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Ju-Hsiou Liao

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**HYDROTHERMAL (SOLVOTHERMAL) AND MOLTEN
POLYCHALCOGENIDE SALT SYNTHESIS OF TERNARY
AND QUATERNARY CHALCOGENIDES**

Volume I

By

Ju-Hsiou Liao

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ABSTRACT

HYDROTHERMAL (SOLVOTHERMAL) AND MOLTEN POLYCHALCOGENIDE SALT SYNTHESIS OF TERNARY AND QUATERNARY CHALCOGENIDES

By

Ju-Hsiou Liao

Metal (poly)chalcogenides have received great attention because they exhibit interesting electronic, optical and catalytic properties which can be applied in nonlinear optics, rechargeable battery cathodes, optical storage, radiation detection, solar energy conversion or catalysts.

A lot of effort has been expended synthesizing metal (poly)chalcogenides by using traditional solution methods at ambient temperatures and solid state methods at high temperatures ($>500^{\circ}\text{C}$). We are interested in investigating two new synthetic techniques for the chalcogenide chemistry to explore new materials. Using polyselenides as starting materials and "mineralizers" under hydrothermal conditions, we successfully synthesized discrete clusters such as $(\text{Me}_4\text{N})_2\text{Mo}_3\text{Se}_{13}$, $\text{K}_2\text{Mo}_3\text{Se}_{13}$, $\alpha\text{-K}_8\text{Mo}_9\text{Se}_{40}\cdot 4\text{H}_2\text{O}$, $\beta\text{-K}_8\text{Mo}_9\text{Se}_{40}$, $\text{K}_6\text{Mo}_6\text{Se}_{27}\cdot 6\text{H}_2\text{O}$, $\text{K}_{12}\text{Mo}_{12}\text{Se}_{56}$, $\text{Cs}_2\text{Mo}_2\text{O}_2\text{Se}_6$ and $(\text{Me}_4\text{N})_4\text{Sn}_4\text{Se}_{10}$, and extended structures such as $\text{K}_2\text{Mo}_3\text{Se}_{18}$, $\text{K}_{10}\text{Mo}_{12}\text{Se}_{58}$ and $(\text{Me}_4\text{N})_2\text{Sn}_3\text{Se}_7\cdot 2\text{H}_2\text{O}$. All the molybdenum compounds contain polyselenide ligands and special trinuclear $[\text{Mo}_3\text{Se}_7]^{4+}$ cores except for $\text{Cs}_2\text{Mo}_2\text{O}_2\text{Se}_6$. Using methanol as solvent

under the similar conditions, we synthesized dimeric $K_4V_2O_2Se_{10} \cdot 2MeOH$ and $K_4V_2O_2Se_8 \cdot 0.65MeOH$ clusters, as well as K_3NbOSe_3 and $K_2[(WO_2Se_2)_{0.5}(WOSe_3)_{0.5}]$ anions.

Molten polychalcogenide fluxes serve as good reaction media. The preparation of novel Sn (poly)chalcogenide compounds, $K_2Sn_2S_8$, α - $Rb_2Sn_2S_8$, β - $Rb_2Sn_2S_8$, $K_2Sn_2S_5$, $Cs_2Sn_2S_6$, Cs_2SnS_{14} and K_2SnTe_5 , reveals the structural diversity of the (poly)chalcogenide ligands. We further investigated mixed metal systems which potentially allow larger structural varieties and may lead to interesting physical properties. Using $[MQ_4]^{4-}$ and $[M_2Q_6]^{4-}$ ($M=Ge, Sn$; $Q=S, Se$) anions as building blocks in polychalcogenide fluxes mixed with other cations with different coordination preference, size and charge, we synthesized novel quaternary chalcogenide compounds, $Rb_2Cu_2SnS_4$, $A_2Cu_2Sn_2Q_6$ ($A=Na, K, Rb, Cs$; $Q=S, Se$), $K_2Au_2SnS_4$, $K_2Au_2Sn_2S_6$, $K_2HgSn_2S_6$, $K_2GeIn_2S_6$, $K_2Hg_3Sn_2S_8$, $K_2Hg_3Ge_2S_8$, $K_6Zn_4Sn_5S_{17}$, $Rb_2ZnSn_2S_6$, $Cs_2MnSn_2S_6$, K_2MnSnS_4 , $Cs_2In_2Ge_2S_8$, $Cs_2MnSn_3Se_8$ and $Rb_2CdGe_2S_6$. All these compounds are semiconductors. Among them, $A_2Cu_2Sn_2Q_6$ have band gaps comparable to those in photovoltaic materials; $CuInQ_2$, $CdTe$, $GaAs$ and Si , and are potential candidates for solar cell applications. $K_2Hg_3Sn_2S_8$, $K_2Hg_3Ge_2S_8$, $K_6Zn_4Sn_5S_{17}$, $Rb_2ZnSn_2S_6$, $Cs_2MnSn_2S_6$ possess novel noncentrosymmetric structures and could be promising nonlinear optical materials.

In this dissertation, the synthesis, characterization and properties of the above compounds will be discussed.

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To My Parents, Pei-Chen Liao and Su-Jane Lin

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CHAPTER 1

1. Introduction to Metal Chalcogenide Chemistry

In the last 15 years, metal (poly)chalcogenides have received great attention in the field of coordination chemistry and solid state science due to their interesting structural, reactivity, electronic, optical and catalytic properties.¹⁻⁵ The metal (poly)chalcogenides exhibit large structural diversity because: (a) various lengths of Q_x^{2-} ($x=1$ to 9) ligands are available, (b) both terminal and internal chalcogen atoms of Q_x^{2-} ligands are capable of binding to one or more metal centers and (c) various metal to ligand ratios are possible with appropriate number and size of counterions to balance the charge and to stabilize a crystal lattice. The various bonding modes have been summarized elsewhere.⁶ The special ability of the chalcogen atom to bind multiple metal centers also provides a synthetic route to heterometallic clusters. For example, tetrathiomallates, $[MS_4]^{2-}$, have been used as precursors to bind other transition metals M' via S atoms to form $[M'(MS_4)_2]^{2-}$ ($M=Mo, W$; $M'=Fe, Co, Ni, Pd, Pt, Zn, Cd, Hg$)⁷. These complexes, especially mixed Mo/Fe/S clusters, are enzymologically interesting.⁸ Heterometallic chalcogenide clusters can also be good candidates as precursors for synthesizing ternary chalcogenide

semiconductors such as CuInQ_2 ($\text{Q}=\text{S}, \text{Se}$) which is a good photovoltaic material for solar energy conversion.⁹ Furthermore, there is a great drive for new materials and this motivates the development of new synthetic strategies.¹⁰ Conventional solution methods and high temperature solid state methods have long been used as synthetic techniques in metal (poly)chalcogenide chemistry. However, the former is limited to produce mostly discrete *molecular* complexes and the latter produces mainly thermodynamically stable metal mono- and di-chalcogenides. We are interested in unusual synthetic approaches such as hydro(solvo)thermal and molten salt methods to synthesize new materials inaccessible by the conventional methods.

2. "Conventional" Preparative Methods

2.1. The "Conventional" Solution Method: Synthesis from Solution at Ambient Conditions

Conventionally, metal (poly)chalcogenide synthesis is approached by using the strategies of common homogeneous coordination chemistry. Those conventional methods are often performed at ambient conditions but differ mostly in the choices of chalcogen sources.¹¹ In the early days, polychalcogenides were produced *in situ* by passing H_2Q ($\text{Q}=\text{S}, \text{Se}, \text{Te}$) through an aqueous NH_3 solution in the presence of elemental chalcogen.¹² However, the toxicity of H_2Q gases and the poor stability of H_2Te (stability: $\text{H}_2\text{S} > \text{H}_2\text{Se} > \text{H}_2\text{Te}$) make this synthetic approach impractical. In non-aqueous solutions, polychalcogenides can be produced by the *in situ*

reactions of alkali metals and elemental chalcogens.¹³ This method is mostly used for polyselenide compounds and can be extended to polytellurides. However, alkali metals are too reactive and in these heterogeneous reactions the stoichiometries cannot be well controlled. So far, the most convenient chalcogen sources are alkali metal polychalcogenides which dissolve in water and polar organic solvents such as DMF, DMSO, acetonitrile, methanol, ethylenediamine etc, forming homogeneous solutions.^{14, 15} In these reactions, stoichiometries can be adjusted easily. Bis(trialkylsilyl)sulfide and bis(trialkylsilyl)selenide are less common chalcogen sources which were primitively designed to replace H₂Q.¹⁶ Other reagents such as SeO₃²⁻, TeO₃²⁻, COSe, CS₂ and CSe₂ also have been occasionally used to synthesize metal chalcogenide compounds.¹⁷ Chalcogen elements oxidize electron-rich unsaturated metal-metal bonds at ambient conditions.¹⁸ They also oxidize metal powder and metal carbonyls with the assistance of a special solvent, N-alkylimidazole (N-Melm).¹⁹

These conventional solution methods have been extensively used and yield primarily discrete *molecular* metal (poly)chalcogenide complexes with few exceptions which give extended structures.¹⁴ Large organic cations such as tetraalkylammonium and tetralkylphosphonium are often used to crystallize the products. Typical examples are shown below:



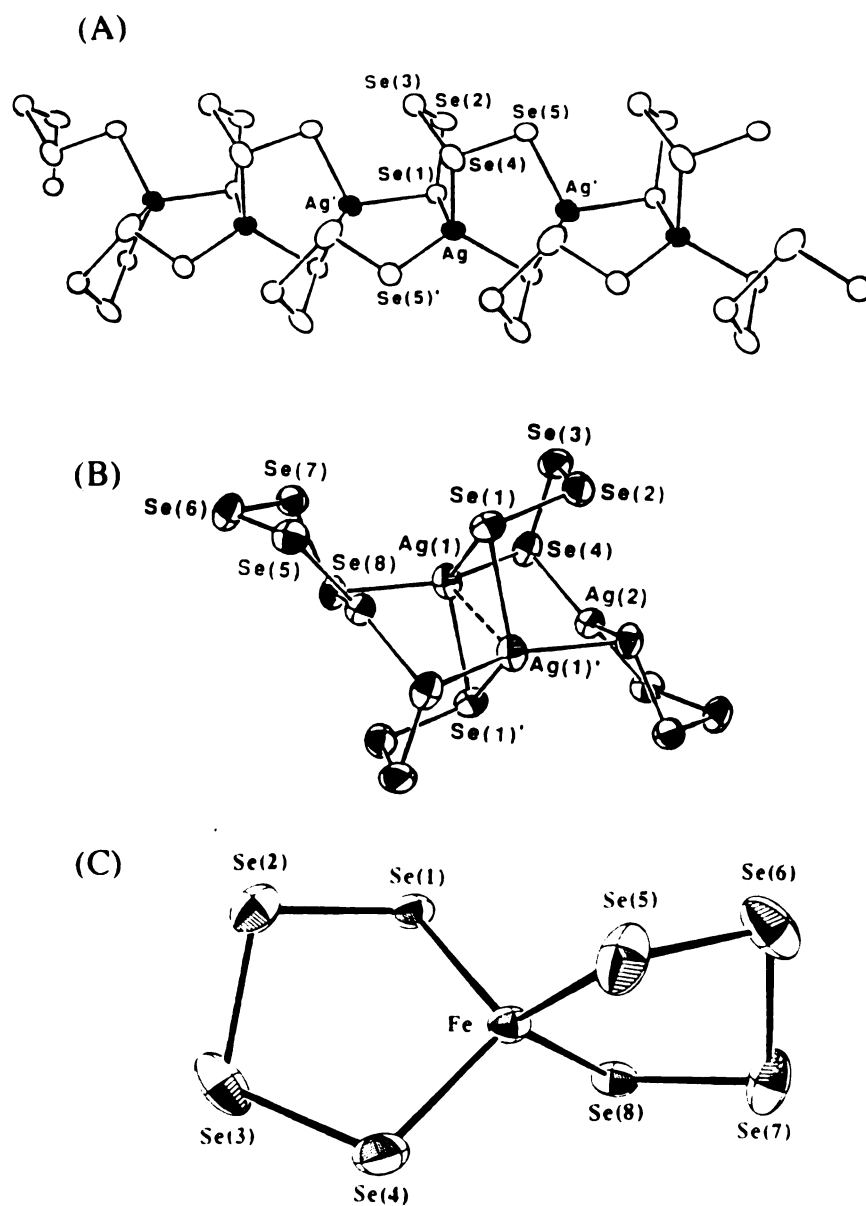


Figure 1-1: ORTEP representation and labeling scheme of (A) $[\text{Ag}(\text{Se}_5)]_n^{n-}$ (B) $[\text{Ag}(\text{Se}_4)]_4^{4+}$ and (C) $[\text{Fe}(\text{Se}_4)_2]^{2-}$.

Eq 1 gives one of the few examples of formation of polymeric complexes anions by room temperature solution synthesis. The structures of (I)~(III) are shown in Figure 1-1. The polychalcogenide ligands observed in these products do not necessarily have the same length as the starting polychalcogenides used. The crystallization of metal polychalcogenide compounds is mostly influenced by the choice of organic cations.

2.2. "Conventional" High Temperature Solid State Synthesis

The most common method for the preparation of solid state metal chalcogenides is performed by reacting the component materials in proper ratios at elevated temperatures ($>500^{\circ}\text{C}$). If all the components are solids, it is called the "ceramic method".²⁰ These typical solid state reactions are different from "wet" reactions because they are limited by (1) the diffusibility of reacting species, (2) the surface area of particles and (3) the rate of nucleation of the product phase. Factor (1) can be overcome by increasing the reaction temperature. The reaction temperature however not only kinetically enhances the reaction rate, but also determines thermodynamically which phase will be formed. Since the total surface area depends inversely on the particle size, factor (2) can be overcome by using fine powder for the reaction. Pressing the reacting powder into a pellet at high temperature will also increase the contact area of reactants. Factor (3) involves the reorientation and rearrangement of the building blocks in starting materials and products and is controlled by their structural similarity. Choice of starting materials is crucial for factor (3) and elevated reaction temperature will assist the required bond-breaking and bond-forming process.

Despite the limitations of the conventional high temperature solid state method, it has been widely used to synthesize various metal chalcogenide compounds. Various structure types of metal chalcogenides form based on (a) stoichiometry (MQ , M_2Q_3 , MQ_2 , MQ_3 , $\text{MM}'\text{Q}_2$, $\text{MM}'\text{Q}_3$ etc), (b) coordination number, (c) relative ionic size and (d) the structure preference of metal centers.

The most common binary metal chalcogenides structure types with the composition of MQ are (1) Rocksalt or NaCl -type (octahedral metal centers), (2) Zinc blende (tetrahedral metal centers), (3) Wurtzite (tetrahedral metal centers), and (4) Hexagonal NiAs -type (trigonal prismatic metal centers). These four common MQ structure types are shown in Figure 1-2 and their examples are listed in Table 1-1. Other less common MQ structure types are SnS , PtS and HgS whose structures do not belong to the above structure types because of the special structure preferences of the metal centers, as shown in Figure 1-3. In SnS , the metal centers possess stereochemically active $4s^2$ electron pairs, while in HgS and PtS the metal centers adopt linear and square-planar geometries respectively. A form of FeS adopts the PbO -type structure as shown in Figure 1-4. This structure type can also be found in the $[\text{CuTe}]_n^{n-}$ layers of NaCuTe and in the $[\text{M}_2\text{Q}_2]_n^{n-}$ layers of the ThCr_2Si_2 structure type. Many ternary metal chalcogenides are derivatives of the above common structure types. A typical example is chalcopyrite, CuFeS_2 , which consists of ordered monovalent Cu^+ and trivalent Fe^{3+} cations at the zinc sites of ZnS structure. There are many more derivative structure types formed via defects or atom substitutions.

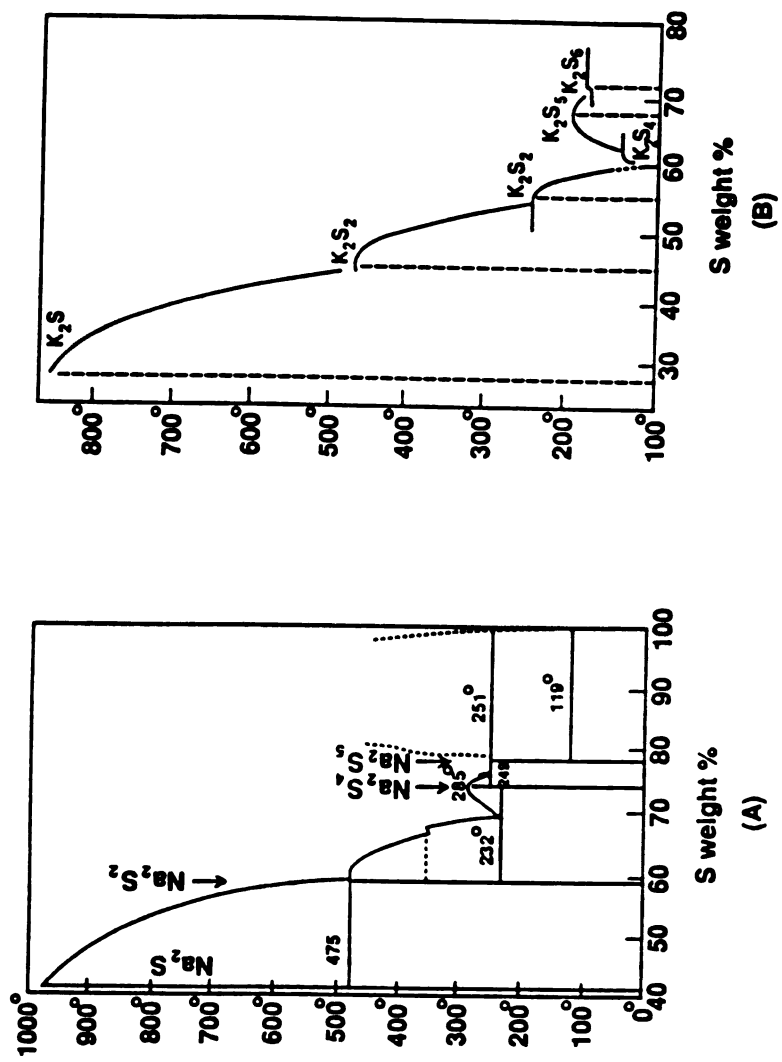
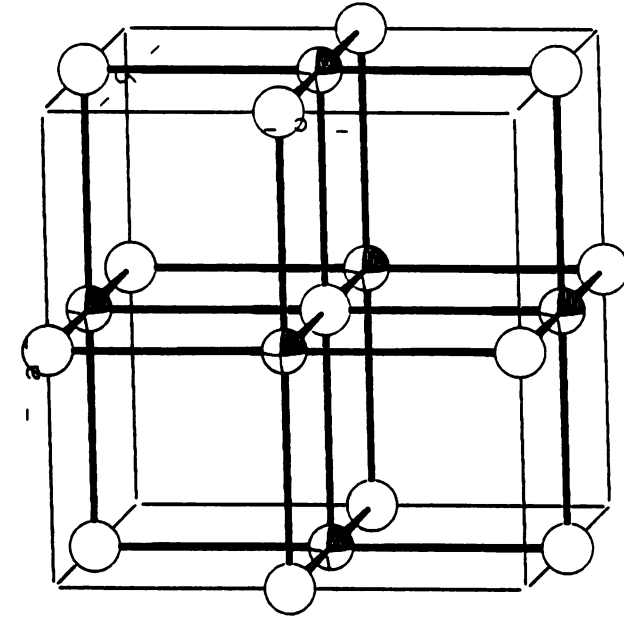
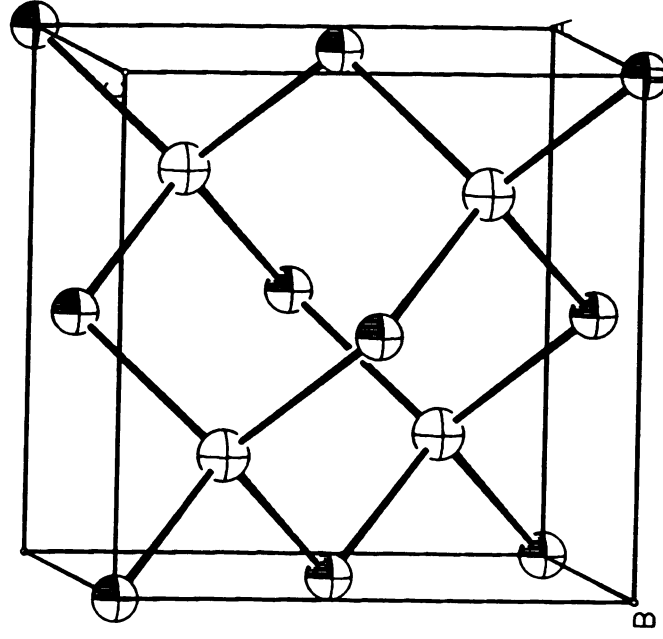


Figure 1-2: Phase diagrams of (A) Na_2S_x (B) K_2S_x system. Temperature ($^{\circ}\text{C}$) vs. % weight of sulfur.



(A)



(B)

Figure 1-3: Crystal structures of common MQ structure types: (A) rocksalt (NaCl) (B) zinc blende (ZnS) (C) wurtzite (ZnS) (D) NiAs.

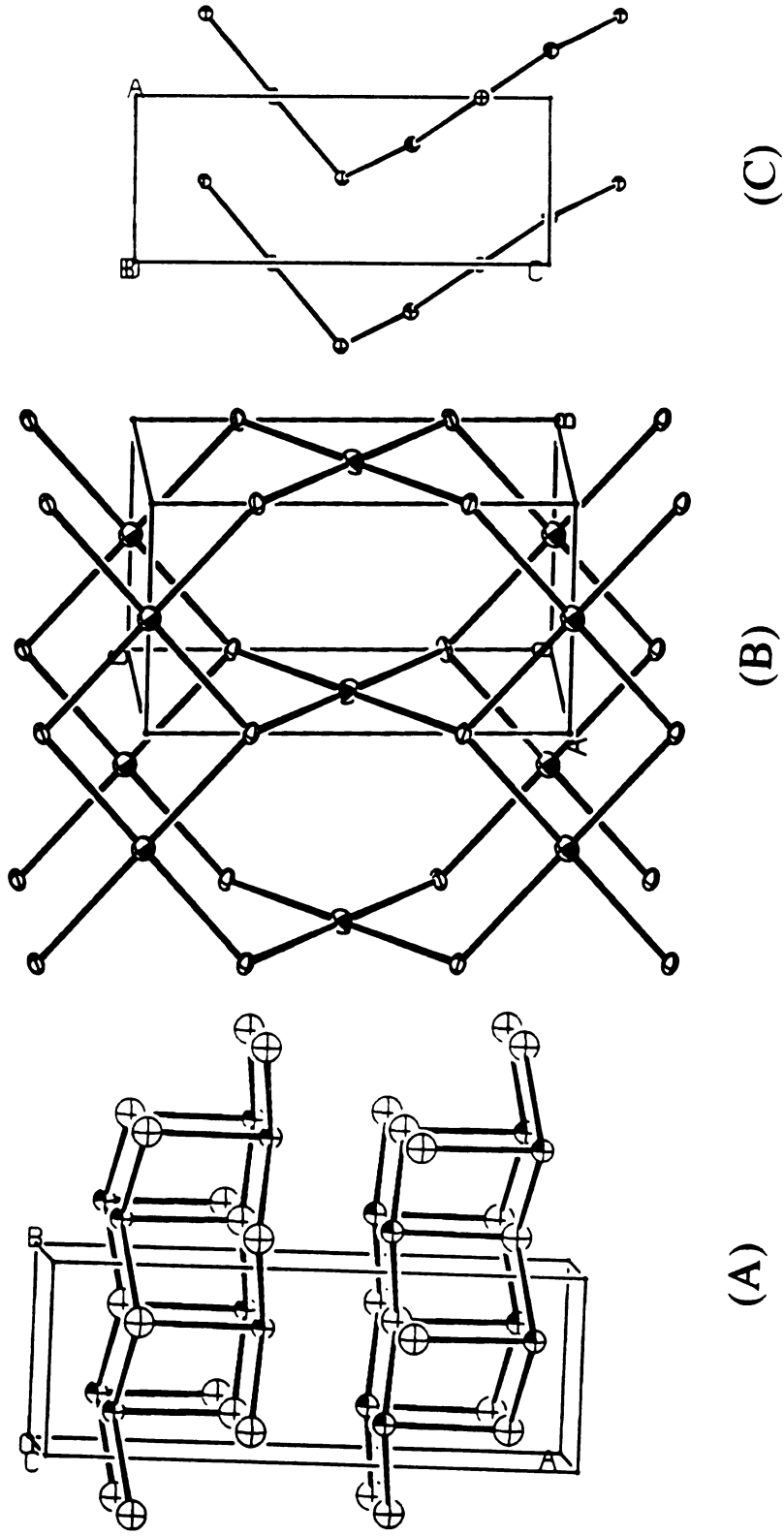


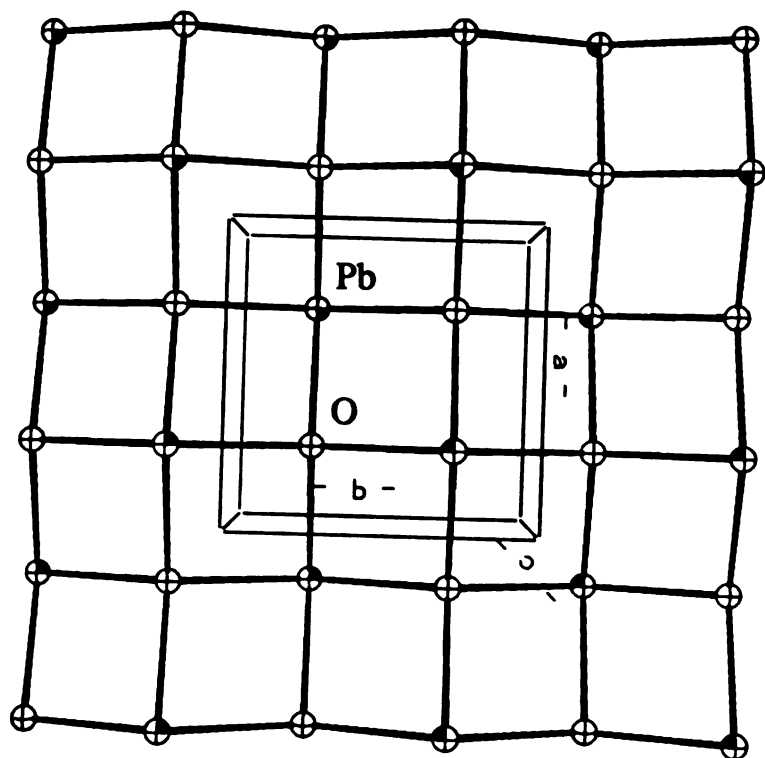
Figure 1-4: Crystal structures of (A) SnS (B) PtS and (C) HgS.

Table 1-1. Examples for Four Common MQ Structure Types: Rocksalt, Zinc Blende, Wurtzite and NiAs-Type

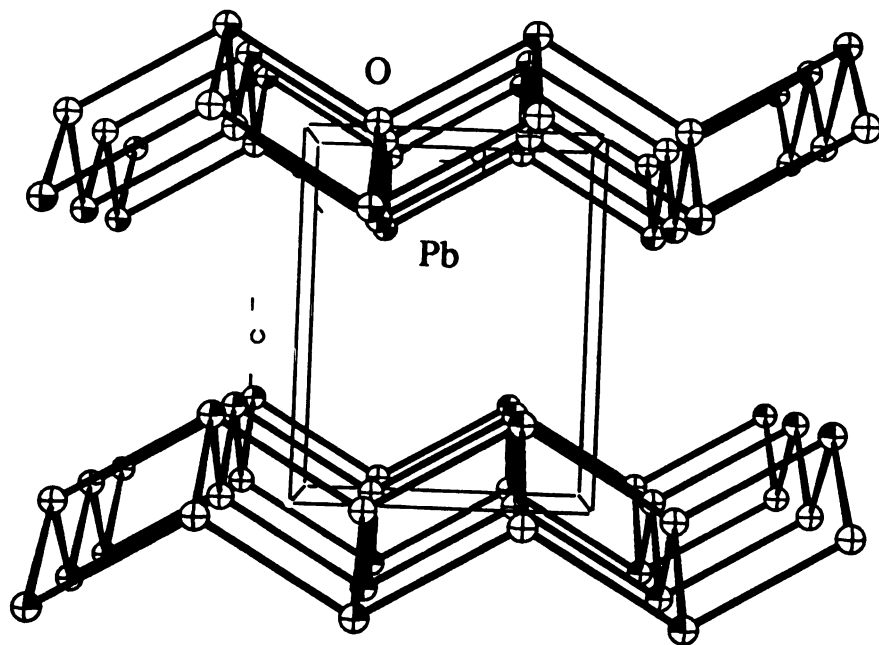
Structure type	Example
Rocksalt	MgS, CaS, SrS, BaS, MgSe, CaSe, SrSe, BaSe, CaTe, SrTe, BaTe
Zinc Blende	β -MnS(red), β -MnSe, BeS, BeSe, BeTe, β -ZnS, ZnSe, ZnTe, β -CdS, CdSe, CdTe, HgS, HgSe, HgTe
Wurtzite	ZnS, ZnSe, ZnTe, CdS, CdSe, MnS, MnSe
NiAs-type	NiS, NiSe, NiTe, FeS, FeSe, FeTe, CoS, CoSe, CoTe, CrSe, CrTe, MnTe

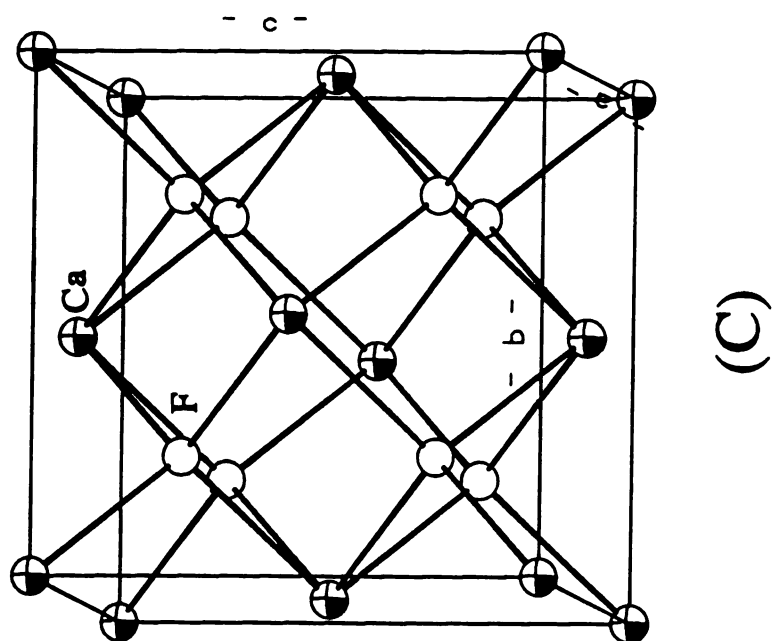
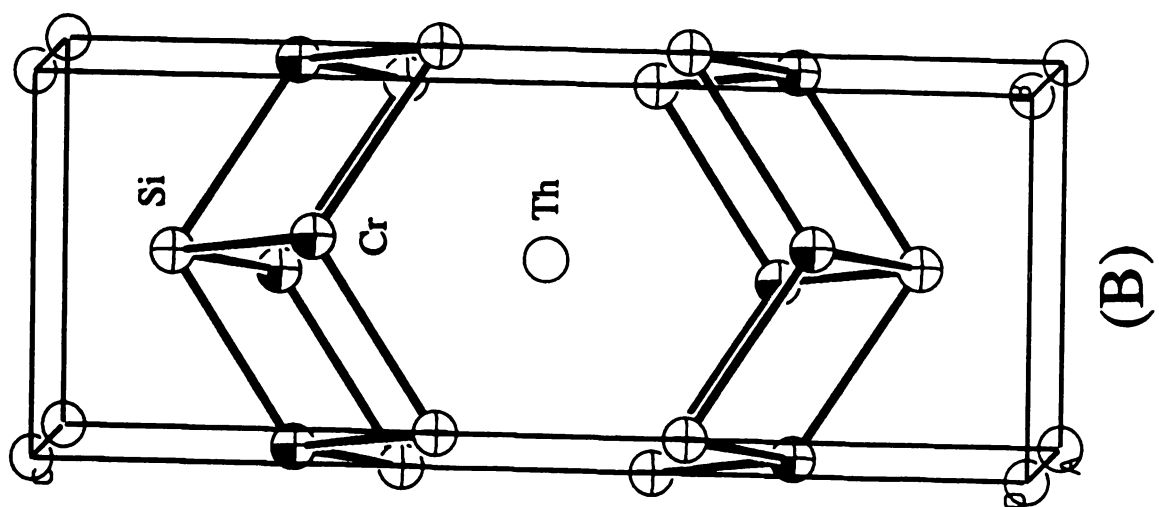
Among MQ₂ structures are the fluorite(CaF₂), rutile(TiO₂), pyrite(FeS₂), MoS₂, TiS₂(CdI₂), SiS₂, while MQ₃ includes ZrSe₃, TaSe₃, NbSe₃ structure types. Perovskite (ABQ₃) and spinel (AB₂Q₄) are also structure types adopted by some chalcogenides. Fluorite and rutile are not common structure types for chalcogenides. Perfect cubic perovskite is not a stable phase for chalcogenides which usually form distorted perovskites with lower symmetry. These non-MQ structure types are illustrated in Figure 1-5 and their examples are given in Table 1-2. The large variety and quantity of compounds reflects the richness and structural diversity of solid state metal chalcogenide compounds.

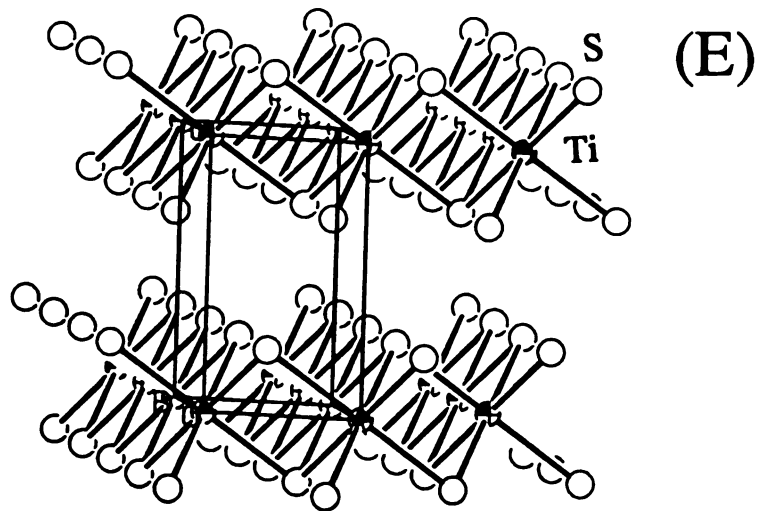
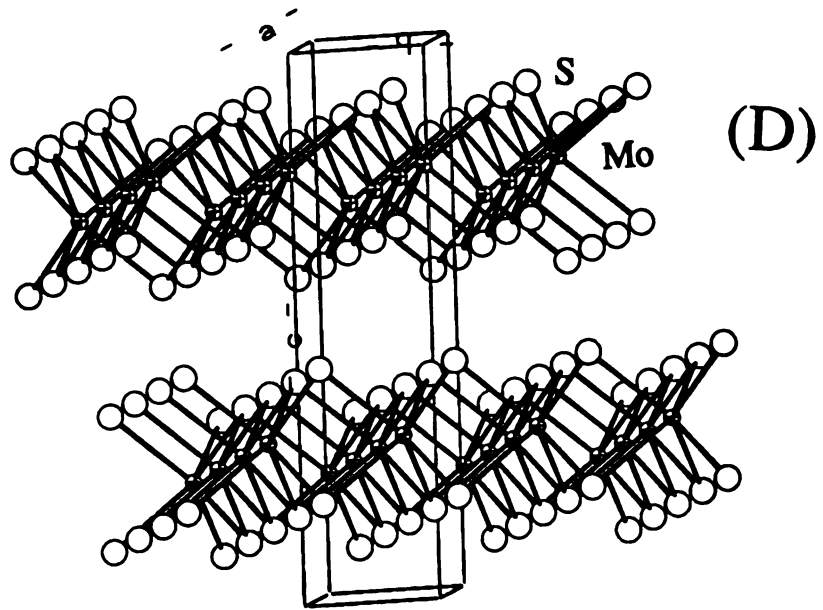
Figure 1-5: Crystal structures of (A) PbO (B) ThCr₂Si₂ (C) fluorite (CaF₂) (D) MoS₂ (E) TiS₂ (CdI₂-type) (F) SiS₂ (G) FeS₂ (H) TiO₂ (I) ZrSe₃ (J) NbSe₃ (K) TaSe₃ (L) perovskite (ABQ₃) and (M) stereoviews of spinel (AB₂Q₄), A: octant-shaded circles; B: octant circles; Q: open circles.

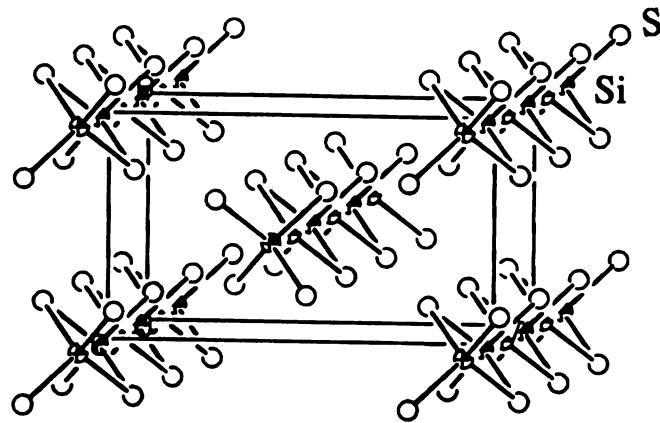


(A)

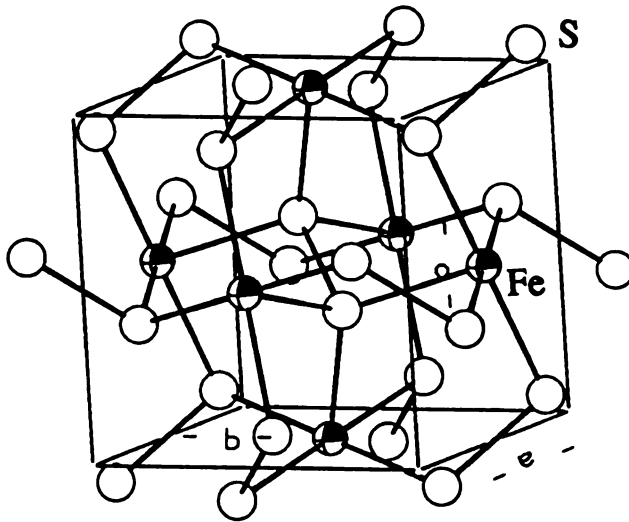




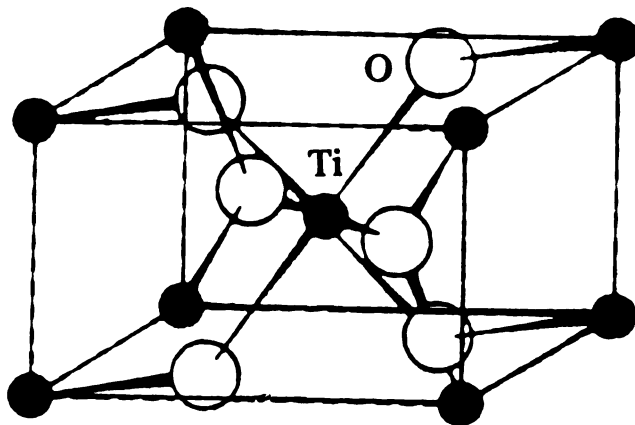




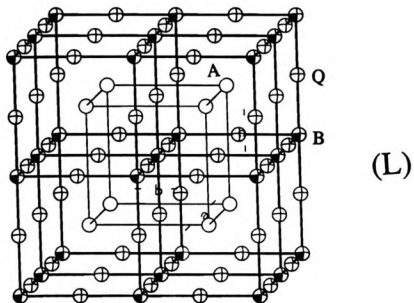
(F)



(G)



(H)



(M)

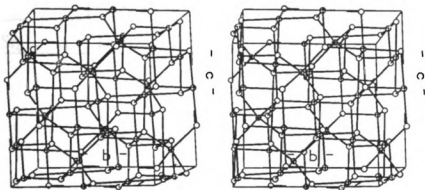


Table 1-2. Examples of Other Common Chalcogenide Structure Types

Structure type	Example
Pyrite $M(Q_2) \leftrightarrow NaCl$	FeS_2 , $FeSe_2$, $FeTe_2$, CuS_2 , $CuSe_2$, $CuTe_2$, CdS_2 , $CdSe_2$, CoS_2 , $CoSe_2$, $CoTe_2$, MnS_2 , $MnSe_2$, $MnTe_2$, NiS_2 , $NiSe_2$, $NiTe_2$, RhS_2 , $RhSe_2$, $RhTe_2$, RuS_2 , $RuSe_2$, $RuTe_2$
MoS_2	MoS_2 , $MoSe_2$, $MoTe_2$, WS_2 , WSe_2 , WTe_2 , α - $NbSe_2$, α - TaS_2 , α - $TaSe_2$
CdI_2	TiS_2 , $TiSe_2$, $CoSeTe$, $NbTe_2$, $NiSeTe$, VS_2 , VSe_2 , $NiTe_2$, $PrTe_2$, $RhTe_2$, TaS_2 , $TaSe_2$, ZrS_2 , $ZrSe_2$, SnS_2
Fluorite(CaF_2)	Li_2S , Na_2S , K_2S , Rb_2S (anti-fluorite)
Perovskite (ABQ_3)	$CaSiS_3$, $SrSiS_3$, $BaZrS_3$, $SrZrS_3$, $BaTiS_3$, $SrTiS_3$, $PbTiS_3$, $PbZrS_3$
Spinel (AB_2Q_4)	Cr_3S_4 , $CoSe_4$, $HgCr_2S_4$, $HgCr_2Se_4$, $ZnCr_2Se_4$, $MnCrInS_4$, $NiCrInS_4$, Fe_3S_4 , Ni_3S_4 , $MgYb_2S_4$, $MgScS_4$, $MgScSe_4$, $ZnMn_2S_4$, $ZnMn_2Se_4$
$ThCr_2Si_2$	$TlCo_2S_2$, $TlFe_2Se_2$, $TlCu_2Se_2$

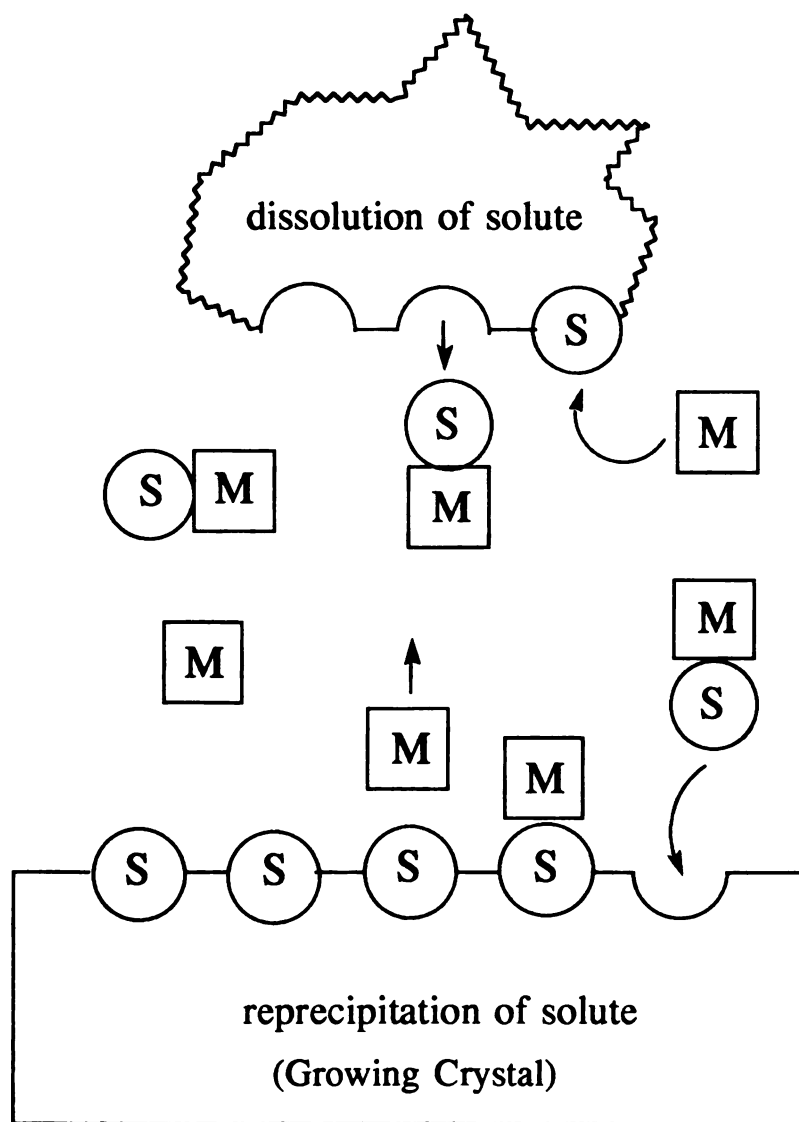
3. Unusual Preparative Methods

3.1. Solvothermal Synthetic Methods

Hydrothermal conditions (aqueous medium over 100°C and autogenous pressure) can be found beneath the surface of the earth. A number of minerals have formed under such conditions. Thus, the

hydrothermal synthetic method has been extensively studied by geologists attempting to simulate the reaction conditions in nature that give rise to minerals. It has been successfully applied in industry for the growth of quartz crystals of large size and extreme purity and for the synthesis of zeolites²¹. Growth of single crystals of reasonable size and purity is important for structure determination and measurements of physical properties of solids. Most chemists grow crystals from solutions at ambient or near-ambient conditions. Under such conditions, some materials do not grow because they are insoluble. For example, quartz (SiO_2) is nearly insoluble in water at ambient temperature. The low solubility problem can be overcome by hydrothermal conditions because at elevated temperature the solubility of solutes increases. Often an additional agent called mineralizer can be added to form soluble complexes with the solute and this increases the overall solubility. The mineralizer effect is illustrated in Scheme (I). The complexes formed with mineralizers are labile. They easily dissociate and redeposit the solute species on the surface of crystals. This dissolution/reprecipitation process or chemical transport process, enhanced by mineralizers, is necessary for single crystal growth.

The hydrothermal technique has been successfully used as a synthetic tool²² to make new materials especially with extended microporous frameworks which are often inaccessible under ambient conditions.



M :mineralizer **S** :solute

S **M** : soluble complex

Scheme (I)

De Sénarmont was the first to introduce hydrothermal synthesis into geological science and synthesized numerous oxide, carbonate, fluoride, sulfate and sulfide minerals during mid nineteenth century.²³ Today, the hydrothermal technique is routinely used for the synthesis of zeolites. Haushalter *et al.*²⁴ and Jacobson *et al.*²⁵ reported great success in synthesizing transition metal phosphates and organophosphonates respectively, using hydrothermal techniques. Some of these phosphate compounds contain open frameworks which provide the size and shape selectivity of zeolites and, in addition, provide d-block transition metals as possible reaction centers for redox chemistry.

Application of hydrothermal techniques on metal chalcogenides²⁶ is less extensively studied than on metal oxides but it is an exciting field to explore because metal-chalcogen based microporous solids resembling their metal-oxides counterparts could lead heterogeneous catalysis into a new era. Schäfer²⁷, Krebs²⁸ and Sheldrick²⁹ have been using alkali metal carbonates as mineralizers to synthesize a series of germanium and tin chalcogenides. The reaction solvents used in these systems were water and in some cases methanol. One advantage of hydrothermal (solvo)thermal reactions over conventional solid state reactions is that organic cations can be used as structure directing templates for microporous material synthesis since they are still thermally stable under hydrothermal conditions. Even though the pursuit of the chalcogen-based "zeolites" is still at a very early stage, some main group metal chalcogenides with open frameworks have been made hydrothermally by using tetraalkylammonium cations as template agents.^{26,30}

Our research approach is to investigate the feasibility of using *polychalcogenides* as reactants and mineralizers in the hydro(solvo)thermal

reactions to synthesize new metal (poly)chalcogenide compounds. The exploration of this synthetic technique on Mo systems gave a series of *molecular* and *polymeric* Mo polychalcogenide compounds with interesting structural features. The results will be described in Chapter 2. The investigations of a main group metal (Sn) and other early transition metals (V, Nb, W) will be discussed in Chapters 3 and 4 respectively.

3.2. Molten Salt (Flux) Synthetic Methods at Intermediate Temperature

Solvents play a very important role in the development of chemistry. Most chemical reactions cannot proceed without using solvents as reaction media. The term, "solvent", is dominantly represented by water and other non aqueous room temperature liquids simply due to their abundance and convenience of handling. In fact, liquid phases in other temperature ranges, lower or higher than ambient temperature, can also serve as reaction media with special functions. For example, liquid ammonia is a good low-temperature solvent to dissolve alkali metals due to the excellent ability of ammonia molecules to solvate alkali cations and electrons. Molten salts are high temperature solvents which form by melting ionic solids such as metal halides, metal chalcogenides and alkali polychalcogenides. They possess comparable common liquid phase properties of conventional room temperature solvents such as diffusibility, viscosity, surface tension, etc., and therefore can also be used for the purpose of reaction media and crystal growth. In spite of the obvious difficulties of handling, molten salts have some advantages not offered by common room temperature solvents.

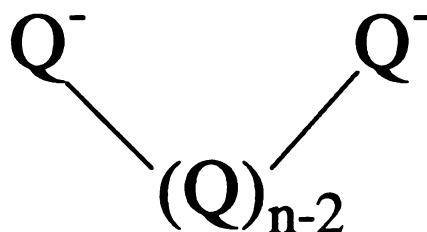
(1) Wide temperature range: The applicable melting temperature of inorganic molten salts can be as low as 89°C (melting point of eutectic mixture of $\text{AlCl}_3 + \text{NaCl} + \text{KCl}$) or as high as thousands of degrees.

(2) Special solubility: Molten salts can dissolve minerals such as metal oxides which are not soluble in conventional room temperature solvents. Noble gases have also been found to dissolve in molten salts.³¹ Most organic compounds decompose at elevated temperatures and therefore molten salts cannot be employed as reaction media. However, some chemical reactions were found between organic materials dissolved in molten salts.³² Acetylene undergoes chlorination with Cl_2 and CCl_4 in a $\text{NaCl} + \text{AlCl}_3 + \text{FeCl}_3$ melt at 200°C, where the molten salt also serves as catalyst. Some organic compounds can "survive" in inorganic melts at low enough temperature. An interesting example is the synthesis of $(\text{Ph}_4\text{P})[\text{InSe}_{12}]$ by reacting In metal in molten $(\text{Ph}_4\text{P})_2\text{Se}_x$ at 200°C. $(\text{Ph}_4\text{P})^+$ survives at this temperature and serves as a charge-compensating and space-filling (structure directing) cation for the open anionic framework.³³

(3) High reactivity: Some molten salts are reactive solvents and take part in chemical reactions. Molten salts have a wide range of oxidizing ability and different acidities. For example, Na_2S is very reducing and basic while Na_2S_5 is more oxidizing and considerably less basic. Therefore, different choices of molten salts as reaction media will lead to different reaction chemistry.

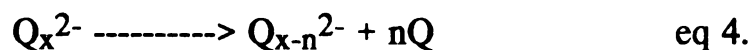
(4) High ionic conductivity: Numerous molten salts possess good ionic conductivity and can be utilized as solid electrolytes for electrochemical reactions.

Our research group is interested in applying alkali polychalcogenide molten salts for synthesis of new metal (poly)chalcogenide compounds. Scheel *et al.* had noticed the "solvent" properties of sodium polysulfide melts and used them to grow single crystals of numerous known binary and ternary metal sulfides such as ZnS, CdS, MnS, PbS, HgS, FeS₂, NiS₂, CoS₂, MoS₂, NbS₂, LaS_{2-x}, NaCrS₂, KCrS₂, NaInS₂, KFeS₂, Cu₃VS₃ at high temperatures (>700°C).³⁴ During his studies, he was aware of the potential reactivity of polysulfides for use as reactants. However he did not proceed further to investigate. The polychalcogenide, Q_n²⁻, anion as depicted in scheme (II), has negative charges formally located at the two terminal chalcogen atoms. The internal atoms are neutral and can serve as electron acceptors or oxidizing agents.



Scheme (II)

All chalcogen atoms, especially the negatively charged terminal atoms, are effective binding sites, which make polychalcogenides good multi-dentate nucleophiles capable of forming strong bonds with metal ions. However, polychalcogenide ligands are not stable at high temperatures and split into shorter chains and elemental chalcogen as shown in eq 4.



The temperature at which this happens depends on x and on Q . A typical example is the transformation of $\text{TiS}(\text{S}_2)$ to TiS_2 and S above 500°C .³⁵ To incorporate polychalcogenide into solid state structures, lower temperature reactions have to be used. As shown in the phase diagrams of $\text{Na}_2\text{S}/\text{S}$ ³⁶ and $\text{K}_2\text{S}/\text{S}$ systems,³⁷ the melting points of Na_2S_x and K_2S_x are well below 400°C when $x > 3$ and reach to 145°C for K_2S_4 . This allows the polysulfide molten salt reactions to be performed in such a medium temperature regime. A list of the melting points of known polychalcogenides is given in Table 1-3

Table 1-3. Melting Points ($^\circ\text{C}$) of Some Known Alkali Metal Polychalcogenides^{36~39}

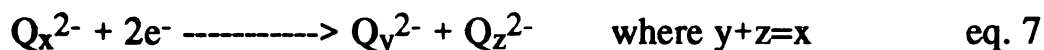
Li_2S 900-975	Li_2S_2 369.5				
Na_2S 1180	Na_2S_2 490	Na_2S_3 228.8	Na_2S_4 275	Na_2S_5 251.8	
Na_2Se >875	Na_2Se_2 495	Na_2Se_3 313	Na_2Se_4 290		Na_2Se_6 258
Na_2Te 953	Na_2Te_2 348				Na_2Te_6 436
K_2S 840	K_2S_2 470	K_2S_3 252	K_2S_4 145	K_2S_5 206	K_2S_6 189
K_2Se	K_2Se_2 460	K_2Se_3 380	K_2Se_4 205	K_2Se_5 190	
Rb_2S 530	Rb_2S_2 420	Rb_2S_3 213	Rb_2S_4 160	Rb_2S_5 225	Rb_2S_6 201
Cs_2S	Cs_2S_2 460	Cs_2S_3 217	Cs_2S_4 160	Cs_2S_5 210	Cs_2S_6 186

The formation of alkali polychalcogenides can be achieved either by reacting stoichiometric amounts of alkali metal and chalcogen in liquid ammonium or by heating stoichiometric amounts of alkali monochalcogenide and chalcogen at appropriate temperatures as illustrated by eq 5.



Most alkali polychalcogenides are air and moisture sensitive and need to be handled under inert atmosphere. They dissolve in water and other nonaqueous polar solvents such as MeOH, DMF and acetonitrile and are therefore easy to remove from the products during isolation. The melting point, acidity and the oxidizing power of alkali polychalcogenides relies on the chain lengths which can be controlled by adjusting the parameters of eq. 5.

Redox chemistry is involved in the reactions of metals with A_2Q_x as shown in eq. 6 and 7.



Metals are oxidized by polychalcogenides, Q_x^{2-} , while polychalcogenides are reduced and split into shorter chains. The resulting M^{n+} cations, alkali metal cations and various (poly)chalcogenides chains, in the fluxes, associate to form various structures, depending on their relative concentrations, the distribution of polychalcogenide lengths, the size of alkali cations, the nature of the M^{n+} centers and the reaction temperatures.

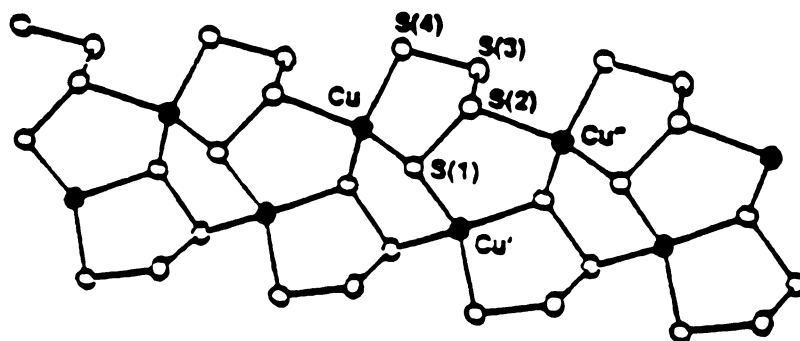
In 1987, Ibers, *et al.* published the first use of reactive polychalcogenide fluxes to synthesize new metal chalcogenide compounds

at 375-470°C, $\text{K}_4\text{Ti}_3\text{S}_{14}$ ⁴⁰ and $\text{Na}_2\text{Ti}_2\text{Se}_8$.⁴¹ These compounds are one-dimensional chains which are composed of Ti^{4+} and Q_2^{2-} and Q^{2-} ligands. No longer polychalcogenide ligands (Q_x^{2-} , $x > 2$) were obtained because of the relatively high temperatures used.

In our laboratory, Y. Park has extensively explored the lower temperature regime (215°C-450°C) on late transition metal systems in which a large number of new metal (poly)chalcogenides containing longer Q_x^{2-} ($x=2,3,4$ and 5) were obtained.⁴² As shown by the results of his work summarized in Table 1-4, all the polychalcogenide compounds were synthesized in the 215°C~310°C regime and all of them are low-dimensional structures. These polychalcogenides are limited to polysulfides and polyselenides while no polytellurides were found. In fact, as shown in Table 1-4, sulfur and selenium undergo similar chemistry while tellurium deviates to form its own category. The effect of reaction temperature is demonstrated by the formation of $\alpha\text{-KCuS}_4$ and $\beta\text{-KCuS}_4$. See Figure 1-6. The thermodynamically more stable $\beta\text{-KCuS}_4$ was obtained at slightly higher temperature (250°C) than the α -phase (215°C) in K_2S_5 flux. The effect of alkali metal cation size can be shown by comparing the structures of KAuSe_2 (one-dimensional) and NaAuSe_2 (two-dimensional). See Figure 1-7. Substitution of smaller Na^+ for K^+ in KAuSe_2 brings the $[\text{AuSe}_2]_n^{n-}$ chains closer and destabilizes the anionic framework due to coulombic repulsion. This forces the $[\text{AuSe}_2]_n^{n-}$ chains to rearrange to form two-dimensional frameworks.

Besides the extensively studied alkali metal containing ternary chalcogenides, this new synthetic technique also shows great potential for preparing new structures by incorporating different metals and different chalcogens. This makes it possible to fine-tune the physical properties.

(A)



(B)

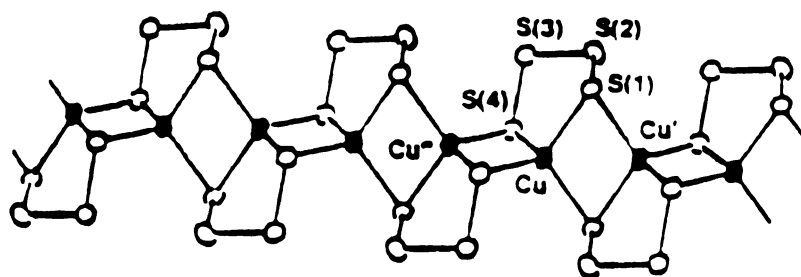


Figure 1-6: ORTEP representation and labeling scheme of (A) α -[CuS₄]⁻ and (B) β -[CuS₄]⁻.

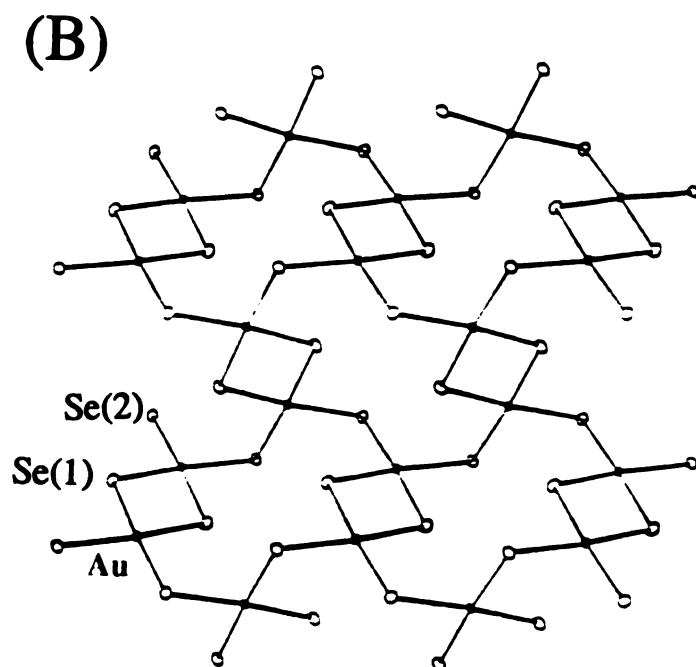
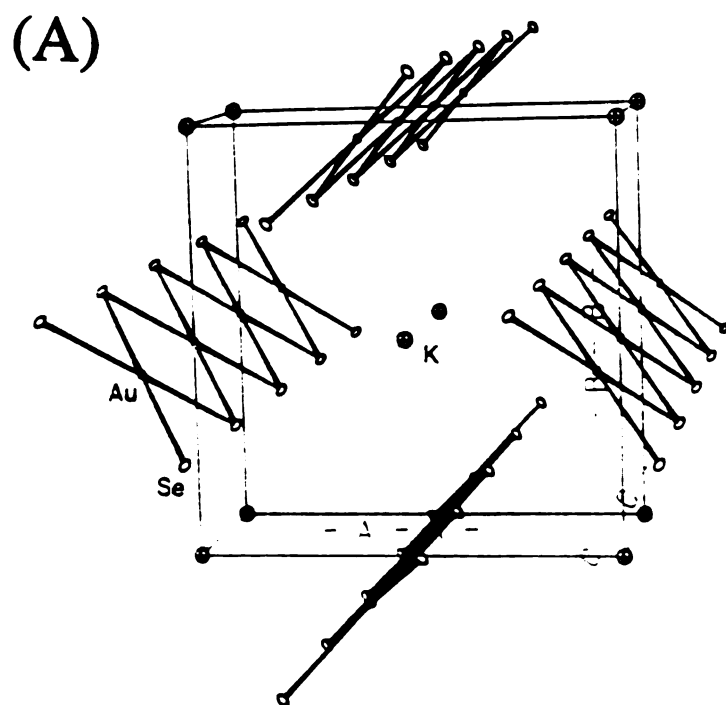


Figure 1-7: ORTEP representation and labeling scheme of (A) KAuSe_2 and (B) an anionic layer of NaAuSe_2 .

Encouraged by Park's success, I continued the exploration of a main group metal, Sn, and expanded to mixed metal quaternary systems using alkali metal polychalcogenide fluxes at temperatures below 500°C. The results will be illustrated in Chapters 5~7.

Table 1-4. Summary of Younbong Park's Work on Molten Salt Synthesis of Late Transition Metal Chalcogenides with Dimensionality and Synthetic Temperatures Given in the Parentheses.^a

Cu	α - KCuS₄ (1D, 215°C), β - KCuS₄ (1D, 250°C), α - KCuSe₄ (1D, 250°C), α - CsCuSe₄ (1D, 250°C), Na₃Cu₄Se₄ (1D, 350°C), Na_{1.9}Cu₂Se₂·Cu₂O (2D, 340°C), K₂Cu₅Te₅ (2D, 350°C), NaCuTe (2D, 400°C), K₄Cu₈Te₁₁ (3D, 350°C), Cs₃Cu₈Te₁₀ (2D, 450°C), KCu₄S₂Te (2D, 450°C), K₃Cu₈S₄Te₂ (2D, 450°C), Cu_{17.6}Te₈S₂₆ (3D, 350°C)
Au	KAuS₅ (1D, 250°C), KAuSe₅ (1D, 250°C), CsAuSe₃ (1D, 350°C), K₃AuSe₁₃ (1D, 250°C), KAuSe₂ (1D, 290°C), Na₃AuSe₈ (1D, 310°C), NaAuSe₂ (2D, 290°C)
Hg	K₂Hg₃S₄ (1D, 220°C), K₂Hg₃Se₄ (1D, 250°C), Cs₂Hg₃Se₄ (1D, 250°C), K₂Hg₆S₇ (3-D, 370°C), Cs₂Hg₆Se₇ (3D, 375°C)
Cu/Au	AuCuSe₄ (3D, 310°C)

^a Compounds in bold contain polychalcogenides.

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CHAPTER 2

Hydrothermal Synthesis and Characterization of New Molybdenum Polyselenides

1. Introduction

Molybdenum-sulfur chemistry has been extensively studied in the last two decades. Interest in this chemistry arises from the industrial application of sulfide-based catalysts for the hydrodesulfurization reaction¹ (HDS) as well as the importance of the active sites of molybdoenzymes² in biological systems. To date, a variety of molybdenum polysulfide complexes³ have been synthesized and structurally characterized. In contrast, no corresponding Mo/Se chemistry has been reported except for $[\text{MoSe}_4]^{2-}$ and $[\text{MoSe}_9]^{2-}$.⁴ Conventionally, syntheses of molybdenum chalcogenides are carried out in solution at ambient temperature. High temperature solid state reactions of molybdenum/chalcogen systems gave thermodynamically stable binary phases⁵ and ternary Chevrel phases⁶ which are electronically and catalytically interesting. The products obtained from high temperature reactions are often extended structures and contain monochalcogenides. Our interest in exploring unusual conditions for the stabilization and

crystallization of new molybdenum-chalcogenide frameworks led us to consider hydrothermal techniques as a possible alternative. Hydrothermal and methanothermal conditions with CO_3^{2-} and OH^- as mineralizers were used to digest sulfides and selenides of main group metals to yield new phases such as $\text{Cs}_4\text{Sn}_5\text{S}_{12}\cdot 2\text{H}_2\text{O}^{7a}$, $\text{RbSb}_3\text{Se}_5^{7b}$, $\text{Rb}_2\text{Sb}_4\text{S}_7^{7c}$, $\text{KAsSe}_3\cdot\text{H}_2\text{O}^{7d}$, $\text{RbAsSe}_3\cdot 0.5\text{H}_2\text{O}^{7d}$, $\text{CsAsSe}_3\cdot 0.5\text{H}_2\text{O}^{7d}$, $\text{Cs}_4\text{Sn}_2\text{Se}_6^{7e}$ and $\text{K}_4\text{Sn}_3\text{Se}_8^{7f}$. Furthermore, Bedard *et al.* reported that novel germanium-sulfide network structures could be synthesized by hydrothermal methods similar to those used for zeolites.⁸ The first three compounds are extended structures and all of them contain only monochalcogenides. We felt that if polychalcogenide ligands were used instead as mineralizers as well as reagents, new polychalcogenide phases with extended frameworks might be accessible. In this chapter, we illustrate the hydrothermal synthesis of a series of ternary molybdenum polyselenide compounds with unusual structures: $(\text{Me}_4\text{N})_2\text{Mo}_3\text{Se}_{13}$,⁹ $\text{K}_2\text{Mo}_3\text{Se}_{13}$,⁹ $\alpha\text{-K}_8\text{Mo}_9\text{Se}_{40}\cdot 4\text{H}_2\text{O}$,¹⁰ $\beta\text{-K}_8\text{Mo}_9\text{Se}_{40}$, $\text{K}_6\text{Mo}_6\text{Se}_{27}\cdot 6\text{H}_2\text{O}$, $\text{K}_2\text{Mo}_3\text{Se}_{18}$,¹⁰ $\text{K}_{12}\text{Mo}_{12}\text{Se}_{56}$,¹¹ $\text{K}_{10}\text{Mo}_{12}\text{Se}_{58}$ and $\text{Cs}_2\text{Mo}_2\text{O}_2\text{Se}_6$. All of them except $[\text{Mo}_2\text{O}_2\text{Se}_6]^{2-}$ contain trinuclear $[\text{Mo}_3\text{Se}(\text{Se}_2)_3]^{4+}$ cores which appear to be very stable under hydrothermal conditions.

2. Experimental Section

2.1. Reagents

Mo was purchased from Alpha Products Inc. Molybdenum trioxide (MoO_3), 99.95%, Johnson, Matthey Catalog Co., Ward Hill, MA. Selenium powder, -100 mesh, 99.5+%; Tetramethylammonium chloride (Me_4NCl),

97%, Aldrich Chemical Co., Inc., Milwaukee, WI. Cesium metal, 99.98% purity, AESAR, Johnson Matthey, Seabrook, NH. Potassium metal, Baker analyzed, J. T. Baker, Inc., Phillipsburg, NJ 08865. Sodium metal, analytical reagents, Mallinckrodt Inc., Paris, K. Y. Methanol, anhydrous, reagent grade; Ether, anhydrous, reagent grade, E. Merck, Darmstadt, Germany.

2.2. Physical Measurements

Far-IR spectra ($600\text{--}100\text{ cm}^{-1}$) were recorded as CsI pellets while Mid-IR spectra ($4000\text{--}400\text{ cm}^{-1}$) were recorded as KBr pellets. Each sample was ground with dry CsI or KBr homogeneously into a fine powder and a pressure of ~ 6 tons was applied to the mixture to make a translucent pellet. The spectra were recorded with a Nicolet 740 Fourier Transform infrared spectrometer in 4 cm^{-1} resolution.

Quantitative microprobe analysis was performed on a JEOL 35CF scanning electron microscope (SEM) equipped with Tracor Northern TN5500 X-ray microanalysis attachment. Single crystals of each sample were mounted on an aluminum stub which was coated with conducting graphite paint to avoid charge accumulation on the sample surface under the bombardment of the electron beam during measurements. Energy Dispersive Spectra (EDS) were obtained by using the following experimental set-up:

X-ray detector position : 55 mm

Working distance : 39 mm

Accelerating voltage : 20 KV

Take-off angle : 27 deg

Beam current : 200 picoamps

Accumulation time : 60 seconds

Window : Be

A standardless quantitative (SQ) analysis program was used to analyze the X-ray spectra obtained. The selenium ratio is always underestimated due to an artifact of the program. An empirical correction factor ($\times 1.6$) was applied to the Mo/Se compounds to correctly evaluate the selenium content. The analyses reported here are based on the average of more than three independent measurements on different crystals of each compound.

^{77}Se ($I=1/2$, natural abundance 7.58%) NMR Spectra were measured on a Varian VXR-500 (superconducting cryomagnet; 11.74 T) pulse spectrometer equipped with a Sun/360 workstation. The spectra were recorded at various temperatures (-55°C to 20°C) by using a broad-band 5-mm probe (frequency range 50-202 MHz). The observing frequency for ^{77}Se was 95.358 MHz. The acquisition time was 6 ms, and no relaxation delay was applied. The number of free induction decays accumulated were 36000. A line broadening of 80 Hz was applied. The spectra were referenced relative to Me_2Se at $\delta=0$ ppm in DMF. Solutions of Ph_2Se_2 ($\delta=460$ ppm) in DMF were used as an external reference. The convention used in reporting the chemical shifts is that a positive sign signifies a shift to higher frequency compared to that of the reference compound.

Optical diffuse reflectance spectra were measured at room temperature with a Shimadzu UV-3101PC double beam, double monochromated spectrophotometer. The sample was ground into powder and pressed into a thin layer above BaSO_4 on a sample holder. BaSO_4 powder was used as reference. The absorption spectrum was calculated from the reflectance data by using the Kubelka-Munk function¹²: $\alpha/S=(1-$

$R)^2/2R$. R is the reflectance, α is the absorption coefficient and S is the scattering coefficient which is practically wavelength independent when the particle size is larger than $5\text{ }\mu\text{m}$.

2.3. Synthesis

Synthesis: All preparations and handling were done under a nitrogen atmosphere in a glovebox. K_2Se_2 , K_2Se_3 , K_2Se_4 , Cs_2Se_2 and Na_2Se_2 starting materials were prepared by using a modified procedure described in the literature.¹³

K_2Se_2 : An amount of 14.772 g (0.187 mol) of selenium was combined with 7.135g (0.187 mol) of sliced potassium metal under nitrogen in a 250-ml round-bottom flask equipped with a Teflon valve and a stirring bar. Approximately 80-ml volume of liquid ammonia was condensed into the flask which was kept at -78°C by a dry ice/acetone bath. The mixture was stirred for a couple of hours until the potassium metal was dissolved completely. When a dark blue solution formed, the ammonia was removed slowly by evaporation as the cold bath was allowed to warm to room temperature under a flow of nitrogen. The resulting air-sensitive reddish brown solid was dried in vacuum overnight, flame-dried, ground to fine powder and kept in a dry nitrogen glovebox. Yield: 98%.

K_2Se_3 , K_2Se_4 , Na_2Se_2 : The preparation procedure of K_2Se_3 , K_2Se_4 , Na_2Se_2 is the same as that of K_2Se_2 .

Cs₂Se₂. An amount of 5.258 g (0.040 mol) of cesium metal was placed in a 250-ml round-bottom flask equipped with a Teflon valve in a N₂ glove box. **Because cesium metal will react with Teflon and sulfur vigorously upon contact in the solid state (caution!),** around a 40-ml volume of liquid ammonia was first condensed into the flask kept at -78°C by a dry ice/acetone bath to dissolve the cesium metal. A sample of 3.158 g (0.040 mol) elemental selenium and a Teflon stirring bar were then added to the dark blue solution. Approximately an additional 40 ml of liquid ammonia was condensed into the flask. The mixture was stirred for about 1 hour. The subsequent procedure is the same as that for K₂Se₂. The resulting air-sensitive reddish brown fine powder was kept in a dry nitrogen glovebox.

(Me₄N)₂Mo₃Se₁₃ (I): A mixture of MoO₃ (0.072 g, 0.50 mmol), Na₂Se₂ (0.306g, 1.5 mmol) and Me₄NCl (0.109 g, 1.0 mmol) was loaded into an ~5 ml heavy-wall Pyrex tube in which 0.3 ml of degassed water was added. The tube was frozen in liquid nitrogen and sealed under a vacuum of ~10⁻³ torr. The reaction ampoule was maintained at 135°C under autogenous pressure for 3 days and then cooled to room temperature. The growth of needlelike crystals was observed under 135°C. The product was isolated with DMF and water to remove excess Se_x²⁻ and NaCl and dried with acetone and ether. Dark red needlelike crystals were obtained in ~68% yield (based on MoO₃). Semiquantitative elemental analysis performed on SEM/EDS indicated Mo_{1.0}Se_{3.7}. A mid-IR spectrum indicated the presence of Me₄N⁺. The product was found insoluble in H₂O, DMF, DMSO and other common solvents, therefore no solution UV-Vis and ⁷⁷Se NMR spectra of this compound were measured.

K₂Mo₃Se₁₃ (II): A mixture of MoO₃ (0.36 g, 2.5 mmol) and K₂Se₂ (1.18 g, 5.0 mmol) was loaded into a 21-ml autoclave to which 1.5 ml of degassed water was added. The autoclave was maintained at 135°C under autogenous pressure for ~27 days and then cooled to room temperature. The product was isolated with methanol and dried with ether. Yield: 61% (based on MoO₃). The needlelike crystals are stable in air. They were put in H₂O and DMF for one month and found to be insoluble in both solvents and other common organic solvents like DMSO, acetonitrile, ethylenediamine etc. Semiquantitative elemental analysis performed on SEM/EDS indicated K_{0.87}Mo_{1.0}Se_{3.8}.

α-K₈Mo₉Se₄₀·4H₂O (III): The reaction of MoO₃ (0.072 g, 0.5 mmol), K₂Se₂ (0.236 g, 1.0 mmol) and 0.2 ml H₂O in an ~5-ml heavy-wall Pyrex tube at 135°C for 3 days yielded black chunky crystals of α-K₈Mo₉Se₄₀·4H₂O (III). The products were isolated by filtration and washed with methanol in ~20% yield (based on MoO₃). The black crystals degrade in air and dissolve slowly in water, DMF and DMSO. SEM/EDS semiquantitative elemental analysis indicated K_{0.77}Mo_{1.0}Se_{4.4}.

β-K₈Mo₉Se₄₀ (IV): The reaction of MoO₃ (0.288 g, 2.0 mol), K₂Se₂ (2.832 g, 12.0 mol), Et₄NCl (1.324 g, 8.0 mol) and 2.0-ml degassed H₂O in a 21 ml autoclave at 135°C for 80 hours afforded black rectangular crystals of β-K₈Mo₉Se₄₀ (IV) in ~10% yield (based on MoO₃). The product was washed with MeOH in a dry nitrogen glovebox. The crystals are stable in air and insoluble in water, DMF, DMSO, acetonitrile and

other common organic solvents. SEM/EDS indicated $\text{K}_{0.9}\text{Mo}_{1.0}\text{Se}_{4.8}$. Mid-IR spectrum indicated the crystals do not contain Et_4N^+ .

$\text{K}_6\text{Mo}_6\text{Se}_{27}\cdot 6\text{H}_2\text{O}$ (V): The reaction of MoO_3 (0.072 g, 0.50 mmol), K_2Se_2 (0.472 g, 2.0 mmol) and 0.3-ml H_2O in an ~5 ml heavy-wall Pyrex tube at 135°C for 3 days afforded black chunky crystals of $\text{K}_6\text{Mo}_6\text{Se}_{27}\cdot 6\text{H}_2\text{O}$ (V) in ~34% yield (based on MoO_3). The product was isolated with methanol to remove excess Se_x^{2-} and dried with ether. The black crystals degrade slowly in air and are very soluble in DMF and water forming reddish brown solutions which are unstable in air and become cloudy in several minutes. SEM/EDS semiquantitative elemental analysis indicated $\text{K}_{1.0}\text{Mo}_{2.0}\text{Se}_{4.8}$.

$\text{K}_2\text{Mo}_3\text{Se}_{18}$ (VI): The reaction of Mo (0.048 g, 0.5 mmol), K_2Se_4 (0.296 g, 0.75 mmol) and 0.2-ml degassed H_2O in an ~5-ml heavy-wall Pyrex tube at 135°C for 3 days afforded plate-like crystals of $\text{K}_2\text{Mo}_3\text{Se}_{18}$ (VI) in ~20% yield (based on Mo). The product was isolated by filtration and washed with methanol. The crystals are stable in air and insoluble in water, DMF, DMSO, acetonitrile and other common organic solvents. SEM/EDS semiquantitative elemental analysis indicated $\text{K}_{0.8}\text{Mo}_{1.0}\text{Se}_{5.7}$.

$\text{K}_{12}\text{Mo}_{12}\text{Se}_{56}$ (VII): The reaction of Mo (0.144 g, 1.5 mmol), MoO_3 (0.144 g, 1.0 mmol), K_2Se_3 (0.945 g, 3.0 mmol) and 0.3-ml degassed H_2O in an ~5-ml heavy-wall Pyrex tube at 135°C for 3 days afforded black chunky crystals of $\text{K}_{12}\text{Mo}_{12}\text{Se}_{56}$ (VII) in ~10.5% yield (based on Mo). The product was isolated with methanol to remove excess Se_x^{2-} and dried with ether. A very small amount of unreacted Mo metal powder was

obtained as contamination. The crystals are stable in air and insoluble in water and common organic solvents. SEM/EDS semiquantitative elemental analysis indicated $\text{K}_{1.0}\text{Mo}_{2.0}\text{Se}_{4.8}$.

$\text{K}_{10}\text{Mo}_{12}\text{Se}_{58}$ (VIII): The reaction of Mo (0.048 g, 0.50 mmol) and K_2Se_4 (0.236 g, 1.00 mmol) 0.3-ml degassed water in an ~5 ml heavy-wall Pyrex tube at 135°C for 3 days afforded black needle-like crystals contaminated with unreacted Mo metal in ~15 % yield (based on Mo). The product was isolated with methanol to remove excess Se_x^{2-} and dried with ether. The crystals are stable in air and are insoluble water and common organic solvents. SEM/EDS semiquantitative elemental analysis indicated $\text{K}_{1.0}\text{Mo}_{1.0}\text{Se}_{4.8}$.

$\text{Cs}_2\text{Mo}_2\text{O}_2\text{Se}_6$ (IX): The reaction of MoO_3 (0.072 g, 0.50 mmol), Cs_2Se_2 (0.318 g, 7.5 mmol) and 0.3-ml of degassed water in an ~5 ml heavy-wall Pyrex tube at 135°C for 36 hours afforded black chunky crystals in low yield (less the 5%). The product was isolated with MeOH and dried with ether. The crystals degrade slowly in air and are soluble in water and DMF. SEM/EDS semiquantitative elemental analysis indicated $\text{Cs}_{1.5}\text{Mo}_{1.0}\text{Se}_{2.5}$.

2.4. X-Ray Crystallography

X-ray diffraction (XRD) powder patterns were used for the purpose of phase characterization and identification. The XRD patterns were recorded with a Phillips XRD-3000 controlled by PDP 11 computer and operating at 40 kV/35mA. Graphite-monochromated Cu radiation was

used. In order to ensure the homogeneity, d-spacings obtained from XRD powder measurements of the products were compared, and found to be identical, with those calculated from using the atomic coordinates determined from the single crystal data. The calculation of d-spacings was performed by using the POWD 10¹⁴ program. The comparison tables between the calculated and observed d-spacings for these compounds are shown in Tables 2-1~2-7.

The crystallographic data for α -K₈Mo₉Se₄₀·4H₂O (III) and K₂Mo₃Se₁₈ (VI) were collected on a Nicolet P3/F diffractometer with graphite monochromated Mo K α radiation using an ω -2 θ scan mode. The data for (Me₄N)₂Mo₃Se₁₃ (I), K₂Mo₃Se₁₃ (II), K₆Mo₆Se₂₇·6H₂O (V) and K₁₂Mo₁₂Se₅₈ (VIII) were collected on a Rigaku AFC6S diffractometer with graphite monochromated Mo K α radiation using an ω -2 θ scan mode for (I), (II) and ω scan mode for (V), (VIII). The data for β -K₈Mo₉Se₄₀ (IV) and K₁₂Mo₁₂Se₅₆ (VII) were collected on a Rigaku AFC6R with a graphite monochromated Mo K α radiation and a rotating anode generator using an ω -2 θ scan mode. The data for Cs₂Mo₂O₂Se₆ (IX) were collected on a Nicolet P3 diffractometer with graphite monochromated Cu K α radiation and rotating anode tube using an ω -2 θ scan mode. The crystals of (I)~(VIII) were mounted on the tip of glass fibers. The crystal of (IX) was sealed in a capillary. Accurate unit cell parameters for all compounds were obtained from the least-squares refinement of the 2 θ , ω , χ , ϕ values of 20-25 machine-centered reflections. The intensities of three check reflections were monitored every 100 (Nicolet) or 150 (Rigaku) reflections to detect possible decay during the data collection period. An empirical absorption correction was applied to all data based on ψ scans for three reflections. An additional absorption correction following the DIFABS¹⁵



procedure was applied to isotropically refined data. Structures of (III), (VI) and (IX) were refined by full-matrix least-squares techniques with the SDP¹⁶ package of crystallographic programs running on a VAXstation 2000 computer. The structures were solved with direct methods by using SHELXS-86¹⁷ and were refined normally. The structures (I), (II), (IV), (V), (VII) and (VIII) were refined with the TEXSAN¹⁸ package of crystallographic programs running on a VAXstation 3100/76 computer. The enantiomorphs of (I), (II), (VI) and (VII) were checked by refining their (-x, -y, -z) coordinates and no significant improvement of R/R_w values and standard deviations of bond distances and bond angles was observed. (IV) decomposed during data collection with 2 θ between 30-40°. The structure of (IV) was refined by using the incomplete data set. The structures of (VIII) and (IX) were solved but cannot be refined to reasonable R values due to an insufficient number of observed reflections and a serious absorption problem of Cu K α radiation, respectively. The data collection parameters and details of the structure solution and refinement are given in Table 2-8. The final atomic coordinates, temperature factors and their estimated standard deviations for (I)~(VII) are given in Tables 2-9~2-15.

Table 2-1. Calculated and Observed X-Ray Powder Diffraction Pattern for $(\text{Me}_4\text{N})_2\text{Mo}_3\text{Se}_{13}$

h	k	l	$d_{\text{calc.}}(\text{\AA})$	$d_{\text{obs.}}(\text{\AA})$	%I _{obs.}
1	0	0	10.0268	10.2409	100.00
0	0	1	6.1100	6.0965	17.98
1	1	0	5.7890	5.8713	25.64
1	0	1	5.2176	5.2413	31.73
1	1	1	4.2023	4.2215	10.01
3	0	0	3.3423	3.3733	17.87
2	1	1	3.2206	3.2356	43.32
3	0	1	2.9322	2.9171	42.49
2	2	0	2.8945		
1	1	2	2.7019	2.7004	14.47
2	2	1	2.6158	2.6251	25.14
3	1	1	2.5311	2.5404	32.43
4	0	1	2.3191	2.3109	24.36
3	2	0	2.3003		
4	1	0	2.1880	2.1904	50.25
3	2	1	2.1528	2.1653	50.25
1	0	3	1.9959	2.0058	19.44
1	1	3	1.9212		
5	0	1	1.9054	1.9063	12.12
3	3	1	1.8401	1.8379	22.54
3	2	2	1.8376		
3	0	3	1.7392	1.7337	4.10
5	1	1	1.7274		
6	0	0	1.6711	1.6798	13.55
3	3	2	1.6315	1.6425	23.13

Table 2-2. Calculated and Observed X-Ray Powder Diffraction Pattern for $K_2Mo_3Se_{13}$

h	k	l	d _{calc.} (Å)	d _{obs.} (Å)	%I _{obs.}
1	1	0	8.9768	9.1597	100.00
0	2	0	8.4170	8.7021	24.61
1	1	-1	5.4944	5.6006	46.15
2	0	0	5.3057	5.3734	15.38
0	0	1	5.2007	5.2504	20.00
1	3	0	4.9605	5.1023	22.31
3	1	0	3.4615	3.4898	27.69
2	4	0	3.2972	3.3124	61.54
0	4	1	3.2715	3.2731	20.10
2	4	-1	3.2201	3.2210	16.92
1	5	0	3.2091		
3	3	0	2.9923	3.0138	58.46
1	5	-1	2.9134	2.9272	14.61
0	6	0	2.8057	2.8194	20.12
4	2	-1	2.7934		
4	0	0	2.6528	2.6712	18.46
0	0	2	2.6003	2.6268	13.84
1	5	1	2.5791	2.5916	23.84
2	4	1	2.4886	2.4945	26.15
3	3	-2	2.4843	2.4815	35.38
0	6	1	2.4693		
3	5	0	2.4387	2.4502	27.69
4	2	-2	2.3970	2.3754	26.15
2	4	-2	2.3915		
5	1	-1	2.3490	2.3530	23.05
1	7	0	2.3454		
1	1	2	2.2773	2.2885	21.54
5	3	-1	2.1849	2.1775	12.31
3	5	-2	2.1393	2.1184	15.64
5	1	0	2.1056		
2	6	1	2.0759	2.0843	16.95
				2.0708	18.56
1	7	1	2.0627		
3	7	-1	2.0368	2.0521	23.05
4	6	-1	2.0367		
4	0	1	2.0240	2.0318	12.28
2	0	2	2.0063	2.0126	11.08
3	7	0	1.9887	1.9943	19.38
5	3	0	1.9850		
3	1	-3	1.9249		
2	0	-3	1.9219	1.9477	19.35
6	0	-2	1.9156	1.9187	21.85
6	2	-1	1.9130		
0	6	2	1.9072		
2	2	-3	1.8737	1.8878	24.0
4	6	-2	1.8667		
5	5	-2	1.8394	1.8303	12.0

Table 2-2. (cont'd)

h	k	l	d _{calc.} (Å)	d _{obs.} (Å)	%I _{obs.}
5	5	0	1.7954	1.8034	16.95
3	1	2	1.7437	1.7421	16.83
2	8	1	1.7385		
0	10	0	1.6834	1.6891	13.8
3	9	-1	1.6808		
3	9	0	1.6535	1.6505	12.62
4	8	-2	1.6100	1.6007	10.92
7	3	-1	1.6011	1.5944	8.92

Table 2-3. Calculated and Observed X-ray Powder Diffraction Pattern for α - $\text{K}_8\text{Mo}_9\text{Se}_{40}\cdot 4\text{H}_2\text{O}$

h	k	l	$d_{\text{calc.}}(\text{\AA})$	$d_{\text{obs.}}(\text{\AA})$	%I _{obs.}
0	1	1	13.3261	13.7031	11.1
0	0	2	9.2700	9.5274	73.3
-1	0	1	8.8271	9.0181	83.5
1	1	1	8.5559	8.7747	70.4
-1	-1	1	8.1904	8.3456	29.8
0	-2	2	6.4206	6.5356	35.7
1	-2	1	6.1525	6.2420	100.0
0	3	0	6.1451		
0	-3	1	5.7685	5.8520	32.4
1	-2	2	5.3312	5.4254	24.4
-1	1	3	4.9824	5.0522	21.7
-1	3	1	4.8840	4.9295	17.6
0	4	1	4.5127	4.5532	12.7
-2	2	0	4.2947	4.3226	11.5
0	-1	5	3.6090	3.6588	21.7
2	3	3	3.5397	3.5332	20.6
1	0	5	3.5303		
0	2	5	2.4859	2.4262	40.7
-2	0	4	3.3737	3.3294	26.8
3	2	1	3.2935	3.2973	38.5
3	-1	1	3.2646	3.2618	46.0
-1	-2	5	3.2362	3.2012	36.4
1	3	5	3.1600	3.1001	28.6
2	5	2	3.0349	3.0275	19.1
-3	-1	3	2.9381	2.9596	50.8
-1	-1	6	2.8886	2.9264	24.4
0	3	6	2.8034	2.8330	29.8
3	4	3	2.6763	2.7014	14.0
0	7	0	2.6336	2.6416	35.0
2	6	3	2.5757	2.5842	24.4
-4	0	1	2.5248	2.5270	26.2
-2	6	0	2.5231		
0	-4	6	2.5229		
-1	6	4	2.4629	2.4681	44.4
-3	-5	5	2.4600		
2	6	4	2.4361	2.4276	47.6
-3	1	5	2.4286		
1	7	4	2.3236	2.3225	31.7
2	5	6	2.2702	2.2765	22.2
-1	-8	1	2.2692		
2	-2	7	2.2691		
-2	-7	3	2.2347	2.2351	34.4
-1	-1	8	2.2220		
3	4	6	2.1724	2.1685	20.6
1	-7	4	2.1696		
3	1	7	2.1422	2.1371	19.1

Table 2-4. Calculated and Observed X-Ray Powder Diffraction Pattern for β -K₈Mo₉Se₄₀

h	k	l	d _{calc.} (Å)	d _{obs.} (Å)	%I _{obs.}
1	-1	0	14.4218	14.5326	100.00
0	2	0	10.1303	10.2054	5.64
0	1	-1	10.0250	10.0521	6.54
1	0	-1	9.4574	9.5053	10.25
1	1	-1	9.0797	9.0832	64.28
1	0	1	8.7075	8.7129	21.42
1	-1	1	8.6625	8.6705	36.94
1	2	0	8.6600		
0	1	1	8.5325	8.5434	18.65
2	1	0	8.3450	8.3365	9.15
1	-2	1	7.3849	7.3852	3.64
2	-2	0	7.2109	7.2265	21.03
0	3	0	6.7536	6.7602	6.25
2	-1	1	6.7027	6.7068	8.10
1	-3	0	6.5254	6.5264	8.11
3	-1	0	6.1758	6.1750	8.27
2	-3	0	5.7166	5.7156	11.23
3	-2	0	5.5634	5.5670	7.24
2	0	-3	3.3380	3.3291	4.21
2	1	3	3.0052	2.9943	4.05
4	5	0	2.9687	2.9614	3.94
4	2	-3	2.9026	2.9027	3.66
1	5	-3	2.8992		

Table 2-5. Calculated and Observed X-Ray Powder Diffraction Pattern for $K_6Mo_6Se_{27} \cdot 6H_2O$

h	k	l	$d_{calc.} (\text{\AA})$	$d_{obs.} (\text{\AA})$	% $I_{obs.}$
0	2	0	8.9210	8.7682	100.00
1	1	-1	8.6967		
1	1	1	8.0321	8.0716	18.85
0	0	4	6.6791	6.7197, 6.341	45.48, 20.22
1	2	3	5.1023	5.0998	20.22
1	5	0	3.3643	3.3881	16.88
0	6	0	2.9737	2.9536	23.10
2	4	-5	2.9726		
3	3	-1	2.9537		
0	6	2	2.9026	2.8834	26.18
2	4	4	2.8740		
1	2	8	2.8728		
3	3	1	2.8693		
2	5	1	2.8690		
2	4	-7	2.6515	2.6576	11.11
3	1	5	2.6387		
0	4	9	2.4712	2.4723	20.22
0	2	11	2.3434	2.3258	13.58
3	4	-7	2.3354		
3	5	-5	2.3260		
2	3	-10	2.3258		
4	3	0	2.3226		
1	5	8	2.3117		
3	3	-9	2.2396	2.2220	12.17
1	1	-12	2.2303		
1	2	11	2.2116		
2	6	-7	2.2083	2.1892	17.52
3	6	1	2.2018		
4	0	-8	2.1806		
2	3	-11	2.1718		
4	4	-5	2.1339	2.1343	13.85
0	7	7	2.1196		
4	2	-8	2.1182		
4	0	6	2.0634	2.0578	21.63
1	1	-13	2.0632		
3	1	9	2.0595		
3	6	4	2.0518		
4	1	7	1.9582	1.9581	10.60
3	3	9	1.9578		
3	2	-12	1.9549		
4	5	3	1.9540		
2	3	11	1.9531		
1	7	8	1.9517		
6	3	0	1.6185	1.6178	8.23
5	3	7	1.6174		
2	5	13	1.6133		
5	5	-9	1.6091		

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Table 2-6. Calculated and Observed X-ray Powder Diffraction Pattern for $K_2Mo_3Se_{18}$

h	k	l	$d_{calc.}(\text{\AA})$	$d_{obs.}(\text{\AA})$	%I _{obs.}
0	0	1	9.4804	9.3686	27.1
1	0	0	9.1712		
0	1	1	7.5879	7.7304	41.4
1	1	0	7.4265	7.3969	44.4
-1	1	1	7.2783		
0	2	0	6.3285	6.4316	19.2
0	2	1	5.2635	5.2801	39.2
1	2	0	5.2088	5.1985	34.9
-2	0	2	4.4481	4.4949	23.6
1	2	1	4.1393	4.1064	7.6
2	2	0	3.7132	3.7449	12.7
-2	2	2	3.6391	3.6718	15.8
2	1	1	3.4162	3.4092	27.1
-2	1	3	3.3031	3.3024	37.0
0	4	0	3.1642	3.1813	39.2
0	0	3	3.1601		
-1	2	3	3.0736	3.0817	37.7
0	1	3	3.0660		
-2	2	3	3.0099	3.0118	46.8
1	4	0	2.9912	2.9913	50.1
-3	2	1	2.9886		
-3	1	3	2.8872	2.9067	25.9
1	4	1	2.7392	2.7594	26.5
-1	4	2	2.7165	2.7136	14.9
2	4	0	2.6044	2.6033	55.2
-1	0	4	2.5960		
-2	1	4	2.5926		
-4	0	2	2.5675	2.5519	24.1
-1	1	4	2.5430		
-4	1	2	2.5163	2.5293	37.7
2	2	2	2.5114		
-4	1	1	2.4539	2.4499	62.3
-3	1	4	2.4492		
-4	1	3	2.4109	2.4089	56.0
-4	2	2	2.3792	2.3861	19.8
-1	4	3	2.3521	2.3332	26.5
0	1	4	2.3296		
1	5	1	2.2975	2.3073	46.0
2	3	2	2.2956		
-4	2	3	2.2893		
			2.2433	2.2364	100.0
			2.2379		
			2.2357		
4	2	0	2.1557	2.1606	31.5

Table 2-6 (cont'd)

h	k	l	d _{calc.} (Å)	d _{obs.} (Å)	%I _{obs.}
-3	3	4	2.1485	2.1385	16.3
3	1	2	2.1319		
1	5	2	2.0707	2.0707	30.9
2	4	2	2.0696		
0	3	4	2.0664		
2	2	3	2.0651		
3	2	2	2.0466	2.0403	19.2
-2	5	3	2.0350		
-2	2	5	2.0126	2.0099	14.9
-5	1	3	2.0084		
-1	4	4	2.0070		
-4	4	2	1.9938	1.9824	18.7
-3	2	5	1.9825		
-5	0	1	1.9747	1.9599	37.7
-2	3	5	1.8963	1.9022	24.7
0	0	5	1.8961		
0	1	5	1.8751	1.8721	11.1
-3	3	5	1.8711		
-1	3	5	1.8433	1.8399	13.6
5	0	0	1.8342		
-5	3	3	1.8323		
-2	5	4	1.8300		
3	4	2	1.7855	1.7828	17.7
-3	6	2	1.7847		
2	1	4	1.7821		
-4	3	5	1.7762	1.7685	19.8
0	7	1	1.7761		
1	7	0	1.7740		
-5	4	2	1.7205	1.7167	18.7
-1	4	5	1.7200		
5	3	0	1.6821	1.6804	11.9
2	7	0	1.6821		
-6	1	2	1.6803		
-5	4	1	1.6752		
-6	2	3	1.6523	1.6583	11.1
5	1	1	1.6518		
-4	6	1	1.6156	1.6153	8.4
-3	6	4	1.6113		
0	0	6	1.5801	1.5785	25.3

Table 2-7. Calculated and Observed X-Ray Powder Diffraction Pattern for $K_{12}Mo_{12}Se_{56}$

h	k	l	$d_{calc.}(\text{\AA})$	$d_{obs.}(\text{\AA})$	% $I_{obs.}$
1	1	0	14.1892	14.6270	8.00
1	1	2	8.2912	8.1495	16.32
0	2	1	8.1218		
2	0	2	7.7423	7.7762	33.73
2	2	0	7.0946	7.1182	100.00
2	2	1	6.7021	6.7197	58.16
0	2	2	6.6898		
0	2	3	5.3980	5.4303	16.74
4	0	2	5.1305	5.1498	28.12
4	2	2	4.4387	4.4453	17.57
0	4	0	4.4255		
0	2	4	4.4244		
0	2	5	3.7104	3.7114	4.50
6	2	1	3.5559	3.5495	17.57
4	2	4	3.5467		
2	2	5	3.5413		
6	2	3	3.1904	3.1992	18.00
0	2	6	3.1785		
4	4	3	3.1462	3.1401	13.59
4	2	5	3.1458		
6	0	4	3.1274		
8	0	0	2.9664	2.9740	24.50
4	0	6	2.9536		
6	2	4	2.9487		
6	4	1	2.9188	2.9232	21.12
4	4	4	2.9137		
4	2	6	2.8017	2.7914	28.12
8	2	1	2.7863		
6	4	3	2.7063	2.7078	18.00
2	2	7	2.6996		
0	4	6	2.6990		
4	4	5	2.6789		
4	6	1	2.6199	2.6251	39.86
6	4	4	2.5540	2.5588	30.86
2	0	8	2.4970	2.4990	17.15
6	2	6	2.4776		
8	4	0	2.4640	2.4692	26.54
8	4	2	2.3954	2.4001	26.54
3	7	1	2.3922		
6	6	1	2.3492	2.3491	18.00
4	6	4	2.3465		
2	6	5	2.3449		
10	2	1	2.2779	2.2728	9.49
3	7	3	2.2709		
4	2	8	2.2677		

Table 2-7. (cont's)

h	k	l	d _{calc.} (Å)	d _{obs.} (Å)	%I _{obs.}
8	0	6	2.2368	2.2269	58.93
10	2	2	2.2365		
6	6	3	2.2340		
6	4	6	2.2294	2.1675	16.74
0	8	2	2.1626		
0	6	7	2.0751		
4	4	8	2.0728	2.0769	15.12
2	8	3	2.0721		
8	6	2	2.0493		
6	6	5	2.0469	2.0490	19.31
0	0	10	2.0434		
2	8	4	2.0014		
8	6	3	1.9997	2.0032	41.14
8	4	6	1.9963		
0	8	5	1.9458		
7	7	3	1.9428	1.9451	13.22
10	4	4	1.9355		
2	6	8	1.9060		
10	2	6	1.9016	1.9040	9.18
3	9	1	1.9005		
0	8	6	1.8555		
0	4	10	1.8552	1.8572	6.38
8	6	6	1.7825		
10	4	6	1.7822		
11	5	5	1.6795	1.7858	16.32
0	10	4	1.6726		
0	8	8	1.6725		
0	2	12	1.6722	1.6757	12.14
6	2	11	1.6519		
8	4	10	1.5729		
				1.5748	11.11

Table 2-8. Summary of Crystallographic Data for (Me₄N)₂Mo₃Se₁₃, K₂Mo₃Se₁₃, α -K₈Mo₉Se₄₀·4H₂O, β -K₈Mo₉Se₄₀, K₆Mo₆Se₂₇·6H₂O, K₂Mo₃Se₁₈, K₁₂Mo₁₂Se₅₆, K₁₀Mo₁₂Se₅₈ and Cs₂Mo₂O₂Se₆.

	(I)	(II)	(III)
formula	(Me ₄ N) ₂ Mo ₃ Se ₁₃	K ₂ Mo ₃ Se ₁₃	α -K ₈ Mo ₉ Se ₄₀ ·4H ₂ O
fw	1462.59	1392.50	4398.7
a, Å	11.578(1)	11.874(3)	10.312(8)
b, Å	11.578(1)	16.834(3)	18.55(3)
c, Å	6.110(2)	5.820(3)	18.57(2)
α , deg	90.0	90.0	87.6(1)
β , deg	120.0	116.65(2)	87.57(7)
γ , deg	90.0	90.0	84.0(1)
Z, V, Å ³	1, 709.4(3)	2, 1040(1)	2, 3523(8)
space group	P3 ₁ m (#157)	Cm (#8)	P $\bar{1}$ (#2)
d _{calc} , g/cm ³	3.423	4.448	4.08
radiation	Mo K α (λ =0.71069 Å)	Mo K α (λ =0.71069 Å)	Mo K α (λ =0.71069 Å)
μ (Mo K α), cm ⁻¹	177.96	246.64	224
2 θ _{max} , deg	49.9	50.1	45
scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
scan rate, °/min	4	4	2
no. of data collected	992	997	9888
no. of unique data	502	951	8638
no. of observed data	438 (I>3 σ (I))	849 (I>3 σ (I))	3592 (I>4 σ (I))
no. of variables	42	89	546
final R/R _w , %	6.0/7.5	5.1/6.3	9.2/10.8
temperature, °C	23	-100	-120

Table 2-8. (cont'd)

	(IV)	(V)	(VI)
formula	β -K ₈ Mo ₉ Se ₄₀	K ₆ Mo ₆ Se ₂₇ ·6H ₂ O	K ₂ Mo ₃ Se ₁₈
fw	4334.65	3044.20	1724.3
a, Å	19.10(2)	10.21(2)	10.277(6)
b, Å	20.71(2)	17.84(1)	12.66(1)
c, Å	10.56(1)	27.04(2)	10.624(8)
α , deg	101.04(8)	90.0	90.0
β , deg	94.9(1)	98.8(3)	116.82(5)
γ , deg	93.4(1)	90.0	90.0
Z, V, Å ³	2, 4070(16)	4, 4868(21)	2, 1233(2)
space group	P $\bar{1}$ (#2)	P2 ₁ /n (#14)	P2 ₁ (#4)
d _{calc} , g/cm ³	3.536	4.153	4.644
radiation	Mo K α (λ =0.71069 Å)	Mo K α (λ =0.71069 Å)	Mo K α (λ =0.71069 Å)
μ (Mo K α), cm ⁻¹	194.46	219.98	266.53
2 θ _{max} , deg	45	48.0	45
scan type	$\omega/2\theta$	ω	$\omega/2\theta$
scan rate, °/min	8	2	2
no. of data collected	9535	8706	1824
no. of unique data	9057	7920	1608
no. of observed data	2946 (I>3 σ (I))	3520 (I>3 σ (I))	1382 (I>3 σ (I))
no. of variables	249	391	207
final R/R _w , %	8.8/10.9	7.2/9.2	5.2/8.6
temperature, °C	23	-130	-120

Table 2-8. (cont'd)

	(VII)	(VIII)	(IX)
formula	K ₁₂ Mo ₁₂ Se ₅₆	K ₁₀ Mo ₁₂ Se ₅₈	Cs ₂ Mo ₂ O ₂ Se ₆
fw	6042.26	6121.94	995.448
a, Å	23.73(2)	17.900(6)	22.219(5)
b, Å	17.70(1)	24.611(6)	8.685(3)
c, Å	20.434(9)	10.457(5)	20.162(5)
α , deg	90.0	92.17(4)	90.0
β , deg	90.0	90.47(3)	49.64(2)
γ , deg	90.0	83.26(2)	90.0
Z, V, Å ³	4, 8584(9)	2, 4571(5)	8, 2964(2)
space group	Cmc21	P $\bar{1}$ (#2)	C2/c
d _{calc} , g/cm ³	4.675	4.447	4.460
radiation	Mo K α (λ =0.71069 Å)	Mo K α (λ =0.71069 Å)	Cu K α (λ =1.541780 Å)
μ (Mo K α), cm ⁻¹	257.75	248.97	702.79
2 θ _{max} , deg	50.1°	50	50
scan type	ω -2 θ	ω	ω
scan rate, °/min	8	2	4
no. of data collected	4153	8865	2420
no. of unique data	2531	8495	2359
no. of observed data	2394 (I>3 σ (I))	2668 (I>2.5 σ (I))	1361 (I>3 σ (I))
no. of variables	174	293	99
final R/R _w , %	8.0/5.1	17.9/21.2	12.4/14.5
temperature, °C	23	23	23

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Se

Se

Se

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C 1

C 2

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Table

K₂M

atom

Mo 1

Mo 2

Se 1

Se 2

Se 3

Se 4

Se 5

Se 6

Se 7

Se 8

Se 9

7 1

²B eq

Table 2-9. Positional Parameters and Equivalent Isotropic Displacement Values ($\text{\AA}^2$)^a for $(\text{Me}_4\text{N})_2\text{Mo}_3\text{Se}_{13}$ with Estimated Standard Deviations in Parentheses

atom	x	y	z	B (eq)
Mo	0	0.1388 (3)	0.5262	1.6 (2)
Se (1)	0	0	0.827 (1)	2.3 (2)
Se (2)	-0.2596 (4)	0	0.562 (1)	2.3 (2)
Se (3)	-0.1719 (4)	0	0.2265 (9)	2.1 (2)
Se (4)	0	0.3585 (4)	0.423 (1)	3.1 (2)
Se (5)	0	0.3057 (4)	0.790 (1)	2.9 (2)
N	1/3	2/3	1.014 (8)	3 (1)
C (1)	1/3	2/3	0.74 (1)	0.1
C (2)	0.208 (5)	0.657 (5)	1.055 (7)	5 (1)

$$^a B(\text{eq}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}].$$

Table 2-10. Positional Parameters and Equivalent Isotropic Displacement Values ($\text{\AA}^2$)^a for $\text{K}_2\text{Mo}_3\text{Se}_{13}$ with Estimated Standard Deviations in Parentheses

atom	x	y	z	B (eq)
Mo (1)	1.0000	0	0	1.0 (1)
Mo (2)	0.7735 (4)	0.0824 (1)	-0.2025 (8)	0.86 (9)
Se (1)	0.8460 (9)	0	0.1617	6.4 (4)
Se (2)	0.5660 (5)	0	-0.340 (1)	1.4 (2)
Se (3)	0.6607 (6)	0	-0.610 (1)	1.1 (1)
Se (4)	0.6490 (5)	0.2123 (2)	-0.415 (1)	1.8 (1)
Se (5)	0.6854 (5)	0.1837 (2)	0.006 (1)	2.0 (1)
Se (6)	0.9896 (5)	0.1548 (2)	0.043 (1)	1.4 (1)
Se (7)	0.9415 (4)	0.1026 (2)	-0.3572 (9)	1.1 (1)
Se (8)	1.2374 (6)	0	0.104 (1)	3.0 (2)
Se (9)	1.1883 (6)	0	0.452 (1)	1.7 (2)
K (1)	0.851 (1)	0.3275 (6)	0.459 (3)	4.3 (4)

$$^a B(\text{eq}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}].$$

Table 2-11. Positional Parameters and Equivalent Isotropic Displacement Values ($\text{\AA}^2$)^a for $\alpha\text{-K}_8\text{Mo}_9\text{Se}_{40}\cdot 4\text{H}_2\text{O}$ with Estimated Standard Deviations in Parentheses

atom	x	y	z	B (eq)
Mo1	0.1803 (6)	0.9003 (5)	0.6476 (3)	3.9 (2)
Mo2	-0.0490 (5)	0.8866 (4)	0.7266 (3)	2.9 (2)
Mo3	-0.0189 (5)	0.8364 (5)	0.5891 (3)	3.5 (2)
Mo4	0.3960 (6)	0.6065 (4)	0.7706 (3)	2.6 (2)
Mo5	0.1642 (5)	0.5922 (4)	0.8506 (3)	2.2 (1)
Mo6	0.2030 (6)	0.5328 (5)	0.7159 (4)	3.9 (2)
Mo7	0.4907 (5)	1.1616 (4)	0.9112 (4)	3.0 (2)
Mo8	0.5137 (6)	1.1808 (4)	0.7625 (4)	3.4 (2)
Mo9	0.2701 (6)	1.1849 (4)	0.8295 (4)	3.7 (2)
Se1	-0.0321 (7)	0.9677 (6)	0.6152 (5)	5.0 (2)
Se2	0.4325 (7)	0.9059 (6)	0.6513 (4)	4.9 (2)
Se3	0.3065 (8)	1.0096 (6)	0.6130 (5)	7.7 (3)
Se4	-0.2191 (8)	0.9774 (5)	0.7875 (5)	5.1 (2)
Se5	-0.1576 (7)	0.8691 (5)	0.8532 (4)	3.5 (2)
Se6	-0.0761 (7)	0.7380 (7)	0.5025 (4)	5.6 (3)
Se7	-0.1505 (7)	0.8596 (6)	0.4743 (4)	6.1
Se8	0.1712 (6)	0.8317 (5)	0.7708 (3)	2.2 (2)
Se9	0.1370 (7)	0.9560 (5)	0.7735 (5)	4.7 (2)
Se10	-0.0767 (6)	0.7550 (5)	0.6984 (3)	2.2 (2)
Se11	-0.2432 (6)	0.8414 (5)	0.6611 (3)	3.1 (2)
Se12	0.1893 (7)	0.8655 (7)	0.5123 (4)	6.5 (3)
Se13	0.2109 (6)	0.7731 (6)	0.5994 (3)	4.0 (2)
Se14	0.1809 (6)	0.6665 (5)	0.7371 (3)	2.9 (2)
Se15	0.6473 (7)	0.6193 (6)	0.7652 (4)	4.4 (2)
Se16	0.5091 (7)	0.7205 (5)	0.7260 (4)	3.8 (2)
Se17	-0.0092 (6)	0.6902 (5)	0.9013 (3)	2.7 (2)
Se18	0.0403 (7)	0.5857 (6)	0.9778 (4)	3.8 (2)
Se19	0.0764 (8)	0.5489 (7)	0.5990 (4)	6.7 (3)
Se20	0.152 (1)	0.4308 (6)	0.6312 (5)	8.6 (3)
Se21	0.3896 (7)	0.5449 (5)	0.8963 (4)	3.6 (2)

Table 2-11. (cont'd)

atom	x	y	z	B (eq)
Se22	0.3396 (7)	0.6722 (5)	0.8912 (3)	2.6 (2)
Se23	0.1574 (7)	0.4574 (5)	0.8306 (5)	4.1 (2)
Se24	-0.0206 (6)	0.5374 (5)	0.7888 (4)	3.1 (2)
Se25	0.4327 (7)	0.4731 (6)	0.7361 (5)	5.2 (2)
Se26	0.4078 (7)	0.5663 (6)	0.6399 (4)	5.8 (2)
Se27	0.4284 (7)	1.0723 (5)	0.8250 (4)	2.8 (2)
Se28	0.5779 (7)	1.0630 (5)	1.0027 (4)	4.2 (2)
Se29	0.5972 (7)	1.1821 (5)	1.0349 (4)	4.5 (2)
Se30	0.6352 (7)	1.1007 (6)	0.6644 (4)	4.1 (2)
Se31	0.6466 (8)	1.2269 (6)	0.6498 (5)	5.3 (2)
Se32	0.0675 (7)	1.1164 (6)	0.8226 (5)	4.9 (2)
Se33	0.0277 (8)	1.2433 (7)	0.8226 (8)	9.4 (4)
Se34	0.6112 (7)	1.2610 (5)	0.8488 (5)	4.1 (2)
Se35	0.7164 (6)	1.1434 (5)	0.8400 (4)	3.2 (2)
Se36	0.3034 (7)	1.1832 (6)	0.6900 (5)	5.2 (2)
Se37	0.3430 (7)	1.2875 (6)	0.7498 (6)	5.4 (2)
Se38	0.3142 (7)	1.2678 (6)	0.9286 (6)	5.4 (3)
Se39	0.2575 (7)	1.1514 (6)	0.9676 (5)	4.9 (2)
Se40	0.4239 (8)	0.3935 (6)	0.8667 (7)	6.9 (3)
K1	0.474 (2)	0.137 (2)	0.5158 (9)	7.8 (8)
K2	0.516 (2)	0.893 (1)	0.817 (1)	5.2 (5)
K3	0.053 (2)	0.847 (2)	0.332 (1)	9.2 (9)
K4	0.329 (2)	0.293 (1)	0.101 (1)	6.4 (6)
K5	0.090 (2)	0.821 (2)	0.002 (2)	6 (1)
K5'	0.097 (3)	-1.026 (2)	0.050 (2)	4.5 (9)
K6	0.270 (3)	0.565 (2)	0.110 (1)	6 (1)
K6'	0.137 (3)	0.718 (3)	0.048 (2)	2.9 (8)
K7	-0.233 (4)	0.506 (3)	0.639 (2)	4 (1)
K7'	0.260 (3)	0.431 (3)	0.051 (2)	7 (1)
K8	-0.527 (4)	1.375 (3)	0.547 (2)	7 (1)
K8'	0.345 (5)	0.521 (3)	0.474 (3)	9 (1)

Table 2-11. (cont'd)

atom	x	y	z	B (eq)
O1	0.238 (6)	0.621 (5)	0.453 (4)	10 (2)
O2	0.086 (6)	0.668 (5)	0.353 (3)	9 (2)
O3	0.398 (5)	0.281 (4)	0.455 (3)	6 (1)
O4	0.195 (4)	0.613 (3)	0.253 (2)	5 (1)

$$^a B(\text{eq}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}].$$

Table 2-12. Positional Parameters and Equivalent Isotropic Displacement Values ($\text{\AA}^2$)^a for β -K₈Mo₉Se₄₀ with Estimated Standard Deviations in Parentheses

atom	x	y	z	B (eq)
Mo (1)	0.7565 (5)	0.1959 (3)	0.1881 (6)	3.1 (2)
Mo (2)	0.8325 (5)	0.2369 (3)	0.0008 (6)	3.2 (2)
Mo (3)	0.7341 (5)	0.1277 (3)	-0.0669 (6)	3.1 (2)
Mo (4)	0.8192 (5)	0.5530 (3)	0.1353 (6)	2.8 (2)
Mo (5)	0.8829 (5)	0.5879 (3)	0.3889 (6)	3.3 (2)
Mo (6)	0.7449 (5)	0.5231 (3)	0.3350 (6)	3.1 (2)
Mo (7)	0.5431 (5)	0.7894 (3)	0.4816 (6)	2.7 (2)
Mo (8)	0.5108 (5)	0.7268 (3)	0.2263 (6)	2.9 (2)
Mo (9)	0.5724 (5)	0.8531 (3)	0.2825 (6)	2.7 (2)
Se (1)	0.8490 (6)	0.1338 (4)	0.0762 (8)	3.9 (2)
Se (2)	0.7971 (6)	0.1621 (4)	0.4033 (8)	4.0 (2)
Se (3)	0.7003 (6)	0.2294 (4)	0.4101 (8)	4.1 (2)
Se (4)	0.9665 (6)	0.2611 (4)	-0.0295 (9)	4.8 (2)
Se (5)	0.8907 (6)	0.3379 (4)	-0.0757 (8)	3.7 (2)
Se (6)	0.7401 (6)	0.0085 (4)	-0.1753 (8)	4.4 (2)
Se (7)	0.6427 (6)	0.0590 (4)	-0.2483 (8)	3.6 (2)
Se (8)	0.8606 (6)	0.2916 (4)	0.2453 (8)	3.8 (2)
Se (9)	0.7538 (6)	0.3088 (4)	0.1393 (7)	3.3 (2)
Se (10)	0.6705 (5)	0.0872 (4)	0.1176 (7)	3.3 (2)
Se (11)	0.6350 (5)	0.1788 (4)	0.0524 (7)	3.0 (2)
Se (12)	0.8192 (6)	0.1612 (4)	-0.2327 (8)	3.9 (2)
Se (13)	0.7267 (5)	0.2262 (4)	-0.1717 (8)	3.4 (2)
Se (14)	0.8553 (6)	0.4738 (4)	0.2695 (8)	3.9 (2)
Se (15)	0.8581 (6)	0.4863 (4)	-0.0760 (8)	4.2 (2)
Se (16)	0.8127 (6)	0.5836 (4)	-0.0932 (8)	4.2 (2)
Se (17)	1.0046 (6)	0.5719 (5)	0.506 (1)	5.6 (3)
Se (18)	0.9677 (6)	0.6738 (4)	0.5637 (9)	4.8 (2)
Se (19)	0.6832 (6)	0.4174 (4)	0.3882 (8)	4.3 (2)
Se (20)	0.6184 (6)	0.5078 (4)	0.4192 (8)	4.7 (2)

Table 2-12. (cont'd)

atom	x	y	z	B (eq)
Se(21)	0.9537 (6)	0.6014 (4)	0.1930 (8)	3.9 (2)
Se(22)	0.8637 (6)	0.6693 (4)	0.2446 (7)	3.4 (2)
Se(23)	0.8175 (6)	0.5435 (4)	0.5647 (8)	3.9 (2)
Se(24)	0.7742 (6)	0.6323 (4)	0.4891 (8)	3.5 (2)
Se(25)	0.6943 (6)	0.4818 (4)	0.0914 (8)	4.0 (2)
Se(26)	0.6979 (6)	0.5926 (4)	0.1789 (8)	3.9 (2)
Se(27)	0.4497 (6)	0.8179 (4)	0.3291 (8)	3.4 (2)
Se(28)	0.4724 (6)	0.8095 (4)	0.6851 (8)	4.0 (2)
Se(29)	0.5891 (6)	0.7836 (4)	0.7207 (8)	3.9 (2)
Se(30)	0.3931 (6)	0.6697 (4)	0.0840 (8)	3.6 (2)
Se(31)	0.4979 (6)	0.6156 (4)	0.0577 (8)	4.1 (2)
Se(32)	0.5341 (6)	0.9585 (4)	0.2137 (8)	3.5 (2)
Se(33)	0.6569 (6)	0.9408 (4)	0.2076 (8)	4.1 (2)
Se(34)	0.4704 (6)	0.6746 (4)	0.4177 (8)	3.3 (2)
Se(35)	0.5957 (6)	0.6858 (4)	0.3886 (8)	3.5 (2)
Se(36)	0.5278 (6)	0.7936 (4)	0.0469 (8)	3.4 (2)
Se(37)	0.6310 (5)	0.7606 (4)	0.1516 (7)	3.2 (2)
Se(38)	0.5834 (5)	0.9137 (4)	0.5244 (7)	3.1 (2)
Se(39)	0.6673 (6)	0.8404 (4)	0.4593 (8)	3.4 (2)
Se(40)	0.7358 (6)	0.7291 (5)	0.3388 (9)	5.1 (3)
K(1)	0.578 (1)	-0.0663 (8)	-0.107 (2)	3.5 (5)
K(2)	1.016 (1)	0.411 (1)	0.173 (2)	4.7 (5)
K(3)	0.635 (1)	0.075 (1)	0.438 (2)	5.6 (6)
K(4)	0.457 (1)	0.670 (1)	0.777 (2)	6.3 (6)
K(5)	0.538 (2)	0.500 (1)	0.781 (2)	3.9 (7)
K(5')	0.330 (3)	-0.487 (2)	0.270 (4)	3 (1)
K(6)	0.731 (2)	0.378 (1)	0.711 (2)	4.1 (7)
K(6')	0.830 (4)	0.366 (3)	-0.420 (5)	4 (2)

Table 2-12. (cont'd)

atom	x	y	z	B (eq)
K (8)	0.918 (2)	0.272 (1)	-0.384 (2)	3.2 (7)
K (8')	0.992 (3)	0.125 (2)	-0.394 (5)	4 (1)
K (9)	1.015 (4)	0.021 (3)	-0.350 (6)	6 (2)
K (9')	0.951 (4)	0.082 (3)	-0.607 (5)	5 (2)
K (9*)	0.914 (4)	0.054 (3)	-0.286 (5)	4 (1)

$$^a B(\text{eq}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}].$$

Table 2-13. Positional Parameters and Equivalent Isotropic Displacement Values ($\text{\AA}^2$)^a for $\text{K}_6\text{Mo}_6\text{Se}_{27}\cdot 6\text{H}_2\text{O}$ with Estimated Standard Deviations in Parentheses

atom	x	y	z	B (eq)
Mo (1)	0.3963 (4)	0.2027 (3)	0.1598 (1)	0.6 (2)
Mo (2)	0.5921 (4)	0.2652 (2)	0.1116 (1)	0.6 (2)
Mo (3)	0.3746 (4)	0.3501 (3)	0.1285 (1)	0.5 (2)
Mo (4)	0.4471 (4)	0.2783 (2)	0.3877 (1)	0.6 (2)
Mo (5)	0.6723 (4)	0.3551 (2)	0.4287 (2)	0.7 (2)
Mo (6)	0.6888 (4)	0.2051 (2)	0.4053 (2)	0.7 (2)
Se (1)	0.3590 (5)	0.2417 (3)	0.0701 (2)	1.0 (2)
Se (2)	0.5894 (5)	0.1233 (3)	0.1321 (2)	1.1 (2)
Se (3)	0.6385 (5)	0.2090 (3)	0.1991 (2)	1.0 (2)
Se (4)	0.5450 (5)	0.3987 (3)	0.0737 (2)	0.9 (2)
Se (5)	0.6123 (5)	0.3876 (3)	0.1611 (2)	0.9 (2)
Se (6)	0.1841 (5)	0.2809 (3)	0.1629 (2)	1.2 (2)
Se (7)	0.3771 (5)	0.3112 (3)	0.2187 (2)	0.8 (2)
Se (8)	0.2502 (5)	0.0846 (3)	0.1411 (2)	1.5 (2)
Se (9)	0.3325 (6)	0.1068 (3)	0.2262 (2)	1.5 (2)
Se (10)	0.6930 (5)	0.2315 (3)	0.0315 (2)	1.3 (2)
Se (11)	0.8472 (5)	0.2659 (3)	0.1023 (2)	1.1 (2)
Se (12)	0.1955 (6)	0.4260 (3)	0.0709 (2)	1.6 (2)
Se (13)	0.2804 (6)	0.4819 (3)	0.1475 (2)	1.7 (2)
Se (14)	0.5704 (5)	0.2528 (3)	0.4735 (2)	0.8 (2)
Se (15)	0.4359 (5)	0.4148 (3)	0.4213 (2)	0.9 (2)
Se (16)	0.5288 (5)	0.3937 (3)	0.3469 (2)	0.9 (2)
Se (17)	0.8898 (5)	0.2778 (3)	0.4525 (2)	1.0 (2)
Se (18)	0.8201 (5)	0.3056 (3)	0.3679 (2)	0.7 (2)
Se (19)	0.4646 (5)	0.1336 (3)	0.3766 (2)	0.7 (2)
Se (20)	0.5495 (5)	0.2130 (3)	0.3198 (2)	0.8 (2)
Se (21)	0.2109 (5)	0.2561 (3)	0.4099 (2)	1.1 (2)

Table 2-13. (cont'd)

atom	x	y	z	B (eq)
Se(22)	0.2231 (5)	0.2878 (3)	0.3267 (2)	1.3 (2)
Se(23)	0.7476 (6)	0.4285 (3)	0.5103 (2)	1.4 (2)
Se(24)	0.7879 (5)	0.4877 (3)	0.4376 (2)	1.2 (2)
Se(25)	0.7873 (5)	0.0876 (3)	0.4560 (2)	1.1 (2)
Se(26)	0.8259 (6)	0.0965 (3)	0.3715 (2)	1.3 (2)
Se(27)	0.6584 (5)	0.3396 (3)	0.2665 (2)	1.0 (2)
K(1)	0.378 (1)	0.5822 (8)	0.0518 (5)	3.1 (3)
K(2)	0.610 (1)	-0.0474 (7)	0.3999 (4)	1.6 (2)
K(3)	0.063 (2)	0.1357 (9)	0.2919 (5)	3.7 (3)
K(4)	0.955 (1)	0.1028 (8)	0.0548 (5)	2.5 (3)
K(5)	0.593 (2)	0.076 (1)	0.9385 (6)	4.1 (4)
K(6)	0.626 (2)	0.008 (1)	0.2429 (6)	4.2 (4)
O(1)	0.134 (4)	0.605 (2)	-0.002 (1)	2.6 (8)
O(2)	0.499 (3)	-0.071 (2)	0.302 (1)	1.3 (7)
O(3)	0.887 (4)	0.029 (2)	0.247 (1)	2.3 (8)
O(4)	-0.031 (4)	0.124 (2)	0.177 (1)	4 (1)
O(5)	-0.050 (5)	0.279 (3)	0.243 (2)	6 (1)
O(6)	0.462 (5)	-0.059 (3)	0.165 (2)	5 (1)

$$^a B(\text{eq}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}].$$

Table 2-14. Positional Parameters and Equivalent Isotropic Displacement Values ($\text{\AA}^2$)^a for $\text{K}_2\text{Mo}_3\text{Se}_{18}$ with Estimated Standard Deviations in Parentheses

atom	x	y	z	B (eq)
Mo1	0.9101 (5)	0.2306 (4)	0.5096 (5)	0.6 (1)
Mo2	0.7514 (5)	0.239	0.6609 (5)	0.7 (1)
Mo3	1.0540 (5)	0.2517 (4)	0.8013 (5)	0.6 (1)
Se1	0.8955 (6)	0.3909 (6)	0.6358 (6)	1.3 (1)
Se2	0.9100 (7)	0.1551 (6)	0.2759 (7)	1.7 (2)
Se3	0.8919 (7)	0.3381 (6)	0.2923 (6)	1.3 (1)
Se4	0.8894 (7)	0.9054 (6)	0.6891 (7)	2.0 (2)
Se5	1.1006 (6)	0.1014 (6)	0.6678 (6)	1.2 (1)
Se6	1.1909 (6)	0.2642 (6)	0.6409 (7)	1.5 (1)
Se7	0.8928 (7)	0.2820 (6)	0.9308 (6)	1.3 (1)
Se8	0.9077 (6)	0.1111 (5)	0.8543 (6)	1.1 (1)
Se9	0.7363 (6)	0.0857 (5)	0.4960 (6)	1.1 (1)
Se10	0.6269 (6)	0.2450 (6)	0.3854 (6)	1.1 (1)
Se11	1.1740 (7)	0.4348 (6)	0.9024 (7)	1.8 (2)
Se12	1.4217 (7)	0.4282 (6)	1.0738 (6)	1.5 (1)
Se13	0.5642 (7)	-0.0363 (6)	0.7027 (7)	1.5 (1)
Se14	0.5263 (6)	0.1495 (5)	0.6714 (6)	1.1 (1)
Se15	1.2831 (7)	0.1891 (6)	1.0340 (7)	1.4 (1)
Se16	1.2375 (8)	0.0043 (6)	1.0190 (8)	2.2 (2)
Se17	0.5389 (6)	0.4265 (6)	0.8310 (6)	1.3 (1)
Se18	0.5544 (6)	0.3871 (6)	0.6217 (6)	1.5 (1)
K1	0.736 (2)	0.652 (2)	0.661 (2)	3.2 (4)
K2	0.585 (2)	0.190 (2)	1.007 (2)	3.7 (5)

^a $B(\text{eq}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table 2-15. Positional Parameters and Equivalent Isotropic Displacement Values ($\text{\AA}^2$)^a for $\text{K}_{12}\text{Mo}_{12}\text{Se}_{56}$ with Estimated Standard Deviations in Parentheses

atom	x	y	z	B (eq)
Mo (1)	0.3142 (2)	0.4543 (3)	0.5756	0.0 (1)
Mo (2)	0.2534 (2)	0.4914 (3)	0.6860 (4)	0.3 (1)
Mo (3)	0.1978 (2)	0.4496 (3)	0.5731 (4)	0.1 (1)
Mo (4)	0.0576 (2)	0.6945 (3)	0.3933 (3)	-0.2 (1)
Mo (5)	0	3/4	0.2878 (5)	0.2 (2)
Mo (6)	0.0569 (2)	0.2338 (3)	0.3911 (3)	0.1 (1)
Mo (7)	0	1/4	0.2757 (5)	0.1 (2)
Se (1)	0.2534 (3)	0.5699 (4)	0.5848 (4)	0.4 (1)
Se (2)	0.4076 (3)	0.3953 (4)	0.5311 (4)	1.0 (1)
Se (3)	0.3914 (3)	0.5244 (4)	0.5099 (4)	0.9 (1)
Se (4)	0.2540 (3)	0.4826 (4)	0.8166 (4)	1.1 (1)
Se (5)	0.2517 (3)	0.6043 (4)	0.7691 (4)	1.1 (1)
Se (6)	0.2581 (3)	0.4318 (4)	0.4689 (4)	0.4 (1)
Se (7)	0.2587 (3)	0.3361 (4)	0.5499 (4)	0.3 (1)
Se (8)	0.3625 (3)	0.5079 (4)	0.6836 (4)	0.6 (1)
Se (9)	0.3240 (3)	0.3825 (4)	0.6842 (4)	0.6 (1)
Se (10)	0.1440 (3)	0.5058 (4)	0.6736 (4)	0.6 (1)
Se (11)	0.1898 (3)	0.3745 (4)	0.6825 (4)	0.4 (1)
Se (12)	0.2527 (3)	0.2570 (4)	0.6762 (4)	0.9 (1)
Se (13)	0.1223 (3)	0.5155 (4)	0.4968 (4)	0.5 (1)
Se (14)	0.1107 (3)	0.3593 (4)	0.5510 (4)	0.5 (1)
Se (15)	0	0.8104 (6)	0.4008 (5)	0.6 (2)
Se (16)	0.1530 (3)	0.6236 (4)	0.4334 (4)	0.6 (1)
Se (17)	0.1344 (3)	0.7495 (4)	0.4726 (4)	0.8 (1)
Se (18)	0	0.5749 (6)	0.4081 (5)	0.6 (2)
Se (19)	0	0.6571 (6)	0.4984 (5)	0.3 (2)
Se (20)	0	0.8761 (7)	0.2244 (6)	1.7 (2)

Table 2-15. (cont'd)

atom	x	y	z	B (eq)
Se(21)	0	0.7634 (7)	0.1621 (6)	1.7 (2)
Se(22)	0.1100 (3)	0.7651 (4)	0.2995 (4)	0.5 (1)
Se(23)	0.0670 (3)	0.6389 (4)	0.2783 (4)	0.5 (1)
Se(24)	0	0.5203 (6)	0.2673 (6)	1.0 (2)
Se(25)	0	0.3508 (6)	0.3672 (5)	0.4 (2)
Se(26)	0.1346 (3)	0.3151 (4)	0.4455 (4)	0.5 (1)
Se(27)	0.1507 (3)	0.1855 (4)	0.4507 (4)	1.0 (1)
Se(28)	0	0.2355 (6)	1/2	0.4 (2)
Se(29)	0	0.1224 (5)	0.4341 (5)	0.3 (2)
Se(30)	0	0.3595 (6)	0.1894 (6)	0.9 (2)
Se(31)	0	0.2357 (7)	0.1480 (6)	1.4 (2)
Se(32)	0.1095 (3)	0.2734 (4)	0.2854 (4)	0.9 (1)
Se(33)	0.0680 (3)	0.1440 (4)	0.2962 (4)	0.6 (1)
Se(34)	0	0.0279 (7)	0.3221 (6)	1.8 (2)
K(1)	1/2	0.467 (2)	0.635 (2)	3.2 (7)
K(2)	0.3726 (8)	0.184 (1)	0.619 (1)	2.4 (4)
K(3)	0.253 (1)	0.222 (1)	0.340 (1)	3.0 (4)
K(4)	0.378 (1)	0.441 (1)	0.360 (1)	3.1 (5)
K(5)	0.1297 (8)	0.185 (1)	0.621 (1)	2.4 (4)
K(6)	0	0.480 (2)	0.593 (1)	3.2 (6)
K(7)	0.1240 (7)	0.460 (1)	0.3299 (9)	1.6 (3)

$$^a B(\text{eq}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}].$$

3. Results and Discussion

3.1. Synthesis

The syntheses of (I)~(IX) were performed in either thick wall Pyrex-glass tubes or autoclaves at ~135 °C. A very small amount of water is used (~6% filling), and at no time during the reaction is it completely evaporated. The crystals grow in the liquid phase of the container. The small volume of water used is beneficial because it generates supersaturation conditions and promotes crystal growth. The crystals formed during the isotherm of 135°C and not during the cool-down period. These reactions involve complicated redox chemistry between Mo metal and Se_4^{2-} or between MoO_3 and Se_2^{2-} . All the structures except (IX) contain trimeric $[\text{Mo}_3\text{Se}_7]^{4+}$ cores as building blocks in which the formal oxidation state of Mo can be assigned as +4. (IX) contains a dimeric $[\text{Mo}_2\text{O}_2\text{Se}_2]^{2+}$ core in which the formal oxidation state of Mo is +5. MoO_3 was chosen as a starting material because it possesses the advantage of giving clean reactions by replacing oxygen atoms with Se, forming $[\text{MoSe}_x\text{O}_{4-x}]^{2-}$ and hydroxide in aqueous solution. $[\text{MQ}_4]^n-$ (M=Mo, W; Q=S, Se) have been used as starting materials⁴ in chalcogenides synthesis at ambient temperature. Subsequent reactions are presumingly intramolecular electron transfer or self-redox reactions followed by assembling of metal centers and chelating polychalcogenide ligands. The x values of Se_x^{2-} polyselenide chains are crucial for these reactions. Longer polyselenide chains serve as oxidizing agents which accept electrons from Mo metal and break apart into shorter (poly)selenide chains. Heating long polyselenides

($x \geq 4$) themselves at the same hydrothermal condition results in the formation elemental Se crystals and shorter Se_y^{2-} ($y < 4$) species due to the self-redox chemistry between the polyselenides. MoO_3 , in which Mo has the +6 oxidation state, also serves as an oxidizing agent. It is thus not surprising that the reaction of MoO_3 and Se_4^{2-} also gives elemental Se crystals. To avoid the formation of elemental selenium, shorter polyselenide chains have to be used. Se_2^{2-} was found to be the best polyselenide length if MoO_3 is used as the molybdenum source. To use longer polyselenide chains as starting material, molybdenum metal was found suitable because it is a reducing agent, giving electrons to break polyselenides into shorter chains, and thus driving the reactions away from selenium formation.

It is interesting to comment on how these K/Mo/Se phases might form. The fact that the $[\text{Mo}_3\text{Se}_7]^{4+}$ core occurs in all eight phases characterized thus far suggests that the core has considerable thermodynamic stability and forms readily under hydrothermal conditions. In solution the trinuclear $[\text{Mo}_3\text{Se}_7]^{4+}$ core is probably ligated by Se_x^{2-} ligands. The various $\{[\text{Mo}_3\text{Se}_7](\text{Se}_x)_n\}^{z-}$ complexes present in solution during the reaction provide an efficient mass-transport and dissolution-precipitation mechanism, both of which are necessary for crystal growth. Thus the excess Se_x^{2-} ligands act as effective "mineralizers". The role of counterion in phase formation is not clear at the moment but preliminary observations indicate that it must be significant. For example, the formation and crystallization of $[\text{Mo}_2\text{O}_2\text{Se}_6]^{2-}$ in the presence of Cs^+ suggests that more than one species other than $[\text{Mo}_3\text{Se}_7]^{4+}$ exist in the polyselenide solutions. So far, no $[\text{Mo}_3\text{Se}_7]^{4+}$ containing phase has been

isolated as a Cs^+ salt. The size of counterion is an important factor for the crystallization of certain species.

The reaction of MoO_3 and K_2Se_2 in 1:2 ratio for three days consistently gave crystals of $\alpha\text{-K}_6[\text{Mo}_3\text{Se}_{13}]_3\cdot(\text{K}_2\text{Se})\cdot 4\text{H}_2\text{O}$ (III). Surprisingly, the same reaction for an elongated reaction time afforded $\text{K}_2\text{Mo}_3\text{Se}_{13}$ (II) crystals. However, the reaction is not consistent. Sometimes a few very large crystals (up to ~ 7 mm in length) of $\alpha\text{-K}_6[\text{Mo}_3\text{Se}_{13}]_3\cdot(\text{K}_2\text{Se})\cdot 4\text{H}_2\text{O}$ (III) were obtained with prolonged reaction time. $\text{K}_2\text{Mo}_3\text{Se}_{13}$ is likely to be slightly more thermodynamically stable (insoluble) than $\alpha\text{-K}_6[\text{Mo}_3\text{Se}_{13}]_3\cdot(\text{K}_2\text{Se})\cdot 4\text{H}_2\text{O}$ (III). Therefore small fluctuations in reaction conditions may alter the reaction route to the growth of larger crystals of $\text{K}_6[\text{Mo}_3\text{Se}_{13}]_3\cdot(\text{K}_2\text{Se})\cdot 4\text{H}_2\text{O}$ (III). With the addition of $[\text{Me}_4\text{N}]^+$, $[\text{Mo}_3\text{Se}_{13}]^{2-}$ can be crystallized consistently as an organic counterion salt, $(\text{Me}_4\text{N})_2[\text{Mo}_3\text{Se}_{13}]$ (I). No $[(\text{Mo}_3\text{Se}_{13})_n(\text{Se})]^{2(n+1)-}$ phases were observed with the addition of organic counterions. Na_2Se_2 was used as starting material to avoid the competition of K/Mo/Se phases.

$\beta\text{-K}_8\text{Mo}_9\text{Se}_{40}$ (IV) formed consistently only at the presence of $[\text{Et}_4\text{N}]^+$ but did not include the organic cations in the crystal lattice. The function of $[\text{Et}_4\text{N}]^+$ is not clear. Based on the fact that (IV) does not contain solvated water molecules and is insoluble in water, it is likely the (IV) crystallized in a hydrophobic phase provided by the organic Et_4N^+ cation.

$\alpha\text{-K}_8\text{Mo}_9\text{Se}_{40}\cdot 4\text{H}_2\text{O}$ (III), $\beta\text{-K}_8\text{Mo}_9\text{Se}_{40}$ (IV) and $\text{K}_6\text{Mo}_6\text{Se}_{27}\cdot 6\text{H}_2\text{O}$ (V) can be expressed by the general formula, $\text{K}_m[\text{Mo}_3\text{Se}_{13}]_n\cdot(\text{K}_2\text{Se})\cdot x\text{H}_2\text{O}$ ($m=6$, $n=3$ for (III) and (IV); $m=4$, $n=2$ for (V)). They are the cocrystallization products of the $[\text{Mo}_3\text{Se}_{13}]^{2-}$ cluster and the Se_2^{2-} anion in the ratio of 3:1 and 2:1, respectively. The tendency of such

cocrystallization is due to the affinity of $[\text{Mo}_3\text{Se}_7]^{4+}$ cores for Se^{2-} anions and will be discussed in Section 3.3. (III) and (IV) are isostructural and differ in the way the $[\text{Mo}_3\text{Se}_{13}]^{2-}$ clusters and Se^{2-} anions are packed in the crystal lattice. (V) was obtained under the same condition as (III) except two more equivalents of K_2Se_2 were added to the reaction mixture. With more Se_x^{2-} ligand in solution, (V), which has a larger K_2Se to $\text{K}_2\text{Mo}_3\text{Se}_{13}$ ratio than (III), is crystallized.

$\text{K}_2\text{Mo}_3\text{Se}_{18}$ (VI) was obtained by reacting Mo and K_2Se_4 in 1:1.5 ratio. Upon using 2~3 equivalents of K_2Se_4 , $\text{K}_{10}\text{Mo}_{12}\text{Se}_{58}$ (VIII) was obtained. Unlike the crystals of (I)~(V), plate-like crystals of (VI) rarely grow larger than 0.5 mm. (VIII) tends to grow tiny hair-like crystals with poor crystallinity. Both (VI) and (VIII) are extended structures with $[\text{Mo}_3\text{Se}_7]^{4+}$ cores linked by tetraselenides in (VI) and diselenide, hexaselenides in (VIII) (see Section 3.2.3 and 3.2.5). This indicates the Mo metal is oxidized by Se_4^{2-} and similar $\{[\text{Mo}_3\text{Se}_7](\text{Se}_x)_n\}^{z-}$ complexes are present in the polyselenide solutions. The formation of (VI) and (VIII) instead of $\text{K}_m[\text{Mo}_3\text{Se}_{13}]_n \cdot (\text{K}_2\text{Se})$ phases in the $\text{Mo}/\text{Se}_4^{2-}$ solutions is likely because more longer Se_x^{2-} chains are available and thus direct the reactions to the crystallization of (VI) and (VIII). In very few instances, the reaction of Mo and K_2Se_4 in a 1:2 ratio gave crystals of $\text{K}_{12}\text{Mo}_{12}\text{Se}_{56}$ (VII), which were found to be reproducible by reacting a mixture of Mo, MoO_3 and K_2Se_3 in a ratio of 3:2:6. Since both Mo and MoO_3 were used in this reaction, Se_3^{2-} which has medium polyselenide length between Se_2^{2-} and Se_4^{2-} was chosen.

We note here that known Mo/Se anions such as $[\text{MoSe}_4]^{2-}$ and $[\text{MoSe}_9]^{2-}$,⁴ typically synthesized at ambient temperature by using conventional solution methods, were not observed under our hydrothermal

conditions nor did we observe any MoSe₂ impurity. We also did not detect formation of reduced Mo/Se Chevrel phases, such as the members of the A_{n-2}[Mo_{3n}Se_{3n+2}] (A=alkali ion) family⁶, typically prepared by high temperature ceramic methods.

3.2. Description of Structures

Structures of (Me₄N)₂Mo₃Se₁₃ (I) and K₂Mo₃Se₁₃ (II)

The structures of (I) and (II) contain the same [Mo₃Se₁₃]²⁻ anion. The [Mo₃Se₁₃]²⁻ anion is isostructural to [Mo₃S₁₃]²⁻ and is shown in Figure 2-1. It is composed of a Mo₃ triangular core, a triply bridging monoselenide, three doubly bridging diselenides and three terminal diselenides in an overall C_{3v} symmetry. Therefore, the formula can be expressed as [Mo₃(μ₃-Se)(μ₂-Se₂)₃(Se₂)₃]²⁻. By assigning the charges to Se²⁻ and Se₂²⁻, the formal oxidation state of Mo atoms is 4+. The three axial Se atoms of the three bridging diselenides (Se(3)) are in the opposite side of the Mo₃ plane to that of the triply bridging monoselenide (Se(1)). The other three equatorial Se atoms (Se(2)) lie very close to the Mo₃ plane. This results in a [Mo₃Se₇]⁴⁺ core which has been observed also in Mo₃Se₇X₄ (X=Cl, Br)¹⁹ and Mo₃Se₇(Et₂NCS₂)₄²⁰. Each Mo on the corner of the [Mo₃Se₇]⁴⁺ core is coordinated by a terminal Se₂²⁻ ligand in a side-on fashion. The three terminal diselenides can also be divided into three axial Se atoms (Se(4)) located below the Mo₃ plane and three equatorial Se atoms (Se(5)) slightly above the Mo₃ plane.

Compound (I) crystallizes in a trigonal space group. As shown in the packing diagram of Figure 2-2, all the diselenides are sitting in the three

mirror planes. The charge compensating tetramethylammonium cations are sitting in 3 fold rotation axes. (II) crystallizes in the same monoclinic space group as $(\text{NH}_4)_2\text{Mo}_3\text{S}_{13}$.²¹ The packing diagram of (II) is shown in Figure 2-3. The lattice of (II) has lower symmetry than that of (I) because by replacing tetramethylammonium with smaller K^+ cations, the lattice has to be squeezed to achieve a more efficient packing. This results in a shift of the K^+ cations toward the $[\text{Mo}_3\text{Se}_{13}]^{2-}$ and loss of the three fold rotation axes.

Selected bond distances and bond angles of (I) and (II) are given in Table 2-16 and 2-17 respectively. The average Mo-Mo distances for (I) and (II) are normal at 2.784(6)Å and 2.774(5)Å respectively. The average Mo to the triply bridging Se(1) distance is 2.444(7)Å in (I) and is comparable to those in the $[\text{Mo}_3\text{Se}_7]^{4+}$ containing compounds. However, the corresponding distance in (II) is surprisingly short at 2.37(4)Å. The reason is not clear. Short intercluster Se...Se contacts with a $[\text{Mo}_3\text{Se}_{13}]^{2-}$ below Se(1) as shown by the dashed lines in Figure 2-4b are probably attributed to the shortening of the Mo-Se distances (see discussion below). The Mo to the axial Se (Se(3) in (I); Se(3) and Se(7) in (II)) distances in the bridging diselenides are significantly shorter than those to the equatorial Se atoms (Se(2) in (I); Se(2) and Se(6) in (II)). The former average 2.589(4)Å and 2.549(3)Å; the latter average 2.614(4)Å and 2.621(7)Å for (I) and (II) respectively. The differences in bond strength are consistent with the fact that the equatorial selenides can be extracted by Ph_3P to form $[\text{Mo}_3\text{Se}_4]^{4+}$ cores.²² Similar differences are also observed in the Mo to the terminal diselenide distances. The Mo to the axial Se (Se(5) in (I); Se(5) and Se(9) in (II)) distances average 2.515(6)Å and 2.574(2)Å for (I) and (II) respectively. The Mo to the equatorial Se (Se(4) in (I);

Se(4) and Se(8) in (II)) average 2.620(6)Å and 2.614(10)Å for (I) and (II) respectively. The average bridging diselenide distances are 2.290(6)Å and 2.306(6)Å for (I) and (II); the average terminal diselenide distances are slightly longer at 2.320(7)Å and 2.343(7)Å for (I) and (II) respectively. These values are between the Se-Se distance (2.37Å) of elemental selenium and that of the Se₂ molecule in the gas phase (2.19Å).²³

The [Mo₃Se₁₃]²⁻ anions in (I) and (II) are stacked on top of one another via intercluster Se...Se contacts. The triply bridging Se(1) atom interacts with the three axial selenium atoms of the three bridging diselenides in another [Mo₃Se₁₃]²⁻ anion below it as shown in Figure 2-4. Both Se...Se contacts are significantly shorter than the sum of the van der Waals radius of Se atoms. The Se...Se short contacts are significantly different at 3.147(7)Å and 3.04(1)Å for (I) and (II) respectively. The difference is likely due to the sizes of the counter cations. Potassium cations are smaller than the tetramethylammonium ion so that the [Mo₃Se₁₃]²⁻ are forced to pack more closely in (II). As mentioned earlier, (NH₄)₂Mo₃S₁₃ is isostructural to (II). The size of NH₄⁺ is comparable to K⁺. The corresponding distance of the S...S short contacts is 3.026Å. Since the size of sulfur atoms is smaller, this interaction is not as profound as in the selenium system.

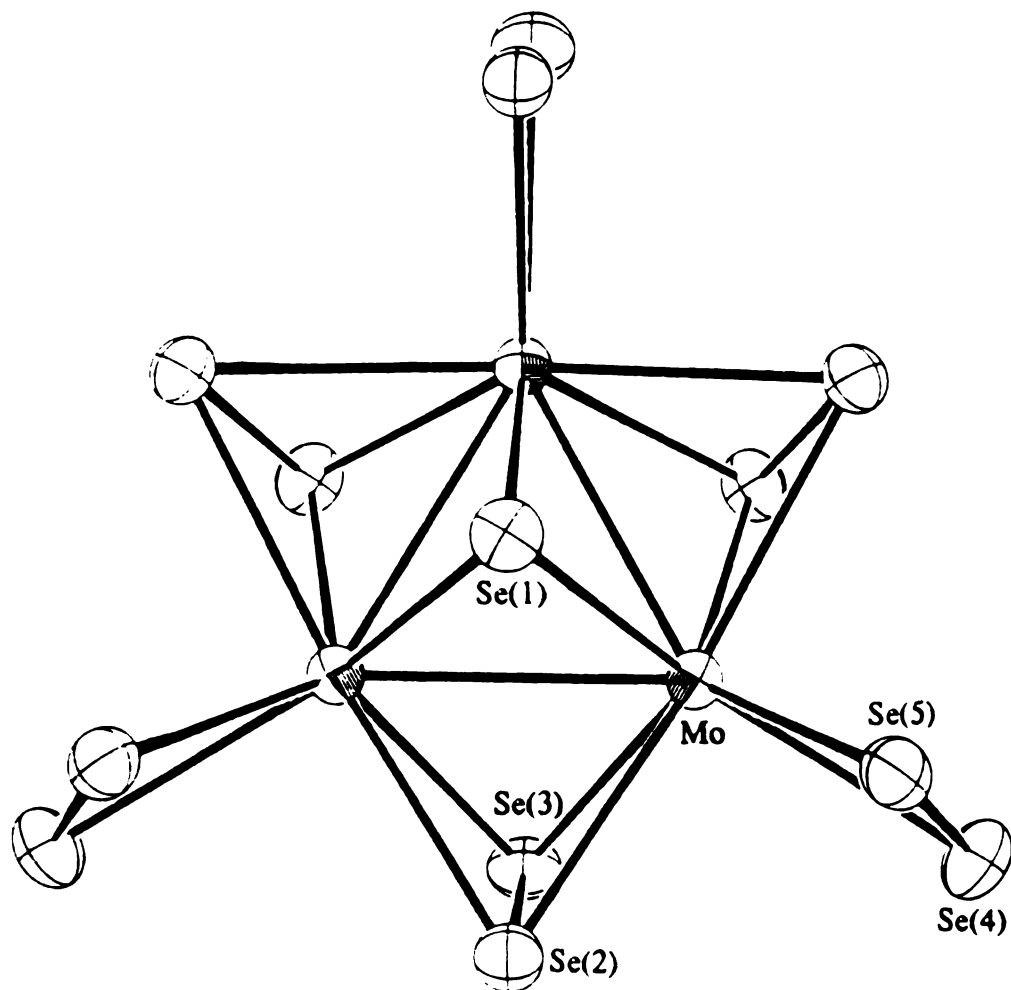


Figure 2-1: ORTEP representation and labeling scheme of [Mo₃Se₁₃]²⁻.

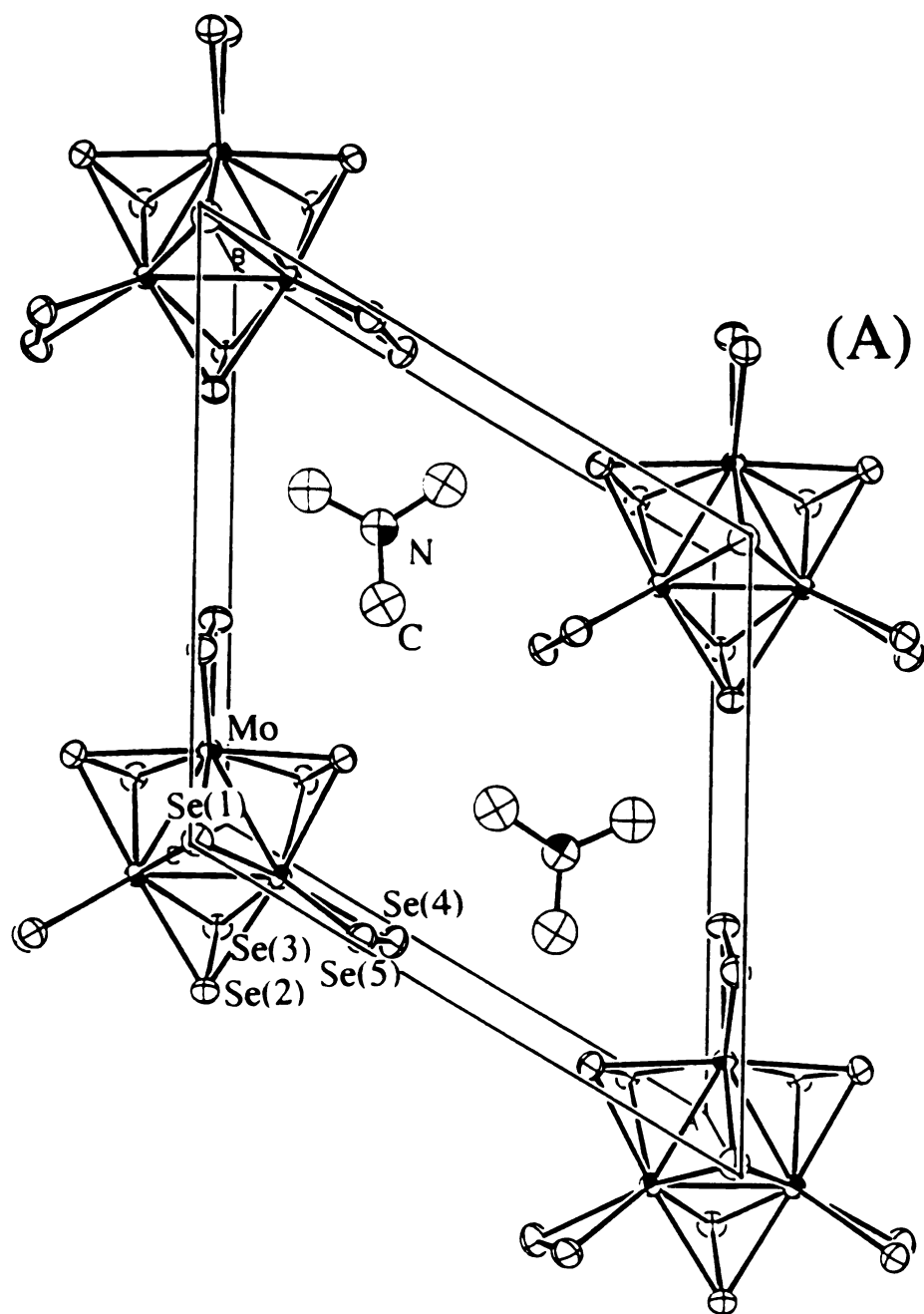
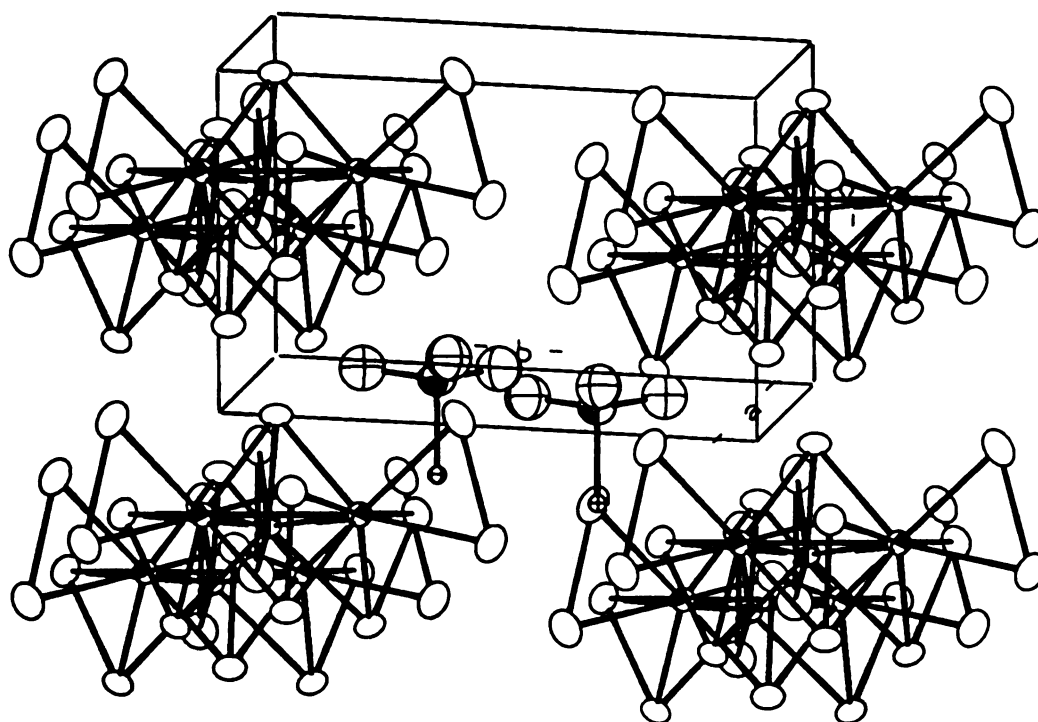


Figure 2-2: Labeling scheme and packing diagram of $(\text{Me}_4\text{N})_2\text{Mo}_3\text{Se}_{13}$.
View down (A) c-axis and (B) a-axis.

(B)

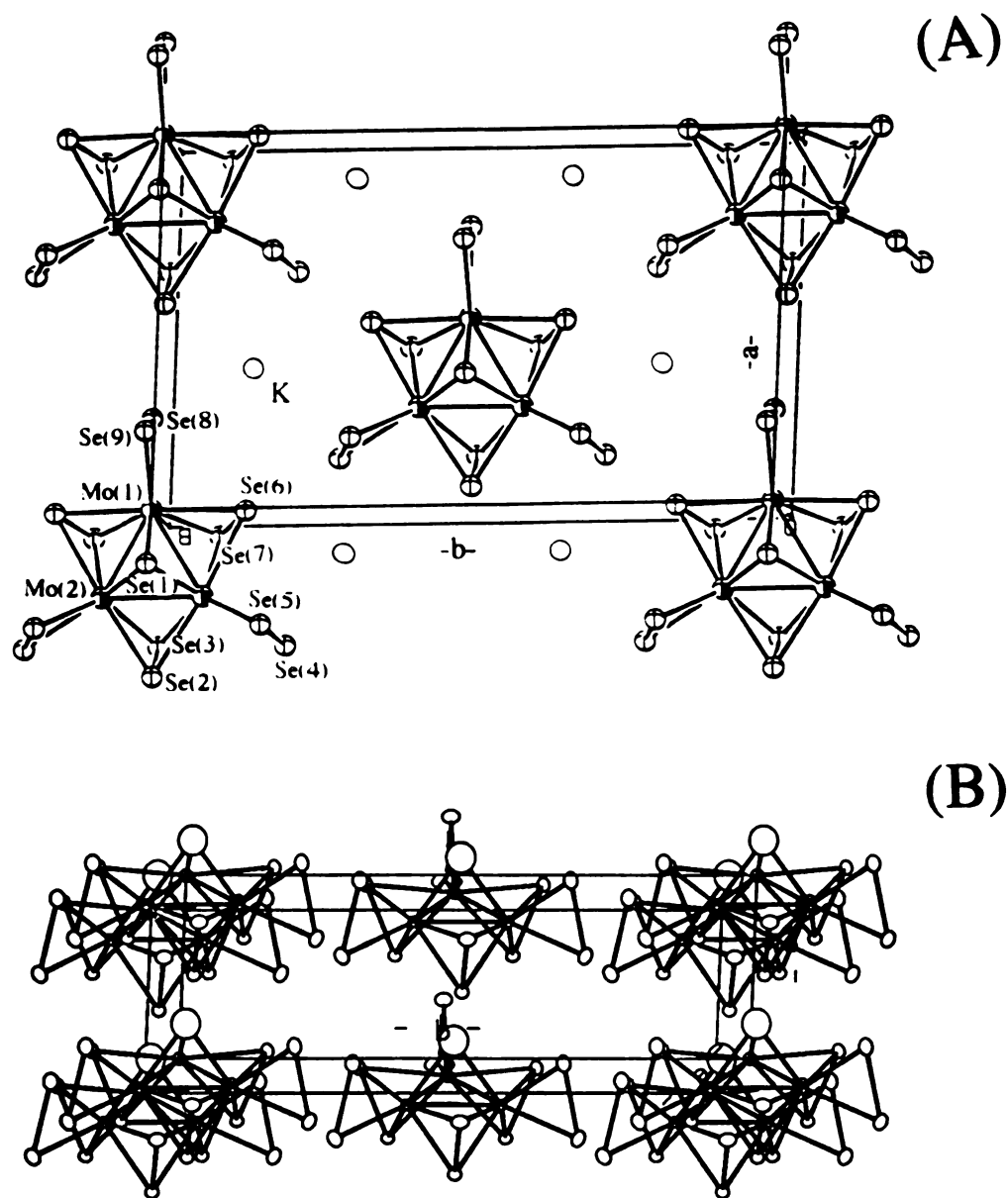


Figure 2-3: Labeling scheme and packing diagram of $\text{K}_2\text{Mo}_3\text{Se}_{13}$. View down (A) c-axis and (B) a-axis.

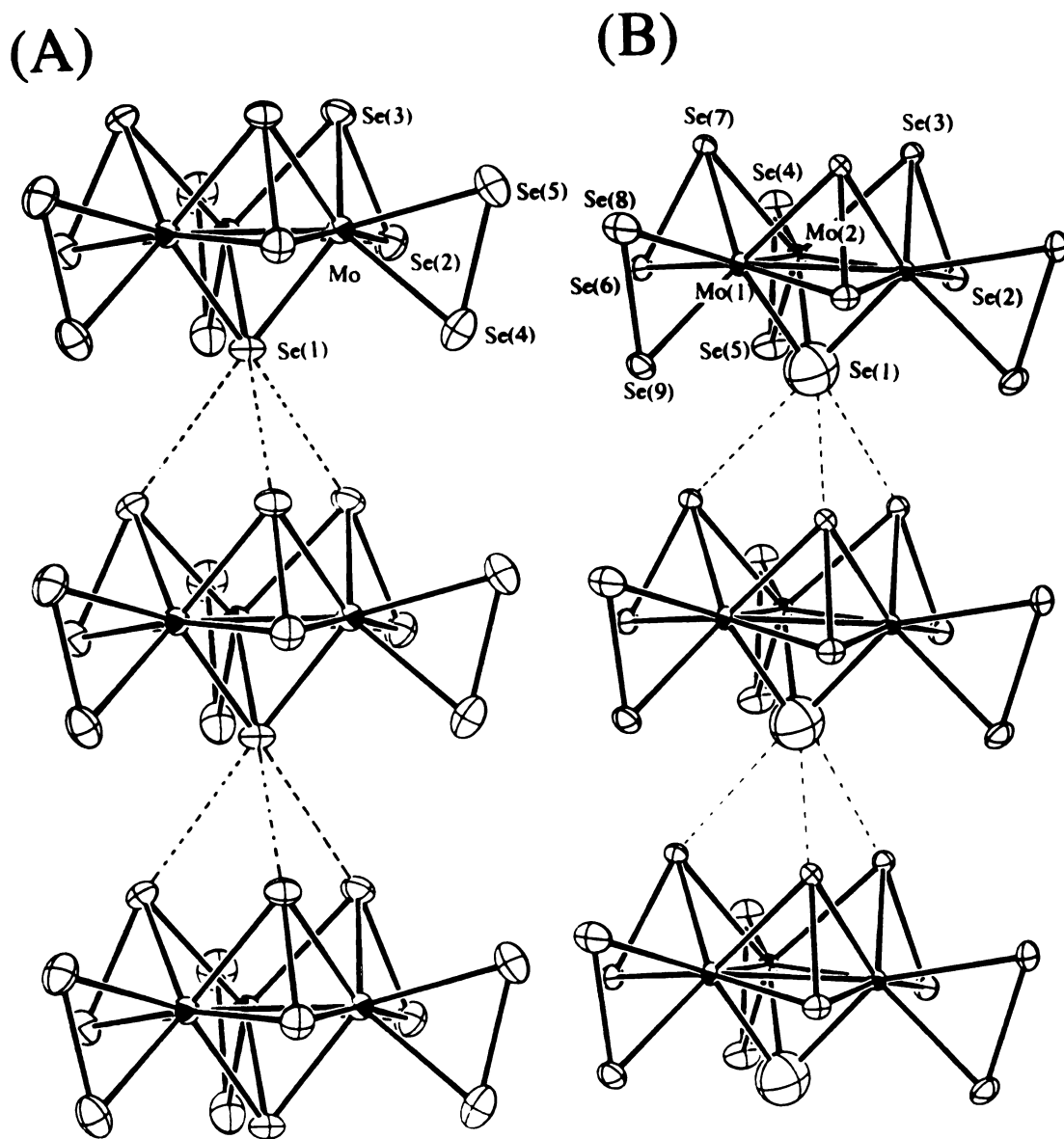


Figure 2-4: Labeling scheme and packing diagram of (A) $(\text{Me}_4\text{N})_2\text{Mo}_3\text{Se}_{13}$ and (B) $\text{K}_2\text{Mo}_3\text{Se}_{13}$. Dashed lines show $\text{Se}\cdots\text{Se}$ contacts.

Table 16. Selected Bond Distances(Å) and Angles(deg) for (Me₄N)₂Mo₃Se₁₃ with Standard Deviations in Parentheses

Selected Bond Distances (Å)			
Mo-Mo	2.784(6)	Mo-Se(5)	2.515(6)
Mo-Se(1)	2.444(7)	Se(2)-Se(3)	2.290(6)
Mo-Se(2)	2.614(4)	Se(4)-Se(5)	2.320(7)
Mo-Se(3)	2.589(4)	N(1)-C(1)	1.67(8)
Mo-Se(4)	2.620(6)	N(1)-C(2)	1.42(4)
Selected Bond Angles (deg)			
Mo-Mo-Mo	60.00	Se(3)-Mo-Se(3)	83.5(2)
Mo-Mo-Se(1)	55.3(1)	Se(3)-Mo-Se(4)	93.4(1)
Mo-Mo-Se(2)	57.83(9)	Se(3)-Mo-Se(5)	129.4(1)
Mo-Mo-Se(3)	57.47(8)	Se(4)-Mo-Se(5)	53.7(2)
Se(1)-Mo-Se(2)	84.8(1)	Mo-Se(1)-Mo	69.4(2)
Se(1)-Mo-Se(3)	112.2(1)	Mo-Se(2)-Mo	64.3(2)
Se(1)-Mo-Se(4)	145.0(2)	Mo-Se(3)-Mo	65.1(2)
Se(1)-Mo-Se(5)	91.3(2)	Mo-Se(2)-Se(3)	63.3(1)
Se(2)-Mo-Se(2)	169.3(3)	Mo-Se(3)-Se(2)	64.5(1)
Se(2)-Mo-Se(3)	52.2(1)	Mo-Se(4)-Se(5)	60.8(2)
Se(2)-Mo-Se(3)	135.5(2)	Mo-Se(5)-Se(4)	65.5(2)
Se(2)-Mo-Se(4)	93.38(9)	C(1)-N-C(2)	100(3)
Se(2)-Mo-Se(5)	88.7(1)	C(2)-N-C(2)	117(2)

Table 17. Selected Bond Distances (Å) and Angles (deg) for K₂Mo₃Se₁₃ with Standard Deviations in Parentheses

Selected Bond Distances (Å)			
Mo(1)-Mo(2)	2.775(4)	Mo(2)-Se(7)	2.553(4)
Mo(2)-Mo(2)	2.773(5)	Se(2)-Se(3)	2.306(6)
Mo(1)-Se(1)	2.40(1)	Se(4)-Se(5)	2.343(5)
Mo(1)-Se(6)	2.626(3)	Se(6)-Se(7)	2.306(5)
Mo(1)-Se(7)	2.548(4)	Se(8)-Se(9)	2.342(7)
Mo(1)-Se(8)	2.603(6)	Se(2)-K	3.70(1)
Mo(1)-Se(9)	2.577(6)	Se(4)-K	3.35(1)
Mo(2)-Se(1)	2.349(4)	Se(4)-K	3.40(1)
Mo(2)-Se(2)	2.620(4)	Se(5)-K	3.47(1)
Mo(2)-Se(3)	2.547(5)	Se(5)-K	3.82(1)
Mo(2)-Se(4)	2.620(4)	Se(8)-K	3.47(1)
Mo(2)-Se(5)	2.573(4)	Se(9)-K	3.47(1)
Mo(2)-Se(6)	2.612(4)		
Selected Bond Angles (deg)			
Mo(2)-Mo(1)-Mo(2)	59.9(1)	Se(3)-Mo(2)-Se(7)	85.0(1)
Mo(1)-Mo(2)-Mo(2)	60.03(6)	Se(4)-Mo(2)-Se(5)	53.6(1)
Mo(2)-Mo(1)-Se(1)	53.4(1)	Se(4)-Mo(2)-Se(6)	94.4(1)
Mo(2)-Mo(1)-Se(6)	57.8(1)	Se(4)-Mo(2)-Se(7)	94.9(1)
Mo(2)-Mo(1)-Se(7)	57.1(1)	Se(5)-Mo(2)-Se(6)	86.6(1)
Mo(2)-Mo(1)-Se(1)	53.4(1)	Se(5)-Mo(2)-Se(7)	128.7(1)
Se(1)-Mo(1)-Se(6)	83.5(1)	Se(6)-Mo(2)-Se(7)	53.0(1)
Se(1)-Mo(1)-Se(7)	110.0(1)	Mo(1)-Mo(2)-Se(1)	55.2(3)
Se(1)-Mo(1)-Se(8)	147.5(2)	Mo(1)-Mo(2)-Se(6)	58.2(1)
Se(1)-Mo(1)-Se(9)	93.7(2)	Mo(1)-Mo(2)-Se(7)	56.9(1)
Se(6)-Mo(1)-Se(6)	165.9(2)	Mo(2)-Mo(2)-Se(1)	53.83(8)
Se(6)-Mo(1)-Se(7)	52.9(1)	Mo(2)-Mo(2)-Se(2)	58.05(7)
Se(6)-Mo(1)-Se(7)	137.9(2)	Mo(2)-Mo(2)-Se(3)	57.02(8)
Se(6)-Mo(1)-Se(8)	94.0(1)	Se(1)-Mo(2)-Se(2)	82.9(2)
Se(6)-Mo(1)-Se(9)	87.7(1)	Mo(1)-Se(1)-Mo(2)	71.5(2)
Se(7)-Mo(1)-Se(7)	85.4(2)	Mo(2)-Se(1)-Mo(2)	72.3(2)
Se(7)-Mo(1)-Se(8)	93.5(1)	Mo(2)-Se(2)-Mo(2)	63.9(1)
Se(7)-Mo(1)-Se(9)	128.8(1)	Mo(2)-Se(2)-Se(3)	61.9(1)

Table 17. (cont'd)

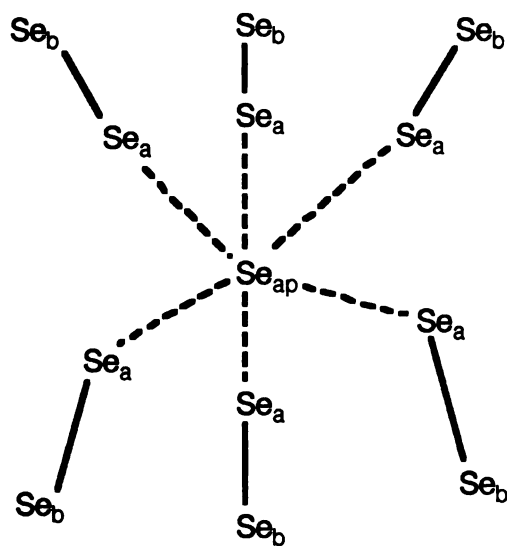
Se(8)-Mo(1)-Se(9)	53.8(2)	Mo(1)-Se(7)-Se(6)	65.3(1)
Se(1)-Mo(2)-Se(3)	110.2(1)	Mo(2)-Se(7)-Se(6)	64.8(1)
Se(1)-Mo(2)-Se(4)	145.1(2)	Mo(1)-Se(8)-Se(9)	62.5(2)
Se(1)-Mo(2)-Se(5)	91.6(2)	Mo(1)-Se(9)-Se(8)	63.7(2)
Se(1)-Mo(2)-Se(6)	84.8(2)	Mo(2)-Se(2)-Se(3)	61.9(1)
Se(1)-Mo(2)-Se(7)	111.6(3)	Mo(2)-Se(3)-Mo(2)	66.0(2)
Se(2)-Mo(2)-Se(3)	53.0(1)	Mo(2)-Se(3)-Se(2)	65.1(1)
Se(2)-Mo(2)-Se(4)	92.5(1)	Mo(2)-Se(4)-Se(5)	62.2(1)
Se(2)-Mo(2)-Se(5)	88.2(1)	Mo(2)-Se(5)-Se(4)	64.2(1)
Se(2)-Mo(2)-Se(6)	166.6(2)	Mo(1)-Se(6)-Mo(2)	64.0(1)
Se(2)-Mo(2)-Se(7)	137.7(2)	Mo(1)-Se(6)-Se(7)	61.8(1)
Se(3)-Mo(2)-Se(4)	93.7(1)	Mo(2)-Se(6)-Se(7)	62.2(1)
Se(3)-Mo(2)-Se(5)	130.2(2)	Mo(1)-Se(7)-Mo(2)	65.9(1)
Se(3)-Mo(2)-Se(6)	137.7(2)		

Structures of α -K₈Mo₉Se₄₀·4H₂O (III), β -K₈Mo₉Se₄₀ (IV) and K₆Mo₆Se₂₇·6H₂O (V)

The formula of (III)~(V) can be expressed as a general form, $[K_m(Mo_3Se_{13})_n \cdot (K_2Se)] \cdot xH_2O$ (where $m=6$, $n=3$ for (III) and (IV); $m=4$, $n=2$ for (V)). They can be viewed as aggregates of n $[Mo_3Se_{13}]^{2-}$ trinuclear clusters and one Se^{2-} . (III) and (IV) have the same formula except that (III) has four cocrystallized water molecules. They differ in the way the three $[Mo_3Se_{13}]^{2-}$ and Se^{2-} are packed. The $[Mo_9Se_{40}]^{8-}$ anions of (III) and (IV) have very unusual and asymmetric structures which are shown in Figure 2-5. They have several unexpected features. They are composed of three different trinuclear molybdenum polyselenide subclusters, (A), (B), (C), in which the trinuclear $[Mo_3(\mu_2-Se)_3(\mu_3-Se)]^{4+}$ core is readily recognizable. In (III), the triply bridging Se(14) atom is part of subcluster (B) by covalently binding its three Mo atoms and at the same time forms unusual $Se \cdots Se$ contacts with the three Se atoms of the bridging Se^{2-} units of subcluster (A). The average bond distance is 3.13(6) Å, which is significantly smaller than the van der Waals distance between two Se atoms. This $Se \cdots Se$ interaction is probably not bonding and does not cause significant bond lengthening of the bridging diselenides in cluster (A). In (IV), the triply bridging Se(14) atoms of subcluster (B) does not have such $Se \cdots Se$ short contacts with subcluster (A) as found in (III). The average Se-Se distances in the bridging Se_2^{2-} ligands in subcluster (A) are 2.31(2) Å and 2.31(4) Å for (III) and (IV) respectively. Selected distances and angles in the Mo/Se framework are shown in Tables 2-18 and 2-19. The coordination around the K^+ ions is not well defined and disorder among the K^+ positions was found in (IV).

Another unprecedented interaction which is a common feature for both (III) and (IV) is that between subcluster (B) and subcluster (C). These subclusters are connected by a Se^{2-} atom which is weakly interacting with six Se atoms of the six Mo-bridging Se_2^{2-} units of the two subclusters. This forms an intriguing $[\text{Se}_{13}]^x$ "double-umbrella" fragment shown in Scheme (1), with long $\text{Se}_{\text{ap}}\text{-Se}_a$ distances as shown in Figure 2-5. The distance between this Se_{ap} atom and the six Se atoms ranges from $2.80(2)\text{\AA}$ to $3.182(9)\text{\AA}$ for (III) and from $2.86(1)\text{\AA}$ to $3.01(1)\text{\AA}$ for (IV). An inverse correlation exists between the $\text{Se}_{\text{ap}}\text{-Se}_a$ distance and the corresponding $\text{Se}_a\text{-Se}_b$ distance. For example, the shortest $\text{Se}_{\text{ap}}\text{-Se}_a$ distance, $2.80(2)\text{\AA}$, results in the maximum lengthening of corresponding diselenide to $2.44(1)\text{\AA}$, which is $0.14\text{\AA}$ longer than average bridging Se-Se distance in (I).

These results make it apparent that the pocket created by the three bridging Se_2^{2-} ligands of a trinuclear $[\text{Mo}_3\text{Se}_7]^{4+}$ core is special and it has affinity for additional electron-rich species such as Se^{2-} anions.



Scheme (1)

Finally, in (III), there is an unusually short intercluster Se(28)···Se(28) distance of 2.98(1) Å between two different [Mo₉Se₄₀]⁸⁻ clusters that involves a terminal diselenide ligand in subcluster (C). The two [Mo₉Se₄₀]⁸⁻ clusters involved in this close Se···Se contact are related by a crystallographic center of symmetry as shown in Figure 2-6. A similar distance was also observed in the electron-poor [W(CO)₅Se₂]₂²⁺ dimer (Se-Se 3.015 Å)²⁵ and Se₄S₂N₂²⁺ cation (Se-Se 3.135 Å)²⁶, in which it was characterized as a bonding weak Se···Se interaction. These short Se···Se contacts are electronic in origin. If the electron deficiency in the Mo(Se₂) fragment was causing this unusual Se···Se contact, shorter than average Mo-Se and Se-Se bonds would be expected. However, the normal Mo-Se and Se-Se distances, around the Mo-Se₂ fragment associated with this close contact, do not hint any lack of electron density in this part of the molecule. Thus, the close Se···Se distance may be the result of crystal packing forces.

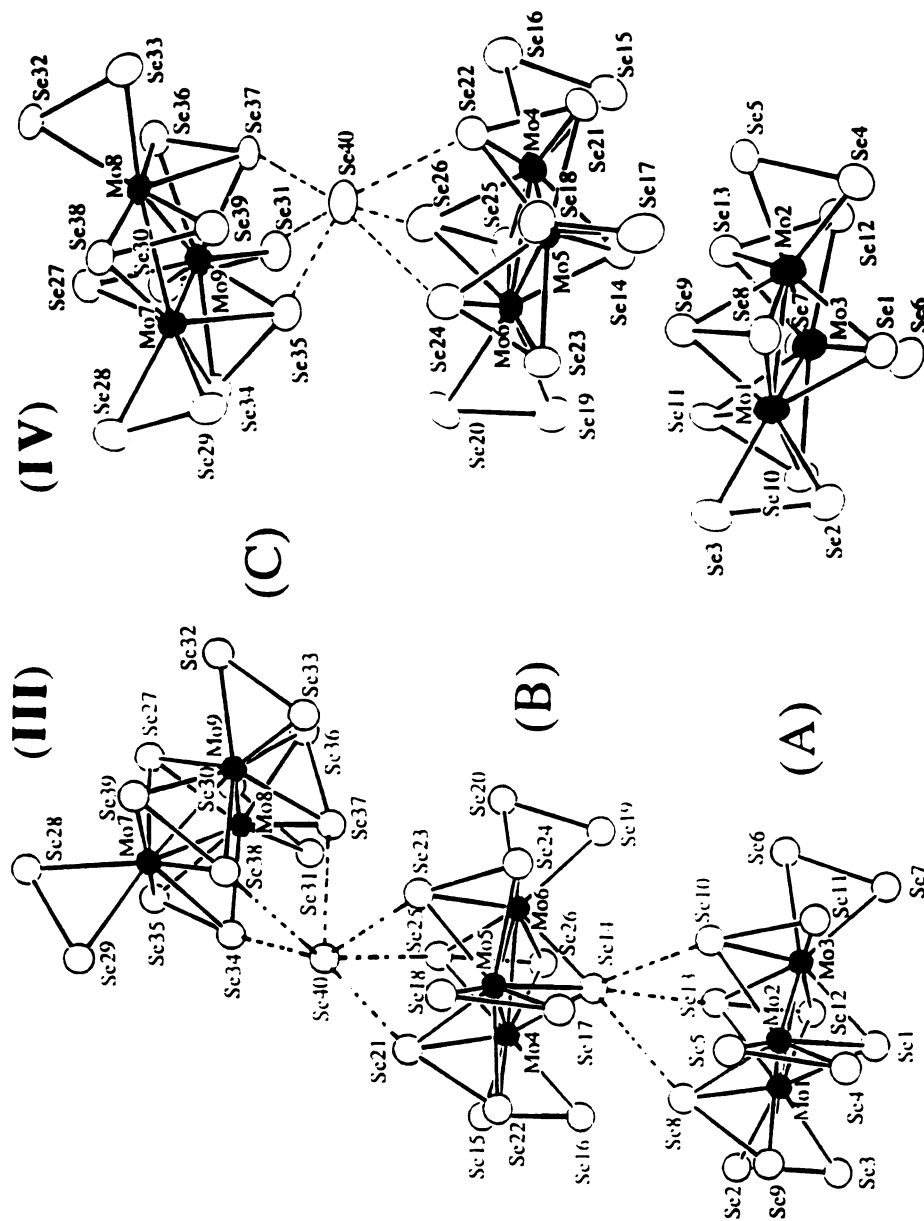


Figure 2-5: ORTEP representation and labeling scheme of α -[Mo₉Se₄₀]⁸⁻ (III) and β -[Mo₉Se₄₀]⁸⁻ (IV). Dashed lines show Se...Se short contacts.

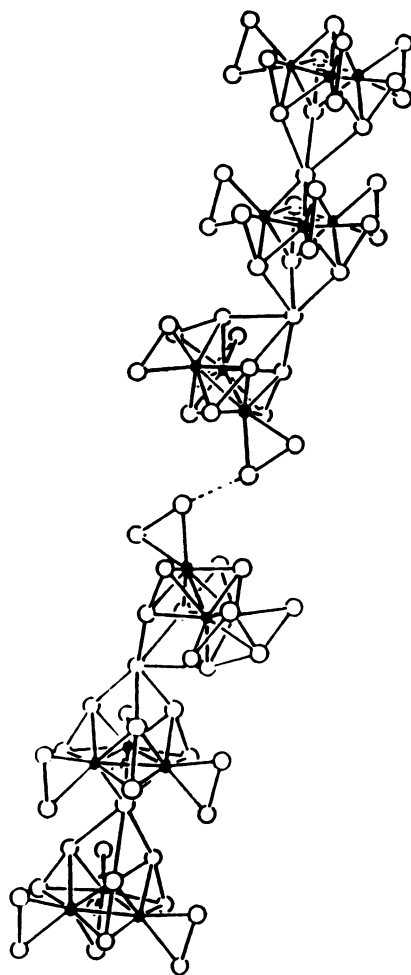


Figure 2-6: ORTEP representation of the centrosymmetric relationship between two clusters of α -[Mo₉Se₄₀]⁸⁻. The short contact between two terminal diselenides is shown by a dashed line. Black circles represent Mo atoms. Open circles represent Se atoms.

Table 2-18. Selected Bond Distances (Å) and Angles (deg) for α -K₈Mo₉Se₄₀·4H₂O with Estimated Standard Deviations in Parentheses

Selected Bond Distances (Å)			
Mo1-Mo2	2.760(6)	Mo6-Se24	2.620(6)
Mo1-Mo3	2.759(5)	Mo6-Se25	2.543(8)
Mo2-Mo3	2.749(6)	Mo6-Se26	2.606(6)
Mo4-Mo5	2.791(5)	Mo7-Se27	2.499(6)
Mo4-Mo6	2.778(5)	Mo7-Se28	2.562(8)
Mo5-Mo6	2.772(6)	Mo7-Se29	2.646(6)
Mo7-Mo8	2.773(6)	Mo7-Se34	2.543(7)
Mo7-Mo9	2.775(5)	Mo7-Se35	2.625(6)
Mo8-Mo9	2.750(6)	Mo7-Se38	2.559(7)
Mo1-Se1	2.489(7)	Mo7-Se39	2.604(6)
Mo1-Se2	2.617(6)	Mo8-Se27	2.503(7)
Mo1-Se3	2.568(8)	Mo8-Se30	2.594(7)
Mo1-Se8	2.574(6)	Mo8-Se31	2.616(7)
Mo1-Se9	2.599(8)	Mo8-Se34	2.536(7)
Mo1-Se12	2.615(7)	Mo8-Se35	2.606(6)
Mo1-Se13	2.542(9)	Mo8-Se36	2.596(5)
Mo2-Se1	2.517(7)	Mo8-Se37	2.517(7)
Mo2-Se4	2.560(8)	Mo9-Se27	2.514(7)
Mo2-Se5	2.584(6)	Mo9-Se32	2.567(6)
Mo2-Se8	2.544(5)	Mo9-Se33	2.624(7)
Mo2-Se9	2.616(6)	Mo9-Se36	2.599(7)
Mo2-Se10	2.565(7)	Mo9-Se37	2.520(8)
Mo2-Se11	2.615(5)	Mo9-Se38	2.531(8)
Mo3-Se1	2.491(9)	Mo9-Se39	2.615(7)
Mo3-Se6	2.609(8)	Se2-Se3	2.32(1)
Mo3-Se7	2.572(5)	Se4-Se5	2.350(9)
Mo3-Se10	2.567(6)	Se6-Se7	2.35(1)
Mo3-Se11	2.617(6)	Se8-Se9	2.297(8)
Mo3-Se12	2.618(6)	Se10-Se11	2.329(7)
Mo3-Se13	2.543(7)	Se12-Se13	2.307(8)

Table 2-18. (cont'd)

Mo4-Se14	2.467(6)	Se15-Se16	2.344(9)
Mo4-Se15	2.624(6)	Se17-Se18	2.380(8)
Mo4-Se16	2.609(7)	Se19-Se20	2.31(1)
Mo4-Se21	2.558(6)	Se21-Se22	2.362(8)
Mo4-Se22	2.608(6)	Se21-Se40	2.866(9)
Mo4-Se25	2.567(8)	Se23-Se24	2.373(8)
Mo4-Se26	2.563(6)	Se23-Se40	2.969(7)
Mo5-Se14	2.481(6)	Se25-Se26	2.44(1)
Mo5-Se17	2.589(6)	Se25-Se40	2.80(1)
Mo5-Se18	2.641(6)	Se28-Se28	2.98(1)
Mo5-Se21	2.563(6)	Se28-Se29	2.342(8)
Mo5-Se22	2.611(6)	Se30-Se31	2.360(9)
Mo5-Se23	2.552(8)	Se32-Se33	2.35(1)
Mo5-Se24	2.584(6)	Se34-Se35	2.340(8)
Mo6-Se14	2.513(8)	Se34-Se40	2.984(8)
Mo6-Se19	2.571(7)	Se36-Se37	2.349(9)
Mo6-Se20	2.617(7)	Se38-Se39	2.37(1)
Mo6-Se23	2.553(8)	Se38-Se40	2.87(1)
		Se37-Se40	3.182(9)
Se1-K3	3.59(2)	Se24-K7	3.72(2)
Se2-K1	3.32(1)	Se24-K7'	3.81(2)
Se2-K2	3.23(1)	Se25-K7	3.93(3)
Se3-K1	3.48(2)	Se26-K7	3.76(3)
Se4-K2	3.30(1)	Se26-K8	3.99(3)
Se4-K5'	3.51(2)	Se26-K8	3.79(3)
Se5-K2	3.44(1)	Se26-K8'	3.33(3)
Se5-K4	3.70(2)	Se26-K8'	3.56(3)
Se5-K5	3.85(2)	Se27-K2	3.37(1)
Se5-K5'	3.60(2)	Se28-K2	3.55(1)
Se6-K3	3.94(2)	Se28-K5'	3.46(2)
Se7-K1	3.32(1)	Se29-K2	3.25(1)
Se7-K3	3.30(2)	Se29-K4	3.48(1)

Table 2-18. (cont'd)

Se8-K2	3.98(1)	Se29-K5	3.27(2)
Se11-K2	3.82(1)	Se29-K6'	3.71(2)
Se12-K1	3.49(1)	Se30-K1	3.30(1)
Se12-K3	3.72(1)	Se30-K3	3.45(1)
Se15-K7	3.33(3)	Se31-K1	3.68(1)
Se15-K7'	3.64(2)	Se31-K3	3.27(1)
Se16-K2	3.68(1)	Se31-K8	3.65(3)
Se16-K4	3.67(1)	Se32-K3	3.20(1)
Se17-K4	3.29(1)	Se32-K5	3.75(2)
Se17-K5	3.39(2)	Se32-K5'	3.36(3)
Se17-K6'	3.27(2)	Se33-K3	3.56(2)
Se17-K7'	3.65(2)	Se33-K5	3.62(3)
Se18-K6	3.46(2)	Se34-K6	3.69(3)
Se18-K6'	3.10(3)	Se34-K6'	3.35(2)
Se18-K7'	3.73(3)	Se35-K3	3.91(2)
Se18-K7'	3.21(2)	Se35-K5	3.74(2)
Se19-K7	3.41(3)	Se35-K5'	3.42(2)
Se19-K8'	3.54(3)	Se35-K6'	3.83(3)
Se20-K8	3.68(3)	Se36-K1	3.71(1)
Se20-K8'	3.88(3)	Se36-K3	3.82(1)
Se21-K6	3.87(2)	Se38-K4	3.26(1)
Se21-K7'	3.79(2)	Se38-K7'	3.84(3)
Se21-K7'	3.86(2)	Se39-K4	3.83(1)
Se22-K4	3.55(1)	Se39-K5	3.59(2)
Se22-K6'	3.60(2)	Se40-K6	3.38(2)
Se24-K6	3.75(2)	Se40-K7'	3.81(2)

Selected Bond Angles (deg)

Subcluster A			
Se2-Mo1-Se3	53.0(2)	Se1-Mo3-Se12	83.0(3)
Se2-Mo1-Se8	92.0(6)	Se6-Mo3-Se7	53.9(2)

Table 2-18. (cont'd)

Se2-Mo1-Se9	92.0(9)	Se10-Mo3-Se13	85.3(2)
Se2-Mo1-Se12	93.9(2)	Se7-Mo3-Se12	88.3(2)
Se2-Mo1-Se13	92.1(2)	Mo1-Se1-Mo2	66.9(2)
Se3-Mo1-Se9	86.9(3)	Mo1-Se1-Mo3	67.3(2)
Se3-Mo1-Se12	89.8(3)	Mo2-Se1-Mo3	66.6(3)
Se8-Mo1-Se9	52.7(2)	Mo1-Se2-Se3	62.4(2)
Se8-Mo1-Se13	83.3(2)	Mo1-Se3-Se2	64.7(2)
Se9-Mo1-Se12	168.4(3)	Mo2-Se4-Se5	63.3(2)
Se12-Mo1-Se13	53.1(2)	Mo2-Se5-Se4	62.3(2)
Se1-Mo1-Se3	92.5(3)	Mo3-Se6-Se7	62.2(2)
Se1-Mo1-Se9	86.0(2)	Mo3-Se7-Se6	63.9(2)
Se1-Mo1-Se12	83.1(2)	Mo1-Se8-Mo2	65.2(2)
Se1-Mo2-Se4	92.4(3)	Mo1-Se8-Se9	64.2(2)
Se1-Mo2-Se9	85.1(2)	Mo2-Se8-Se9	65.2(2)
Se1-Mo2-Se10	113.0(2)	Mo1-Se9-Mo2	63.9(2)
Se1-Mo2-Se11	83.5(2)	Mo1-Se9-Se8	63.2(2)
Se4-Mo2-Se5	54.4(2)	Mo2-Se9-Se8	62.0(2)
Se4-Mo2-Se11	86.6(2)	Mo2-Se10-Mo3	64.8(2)
Se5-Mo2-Se9	94.0(2)	Mo2-Se10-Se11	64.4(2)
Se5-Mo2-Se10	90.5(2)	Mo2-Se11-Mo3	63.4(2)
Se5-Mo2-Se11	93.3(2)	Mo2-Se11-Se10	62.2(2)
Se8-Mo2-Se9	52.8(2)	Mo3-Se11-Se10	62.2(2)
Se8-Mo2-Se10	83.5(2)	Mo1-Se12-Mo3	63.6(2)
Se9-Mo2-Se11	167.9(3)	Mo1-Se12-Se13	61.9(2)
Se10-Mo2-Se11	53.4(2)	Mo3-Se12-Se13	61.8(2)
Se6-Mo3-Se10	90.1(2)	Mo1-Se13-Mo3	65.7(2)
Se6-Mo3-Se11	94.2(2)	Mo1-Se13-Se12	65.1(3)
Se12-Mo3-Se13	53.1(2)	Mo2-Mo1-Mo3	59.8(1)
Se6-Mo3-Se12	93.7(2)	Mo1-Mo2-Mo3	60.1(1)
Se6-Mo3-Se13	90.4(3)	Mo1-Mo3-Mo2	60.1(1)
Se1-Mo3-Se7	93.3(3)	Se11-Se10-Se14	167.6(4)
Se10-Mo3-Se11	53.4(2)	Se8-Se9-Se14	167.5(3)

Table 2-18. (cont'd)

Se7-Mo3-Se11	86.9(2)	Se12-Se13-Se14	166.3(4)
Se1-Mo3-Se11	84.0(2)		
Subcluster B			
Se14-Mo4-Se16	91.1(2)	Se20-Mo6-Se23	93.2(3)
Se14-Mo4-Se22	83.1(2)	Se20-Mo6-Se24	95.1(2)
Se14-Mo4-Se26	83.4(2)	Se20-Mo6-Se25	92.4(3)
Se15-Mo4-Se16	53.2(2)	Se20-Mo6-Se26	94.8(2)
Se15-Mo4-Se21	96.0(2)	Mo3-Se13-Se12	65.1(2)
Se15-Mo4-Se22	97.2(2)	Mo4-Se14-Mo5	68.7(2)
Se15-Mo4-Se25	92.4(2)	Mo4-Se14-Mo6	67.9(2)
Se15-Mo4-Se26	90.9(2)	Mo5-Se14-Mo6	67.4(2)
Se16-Mo4-Se22	87.1(2)	Mo4-Se15-Se16	63.1(2)
Se16-Mo4-Se25	132.1(2)	Mo4-Se16-Se15	63.7(2)
Se16-Mo4-Se26	88.3(2)	Mo5-Se17-Se18	64.1(2)
Se21-Mo4-Se22	54.5(2)	Mo5-Se18-Se17	61.8(2)
Se21-Mo4-Se22	80.3(2)	Mo6-Se19-Se20	64.6(3)
Se22-Mo4-Se25	165.6(3)	Mo6-Se20-Se19	62.5(3)
Se25-Mo4-Se26	56.8(2)	Mo4-Se21-Mo5	66.1(2)
Se17-Mo5-Se24	88.3(2)	Mo4-Se21-Se22	64.0(2)
Se18-Mo5-Se21	95.7(2)	Mo5-Se21-Se22	63.9(2)
Se18-Mo5-Se22	95.4(2)	Mo4-Se22-Mo5	64.6(2)
Se18-Mo5-Se23	93.2(2)	Mo4-Se22-Se21	61.7(2)
Se21-Mo5-Se22	54.3(2)	Mo5-Se22-Se21	61.8(2)
Se21-Mo5-Se23	81.2(2)	Mo5-Se23-Mo6	65.8(2)
Se22-Mo5-Se24	166.7(2)	Mo5-Se23-Se24	63.2(2)
Se23-Mo5-Se24	55.0(2)	Mo4-Se25-Mo6	65.9(2)
Se14-Mo5-Se17	89.6(2)	Mo4-Se25-Se26	61.6(2)
Se14-Mo5-Se22	82.8(2)	Mo6-Se25-Se26	63.1(2)
Se14-Mo5-Se24	84.8(2)	Mo4-Se26-Mo6	65.0(2)
Se17-Mo5-Se18	54.2(2)	Mo4-Se26-Se25	61.7(2)

Table 2-18. (cont'd)

Se17-Mo5-Se22	86.9(2)	Mo6-Se26-Se25	60.5(2)
Se23-Mo6-Se24	54.6(2)	Mo6-Se23-Se24	64.1(2)
Se23-Mo6-Se25	81.0(2)	Mo5-Se24-Mo6	64.4(2)
Se24-Mo6-Se26	164.3(3)	Mo5-Se24-Se23	61.9(2)
Se25-Mo6-Se26	56.5(2)	Mo6-Se24-Se23	61.3(2)
Se14-Mo6-Se19	93.3(3)	Se22-Se21-Se40	165.5(3)
Se14-Mo6-Se24	83.4(2)	Se26-Se25-Se40	165.3(3)
Se14-Mo6-Se26	81.7(2)	Se24-Se23-Se40	162.9(3)
Se19-Mo6-Se20	52.9(3)	Mo5-Mo4-Mo6	59.7(1)
Se19-Mo6-Se24	88.6(2)	Mo4-Mo5-Mo6	59.9(1)
Se19-Mo6-Se26	87.6(2)	Mo4-Mo6-Mo5	60.4(1)
Subcluster C			
Se27-Mo7-Se28	93.6(2)	Se32-Mo9-Se39	85.4(2)
Se27-Mo7-Se35	83.1(2)	Se33-Mo9-Se37	89.8(3)
Se27-Mo7-Se39	84.0(2)	Se33-Mo9-Se38	91.6(3)
Se28-Mo7-Se35	88.5(2)	Se33-Mo9-Se39	95.7(3)
Se29-Mo7-Se39	95.1(2)	Se36-Mo9-Se37	54.6(2)
Se28-Mo7-Se29	53.4(2)	Se36-Mo9-Se39	165.3(3)
Se28-Mo7-Se39	88.5(2)	Se38-Mo9-Se39	54.9(2)
Se29-Mo7-Se35	93.7(2)	Mo8-Se34-Se35	64.4(2)
Se34-Mo7-Se35	53.8(2)	Mo7-Se35-Mo8	64.0(2)
Se34-Mo7-Se38	81.7(2)	Mo7-Se35-Se34	61.3(2)
Se35-Mo7-Se39	166.4(3)	Mo8-Se35-Se34	61.4(2)
Se38-Mo7-Se39	54.7(2)	Mo8-Se36-Mo9	63.9(2)
Se31-Mo8-Se34	94.0(2)	Mo8-Se36-Se37	60.9(2)
Se30-Mo8-Se31	53.9(2)	Mo9-Se36-Se37	61.0(2)
Se30-Mo8-Se35	85.8(2)	Mo8-Se37-Mo9	66.3(2)
Se30-Mo8-Se36	88.5(2)	Mo8-Se37-Se36	64.4(2)
Se31-Mo8-Se36	92.0(2)	Mo9-Se37-Se36	64.4(2)
Se31-Mo8-Se37	91.2(3)	Mo7-Se38-Mo9	66.1(2)

Table 2-18. (cont'd)

Se34-Mo8-Se35	54.1(2)	Mo7-Se38-Se39	63.6(2)
Se34-Mo8-Se37	83.6(2)	Mo9-Se38-Se39	64.4(2)
Se35-Mo8-Se36	165.3(3)	Mo7-Se39-Mo9	64.2(2)
Se36-Mo8-Se37	54.7(2)	Mo7-Se39-Se38	61.7(2)
Se27-Mo8-Se30	91.3(2)	Mo9-Se39-Se38	60.8(2)
Se27-Mo8-Se35	83.4(2)	Se34-Se40-Se38	69.5(2)
Se27-Mo8-Se36	83.2(2)	Se21-Se40-Se23	69.6(2)
Se27-Mo8-Se37	113.2(2)	Se21-Se40-Se25	71.4(2)
Se27-Mo9-Se32	94.4(2)	Se23-Se40-Se25	70.0(2)
Se33-Mo9-Se36	93.1(3)	Se23-Se40-Se38	89.2(2)
Se27-Mo9-Se36	82.9(2)	Se25-Se40-Se34	106.4(3)
Se27-Mo9-Se37	112.7(2)	Se35-Se34-Se40	167.1(3)
Se27-Mo9-Se38	113.1(2)	Se39-Se38-Se40	169.0(3)
Se27-Mo9-Se39	83.5(2)	Mo8-Mo7-Mo9	59.4(1)
Se32-Mo9-Se33	53.7(2)	Mo7-Mo8-Mo9	60.3(1)
Se32-Mo9-Se36	90.2(2)	Mo7-Mo9-Mo8	60.2(1)
Se37-Mo9-Se38	82.5(3)		

Table 2-19. Selected Bond Distances (Å) and Angles (deg) for β -K₈Mo₉Se₄₀ with Standard Deviations in Parentheses

Selected Bond Distances (Å)			
Mo(1)-Mo(2)	2.78(1)	Se(6)-Se(7)	2.33(2)
Mo(1)-Mo(3)	2.78(1)	Se(8)-Se(9)	2.32(1)
Mo(2)-Mo(3)	2.79(1)	Se(10)-Se(11)	2.26(1)
Mo(4)-Mo(5)	2.79(1)	Se(12)-Se(13)	2.34(2)
Mo(4)-Mo(6)	2.78(1)	Se(15)-Se(16)	2.27(1)
Mo(5)-Mo(6)	2.85(1)	Se(17)-Se(18)	2.25(1)
Mo(8)-Mo(9)	2.74(1)	Se(19)-Se(20)	2.29(1)
Mo(7)-Mo(8)	2.76(1)	Se(21)-Se(22)	2.32(1)
Mo(7)-Mo(9)	2.76(1)	Se(23)-Se(24)	2.31(1)
Mo(1)-Se(1)	2.49(1)	Se(25)-Se(26)	2.30(1)
Mo(1)-Se(2)	2.57(1)	Se(28)-Se(29)	2.34(2)
Mo(1)-Se(3)	2.65(1)	Se(30)-Se(31)	2.36(2)
Mo(1)-Se(8)	2.67(1)	Se(32)-Se(33)	2.40(2)
Mo(1)-Se(9)	2.49(1)	Se(34)-Se(35)	2.44(2)
Mo(1)-Se(10)	2.65(1)	Se(36)-Se(37)	2.38(1)
Mo(1)-Se(11)	2.59(1)	Se(38)-Se(39)	2.33(1)
Mo(2)-Se(1)	2.44(1)	Se(6)-K(1)	3.57(2)
Mo(2)-Se(4)	2.64(1)	Se(7)-K(1)	3.45(2)
Mo(2)-Se(5)	2.61(1)	Se(10)-K(1)	3.82(2)
Mo(2)-Se(8)	2.61(1)	Se(28)-K(1)	3.46(2)
Mo(2)-Se(9)	2.53(1)	Se(29)-K(1)	3.32(2)
Mo(2)-Se(12)	2.64(1)	Se(32)-K(1)	3.50(2)
Mo(2)-Se(13)	2.57(1)	Se(32)-K(1)	3.46(2)
Mo(3)-Se(1)	2.54(1)	Se(33)-K(1)	3.50(2)
Mo(3)-Se(6)	2.53(1)	Se(36)-K(1)	3.70(2)
Mo(3)-Se(7)	2.61(1)	Se(4)-K(2)	3.44(2)
Mo(3)-Se(10)	2.62(1)	Se(5)-K(2)	3.44(2)
Mo(3)-Se(11)	2.54(1)	Se(14)-K(2)	3.56(3)
Mo(3)-Se(12)	2.65(1)	Se(15)-K(2)	3.47(2)
Mo(3)-Se(13)	2.51(1)	Se(16)-K(2)	3.45(3)

Table 2-19. (cont'd)

Mo(4)-Se(14)	2.46(1)	Se(17)-K(2)	3.40(2)
Mo(4)-Se(15)	2.58(1)	Se(18)-K(2)	3.56(2)
Mo(4)-Se(16)	2.60(1)	Se(2)-K(3)	3.57(3)
Mo(4)-Se(21)	2.68(1)	Se(3)-K(3)	3.43(2)
Mo(4)-Se(22)	2.52(1)	Se(7)-K(3)	3.39(2)
Mo(4)-Se(25)	2.69(1)	Se(10)-K(3)	3.55(2)
Mo(4)-Se(26)	2.55(1)	Se(27)-K(3)	3.55(2)
Mo(5)-Se(14)	2.46(1)	Se(28)-K(3)	3.60(2)
Mo(5)-Se(17)	2.61(1)	Se(32)-K(3)	3.41(2)
Mo(5)-Se(18)	2.66(1)	Se(33)-K(3)	3.40(2)
Mo(5)-Se(21)	2.61(1)	Se(38)-K(3)	3.73(2)
Mo(5)-Se(22)	2.50(1)	Se(19)-K(4)	3.29(2)
Mo(5)-Se(23)	2.60(1)	Se(28)-K(4)	3.22(2)
Mo(5)-Se(24)	2.55(1)	Se(29)-K(4)	3.52(2)
Mo(6)-Se(14)	2.49(1)	Se(30)-K(4)	3.56(2)
Mo(6)-Se(19)	2.60(1)	Se(31)-K(4)	3.42(2)
Mo(6)-Se(20)	2.67(1)	Se(36)-K(4)	3.56(2)
Mo(6)-Se(23)	2.64(1)	Se(20)-K(5)	3.49(3)
Mo(6)-Se(24)	2.52(1)	Se(31)-K(5)	3.57(3)
Mo(6)-Se(25)	2.63(1)	Se(31)-K(5)	3.27(3)
Mo(6)-Se(26)	2.53(1)	Se(34)-K(5)	3.80(3)
Mo(7)-Se(27)	2.48(1)	Se(19)-K(5')	3.66(5)
Mo(7)-Se(28)	2.61(1)	Se(20)-K(5')	3.46(5)
Mo(7)-Se(29)	2.63(1)	Se(16)-K(5')	3.45(5)
Mo(7)-Se(34)	2.62(1)	Se(23)-K(5')	3.68(6)
Mo(7)-Se(35)	2.49(1)	Se(25)-K(5')	3.82(5)
Mo(7)-Se(38)	2.59(1)	Se(13)-K(6)	3.59(3)
Mo(7)-Se(39)	2.59(1)	Se(15)-K(6)	3.53(3)
Mo(8)-Se(27)	2.41(1)	Se(19)-K(6)	3.71(3)
Mo(8)-Se(30)	2.67(1)	Se(30)-K(6)	3.55(3)
Mo(8)-Se(31)	2.61(1)	Se(3)-K(6')	3.72(6)

Table 2-19. (cont'd)

Mo(8)-Se(34)	2.62(1)	Se(8)-K(6')	3.69(6)
Mo(8)-Se(35)	2.56(1)	Se(17)-K(6')	3.59(7)
Mo(8)-Se(36)	2.58(1)	Se(19)-K(6')	3.64(7)
Mo(8)-Se(37)	2.59(1)	Se(23)-K(6')	3.72(6)
Mo(9)-Se(27)	2.53(1)	Se(2)-K(7)	3.46(7)
Mo(9)-Se(32)	2.56(1)	Se(6)-K(7')	3.74(6)
Mo(9)-Se(33)	2.63(1)	Se(12)-K(7')	2.95(6)
Mo(9)-Se(36)	2.60(1)	Se(2)-K(8)	3.48(3)
Mo(9)-Se(37)	2.52(1)	Se(5)-K(8)	3.38(3)
Mo(9)-Se(38)	2.61(1)	Se(12)-K(8)	3.58(3)
Mo(9)-Se(39)	2.55(1)	Se(18)-K(8)	3.29(3)
Se(2)-Se(3)	2.38(2)	Se(21)-K(8)	3.65(3)
Se(4)-Se(5)	2.31(1)		
Selected Bond Angles (deg)			
Mo(2)-Mo(1)-Mo(3)	60.4(3)	Se(24)-Mo(6)-Se(26)	84.5(4)
Mo(2)-Mo(1)-Se(1)	55.0(3)	Se(25)-Mo(6)-Se(26)	52.8(3)
Mo(2)-Mo(1)-Se(8)	57.3(3)	Mo(8)-Mo(7)-Mo(9)	59.4(3)
Mo(2)-Mo(1)-Se(9)	57.2(3)	Mo(8)-Mo(7)-Se(27)	54.5(3)
Mo(3)-Mo(1)-Se(1)	57.3(3)	Mo(8)-Mo(7)-Se(34)	58.2(3)
Mo(3)-Mo(1)-Se(10)	57.7(3)	Mo(8)-Mo(7)-Se(35)	58.1(3)
Mo(3)-Mo(1)-Se(11)	56.3(3)	Mo(9)-Mo(7)-Se(27)	57.4(3)
Se(1)-Mo(1)-Se(2)	91.3(4)	Mo(9)-Mo(7)-Se(38)	58.2(3)
Se(1)-Mo(1)-Se(3)	145.4(4)	Mo(9)-Mo(7)-Se(39)	56.8(3)
Se(1)-Mo(1)-Se(8)	82.2(4)	Se(27)-Mo(7)-Se(28)	96.1(4)
Se(1)-Mo(1)-Se(9)	111.4(4)	Se(27)-Mo(7)-Se(29)	148.8(5)
Se(1)-Mo(1)-Se(10)	87.9(4)	Se(27)-Mo(7)-Se(34)	81.1(4)
Se(1)-Mo(1)-Se(11)	113.2(4)	Se(27)-Mo(7)-Se(35)	112.0(4)
Se(2)-Mo(1)-Se(3)	54.1(4)	Se(27)-Mo(7)-Se(38)	84.7(4)
Se(2)-Mo(1)-Se(8)	87.4(4)	Se(27)-Mo(7)-Se(39)	113.6(4)
Se(2)-Mo(1)-Se(9)	128.6(4)	Se(28)-Mo(7)-Se(29)	53.0(4)

Table 2-19. (cont'd)

Se(2)-Mo(1)-Se(10)	90.9(4)	Se(28)-Mo(7)-Se(34)	85.9(4)
Se(2)-Mo(1)-Se(11)	131.1(4)	Se(28)-Mo(7)-Se(35)	126.7(4)
Se(3)-Mo(1)-Se(8)	95.0(4)	Se(28)-Mo(7)-Se(38)	89.9(4)
Se(3)-Mo(1)-Se(9)	93.5(4)	Se(28)-Mo(7)-Se(39)	127.5(4)
Se(3)-Mo(1)-Se(10)	92.0(4)	Se(29)-Mo(7)-Se(34)	98.7(4)
Se(3)-Mo(1)-Se(11)	92.9(4)	Se(29)-Mo(7)-Se(35)	93.0(4)
Se(8)-Mo(1)-Se(9)	53.4(3)	Se(29)-Mo(7)-Se(38)	90.4(3)
Se(8)-Mo(1)-Se(10)	169.9(5)	Se(29)-Mo(7)-Se(39)	87.3(4)
Se(8)-Mo(1)-Se(11)	135.5(4)	Se(34)-Mo(7)-Se(35)	57.0(4)
Se(9)-Mo(1)-Se(10)	133.4(5)	Se(34)-Mo(7)-Se(38)	164.7(5)
Se(9)-Mo(1)-Se(11)	82.4(4)	Se(34)-Mo(7)-Se(39)	138.6(4)
Se(10)-Mo(1)-Se(11)	51.1(3)	Se(35)-Mo(7)-Se(38)	135.1(5)
Mo(1)-Mo(2)-Mo(3)	59.8(3)	Se(35)-Mo(7)-Se(39)	81.9(4)
Mo(1)-Mo(2)-Se(1)	56.6(3)	Se(38)-Mo(7)-Se(39)	53.5(3)
Mo(1)-Mo(2)-Se(8)	59.2(3)	Mo(7)-Mo(8)-Mo(9)	60.4(3)
Mo(1)-Mo(2)-Se(9)	55.7(3)	Mo(7)-Mo(8)-Se(27)	56.8(3)
Mo(3)-Mo(2)-Se(1)	57.5(3)	Mo(7)-Mo(8)-Se(34)	58.3(3)
Mo(3)-Mo(2)-Se(12)	58.2(3)	Mo(7)-Mo(8)-Se(35)	55.7(3)
Mo(3)-Mo(2)-Se(13)	55.5(3)	Mo(9)-Mo(8)-Se(27)	58.4(3)
Se(1)-Mo(2)-Se(4)	95.1(5)	Mo(9)-Mo(8)-Se(36)	58.5(3)
Se(1)-Mo(2)-Se(5)	147.3(5)	Mo(9)-Mo(8)-Se(37)	56.3(3)
Se(1)-Mo(2)-Se(8)	84.3(4)	Se(27)-Mo(8)-Se(30)	91.9(4)
Se(1)-Mo(2)-Se(9)	111.5(4)	Se(27)-Mo(8)-Se(31)	145.1(5)
Se(1)-Mo(2)-Se(12)	84.6(4)	Se(27)-Mo(8)-Se(34)	82.4(4)
Se(1)-Mo(2)-Se(13)	112.4(4)	Se(27)-Mo(8)-Se(35)	111.9(4)
Se(4)-Mo(2)-Se(5)	52.2(4)	Se(27)-Mo(8)-Se(36)	86.1(4)
Se(4)-Mo(2)-Se(8)	88.3(4)	Se(27)-Mo(8)-Se(37)	114.4(4)
Se(4)-Mo(2)-Se(9)	128.5(4)	Se(30)-Mo(8)-Se(31)	53.1(4)
Se(4)-Mo(2)-Se(12)	87.7(4)	Se(30)-Mo(8)-Se(34)	88.2(4)
Se(4)-Mo(2)-Se(13)	127.2(4)	Se(30)-Mo(8)-Se(35)	131.6(4)
Se(5)-Mo(2)-Se(8)	92.7(4)	Se(30)-Mo(8)-Se(36)	87.2(4)
Se(5)-Mo(2)-Se(9)	92.1(4)	Se(30)-Mo(8)-Se(37)	129.3(4)

Table 2-19. (cont'd)

Se(5)-Mo(2)-Se(12)	93.9(4)	Se(31)-Mo(8)-Se(34)	95.0(4)
Se(5)-Mo(2)-Se(13)	92.1(4)	Se(31)-Mo(8)-Se(35)	94.6(4)
Se(8)-Mo(2)-Se(9)	53.7(4)	Se(31)-Mo(8)-Se(36)	91.6(3)
Se(8)-Mo(2)-Se(12)	167.8(5)	Se(31)-Mo(8)-Se(37)	91.9(4)
Se(8)-Mo(2)-Se(13)	136.5(5)	Se(34)-Mo(8)-Se(35)	56.3(4)
Se(9)-Mo(2)-Se(12)	136.1(5)	Se(34)-Mo(8)-Se(36)	167.5(5)
Se(9)-Mo(2)-Se(13)	82.9(4)	Se(34)-Mo(8)-Se(37)	135.3(4)
Se(12)-Mo(2)-Se(13)	53.5(4)	Se(35)-Mo(8)-Se(36)	133.8(5)
Mo(1)-Mo(3)-Mo(2)	59.8(3)	Se(35)-Mo(8)-Se(37)	79.2(4)
Mo(1)-Mo(3)-Se(1)	55.7(3)	Se(36)-Mo(8)-Se(37)	54.8(3)
Mo(1)-Mo(3)-Se(10)	58.8(3)	Mo(7)-Mo(9)-Mo(8)	60.2(2)
Mo(1)-Mo(3)-Se(11)	58.2(3)	Mo(7)-Mo(9)-Se(27)	55.5(3)
Mo(2)-Mo(3)-Se(1)	54.3(3)	Mo(7)-Mo(9)-Se(38)	57.5(3)
Mo(2)-Mo(3)-Se(12)	58.0(3)	Mo(7)-Mo(9)-Se(39)	58.0(3)
Mo(2)-Mo(3)-Se(13)	57.8(3)	Mo(8)-Mo(9)-Se(27)	54.2(3)
Se(1)-Mo(3)-Se(6)	94.7(4)	Mo(8)-Mo(9)-Se(36)	57.7(3)
Se(1)-Mo(3)-Se(7)	148.7(4)	Mo(8)-Mo(9)-Se(37)	58.8(3)
Se(1)-Mo(3)-Se(10)	87.6(4)	Se(27)-Mo(9)-Se(32)	93.4(4)
Se(1)-Mo(3)-Se(11)	113.5(4)	Se(27)-Mo(9)-Se(33)	148.4(5)
Se(1)-Mo(3)-Se(12)	82.6(4)	Se(27)-Mo(9)-Se(36)	83.3(4)
Se(1)-Mo(3)-Se(13)	111.5(4)	Se(27)-Mo(9)-Se(37)	112.7(4)
Se(6)-Mo(3)-Se(7)	54.0(4)	Se(27)-Mo(9)-Se(38)	83.3(4)
Se(6)-Mo(3)-Se(10)	88.9(4)	Se(27)-Mo(9)-Se(39)	112.9(4)
Se(6)-Mo(3)-Se(11)	127.8(5)	Se(32)-Mo(9)-Se(33)	55.0(4)
Se(6)-Mo(3)-Se(12)	88.2(4)	Se(32)-Mo(9)-Se(36)	86.0(3)
Se(6)-Mo(3)-Se(13)	128.0(4)	Se(32)-Mo(9)-Se(37)	127.7(4)
Se(7)-Mo(3)-Se(10)	92.5(4)	Se(32)-Mo(9)-Se(38)	89.7(3)
Se(7)-Mo(3)-Se(11)	90.5(4)	Se(32)-Mo(9)-Se(39)	128.9(4)
Se(7)-Mo(3)-Se(12)	94.0(4)	Se(33)-Mo(9)-Se(36)	93.9(4)
Se(7)-Mo(3)-Se(13)	90.6(4)	Se(33)-Mo(9)-Se(37)	90.5(4)
Se(10)-Mo(3)-Se(11)	52.0(3)	Se(33)-Mo(9)-Se(38)	94.9(3)
Se(10)-Mo(3)-Se(12)	169.5(5)	Se(33)-Mo(9)-Se(39)	90.2(4)

Table 2-19. (cont'd)

Se(10)-Mo(3)-Se(13)	134.2(5)	Se(36)-Mo(9)-Se(37)	55.4(3)
Se(11)-Mo(3)-Se(12)	136.2(4)	Se(36)-Mo(9)-Se(38)	165.6(5)
Se(11)-Mo(3)-Se(13)	82.4(4)	Se(36)-Mo(9)-Se(39)	137.7(4)
Se(12)-Mo(3)-Se(13)	54.1(4)	Se(37)-Mo(9)-Se(38)	135.9(4)
Mo(5)-Mo(4)-Mo(6)	61.5(3)	Se(37)-Mo(9)-Se(39)	82.6(4)
Mo(5)-Mo(4)-Se(14)	55.5(3)	Se(38)-Mo(9)-Se(39)	53.7(3)
Mo(5)-Mo(4)-Se(21)	57.1(3)	Mo(1)-Se(1)-Mo(2)	68.5(4)
Mo(5)-Mo(4)-Se(22)	55.9(3)	Mo(1)-Se(1)-Mo(3)	67.0(4)
Mo(6)-Mo(4)-Se(14)	56.4(3)	Mo(2)-Se(1)-Mo(3)	68.1(4)
Mo(6)-Mo(4)-Se(25)	57.5(3)	Mo(1)-Se(2)-Se(3)	64.5(4)
Mo(6)-Mo(4)-Se(26)	56.4(3)	Mo(1)-Se(3)-Se(2)	61.3(4)
Se(15)-Mo(4)-Se(21)	86.9(4)	Mo(2)-Se(4)-Se(5)	63.2(4)
Se(15)-Mo(4)-Se(22)	126.6(4)	Mo(2)-Se(5)-Se(4)	64.6(4)
Se(15)-Mo(4)-Se(25)	90.1(4)	Mo(3)-Se(6)-Se(7)	64.9(4)
Se(15)-Mo(4)-Se(26)	128.6(4)	Mo(3)-Se(7)-Se(6)	61.1(4)
Se(16)-Mo(4)-Se(21)	92.7(4)	Mo(1)-Se(8)-Mo(2)	63.5(3)
Se(16)-Mo(4)-Se(22)	91.9(3)	Mo(1)-Se(8)-Se(9)	59.4(4)
Se(16)-Mo(4)-Se(25)	94.6(4)	Mo(2)-Se(8)-Se(9)	61.5(4)
Se(16)-Mo(4)-Se(26)	93.1(4)	Mo(1)-Se(9)-Mo(2)	67.1(3)
Se(21)-Mo(4)-Se(22)	52.9(4)	Mo(1)-Se(9)-Se(8)	67.2(4)
Se(21)-Mo(4)-Se(25)	168.1(4)	Mo(2)-Se(9)-Se(8)	64.8(4)
Se(21)-Mo(4)-Se(26)	137.1(4)	Mo(1)-Se(10)-Mo(3)	63.5(3)
Se(22)-Mo(4)-Se(25)	136.1(5)	Mo(1)-Se(10)-Se(11)	63.1(4)
Se(22)-Mo(4)-Se(26)	84.4(4)	Mo(3)-Se(10)-Se(11)	62.0(4)
Se(25)-Mo(4)-Se(26)	52.0(3)	Mo(1)-Se(11)-Mo(3)	65.6(4)
Se(14)-Mo(4)-Se(15)	94.8(4)	Mo(1)-Se(11)-Se(10)	65.9(4)
Se(14)-Mo(4)-Se(16)	146.8(4)	Mo(3)-Se(11)-Se(10)	66.0(4)
Se(14)-Mo(4)-Se(21)	83.2(4)	Mo(2)-Se(12)-Mo(3)	63.8(3)
Se(14)-Mo(4)-Se(22)	110.8(4)	Mo(2)-Se(12)-Se(13)	61.8(4)
Se(14)-Mo(4)-Se(25)	85.6(4)	Mo(3)-Se(12)-Se(13)	59.9(4)
Se(14)-Mo(4)-Se(26)	112.3(4)	Mo(2)-Se(13)-Mo(3)	66.7(3)

Table 2-19. (cont'd)

Se(15)-Mo(4)-Se(16)	52.0(3)	Mo(2)-Se(13)-Se(12)	64.7(4)
Mo(4)-Mo(5)-Mo(6)	59.2(3)	Mo(3)-Se(13)-Se(12)	66.0(4)
Mo(4)-Mo(5)-Se(14)	55.4(3)	Mo(4)-Se(14)-Mo(5)	69.1(3)
Mo(4)-Mo(5)-Se(21)	59.3(3)	Mo(4)-Se(14)-Mo(6)	68.4(4)
Mo(4)-Mo(5)-Se(22)	56.7(3)	Mo(5)-Se(14)-Mo(6)	70.2(4)
Mo(6)-Mo(5)-Se(14)	55.4(3)	Mo(4)-Se(15)-Se(16)	64.5(4)
Mo(6)-Mo(5)-Se(23)	57.7(3)	Mo(4)-Se(16)-Se(15)	63.5(4)
Mo(6)-Mo(5)-Se(24)	55.4(3)	Mo(5)-Se(17)-Se(18)	65.9(4)
Se(14)-Mo(5)-Se(17)	98.0(4)	Mo(5)-Se(18)-Se(17)	63.4(4)
Se(14)-Mo(5)-Se(18)	148.4(5)	Mo(6)-Se(19)-Se(20)	65.7(4)
Se(14)-Mo(5)-Se(21)	84.5(4)	Mo(6)-Se(20)-Se(19)	62.8(4)
Se(14)-Mo(5)-Se(22)	111.5(4)	Mo(4)-Se(21)-Mo(5)	63.6(3)
Se(14)-Mo(5)-Se(23)	82.3(4)	Mo(4)-Se(21)-Se(22)	60.2(4)
Se(14)-Mo(5)-Se(24)	110.1(5)	Mo(5)-Se(21)-Se(22)	60.6(4)
Se(17)-Mo(5)-Se(18)	50.6(4)	Mo(4)-Se(22)-Mo(5)	67.4(3)
Se(17)-Mo(5)-Se(21)	85.4(4)	Mo(4)-Se(22)-Se(21)	66.9(4)
Se(17)-Mo(5)-Se(22)	124.5(5)	Mo(5)-Se(22)-Se(21)	65.5(4)
Se(17)-Mo(5)-Se(23)	90.9(4)	Mo(5)-Se(23)-Mo(6)	65.9(3)
Se(17)-Mo(5)-Se(24)	128.5(4)	Mo(5)-Se(23)-Se(24)	62.3(4)
Se(18)-Mo(5)-Se(21)	95.1(4)	Mo(6)-Se(23)-Se(24)	60.9(3)
Se(18)-Mo(5)-Se(22)	92.9(4)	Mo(5)-Se(24)-Se(23)	64.4(4)
Se(18)-Mo(5)-Se(23)	93.1(4)	Mo(6)-Se(24)-Se(23)	66.0(4)
Se(18)-Mo(5)-Se(24)	91.3(4)	Mo(4)-Se(25)-Mo(6)	63.1(3)
Se(21)-Mo(5)-Se(22)	53.9(4)	Mo(4)-Se(25)-Se(26)	61.0(4)
Se(21)-Mo(5)-Se(23)	165.7(4)	Mo(6)-Se(25)-Se(26)	61.4(3)
Se(21)-Mo(5)-Se(24)	138.0(4)	Mo(4)-Se(26)-Mo(6)	66.4(4)
Se(22)-Mo(5)-Se(23)	137.3(5)	Mo(4)-Se(26)-Se(25)	67.0(4)
Se(22)-Mo(5)-Se(24)	84.4(4)	Mo(6)-Se(26)-Se(25)	65.8(4)
Se(23)-Mo(5)-Se(24)	53.3(3)	Mo(7)-Se(27)-Mo(8)	68.8(4)
Mo(4)-Mo(6)-Mo(5)	59.4(3)	Mo(7)-Se(27)-Mo(9)	67.1(4)
Mo(4)-Mo(6)-Se(14)	55.2(3)	Mo(8)-Se(27)-Mo(9)	67.3(4)
Mo(4)-Mo(6)-Se(25)	59.4(3)	Mo(7)-Se(28)-Se(29)	63.8(4)

Table 2-19. (cont'd)

Mo(4)-Mo(6)-Se(26)	57.2(3)	Mo(7)-Se(29)-Se(28)	63.1(4)
Mo(5)-Mo(6)-Se(14)	54.4(3)	Mo(8)-Se(30)-Se(31)	62.1(4)
Mo(5)-Mo(6)-Se(23)	56.5(3)	Mo(8)-Se(31)-Se(30)	64.8(4)
Mo(5)-Mo(6)-Se(24)	56.4(3)	Mo(9)-Se(32)-Se(33)	64.1(4)
Se(14)-Mo(6)-Se(19)	96.9(4)	Mo(9)-Se(33)-Se(32)	60.8(4)
Se(14)-Mo(6)-Se(20)	148.5(4)	Mo(7)-Se(34)-Mo(8)	63.6(3)
Se(14)-Mo(6)-Se(23)	81.0(4)	Mo(7)-Se(34)-Se(35)	58.8(3)
Se(14)-Mo(6)-Se(24)	110.0(5)	Mo(8)-Se(34)-Se(35)	60.6(3)
Se(14)-Mo(6)-Se(25)	86.1(4)	Mo(7)-Se(35)-Mo(8)	66.3(3)
Se(14)-Mo(6)-Se(26)	111.9(4)	Mo(7)-Se(35)-Se(34)	64.2(4)
Se(19)-Mo(6)-Se(20)	51.6(4)	Mo(8)-Se(35)-Se(34)	63.1(4)
Se(19)-Mo(6)-Se(23)	88.6(4)	Mo(8)-Se(36)-Mo(9)	63.8(3)
Se(19)-Mo(6)-Se(24)	126.3(4)	Mo(8)-Se(36)-Se(37)	62.8(4)
Se(19)-Mo(6)-Se(25)	88.5(4)	Mo(9)-Se(36)-Se(37)	60.5(3)
Se(19)-Mo(6)-Se(26)	127.4(5)	Mo(8)-Se(37)-Mo(9)	64.8(3)
Se(20)-Mo(6)-Se(23)	96.3(4)	Mo(8)-Se(37)-Se(36)	62.4(4)
Se(20)-Mo(6)-Se(24)	92.4(4)	Mo(9)-Se(37)-Se(36)	64.1(4)
Se(20)-Mo(6)-Se(25)	92.3(4)	Mo(7)-Se(38)-Mo(9)	64.4(3)
Se(20)-Mo(6)-Se(26)	91.5(4)	Mo(7)-Se(38)-Se(39)	63.2(4)
Se(23)-Mo(6)-Se(24)	53.2(3)	Mo(9)-Se(38)-Se(39)	62.0(3)
Se(23)-Mo(6)-Se(25)	166.3(5)	Mo(7)-Se(39)-Mo(9)	65.1(3)
Se(23)-Mo(6)-Se(26)	137.1(4)	Mo(7)-Se(39)-Se(38)	63.2(4)
Se(24)-Mo(6)-Se(25)	137.2(4)	Mo(9)-Se(39)-Se(38)	64.3(4)

The structure of (V) contains two $[\text{Mo}_3\text{Se}_{13}]^{2-}$ anions attached to a monoselenide, as shown in Figure 2-7. The two $[\text{Mo}_3\text{Se}_{13}]^{2-}$ anions are interacting with a Se^{2-} anion via the six axial Se atoms of the doubly bridging diselenides in the two $[\text{Mo}_3\text{Se}_{13}]^{2-}$ clusters. This is very similar to the interaction between subcluster (B) and (C) in (III) and (IV).

The two $[\text{Mo}_3\text{Se}_{13}]^{2-}$ clusters in (V) also feature interesting structural modifications on the lengthening of bridging diselenides introduced through the special $\text{Se}\cdots\text{Se}$ short contacts mentioned above.

Selected bond distances and bond angles of (V) are given in Table 2-20. The average Mo-Mo distance is $2.77(1)\text{\AA}$. For both bridging and terminal diselenides, the average Mo-(equatorial Se) distance is also longer than the average Mo-(axial Se) distance ($2.61(2)\text{\AA}$ and $2.54\text{\AA}$ for bridging diselenides; $2.63(1)\text{\AA}$ and $2.61(2)\text{\AA}$ for terminal diselenides). The average Mo to the triply bridging selenide (Se(1) and Se(14)) distance is $2.495(9)\text{\AA}$. It is slightly longer than that of (I) but falls in the range of other $[\text{Mo}_3\text{Se}_7]^{4+}$ containing compounds. Interestingly, the average bridging diselenide distance ($2.36(2)\text{\AA}$) is significantly longer than those in (I) and (II), while the average terminal diselenide distance ($2.34(2)\text{\AA}$) remains approximately the same. The distances of the $\text{Se}\cdots\text{Se}$ short contacts between Se(27) and the six axial selenium atoms of the bridging diselenides in the two $[\text{Mo}_3\text{Se}_{13}]^{2-}$ clusters range from $2.81(1)\text{\AA}$ to $3.035(9)\text{\AA}$. As observed earlier in (III) and (IV), it is again the $\text{Se}\cdots\text{Se}$ short contacts that cause the lengthening of the bridging diselenides.

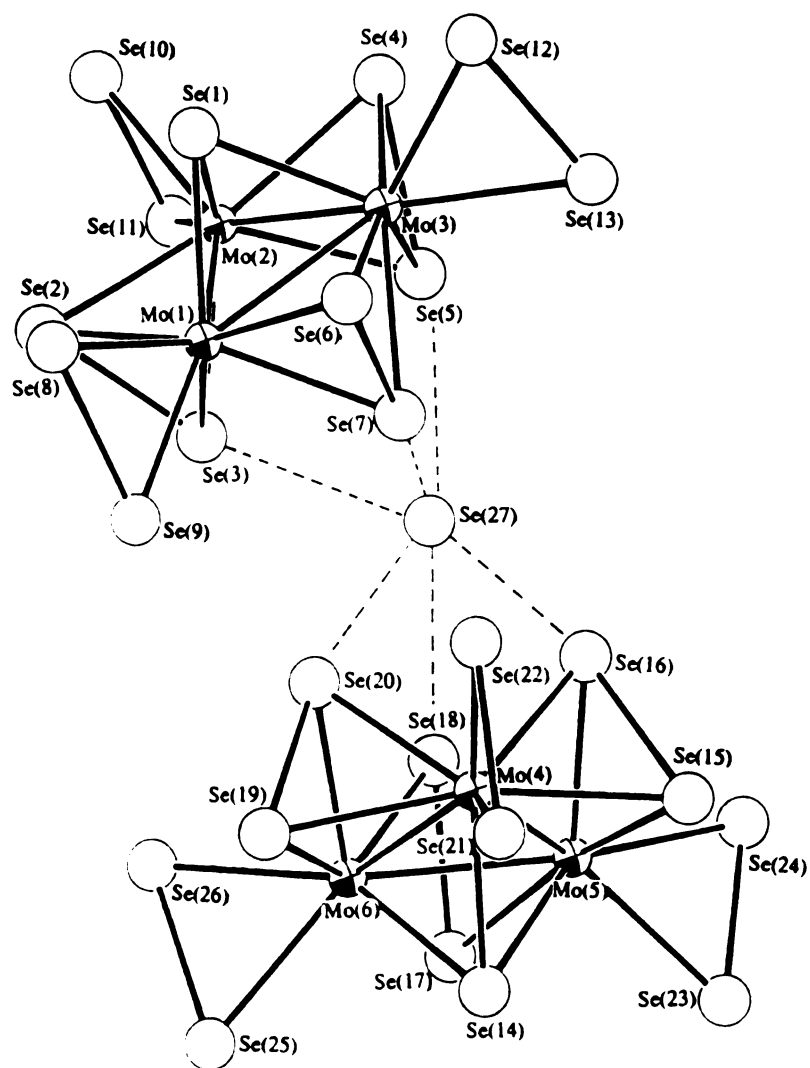


Figure 2-7: ORTEP representation and labeling scheme of $[\text{Mo}_6\text{Se}_{27}]^{6-}$.

Dashed lines represent Se...Se short contacts.

Table 2-20. Selected Bond Distances(Å) and Angles(deg) for K₆Mo₆Se₂₇·6H₂O with Standard Deviations in Parentheses

Selected Bond Distances (Å)			
Mo(1)-Mo(2)	2.781(9)	Se(17)-Se(18)	2.341(8)
Mo(1)-Mo(3)	2.761(7)	Se(19)-Se(20)	2.351(8)
Mo(2)-Mo(3)	2.782(8)	Se(21)-Se(22)	2.341(7)
Mo(4)-Mo(5)	2.759(9)	Se(23)-Se(24)	2.323(8)
Mo(4)-Mo(6)	2.769(8)	Se(25)-Se(26)	2.382(8)
Mo(5)-Mo(6)	2.760(7)	Se(4)-K(1)	3.70(2)
Mo(1)-Se(1)	2.495(7)	Se(4)-K(1)	3.62(2)
Mo(1)-Se(2)	2.629(9)	Se(12)-K(1)	3.43(2)
Mo(1)-Se(3)	2.54(1)	Se(13)-K(1)	3.42(2)
Mo(1)-Se(6)	2.591(8)	Se(21)-K(1)	3.44(2)
Mo(1)-Se(7)	2.535(7)	Se(25)-K(1)	3.46(2)
Mo(1)-Se(8)	2.586(8)	Se(26)-K(1)	3.41(2)
Mo(1)-Se(9)	2.633(8)	Se(4)-K(2)	3.62(2)
Mo(2)-Se(1)	2.51(1)	Se(5)-K(2)	3.68(2)
Mo(2)-Se(2)	2.594(7)	Se(11)-K(2)	3.36(1)
Mo(2)-Se(3)	2.545(7)	Se(12)-K(2)	3.36(2)
Mo(2)-Se(4)	2.609(7)	Se(19)-K(2)	3.57(1)
Mo(2)-Se(5)	2.552(7)	Se(25)-K(2)	3.25(1)
Mo(2)-Se(10)	2.609(9)	Se(26)-K(2)	3.55(1)
Mo(2)-Se(11)	2.656(9)	Se(9)-K(3)	3.53(2)
Mo(3)-Se(1)	2.486(7)	Se(13)-K(3)	3.46(2)
Mo(3)-Se(4)	2.601(9)	Se(22)-K(3)	3.23(2)
Mo(3)-Se(5)	2.542(9)	Se(26)-K(3)	3.55(2)
Mo(3)-Se(6)	2.595(9)	Se(8)-K(4)	3.54(2)
Mo(3)-Se(7)	2.533(6)	Se(10)-K(4)	3.50(2)
Mo(3)-Se(12)	2.59(1)	Se(11)-K(4)	3.43(2)
Mo(3)-Se(13)	2.622(8)	Se(14)-K(4)	3.70(2)
Mo(4)-Se(14)	2.505(9)	Se(15)-K(4)	3.60(1)
Mo(4)-Se(15)	2.607(7)	Se(15)-K(4)	3.56(1)
Mo(4)-Se(16)	2.535(7)	Se(23)-K(4)	3.44(2)

Table 2-20. (cont'd)

Mo(4)-Se(19)	2.609(7)	Se(24)-K(4)	3.25(2)
Mo(4)-Se(20)	2.532(8)	Se(10)-K(5)	3.78(2)
Mo(4)-Se(21)	2.604(9)	Se(15)-K(5)	3.61(2)
Mo(4)-Se(22)	2.61(1)	Se(17)-K(5)	3.39(2)
Mo(5)-Se(14)	2.504(8)	Se(18)-K(5)	3.77(2)
Mo(5)-Se(15)	2.619(9)	Se(21)-K(5)	3.37(2)
Mo(5)-Se(16)	2.55(1)	Se(23)-K(5)	3.28(2)
Mo(5)-Se(17)	2.609(8)	Se(24)-K(5)	3.31(2)
Mo(5)-Se(18)	2.553(9)	Se(24)-K(5)	3.73(2)
Mo(5)-Se(23)	2.580(8)	Se(2)-K(6)	3.61(2)
Mo(5)-Se(24)	2.639(7)	Se(3)-K(6)	3.79(2)
Mo(6)-Se(14)	2.503(9)	Se(9)-K(6)	3.44(2)
Mo(6)-Se(17)	2.592(9)	Se(27)-K(6)	3.76(2)
Mo(6)-Se(18)	2.540(8)	K(1)-O(1)	2.71(4)
Mo(6)-Se(19)	2.632(9)	K(2)-O(1)	2.82(4)
Mo(6)-Se(20)	2.53(1)	K(2)-O(2)	2.75(3)
Mo(6)-Se(25)	2.619(7)	K(3)-O(3)	2.78(4)
Mo(6)-Se(26)	2.635(8)	K(3)-O(4)	3.11(4)
Se(2)-Se(3)	2.365(8)	K(3)-O(5)	3.02(5)
Se(4)-Se(5)	2.365(8)	K(4)-O(4)	3.31(4)
Se(6)-Se(7)	2.35(1)	K(5)-O(6)	2.78(5)
Se(8)-Se(9)	2.358(9)	K(6)-O(2)	2.61(4)
Se(10)-Se(11)	2.36(1)	K(6)-O(3)	2.68(4)
Se(12)-Se(13)	2.343(9)	K(6)-O(6)	2.75(5)
Se(15)-Se(16)	2.381(9)		

Selected Bond Angles (deg)

Mo(2)-Mo(1)-Mo(3)	60.3(2)	Mo(5)-Mo(4)-Mo(6)	59.9(2)
Mo(2)-Mo(1)-Se(1)	56.4(3)	Mo(5)-Mo(4)-Se(14)	56.5(3)
Mo(2)-Mo(1)-Se(2)	57.2(2)	Mo(5)-Mo(4)-Se(15)	58.3(2)
Mo(2)-Mo(1)-Se(3)	56.9(2)	Mo(5)-Mo(4)-Se(16)	57.5(2)
Mo(3)-Mo(1)-Se(1)	56.2(2)	Mo(6)-Mo(4)-Se(14)	56.4(3)
Mo(3)-Mo(1)-Se(6)	57.9(2)	Mo(6)-Mo(4)-Se(19)	58.5(2)

Table 2-20. (cont'd)

Mo(3)-Mo(1)-Se(7)	57.0(2)	Mo(6)-Mo(4)-Se(20)	56.7(3)
Se(1)-Mo(1)-Se(2)	83.3(3)	Se(14)-Mo(4)-Se(15)	83.7(2)
Se(1)-Mo(1)-Se(3)	112.8(4)	Se(14)-Mo(4)-Se(16)	113.4(2)
Se(1)-Mo(1)-Se(6)	83.0(3)	Se(14)-Mo(4)-Se(19)	83.8(2)
Se(1)-Mo(1)-Se(7)	112.5(2)	Se(14)-Mo(4)-Se(20)	112.5(2)
Se(1)-Mo(1)-Se(8)	92.3(3)	Se(14)-Mo(4)-Se(21)	96.4(3)
Se(1)-Mo(1)-Se(9)	145.8(3)	Se(14)-Mo(4)-Se(22)	149.7(3)
Se(2)-Mo(1)-Se(3)	54.4(2)	Se(15)-Mo(4)-Se(16)	55.1(2)
Se(2)-Mo(1)-Se(6)	165.4(2)	Se(15)-Mo(4)-Se(19)	166.4(2)
Se(2)-Mo(1)-Se(7)	136.4(3)	Se(15)-Mo(4)-Se(20)	136.7(2)
Se(2)-Mo(1)-Se(8)	86.6(2)	Se(15)-Mo(4)-Se(21)	88.3(2)
Se(2)-Mo(1)-Se(9)	96.8(3)	Se(15)-Mo(4)-Se(22)	94.5(2)
Se(3)-Mo(1)-Se(6)	136.7(3)	Se(16)-Mo(4)-Se(19)	136.1(3)
Se(3)-Mo(1)-Se(7)	82.4(3)	Se(16)-Mo(4)-Se(20)	81.9(2)
Se(3)-Mo(1)-Se(8)	127.8(3)	Se(16)-Mo(4)-Se(21)	127.0(3)
Se(3)-Mo(1)-Se(9)	94.0(3)	Se(16)-Mo(4)-Se(22)	89.3(2)
Se(6)-Mo(1)-Se(7)	54.7(3)	Se(19)-Mo(4)-Se(20)	54.4(2)
Se(6)-Mo(1)-Se(8)	89.1(3)	Se(19)-Mo(4)-Se(21)	87.6(2)
Se(6)-Mo(1)-Se(9)	91.8(3)	Se(19)-Mo(4)-Se(22)	93.5(2)
Se(7)-Mo(1)-Se(8)	130.3(3)	Se(20)-Mo(4)-Se(21)	126.7(3)
Se(7)-Mo(1)-Se(9)	90.9(2)	Se(20)-Mo(4)-Se(22)	89.5(3)
Se(8)-Mo(1)-Se(9)	53.7(2)	Se(21)-Mo(4)-Se(22)	53.3(2)
Mo(1)-Mo(2)-Mo(3)	59.5(2)	Mo(4)-Mo(5)-Mo(6)	60.2(2)
Mo(1)-Mo(2)-Se(1)	56.0(2)	Mo(4)-Mo(5)-Se(14)	56.6(2)
Mo(1)-Mo(2)-Se(2)	58.4(2)	Mo(4)-Mo(5)-Se(15)	57.9(2)
Mo(1)-Mo(2)-Se(3)	56.8(3)	Mo(4)-Mo(5)-Se(16)	56.9(3)
Mo(3)-Mo(2)-Se(1)	55.8(2)	Mo(6)-Mo(5)-Se(14)	56.5(2)
Mo(3)-Mo(2)-Se(4)	57.6(2)	Mo(6)-Mo(5)-Se(17)	57.7(2)
Mo(3)-Mo(2)-Se(5)	56.7(2)	Mo(6)-Mo(5)-Se(18)	57.0(2)
Se(1)-Mo(2)-Se(2)	83.8(2)	Se(14)-Mo(5)-Se(15)	83.5(3)
Se(1)-Mo(2)-Se(3)	112.3(4)	Se(14)-Mo(5)-Se(16)	112.9(3)
Se(1)-Mo(2)-Se(4)	82.6(2)	Se(14)-Mo(5)-Se(17)	84.1(3)

Table 2-20. (cont'd)

Se(1)-Mo(2)-Se(5)	111.9(3)	Se(14)-Mo(5)-Se(18)	112.9(3)
Se(1)-Mo(2)-Se(10)	93.4(3)	Se(14)-Mo(5)-Se(23)	92.8(2)
Se(1)-Mo(2)-Se(11)	146.7(2)	Se(14)-Mo(5)-Se(24)	145.4(2)
Se(2)-Mo(2)-Se(3)	54.8(2)	Se(15)-Mo(5)-Se(16)	54.8(3)
Se(2)-Mo(2)-Se(4)	165.5(2)	Se(15)-Mo(5)-Se(17)	166.9(3)
Se(2)-Mo(2)-Se(5)	136.6(2)	Se(15)-Mo(5)-Se(18)	136.1(3)
Se(2)-Mo(2)-Se(10)	88.3(2)	Se(15)-Mo(5)-Se(23)	90.5(3)
Se(2)-Mo(2)-Se(11)	93.9(2)	Se(15)-Mo(5)-Se(24)	92.1(2)
Se(3)-Mo(2)-Se(4)	136.2(2)	Se(16)-Mo(5)-Se(17)	135.2(3)
Se(3)-Mo(2)-Se(5)	82.1(2)	Se(16)-Mo(5)-Se(18)	81.6(2)
Se(3)-Mo(2)-Se(10)	129.8(3)	Se(16)-Mo(5)-Se(23)	131.3(3)
Se(3)-Mo(2)-Se(11)	92.6(4)	Se(16)-Mo(5)-Se(24)	91.5(3)
Se(4)-Mo(2)-Se(5)	54.5(2)	Se(17)-Mo(5)-Se(18)	53.9(2)
Se(4)-Mo(2)-Se(10)	87.5(2)	Se(17)-Mo(5)-Se(23)	85.8(3)
Se(4)-Mo(2)-Se(11)	94.7(3)	Se(17)-Mo(5)-Se(24)	95.7(3)
Se(5)-Mo(2)-Se(10)	128.5(2)	Se(18)-Mo(5)-Se(23)	126.7(3)
Se(5)-Mo(2)-Se(11)	92.5(3)	Se(18)-Mo(5)-Se(24)	93.9(3)
Se(10)-Mo(2)-Se(11)	53.4(3)	Se(23)-Mo(5)-Se(24)	52.9(2)
Mo(1)-Mo(3)-Mo(2)	60.2(2)	Mo(4)-Mo(6)-Mo(5)	59.9(2)
Mo(1)-Mo(3)-Se(1)	56.5(2)	Mo(4)-Mo(6)-Se(14)	56.5(3)
Mo(1)-Mo(3)-Se(6)	57.8(2)	Mo(4)-Mo(6)-Se(19)	57.7(2)
Mo(1)-Mo(3)-Se(7)	57.0(2)	Mo(4)-Mo(6)-Se(20)	56.9(3)
Mo(2)-Mo(3)-Se(1)	56.5(3)	Mo(5)-Mo(6)-Se(14)	56.5(2)
Mo(2)-Mo(3)-Se(4)	57.8(2)	Mo(5)-Mo(6)-Se(17)	58.2(2)
Mo(2)-Mo(3)-Se(5)	57.1(2)	Mo(5)-Mo(6)-Se(18)	57.4(2)
Se(1)-Mo(3)-Se(4)	83.2(2)	Se(14)-Mo(6)-Se(17)	84.4(3)
Se(1)-Mo(3)-Se(5)	113.0(3)	Se(14)-Mo(6)-Se(18)	113.4(3)
Se(1)-Mo(3)-Se(6)	83.1(3)	Se(14)-Mo(6)-Se(19)	83.4(3)
Se(1)-Mo(3)-Se(7)	112.9(2)	Se(14)-Mo(6)-Se(20)	112.8(3)
Se(1)-Mo(3)-Se(12)	93.1(3)	Se(14)-Mo(6)-Se(25)	94.4(2)
Se(1)-Mo(3)-Se(13)	146.4(3)	Se(14)-Mo(6)-Se(26)	147.9(3)
Se(4)-Mo(3)-Se(5)	54.7(2)	Se(17)-Mo(6)-Se(18)	54.3(2)

Table 2-20. (cont'd)

Se(4)-Mo(3)-Se(6)	165.3(2)	Se(17)-Mo(6)-Se(19)	167.2(2)
Se(4)-Mo(3)-Se(7)	137.0(3)	Se(17)-Mo(6)-Se(20)	135.6(3)
Se(4)-Mo(3)-Se(12)	87.5(2)	Se(17)-Mo(6)-Se(25)	86.1(3)
Se(4)-Mo(3)-Se(13)	96.3(3)	Se(17)-Mo(6)-Se(26)	96.7(2)
Se(5)-Mo(3)-Se(6)	136.9(2)	Se(18)-Mo(6)-Se(19)	135.5(2)
Se(5)-Mo(3)-Se(7)	82.6(4)	Se(18)-Mo(6)-Se(20)	81.6(2)
Se(5)-Mo(3)-Se(12)	128.2(3)	Se(18)-Mo(6)-Se(25)	126.1(3)
Se(5)-Mo(3)-Se(13)	93.2(2)	Se(18)-Mo(6)-Se(26)	92.3(3)
Se(6)-Mo(3)-Se(7)	54.6(3)	Se(19)-Mo(6)-Se(20)	54.2(3)
Se(6)-Mo(3)-Se(12)	88.0(3)	Se(19)-Mo(6)-Se(25)	90.7(3)
Se(6)-Mo(3)-Se(13)	92.2(3)	Se(19)-Mo(6)-Se(26)	91.5(2)
Se(7)-Mo(3)-Se(12)	128.6(3)	Se(20)-Mo(6)-Se(25)	129.8(2)
Se(7)-Mo(3)-Se(13)	90.4(2)	Se(20)-Mo(6)-Se(26)	88.7(2)
Se(12)-Mo(3)-Se(13)	53.4(2)	Se(25)-Mo(6)-Se(26)	53.9(2)
Mo(1)-Se(1)-Mo(2)	67.6(3)	Mo(4)-Se(14)-Mo(5)	66.9(2)
Mo(1)-Se(1)-Mo(3)	67.3(2)	Mo(4)-Se(14)-Mo(6)	67.1(2)
Mo(2)-Se(1)-Mo(3)	67.7(2)	Mo(5)-Se(14)-Mo(6)	66.9(2)
Mo(1)-Se(2)-Mo(2)	64.4(2)	Mo(4)-Se(15)-Mo(5)	63.7(2)
Mo(1)-Se(2)-Se(3)	60.9(3)	Mo(4)-Se(15)-Se(16)	60.9(2)
Mo(2)-Se(2)-Se(3)	61.6(2)	Mo(5)-Se(15)-Se(16)	61.2(3)
Mo(1)-Se(3)-Mo(2)	66.3(3)	Mo(4)-Se(16)-Mo(5)	65.7(2)
Mo(1)-Se(3)-Se(2)	64.7(3)	Mo(4)-Se(16)-Se(15)	64.0(2)
Mo(2)-Se(3)-Se(2)	63.6(2)	Mo(5)-Se(16)-Se(15)	64.0(2)
Mo(2)-Se(4)-Mo(3)	64.6(2)	Mo(5)-Se(17)-Mo(6)	64.1(2)
Mo(2)-Se(4)-Se(5)	61.5(2)	Mo(5)-Se(17)-Se(18)	61.8(3)
Mo(3)-Se(4)-Se(5)	61.4(3)	Mo(6)-Se(17)-Se(18)	61.7(3)
Mo(2)-Se(5)-Mo(3)	66.2(2)	Mo(5)-Se(18)-Mo(6)	65.6(2)
Mo(2)-Se(5)-Se(4)	64.0(2)	Mo(5)-Se(18)-Se(17)	64.3(2)
Mo(3)-Se(5)-Se(4)	63.9(3)	Mo(6)-Se(18)-Se(17)	64.0(3)
Mo(1)-Se(6)-Mo(3)	64.3(2)	Mo(4)-Se(19)-Mo(6)	63.8(2)
Mo(1)-Se(6)-Se(7)	61.4(2)	Mo(4)-Se(19)-Se(20)	61.1(2)
Mo(3)-Se(6)-Se(7)	61.3(2)	Mo(6)-Se(19)-Se(20)	60.6(3)

Table 2-20. (cont'd)

Mo(1)-Se(7)-Mo(3)	66.0(2)	Mo(4)-Se(20)-Mo(6)	66.4(2)
Mo(1)-Se(7)-Se(6)	63.9(2)	Mo(4)-Se(20)-Se(19)	64.5(2)
Mo(3)-Se(7)-Se(6)	64.0(3)	Mo(6)-Se(20)-Se(19)	65.2(2)
Mo(1)-Se(8)-Se(9)	64.2(3)	Mo(4)-Se(21)-Se(22)	63.5(4)
Mo(1)-Se(9)-Se(8)	62.1(2)	Mo(4)-Se(22)-Se(21)	63.2(3)
Mo(2)-Se(10)-Se(11)	64.3(2)	Mo(5)-Se(23)-Se(24)	64.9(2)
Mo(2)-Se(11)-Se(10)	62.3(3)	Mo(5)-Se(24)-Se(23)	62.3(2)
Mo(3)-Se(12)-Se(13)	63.9(3)	Mo(6)-Se(25)-Se(26)	63.4(2)
Mo(3)-Se(13)-Se(12)	62.7(3)	Mo(6)-Se(26)-Se(25)	62.7(3)

Structure of $[\text{K}_2\text{Mo}_3\text{Se}_{18}]_n$ (VI)

$[\text{Mo}_3\text{Se}_{18}]_n^{2n-}$ (VI) is the first known molybdenum polyselenide polymer. The structure of $[\text{Mo}_3\text{Se}_{18}]_n^{2n-}$ is illustrated in Figure 2-8. It is composed of a zigzag chain-like structure containing the repeating unit shown in Figure 2-9. It is also worthwhile to point out that the compound contains four different polyselenides Se^{2-} , Se_2^{2-} , Se_3^{2-} and Se_4^{2-} as ligands, even though only Se_4^{2-} was used as starting material. The starting tetraselenide is reduced by Mo metal to form shorter selenides, while Mo metal is oxidized to the formal oxidation state of 4+. The presence of all the different polyselenides also attests to the complexity of polyselenide solutions²⁴.

The zigzag chain of $[\text{Mo}_3(\mu_2\text{-Se}_2)_3(\mu_3\text{-Se})(\text{Se}_4)_2(\text{Se}_3)]_n^{2n-}$ can be viewed as parallel $[\text{Mo}_3(\mu_2\text{-Se}_2)_3(\mu_3\text{-Se})]^{4+}$ cores, facing in the same direction and cross-linked by bridging Se_4^{2-} ligands. The latter bond to the two Mo atoms (Mo(2) and Mo(3)) of the $[\text{Mo}_3(\mu_2\text{-Se}_2)_3(\mu_3\text{-Se})]^{4+}$ cores. The zigzag chains are noncentrosymmetric. All the triply bridging Se atoms in the $[\text{Mo}_3(\mu_2\text{-Se}_2)_3(\mu_3\text{-Se})]^{4+}$ units within a single zigzag chain are pointed to the $\langle 010 \rangle$ direction. The third Mo atom, Mo(3) is bonded to a terminal Se_3^{2-} ligand in an unusual fashion. In this triselenide ligand, two adjacent Se atoms, Se(2) and Se(3), are bonded to Mo(3), while the third terminal Se(4) atom is left alone. What is unprecedented is that Se(4) stretches out to the center of a triangle of the three Se atoms of the three bridging diselenides of another $[\text{Mo}_3(\mu_2\text{-Se}_2)_3(\mu_3\text{-Se})]^{4+}$ cluster in a neighboring chain. This generates an unusual fashion of Se...Se short contacts similar to but different from those found above. This fragment is shown in Figure 2-10. The bond distances in the triselenide unit are

2.336(3)Å and 2.327(3)Å respectively, which are in the range of other normal Se-Se distances^{24,25}. The average distance between Se_{ap} and Se_a is 3.15(16)Å (see Scheme (2)). The distance between two parallel [Mo₃(μ₂-Se₂)₃(μ₃-Se)]⁴⁺ triangles in each individual chain is 12.66 Å which allows for the insertion of another such triangle from the neighboring chain. This brings the zigzag chains together side by side in a staggered arrangement to make two dimensional sheets. The single chains interlock in a "zipper fashion". The average distance between these sheets is 9.17Å, with the potassium atoms located in between. Selected distances and angles in the Mo/Se framework are shown in Table 2-21. There are two crystallographically different potassium atoms with coordination numbers of 9 and 10 respectively. The average K-Se distance is 3.6(2)Å.

The average Se-Se distances in the tetraselenide ligands are normal at 2.36(2)Å. The three bridging diselenides in the [Mo₃(μ₂-Se₂)₃(μ₃-Se)]⁴⁺ core have the average bond distance of 2.34(1)Å, which is slightly longer than those in the discrete [Mo₃Se₁₃]²⁻ of (I) and (II).

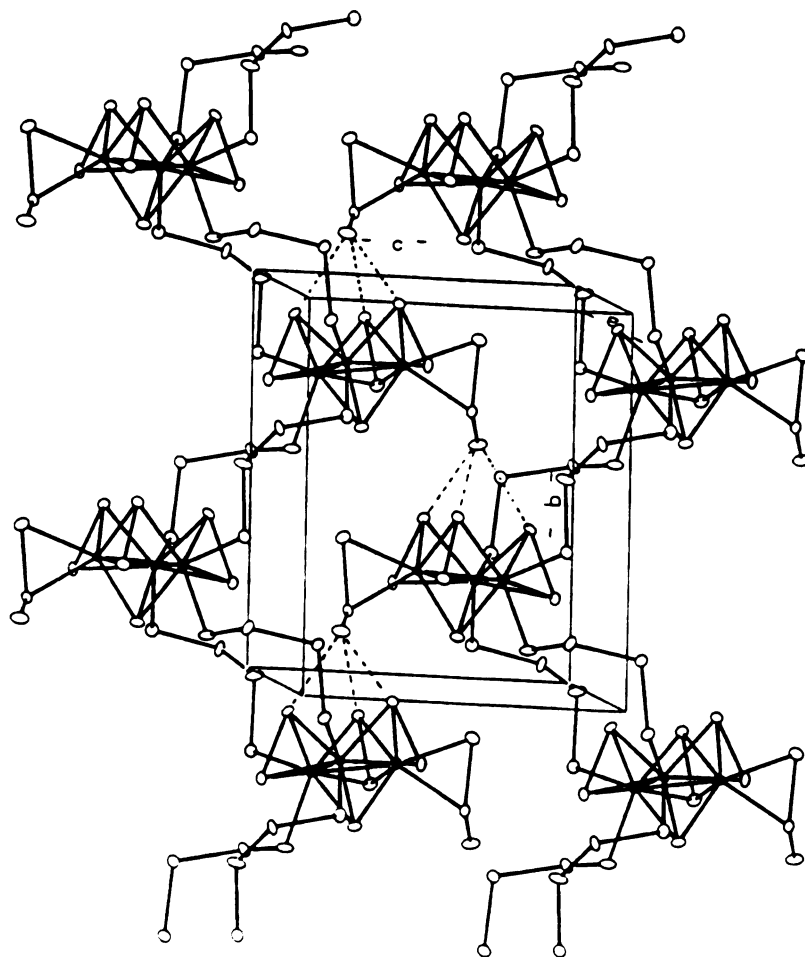


Figure 2-8: ORTEP representation of [Mo₃Se₁₈]ⁿ⁻ chains. Dashed lines show Se...Se short contacts.

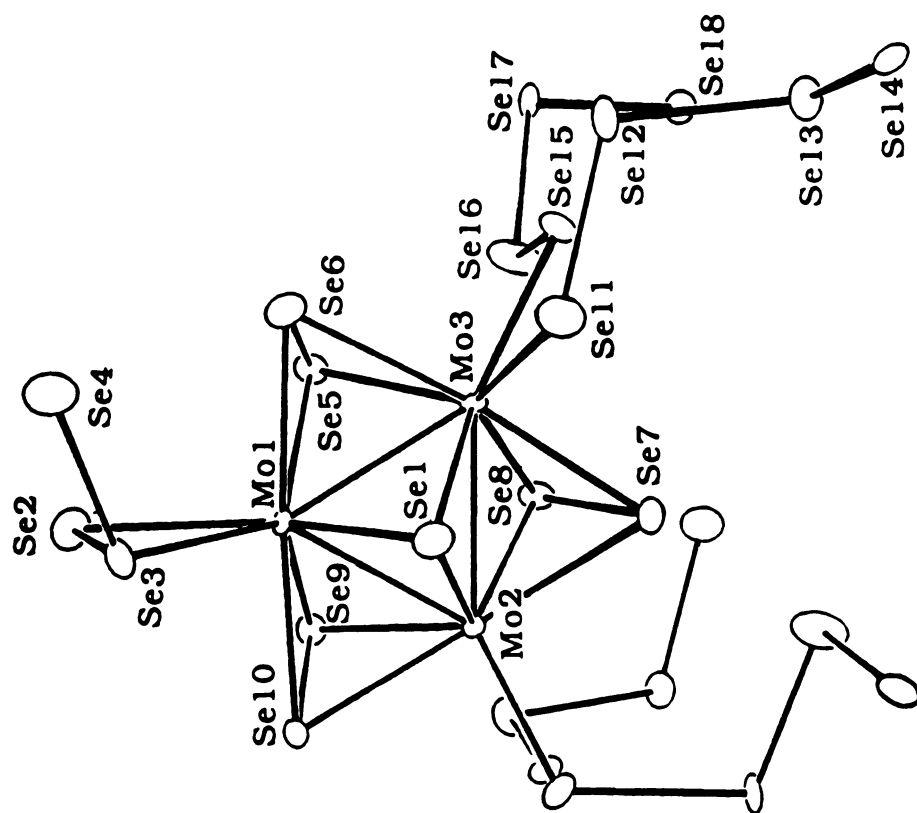


Figure 2-9: Labeling scheme of the repeating unit of $[\text{Mo}_3\text{Se}_{18}]_n^{2n-}$.

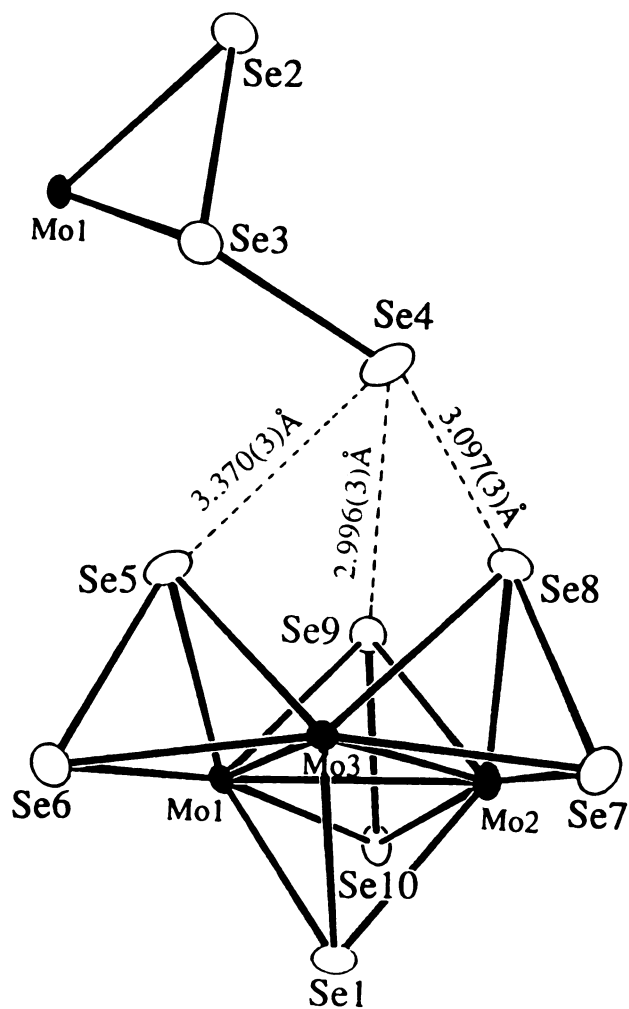


Figure 2-10: ORTEP representation of the interaction between the Se_3^{2-} ligand and the $[\text{Mo}_3(\mu_3\text{-Se})(\mu_2\text{-Se}_2)_4]^{4+}$ core in $[\text{Mo}_3\text{Se}_{18}]_n^{2n-}$.

Table 2-21. Selected Bond Distances (Å) and Angles (deg) for K₂Mo₃Se₁₈ with Standard Deviations in Parentheses

Selected Bond Distances (Å)			
Mo1-Mo2	2.759(2)	Se3-Se4	2.327(3)
Mo1-Mo3	2.779(2)	Se4-Se5	3.370(3)
Mo2-Mo3	2.781(2)	Se4-Se8	3.097(3)
Mo1-Se1	2.473(3)	Se4-Se9	2.996(3)
Mo1-Se2	2.660(3)	Se5-Se6	2.330(3)
Mo1-Se3	2.613(3)	Se7-Se8	2.340(3)
Mo1-Se5	2.522(3)	Se9-Se10	2.350(3)
Mo1-Se6	2.612(3)	Se11-Se12	2.370(3)
Mo1-Se9	2.519(3)	Se13-Se14	2.382(3)
Mo1-Se10	2.604(2)	Se15-Se16	2.376(3)
Mo2-Se1	2.513(3)	Se17-Se18	2.354(3)
Mo2-Se7	2.621(3)	Se1-K1	3.747(7)
Mo2-Se8	2.539(3)	Se4-K1	3.532(7)
Mo2-Se9	2.572(3)	Se10-K1	3.728(6)
Mo2-Se10	2.613(2)	Se14-K1	3.341(6)
Mo2-Se14	2.625(3)	Se18-K1	3.763(7)
Mo2-Se18	2.650(3)	Se2-K2	3.300(6)
Mo3-Se1	2.503(3)	Se3-K2	3.740(6)
Mo3-Se5	2.544(3)	Se7-K2	3.785(7)
Mo3-Se6	2.660(3)	Se10-K2	3.904(7)
Mo3-Se7	2.615(3)	Se12-K2	3.668(7)
Mo3-Se8	2.551(3)	Se14-K2	3.379(7)
Mo3-Se11	2.617(3)	Se15-K2	3.241(7)
Mo3-Se15	2.651(2)	Se17-K2	3.444(7)
Se2-Se3	2.336(3)		
Selected Bond Angles (deg)			
Mo2-Mo1-Mo3	60.27(6)	Mo1-Mo3-Se1	55.53(7)
Mo1-Mo2-Mo3	60.22(6)	Mo1-Mo3-Se5	56.36(6)
Mo1-Mo3-Mo2	59.51(6)	Mo1-Mo3-Se6	57.35(6)

Table 2-21. (cont'd)

Mo2-Mo1-Se1	57.09(7)	Mo2-Mo3-Se1	56.49(7)
Mo2-Mo1-Se9	58.10(7)	Mo2-Mo3-Se7	58.02(6)
Mo2-Mo1-Se10	58.23(6)	Mo2-Mo3-Se8	56.69(6)
Mo3-Mo1-Se1	56.57(7)	Se1-Mo3-Se5	111.18(9)
Mo3-Mo1-Se5	57.11(7)	Se1-Mo3-Se6	82.66(8)
Mo3-Mo1-Se6	59.03(7)	Se1-Mo3-Se7	84.30(8)
Se1-Mo1-Se2	145.7(1)	Se1-Mo3-Se8	112.64(9)
Se1-Mo1-Se3	93.11(9)	Se1-Mo3-Se11	72.64(8)
Se1-Mo1-Se5	112.93(9)	Se1-Mo3-Se15	152.6(1)
Se1-Mo1-Se6	84.23(8)	Se5-Mo3-Se6	53.14(8)
Se1-Mo1-Se9	114.45(9)	Se5-Mo3-Se7	136.58(9)
Se1-Mo1-Se10	83.70(8)	Se5-Mo3-Se8	83.09(8)
Se2-Mo1-Se3	52.58(7)	Se5-Mo3-Se11	135.90(9)
Se2-Mo1-Se5	93.57(8)	Se5-Mo3-Se15	89.12(8)
Se2-Mo1-Se6	95.28(9)	Se6-Mo3-Se7	166.43(9)
Se2-Mo1-Se9	89.03(8)	Se6-Mo3-Se8	135.89(9)
Se2-Mo1-Se10	91.28(8)	Se6-Mo3-Se11	85.55(8)
Se3-Mo1-Se5	130.6(1)	Se6-Mo3-Se15	96.38(8)
Se3-Mo1-Se6	90.48(8)	Se7-Mo3-Se8	53.85(7)
Se3-Mo1-Se9	124.21(9)	Se7-Mo3-Se11	87.00(8)
Se3-Mo1-Se10	84.13(8)	Se7-Mo3-Se15	93.47(8)
Se5-Mo1-Se6	53.94(8)	Se8-Mo3-Se11	138.0(1)
Se5-Mo1-Se9	83.30(8)	Se8-Mo3-Se15	87.12(8)
Se5-Mo1-Se10	137.50(9)	Se11-Mo3-Se15	79.99(8)
Se6-Mo1-Se9	137.17(9)	Mo1-Se1-Mo2	67.20(7)
Se6-Mo1-Se10	166.5(1)	Mo1-Se1-Mo3	67.90(7)
Se9-Mo1-Se10	54.57(8)	Mo2-Se1-Mo3	67.33(7)
Mo1-Mo2-Se1	55.71(7)	Mo1-Se2-Se3	62.67(8)
Mo1-Mo2-Se9	56.26(7)	Mo1-Se3-Se2	64.74(9)
Mo1-Mo2-Se10	57.90(6)	Mo1-Se5-Mo3	66.53(7)
Mo3-Mo2-Se1	56.18(7)	Mo1-Se5-Se6	64.99(8)
Mo3-Mo2-Se7	57.82(7)	Mo3-Se5-Se6	65.98(8)

Table 2-21. (cont'd)

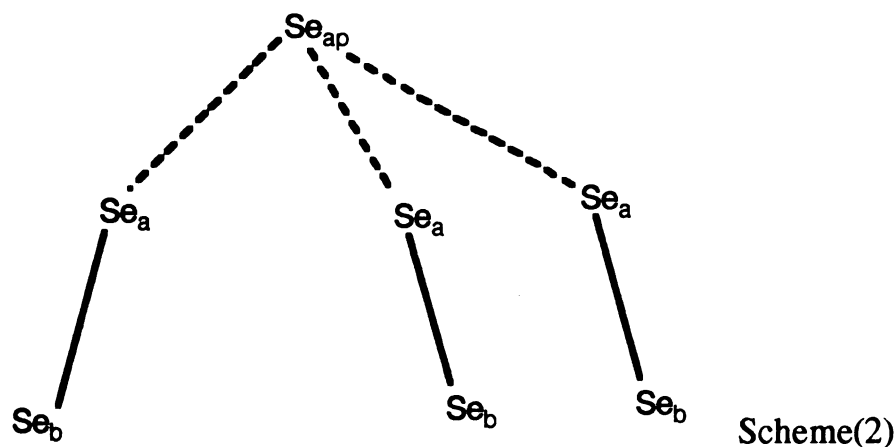
Mo3-Mo2-Se8	57.09(6)	Mo1-Se6-Mo3	63.63(7)
Se1-Mo2-Se7	83.99(8)	Mo1-Se6-Se5	61.08(8)
Se1-Mo2-Se8	112.72(9)	Mo3-Se6-Se5	60.89(8)
Se1-Mo2-Se9	111.28(9)	Mo2-Se7-Mo3	64.16(7)
Se1-Mo2-Se10	82.74(8)	Mo2-Se7-Se8	61.28(8)
Se1-Mo2-Se14	155.3(1)	Mo3-Se7-Se8	61.69(8)
Se1-Mo2-Se18	83.55(8)	Mo2-Se8-Mo3	66.22(7)
Se7-Mo2-Se8	53.90(7)	Mo2-Se8-Se7	64.82(8)
Se7-Mo2-Se9	137.28(9)	Mo3-Se8-Se7	64.47(8)
Se7-Mo2-Se10	165.8(1)	Mo1-Se9-Mo2	65.65(7)
Se7-Mo2-Se14	96.14(9)	Mo1-Se9-Se4	112.05(9)
Se7-Mo2-Se18	91.86(8)	Mo1-Se9-Se10	64.55(8)
Se8-Mo2-Se9	83.75(8)	Mo2-Se9-Se4	104.91(8)
Se8-Mo2-Se10	137.4(1)	Mo2-Se9-Se10	63.95(8)
Se8-Mo2-Se14	86.41(8)	Se4-Se9-Se10	168.9(1)
Se8-Mo2-Se18	137.51(9)	Mo1-Se10-Mo2	63.87(6)
Se9-Mo2-Se10	53.89(8)	Mo1-Se10-Se9	60.87(8)
Se9-Mo2-Se14	85.35(8)	Mo2-Se10-Se9	62.16(8)
Se9-Mo2-Se18	128.29(9)	Mo3-Se11-Se12	115.4(1)
Se10-Mo2-Se14	93.70(8)	Mo2-Se14-Se13	109.9(1)
Se10-Mo2-Se18	81.40(8)	Mo3-Se15-Se16	99.6(1)
Se14-Mo2-Se18	71.72(8)	Mo2-Se18-Se17	112.0(1)

Table 2-21. (cont'd)

Mo3-Mo2-Se8	57.09(6)	Mo1-Se6-Mo3	63.63(7)
Se1-Mo2-Se7	83.99(8)	Mo1-Se6-Se5	61.08(8)
Se1-Mo2-Se8	112.72(9)	Mo3-Se6-Se5	60.89(8)
Se1-Mo2-Se9	111.28(9)	Mo2-Se7-Mo3	64.16(7)
Se1-Mo2-Se10	82.74(8)	Mo2-Se7-Se8	61.28(8)
Se1-Mo2-Se14	155.3(1)	Mo3-Se7-Se8	61.69(8)
Se1-Mo2-Se18	83.55(8)	Mo2-Se8-Mo3	66.22(7)
Se7-Mo2-Se8	53.90(7)	Mo2-Se8-Se7	64.82(8)
Se7-Mo2-Se9	137.28(9)	Mo3-Se8-Se7	64.47(8)
Se7-Mo2-Se10	165.8(1)	Mo1-Se9-Mo2	65.65(7)
Se7-Mo2-Se14	96.14(9)	Mo1-Se9-Se4	112.05(9)
Se7-Mo2-Se18	91.86(8)	Mo1-Se9-Se10	64.55(8)
Se8-Mo2-Se9	83.75(8)	Mo2-Se9-Se4	104.91(8)
Se8-Mo2-Se10	137.4(1)	Mo2-Se9-Se10	63.95(8)
Se8-Mo2-Se14	86.41(8)	Se4-Se9-Se10	168.9(1)
Se8-Mo2-Se18	137.51(9)	Mo1-Se10-Mo2	63.87(6)
Se9-Mo2-Se10	53.89(8)	Mo1-Se10-Se9	60.87(8)
Se9-Mo2-Se14	85.35(8)	Mo2-Se10-Se9	62.16(8)
Se9-Mo2-Se18	128.29(9)	Mo3-Se11-Se12	115.4(1)
Se10-Mo2-Se14	93.70(8)	Mo2-Se14-Se13	109.9(1)
Se10-Mo2-Se18	81.40(8)	Mo3-Se15-Se16	99.6(1)
Se14-Mo2-Se18	71.72(8)	Mo2-Se18-Se17	112.0(1)

Structure of $K_{12}Mo_{12}Se_{56}$

The structure of (VII) is shown in Figure 2-11. (VII) is a discrete molecule which can be viewed as a cluster of four smaller $[Mo_3Se_{14}]^{3-}$ trinuclear, slightly different subclusters. Conceptually, (VII) can be divided into two type (A) subclusters, one type (B) subclusters and one type (C) cluster as shown in Figure 2-12. All the subclusters contain $[Mo_3Se_7]^{4+}$ cores which contain a triply bridging Se^{2-} and three bridging Se_2^{2-} ligands. In cluster (A), two Mo centers each coordinate to a terminal Se_2^{2-} ligand. The third Mo center is bound to two Se_3^{2-} ligands which are linked to cluster (B) and cluster (C) respectively. The bonding mode of the Se_3^{2-} ligand is rare. In cluster (B) and (C), one Mo center coordinates to a terminal Se_2^{2-} ligand and the other two Mo centers each coordinate to one terminal Se_3^{2-} ligand which links the four subclusters. On the top of each $[Mo_3Se_7]^{4+}$ core, an extra Se^{2-} anion interacts with the three Se atoms of the three bridging Se_2^{2-} ligands to form a formally $[Se_7]^{8-}$ "umbrella"-like fragment as shown in Scheme (2). The $Se_{ap}-Se_a$ distances range from 2.56(1) Å to



3.03(1)Å with an average of 2.76(15)Å which is much shorter than the sum of van der Waal radii of two Se atoms. The $[\text{Se}_7]^{8-}$ unit has never been previously observed. The packing diagrams of (VII) in Figure 2-13 show the tetramers are well packed with K^+ cations located between the clusters. The average $\text{K}\cdots\text{Se}$ distance is 3.47(9)Å.

Selected bond distances and angles are give in Table 2-22. The average Mo-Mo distance in (VII) (2.75(2)Å) is slightly shorter than those of the above $[\text{Mo}_3\text{Se}_7]^{4+}$ containing compounds while he average terminal Se_2^{2-} bond length (2.36(3)Å) is comparable. The shorter Mo-Mo distances originate from the stronger $\text{Se}_{\text{ap}}\cdots\text{Se}_{\text{a}}$ interactions in (VII) and will be discussed in Section 3.3. The presence of the apical Se atoms profoundly causes the lengthening of bridging Se_2^{2-} ligands which have an average value of 2.45(7)Å. It is noteworthy that the lengthening of the bridging Se_2^{2-} is inversely proportional to the $\text{Se}_{\text{ap}}\text{-Se}_{\text{a}}$ distances. The effect of the extra Se atom on the lengthening of the bridging Se_2^{2-} is the largest found among the $[\text{Mo}_3\text{Se}_7]^{4+}$ containing compounds.

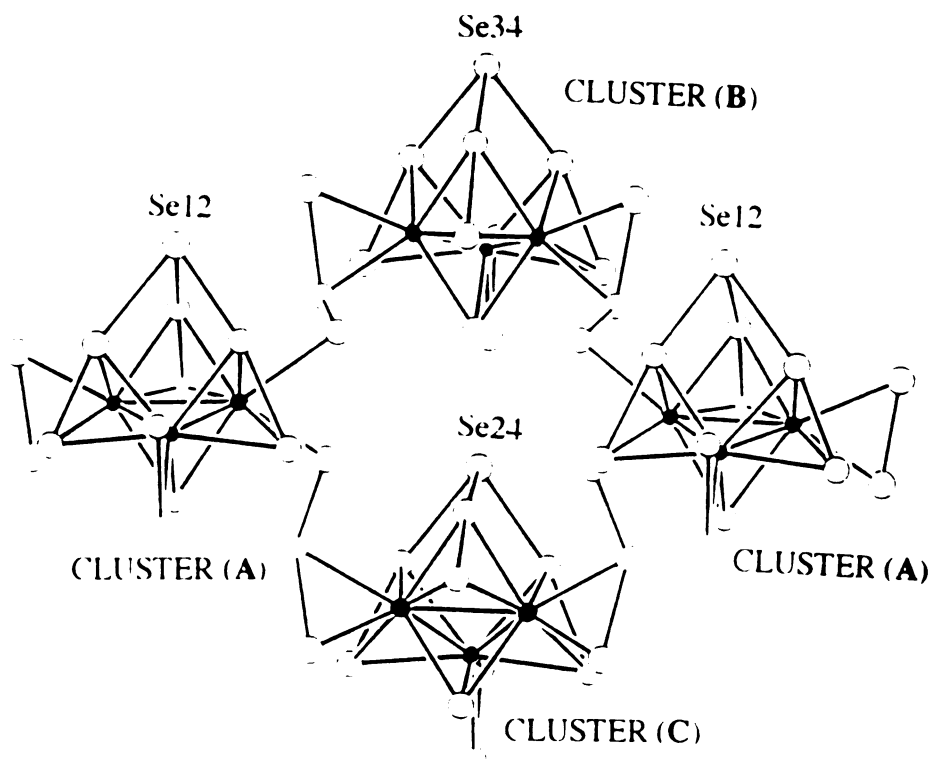


Figure 2-11: ORTEP representation of the molecular structure of the [Mo₁₂Se₅₆]¹²⁻ anion. The black circles represent Mo atoms. The open circles represent Se atoms.

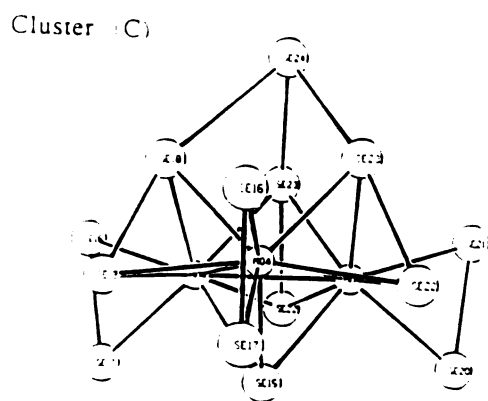
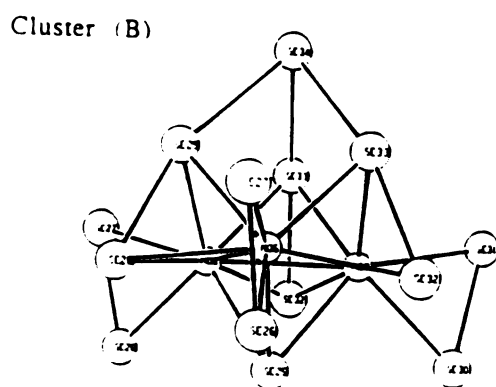
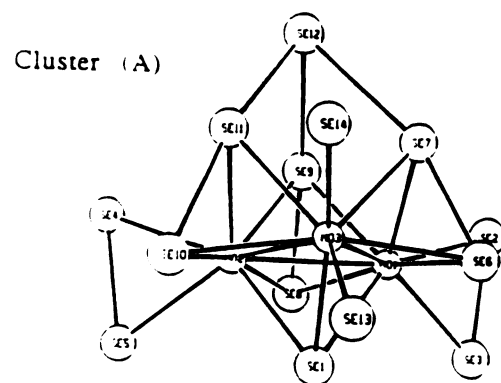


Figure 2-12: The individual structures and labeling scheme of the Mo/Se trinuclear subclusters.

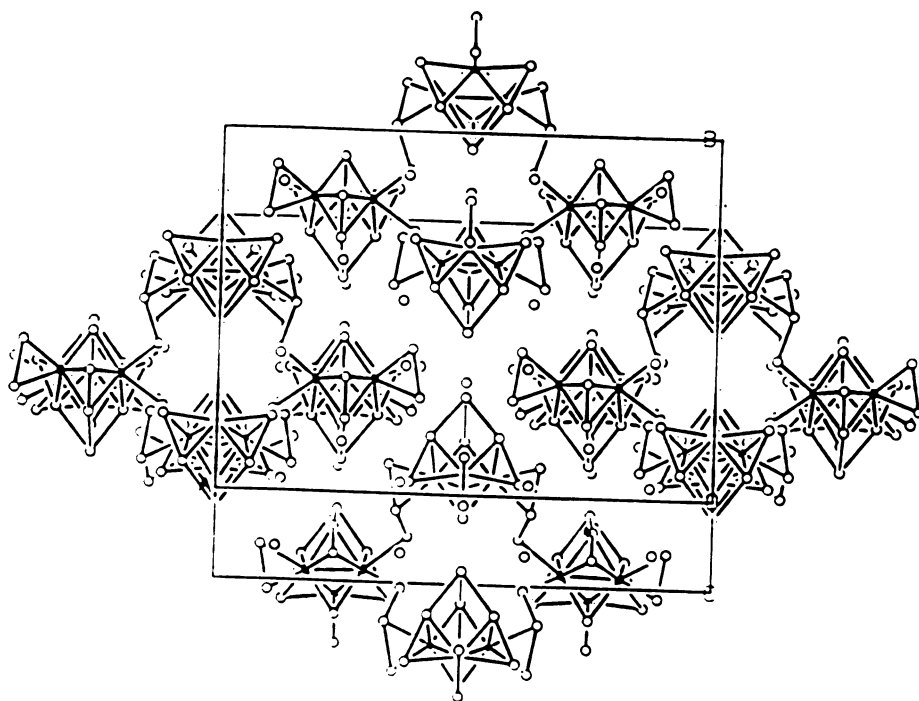


Figure 2-13: Packing diagram of $K_{12}Mo_{12}Se_{56}$.

Table 2-22. Selected Bond Distances (Å) and Angles (deg) for K₁₂Mo₁₂Se₅₆ with Standard Deviations in Parentheses

Selected Bond Distances (Å)			
Mo(1)-Mo(2)	2.758(7)	Mo(4)-Se(17)	2.622(8)
Mo(1)-Mo(3)	2.764(7)	Mo(7)-Se(25)	2.59(1)
Mo(2)-Mo(3)	2.756(7)	Mo(7)-Se(30)	2.62(1)
Mo(4)-Mo(4)	2.73(1)	Mo(7)-Se(31)	2.61(1)
Mo(4)-Mo(5)	2.733(8)	Mo(7)-Se(32)	2.641(7)
Mo(6)-Mo(6)	2.70(1)	Mo(7)-Se(33)	2.515(7)
Mo(6)-Mo(7)	2.735(8)	Se(2)-Se(3)	2.35(1)
Mo(1)-Se(1)	2.505(8)	Se(4)-Se(5)	2.37(1)
Mo(1)-Se(2)	2.611(9)	Se(6)-Se(7)	2.375(9)
Mo(1)-Se(3)	2.586(9)	Se(8)-Se(9)	2.407(9)
Mo(1)-Se(6)	2.593(8)	Se(10)-Se(11)	2.568(9)
Mo(1)-Se(7)	2.533(8)	Se(13)-Se(14)	3.000(9)
Mo(1)-Se(8)	2.664(9)	Se(7)-Se(12)	2.934(9)
Mo(1)-Se(9)	2.557(9)	Se(9)-Se(12)	2.796(9)
Mo(2)-Se(1)	2.489(8)	Se(11)-Se(12)	2.561(9)
Mo(2)-Se(4)	2.669(8)	Se(13)-Se(16)	2.411(9)
Mo(2)-Se(5)	2.620(8)	Se(14)-Se(26)	2.362(9)
Mo(2)-Se(8)	2.617(8)	Se(16)-Se(17)	2.418(9)
Mo(2)-Se(9)	2.553(8)	Se(18)-Se(19)	2.35(1)
Mo(2)-Se(10)	2.618(8)	Se(20)-Se(21)	2.37(2)
Mo(2)-Se(11)	2.561(8)	Se(22)-Se(23)	2.487(9)
Mo(3)-Se(1)	2.522(8)	Se(18)-Se(24)	3.03(1)
Mo(3)-Se(6)	2.589(8)	Se(23)-Se(24)	2.65(1)
Mo(3)-Se(7)	2.518(8)	Se(26)-Se(27)	2.33(1)
Mo(3)-Se(10)	2.613(8)	Se(28)-Se(29)	2.41(1)
Mo(3)-Se(11)	2.598(8)	Se(30)-Se(31)	2.35(1)
Mo(3)-Se(13)	2.658(8)	Se(32)-Se(33)	2.493(9)
Mo(3)-Se(14)	2.647(8)	Se(29)-Se(34)	2.83(1)
Mo(4)-Se(15)	2.486(9)	Se(33)-Se(34)	2.67(1)
Mo(4)-Se(16)	2.712(8)	Se(2)-K(1)	3.30(3)

Table 2-22. (cont'd)

Mo(4)-Se(18)	2.542(9)	Se(3)-K(4)	3.42(2)
Mo(4)-Se(19)	2.633(9)	Se(8)-K(1)	3.49(1)
Mo(4)-Se(22)	2.595(8)	Se(12)-K(2)	3.38(2)
Mo(4)-Se(23)	2.551(8)	Se(12)-K(5)	3.38(2)
Mo(5)-Se(15)	2.54(1)	Se(13)-K(6)	3.58(2)
Mo(5)-Se(20)	2.59(1)	Se(13)-K(7)	3.57(2)
Mo(5)-Se(21)	2.58(1)	Se(14)-K(5)	3.46(2)
Mo(5)-Se(22)	2.629(7)	Se(14)-K(6)	3.51(2)
Mo(5)-Se(23)	2.542(6)	Se(23)-K(7)	3.57(2)
Mo(6)-Se(25)	2.52(1)	Se(24)-K(7)	3.35(2)
Mo(6)-Se(26)	2.595(8)	Se(25)-K(7)	3.60(2)
Mo(6)-Se(27)	2.671(9)	Se(26)-K(7)	3.52(2)
Mo(6)-Se(28)	2.607(5)	Se(27)-K(3)	3.38(2)
Mo(6)-Se(29)	2.545(9)	Se(27)-K(5)	3.54(2)
Mo(6)-Se(32)	2.587(8)	Se(32)-K(7)	3.46(2)
Mo(6)-Se(33)	2.525(8)		
Selected Bond Angles (deg)			
Mo(2)-Mo(1)-Mo(3)	59.9(2)	Se(15)-Mo(5)-Se(20)	94.8(3)
Mo(2)-Mo(1)-Se(1)	56.3(2)	Se(15)-Mo(5)-Se(21)	149.4(3)
Mo(2)-Mo(1)-Se(8)	57.7(2)	Se(15)-Mo(5)-Se(22)	82.8(2)
Mo(2)-Mo(1)-Se(9)	57.3(2)	Se(15)-Mo(5)-Se(23)	113.5(3)
Mo(3)-Mo(1)-Se(1)	56.9(2)	Se(20)-Mo(5)-Se(21)	54.6(4)
Mo(3)-Mo(1)-Se(6)	57.7(2)	Se(20)-Mo(5)-Se(22)	87.6(2)
Mo(3)-Mo(1)-Se(7)	56.6(2)	Se(20)-Mo(5)-Se(23)	129.2(3)
Se(1)-Mo(1)-Se(2)	147.1(3)	Se(21)-Mo(5)-Se(22)	94.6(2)
Se(1)-Mo(1)-Se(3)	93.4(3)	Se(21)-Mo(5)-Se(23)	89.8(3)
Se(1)-Mo(1)-Se(6)	83.9(3)	Se(22)-Mo(5)-Se(23)	57.5(2)
Se(1)-Mo(1)-Se(7)	113.1(3)	Mo(7)-Mo(6)-Se(25)	58.7(2)
Se(1)-Mo(1)-Se(8)	83.9(2)	Mo(7)-Mo(6)-Se(32)	59.4(2)
Se(1)-Mo(1)-Se(9)	113.1(3)	Mo(7)-Mo(6)-Se(33)	57.0(2)
Se(2)-Mo(1)-Se(3)	53.8(2)	Se(25)-Mo(6)-Se(26)	90.6(3)

Table 2-22. (cont'd)

Se(2)-Mo(1)-Se(6)	94.5(3)	Se(25)-Mo(6)-Se(27)	143.0(3)
Se(2)-Mo(1)-Se(7)	92.0(3)	Se(25)-Mo(6)-Se(28)	83.1(3)
Se(2)-Mo(1)-Se(8)	93.9(3)	Se(25)-Mo(6)-Se(29)	114.6(3)
Se(2)-Mo(1)-Se(9)	91.5(3)	Se(25)-Mo(6)-Se(32)	83.0(3)
Se(3)-Mo(1)-Se(6)	90.1(3)	Se(25)-Mo(6)-Se(33)	115.1(3)
Se(3)-Mo(1)-Se(7)	131.0(3)	Se(26)-Mo(6)-Se(27)	52.6(2)
Se(3)-Mo(1)-Se(8)	87.3(3)	Se(26)-Mo(6)-Se(28)	89.9(2)
Se(3)-Mo(1)-Se(9)	128.4(3)	Se(26)-Mo(6)-Se(29)	131.3(3)
Se(6)-Mo(1)-Se(7)	55.2(2)	Se(26)-Mo(6)-Se(32)	82.2(3)
Se(6)-Mo(1)-Se(8)	167.4(3)	Se(26)-Mo(6)-Se(33)	127.2(3)
Se(6)-Mo(1)-Se(9)	134.3(3)	Se(27)-Mo(6)-Se(28)	92.6(2)
Se(7)-Mo(1)-Se(8)	133.9(3)	Se(27)-Mo(6)-Se(29)	91.9(2)
Se(7)-Mo(1)-Se(9)	79.3(2)	Se(27)-Mo(6)-Se(32)	93.8(3)
Se(8)-Mo(1)-Se(9)	54.9(2)	Se(27)-Mo(6)-Se(33)	93.5(3)
Mo(1)-Mo(2)-Mo(3)	60.2(2)	Se(28)-Mo(6)-Se(29)	55.7(3)
Mo(1)-Mo(2)-Se(1)	56.8(2)	Se(28)-Mo(6)-Se(32)	163.8(3)
Mo(1)-Mo(2)-Se(8)	59.4(2)	Se(28)-Mo(6)-Se(33)	136.0(3)
Mo(1)-Mo(2)-Se(9)	57.4(2)	Se(29)-Mo(6)-Se(32)	138.8(3)
Se(5)-Mo(2)-Se(9)	126.6(3)	Se(29)-Mo(6)-Se(33)	80.5(3)
Se(5)-Mo(2)-Se(10)	88.7(3)	Se(32)-Mo(6)-Se(33)	58.4(2)
Se(5)-Mo(2)-Se(11)	128.9(3)	Mo(6)-Mo(7)-Se(25)	56.5(2)
Se(8)-Mo(2)-Se(9)	55.5(2)	Mo(6)-Mo(7)-Se(32)	57.5(2)
Se(8)-Mo(2)-Se(10)	166.3(3)	Mo(6)-Mo(7)-Se(33)	57.4(2)
Se(8)-Mo(2)-Se(11)	132.5(3)	Se(25)-Mo(7)-Se(30)	88.7(3)
Se(9)-Mo(2)-Se(10)	136.1(3)	Se(25)-Mo(7)-Se(31)	141.8(3)
Se(9)-Mo(2)-Se(11)	76.9(2)	Se(25)-Mo(7)-Se(32)	80.8(2)
Se(10)-Mo(2)-Se(11)	59.4(2)	Se(25)-Mo(7)-Se(33)	113.3(3)
Mo(3)-Mo(2)-Se(1)	57.3(2)	Se(30)-Mo(7)-Se(31)	53.2(4)
Mo(3)-Mo(2)-Se(10)	58.2(2)	Se(30)-Mo(7)-Se(32)	86.4(2)
Mo(3)-Mo(2)-Se(11)	58.4(2)	Se(30)-Mo(7)-Se(33)	131.6(3)
Se(1)-Mo(2)-Se(4)	149.6(3)	Se(31)-Mo(7)-Se(32)	95.2(2)
Se(1)-Mo(2)-Se(5)	96.5(3)	Se(31)-Mo(7)-Se(33)	95.4(3)
Se(1)-Mo(2)-Se(8)	85.3(3)	Se(32)-Mo(7)-Se(33)	57.8(2)

Table 2-22. (cont'd)

Se(1)-Mo(2)-Se(9)	113.8(3)	Mo(1)-Se(1)-Mo(2)	67.0(2)
Se(1)-Mo(2)-Se(10)	82.6(3)	Mo(1)-Se(1)-Mo(3)	66.7(2)
Se(1)-Mo(2)-Se(11)	115.3(3)	Mo(2)-Se(1)-Mo(3)	66.7(2)
Se(4)-Mo(2)-Se(5)	53.1(2)	Mo(1)-Se(2)-Se(3)	62.6(3)
Se(4)-Mo(2)-Se(8)	91.2(3)	Mo(1)-Se(3)-Se(2)	63.7(3)
Se(4)-Mo(2)-Se(9)	88.3(3)	Mo(2)-Se(4)-Se(5)	62.4(3)
Se(4)-Mo(2)-Se(10)	96.2(3)	Mo(2)-Se(5)-Se(4)	64.6(3)
Se(4)-Mo(2)-Se(11)	89.1(3)	Mo(1)-Se(6)-Mo(3)	64.5(2)
Se(5)-Mo(2)-Se(8)	86.6(3)	Mo(3)-Se(6)-Se(7)	60.9(2)
Mo(1)-Mo(3)-Mo(2)	59.9(2)	Mo(1)-Se(7)-Mo(3)	66.4(2)
Mo(1)-Mo(3)-Se(1)	56.3(2)	Mo(1)-Se(7)-Se(6)	63.8(2)
Mo(1)-Mo(3)-Se(6)	57.8(2)	Mo(3)-Se(7)-Se(6)	63.8(2)
Mo(1)-Mo(3)-Se(7)	57.1(2)	Se(6)-Se(7)-Se(12)	162.6(3)
Mo(2)-Mo(3)-Se(1)	56.1(2)	Mo(1)-Se(8)-Mo(2)	63.0(2)
Mo(2)-Mo(3)-Se(10)	58.3(2)	Mo(1)-Se(8)-Se(9)	60.3(3)
Mo(2)-Mo(3)-Se(11)	57.1(2)	Mo(2)-Se(8)-Se(9)	60.9(2)
Se(1)-Mo(3)-Se(6)	83.7(3)	Mo(1)-Se(9)-Mo(2)	65.3(2)
Se(1)-Mo(3)-Se(7)	113.0(3)	Mo(1)-Se(9)-Se(8)	64.9(3)
Se(1)-Mo(3)-Se(10)	82.1(3)	Mo(2)-Se(9)-Se(8)	63.6(2)
Se(1)-Mo(3)-Se(11)	112.9(3)	Se(8)-Se(9)-Se(12)	165.0(4)
Se(1)-Mo(3)-Se(13)	92.0(3)	Mo(2)-Se(10)-Mo(3)	63.6(2)
Se(1)-Mo(3)-Se(14)	159.2(3)	Mo(2)-Se(10)-Se(11)	59.2(2)
Se(6)-Mo(3)-Se(7)	55.4(2)	Mo(3)-Se(10)-Se(11)	60.2(2)
Se(6)-Mo(3)-Se(10)	164.5(3)	Mo(2)-Se(11)-Mo(3)	64.6(2)
Se(6)-Mo(3)-Se(11)	133.3(3)	Mo(2)-Se(11)-Se(10)	61.4(2)
Se(6)-Mo(3)-Se(13)	86.7(3)	Mo(2)-Se(11)-Se(12)	108.4(3)
Se(6)-Mo(3)-Se(14)	102.4(3)	Mo(3)-Se(11)-Se(10)	60.8(2)
Se(7)-Mo(3)-Se(10)	137.0(3)	Mo(3)-Se(11)-Se(12)	109.3(3)
Se(7)-Mo(3)-Se(11)	78.3(2)	Se(10)-Se(11)-Se(12)	167.5(3)
Se(7)-Mo(3)-Se(13)	129.1(3)	Mo(3)-Se(13)-Se(14)	55.4(2)
Se(7)-Mo(3)-Se(14)	86.2(2)	Mo(3)-Se(14)-Se(13)	55.8(2)
Se(10)-Mo(3)-Se(11)	59.1(2)	Mo(4)-Se(15)-Mo(5)	65.9(3)
Se(10)-Mo(3)-Se(13)	87.8(3)	Mo(4)-Se(16)-Se(17)	61.2(2)

Table 2-22. (cont'd)

Se(10)-Mo(3)-Se(14)	89.0(3)	Mo(4)-Se(17)-Se(16)	65.0(3)
Se(11)-Mo(3)-Se(13)	133.0(3)	Mo(4)-Se(18)-Se(19)	65.0(3)
Se(11)-Mo(3)-Se(14)	77.5(2)	Mo(4)-Se(19)-Se(18)	61.1(3)
Se(13)-Mo(3)-Se(14)	68.9(2)	Mo(5)-Se(20)-Se(21)	62.6(4)
Mo(5)-Mo(4)-Se(15)	58.0(2)	Mo(5)-Se(21)-Se(20)	62.8(4)
Mo(5)-Mo(4)-Se(22)	59.0(2)	Mo(4)-Se(22)-Mo(5)	63.2(2)
Mo(5)-Mo(4)-Se(23)	57.4(2)	Mo(4)-Se(22)-Se(23)	60.2(2)
Se(15)-Mo(4)-Se(16)	145.8(3)	Mo(5)-Se(22)-Se(23)	59.6(2)
Se(15)-Mo(4)-Se(17)	91.9(3)	Mo(4)-Se(23)-Mo(5)	64.9(2)
Se(15)-Mo(4)-Se(18)	112.8(3)	Mo(4)-Se(23)-Se(22)	62.0(2)
Se(15)-Mo(4)-Se(19)	82.8(3)	Mo(5)-Se(23)-Se(22)	63.0(2)
Se(15)-Mo(4)-Se(22)	84.5(3)	Mo(5)-Se(23)-Se(24)	103.9(2)
Se(15)-Mo(4)-Se(23)	115.1(3)	Se(22)-Se(23)-Se(24)	166.0(3)
Se(16)-Mo(4)-Se(17)	53.9(2)	Mo(6)-Se(25)-Mo(7)	64.9(3)
Se(16)-Mo(4)-Se(18)	91.6(2)	Mo(6)-Se(26)-Se(27)	65.5(3)
Se(16)-Mo(4)-Se(19)	94.0(2)	Mo(6)-Se(27)-Se(26)	62.1(3)
Se(16)-Mo(4)-Se(22)	93.0(3)	Mo(6)-Se(28)-Se(29)	60.8(2)
Se(16)-Mo(4)-Se(23)	91.6(3)	Mo(6)-Se(29)-Se(28)	63.5(3)
Se(17)-Mo(4)-Se(18)	127.5(3)	Mo(7)-Se(30)-Se(31)	63.3(4)
Se(17)-Mo(4)-Se(19)	87.0(2)	Se(24)-Se(30)-Se(31)	171.9(5)
Se(17)-Mo(4)-Se(22)	87.1(3)	Mo(7)-Se(31)-Se(30)	63.5(4)
Se(17)-Mo(4)-Se(23)	130.8(3)	Mo(6)-Se(32)-Mo(7)	63.1(3)
Se(18)-Mo(4)-Se(19)	53.9(3)	Mo(6)-Se(32)-Se(33)	59.6(2)
Se(18)-Mo(4)-Se(22)	138.3(3)	Mo(7)-Se(32)-Se(25)	48.8(2)
Se(18)-Mo(4)-Se(23)	80.7(3)	Mo(7)-Se(32)-Se(33)	58.6(2)
Se(19)-Mo(4)-Se(22)	165.8(3)	Mo(6)-Se(33)-Mo(7)	65.7(3)
Se(19)-Mo(4)-Se(23)	134.3(3)	Mo(6)-Se(33)-Se(32)	62.1(2)
Se(22)-Mo(4)-Se(23)	57.8(2)	Mo(7)-Se(33)-Se(32)	63.6(2)
Mo(4)-Mo(5)-Se(15)	56.1(2)	Mo(7)-Se(33)-Se(34)	102.5(3)
Mo(4)-Mo(5)-Se(22)	57.9(2)	Se(32)-Se(33)-Se(34)	163.7(4)
Mo(4)-Mo(5)-Se(23)	57.7(2)		

Structure of $\text{K}_{10}\text{Mo}_{12}\text{Se}_{58}$ (VIII)

The structure of (VIII) is very complicated as shown in Figure 2-14. Its anionic formula can be written in a more descriptive way: $[(\text{Mo}_3\text{Se}_{15})_2(\text{Mo}_3\text{Se}_{13})_2(\text{Se}_2)]^{10-}$, which contains three separate species cocrystallized in an unit cell: zigzag $[\text{Mo}_3\text{Se}_{15}]^{2-}$ chains, $[\text{Mo}_3\text{Se}_{13}]^{2-}$ trinuclear clusters and Se_2^{2-} anions in a ratio of 2:2:1. The $[\text{Mo}_3\text{Se}_{15}]^{2-}$ chains contain rows of trinuclear $[\text{Mo}_3\text{Se}_7]^{4+}$ cores in which two Mo centers coordinate each to one terminal Se_2^{2-} ligand and the third Mo centers are linked by a Se_2^{2-} ligand and a Se_6^{2-} ligand alternately to form one-dimensional chains. $[\text{Mo}_3\text{Se}_{13}]^{2-}$ clusters are inserted between the $[\text{Mo}_3\text{Se}_{15}]^{2-}$ chains. The triply bridging Se atoms of the $[\text{Mo}_3\text{Se}_{13}]^{2-}$ clusters are right above the three bridging Se_2^{2-} ligands of the $[\text{Mo}_3\text{Se}_7]^{4+}$ cores in the $[\text{Mo}_3\text{Se}_{15}]^{2-}$ chains, forming short Se...Se contacts. Between two $[\text{Mo}_3\text{Se}_{13}]^{2-}$ clusters, one Se_2^{2-} anion is inserted with each of the two negatively charged Se atoms sitting above the three bridging diselenides of the $[\text{Mo}_3\text{Se}_7]^{4+}$ cores in the $[\text{Mo}_3\text{Se}_{13}]^{2-}$ clusters respectively. These special Se...Se interactions are shown by the dashed line in Figure 2-14. Because the X-ray diffraction data set obtained was not intense and enough, positions of potassium cations could not be determined. In addition to the ionic attraction between potassium cations and the anionic species, the special Se...Se attractions appear to be important for the crystallization of the structure.

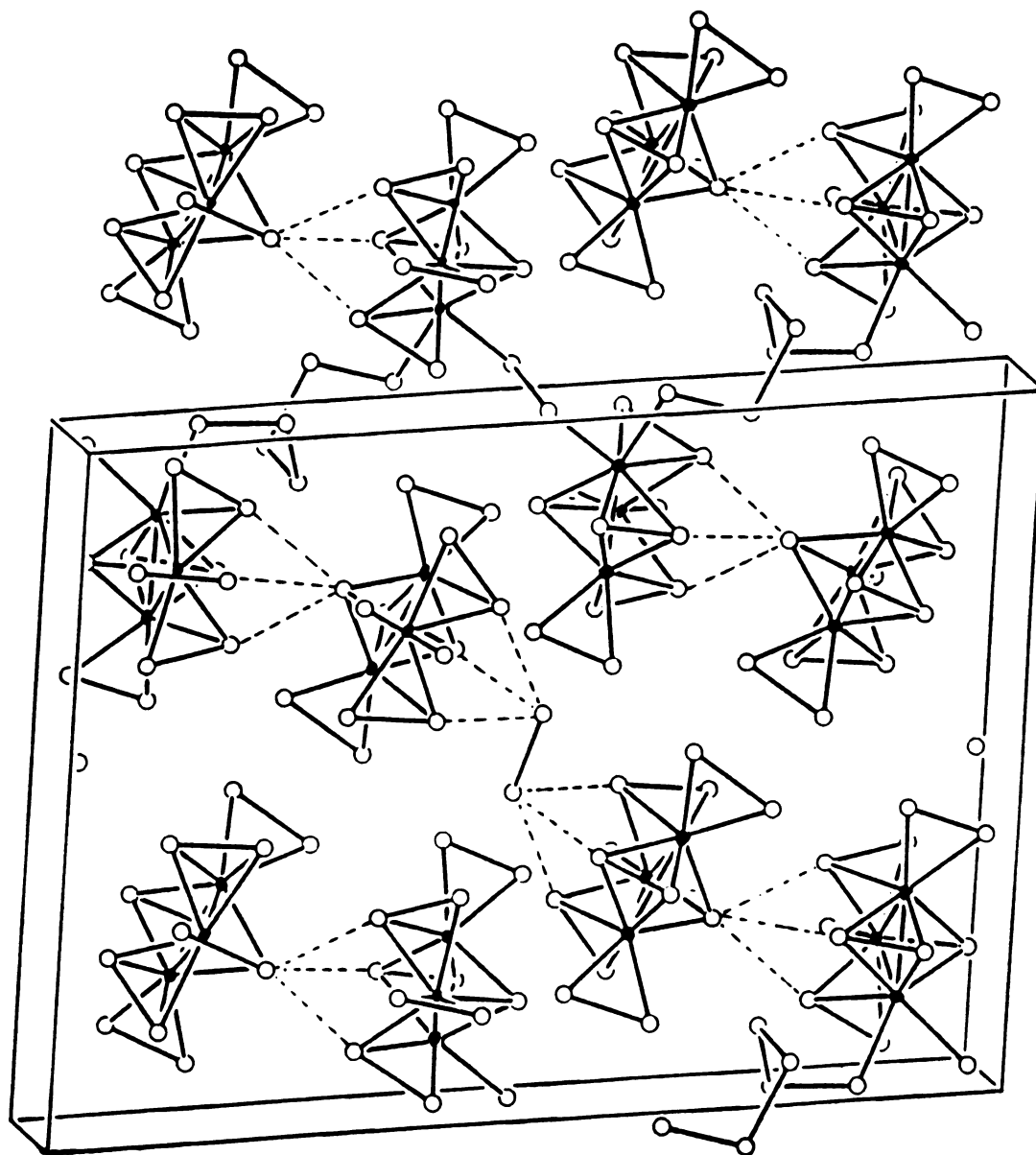


Figure 2-14: ORTEP representation of the structure of $[\text{Mo}_{12}\text{Se}_{58}]^{10-}$.

Black circles represent Mo atoms. Open circles represent Se atoms. Dashed lines indicate Se...Se short contacts.

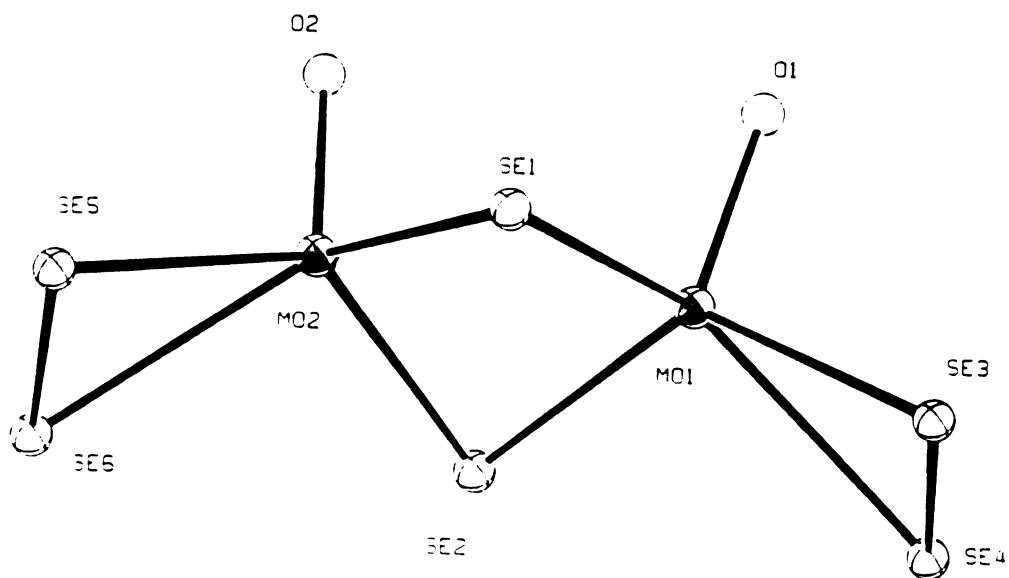


Figure 2-15: ORTEP representation and labeling scheme of [Mo₂O₂Se₆]²⁻.

Structure of $\text{Cs}_2\text{Mo}_2\text{O}_2\text{Se}_6$ (IX)

$[\text{Mo}_2\text{O}_2\text{Se}_6]^{2-}$ has a discrete dimeric structure containing two edge-sharing distorted pyramidal Mo centers. Each Mo atom binds an oxygen atom at its axial position, a terminal Se_2^{2-} ligand and two bridging Se^{2-} ions at its equatorial positions, as shown in Figure 2-15. The structure of (IX) was solved but could not be well refined due to the fast decomposition of the crystal in X-ray beam and its large absorption coefficient with respect to Cu $K\alpha$ radiation. Since (IX) is the selenium analog of $[\text{Mo}_2\text{O}_2\text{S}_6]^{2-}$, no further effort was made to characterize the compound.

3.3. Electron Affinity of $[\text{Mo}_3\text{Se}(\text{Se}_2)_3]^{4+}$ Core

A Molecular Orbital Study

As pointed earlier, the unusual phenomenon observed in all of these molybdenum polyselenide compounds is tendency if the $[\text{Mo}_3\text{Se}_7]^{4+}$ clusters to bind, via $\text{Se}\cdots\text{Se}$ interactions, negatively charged species such as Se^{2-} and Se_x^{2-} . There is an inverse correlation between the $\text{Se}_{\text{ap}}\text{-Se}_a$ and the $\text{Se}_a\text{-Se}_b$ distances, where Se_a and Se_b form the doubly bridging diselenide Se_2^{2-} in the $[\text{Mo}_3(\mu_3\text{-Se})(\mu_2\text{-Se}_2)_3]^{4+}$ core, and Se_{ap} can be a triply bridging selenium from another $[\text{Mo}_3\text{Se}_{13}]^{2-}$ anion, or it can be an isolated Se^{2-} or the terminal Se atom of a Se_x^{2-} ligand. This inverse correlation is clearly demonstrated in Figure 2-16 for various $\text{Se}_{\text{ap}}\text{-Se}_a$ and $\text{Se}_a\text{-Se}_b$ distances.

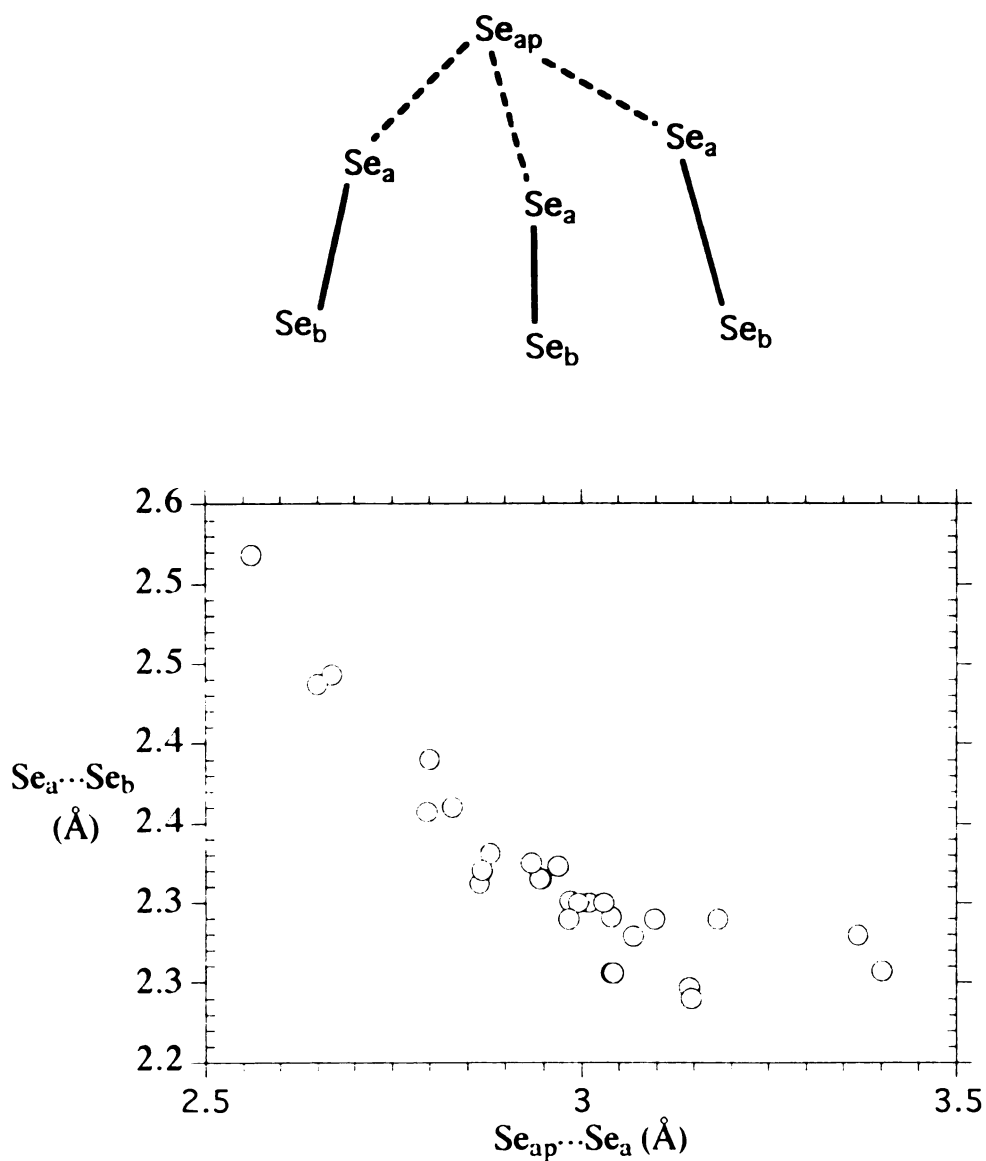
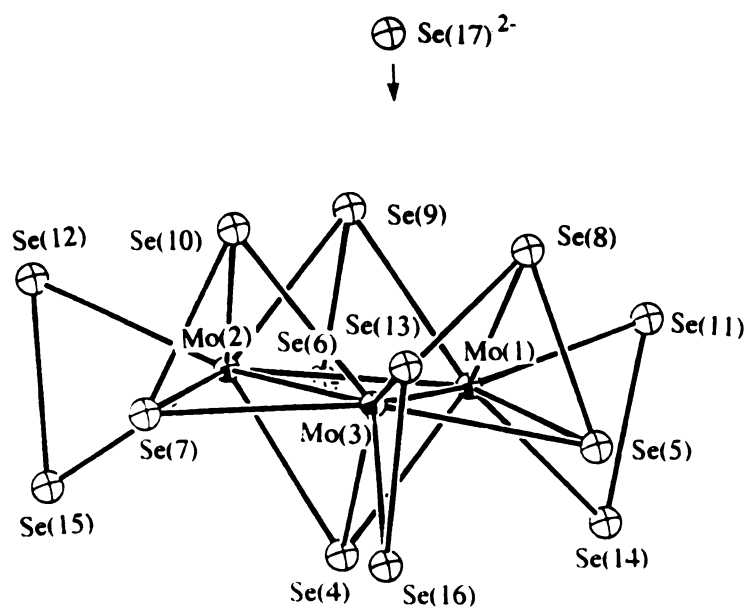


Figure 2-16: Se-Se bond correlation. The horizontal axis represents the Se_{ap}-Se_a bond variation in different Mo selenide molecules, and the corresponding Se_a-Se_b bond is plotted as a function of the Se_{ap}-Se_a distance.



Scheme (3)

To understand the nature of this type of $[\text{Mo}_3\text{Se}_7]^{4+}\cdots\text{Se}$ interaction we have performed a molecular orbital study employing the extended Hückel method²⁶. The atomic parameters and a detailed description of the computations are given in reference 27.

Theoretical investigations on the electronic structures of trinuclear early transition metal clusters have been carried out on several molecular systems, including $[\text{Mo}_3\text{S}_{13}]^{2-}$,²⁸⁻³⁰ $[\text{Mo}_3(\mu_3\text{-X})(\mu_2\text{-Y})_3\text{L}_9]^{4+}$ ($\text{M}=\text{Ti}, \text{Nb}, \text{Mo}, \text{W}$)²⁸, and $[\text{M}_3(\mu_3\text{-X})_2(\mu_2\text{-O}_2\text{Y})_6\text{L}_3]$ ($\text{M}=\text{Mo}, \text{W}$).²⁸ Important bonding features in these trinuclear clusters have been discussed in much detail and are in accordance with our calculation results on the $[\text{Mo}_3\text{Se}_{13}]^{2-}$ cluster. Therefore, our focus in the following discussions will be mainly on the systems in which an additional ligand, such as a Se^{2-} anion, is added to the $[\text{Mo}_3\text{Se}_{13}]^{2-}$ cluster. The bonding interactions between the cluster and the ligand, and the consequence of such interactions will be analyzed.

The model system that we have used in most of our computations consists of a $[\text{Mo}_3\text{Se}_{13}]^{2-}$ trinuclear cluster and a Se^{2-} anions as Se_{ap} . The geometry of $[\text{Mo}_3\text{Se}_{13}]^{2-}$ is taken from the experimental data.³¹ The Se^{2-} approaches the trinuclear cluster from the opposite site of the $\mu_3\text{-Se}$, as shown in Scheme (3). The interatomic distance between $\text{Se}(8)$ and Se^{2-} (or between $\text{Se}(10)$ and Se^{2-} , noting that $\text{Se}(10)$ is equivalent to $\text{Se}(8)$ by symmetry) was chosen to be slightly different from that between $\text{Se}(9)$ and Se^{2-} , as was found in the crystal structure.

Changes in bond strength for various $\text{Se}_{\text{ap}}\text{-Se}_a$ distances are plotted in Figure 2-17 as the difference in the overlap population³² $\Delta(\text{O}) = \text{OP}(\text{d}) - \text{OP}(\infty)$, where $\text{OP}(\text{d})$ is the overlap population at $\text{d}(\text{\AA})$, a perpendicular distance between Se^{2-} and the Mo_3 plane, and $\text{OP}(\infty)$, the corresponding overlap population as d approaches infinity. It is clear from these plots that

our prediction is consistent with the experimental findings: strong bonding interactions are observed between Se_a (labeled Se(8), Se(9) and Se(10)) and Se^{2-} (labeled Se(17)) when Se^{2-} is brought close to the $[\text{Mo}_3\text{Se}_{13}]^{2-}$ trinuclear cluster. At $d=3.6\text{\AA}$, which corresponds to an interatomic distance of $\text{Se(8)-Se(17)}=2.60\text{\AA}$ and $\text{Se(9)-Se(17)}=2.81\text{\AA}$, the overlap populations for the two bonds are increased from zero to 0.106 and 0.018 respectively. At the same time, the decrease in the overlap population between Se_a and Se_b , that is Se(5)-Se(8) (or Se(7)-Se(10) , equivalent by symmetry) and Se(6)-Se(9) , indicates a significant bond weakening between the two atoms. For example at $d=3.6\text{\AA}$, $\Delta(O)$ is -0.154 for Se(5)-Se(8) and is -0.072 for Se(6)-Se(9) . Notice the strong correlation between the $\text{Se}_{ap}\text{-Se}_a$ and $\text{Se}_a\text{-Se}_b$ pairs: at a given d , the stronger the bond between Se_{ap} and Se_a , the bigger the decrease in the $\text{Se}_a\text{-Se}_b$ bond strength. It is also interesting to observe the overlap population increase in the Mo-Mo bonds and the repulsive interactions between these metals and the Se^{2-} atom. At $d=3.6\text{\AA}$, or equivalently at $\text{Se(8)-Se(17)}=2.6\text{\AA}$ and $\text{Se(9)-Se(17)}=2.81\text{\AA}$, the increase in the overlap population is calculated to be 0.019 and 0.026 for the Mo(1)-Mo(2) and Mo(1)-Mo(3) bonds respectively. This metal-metal bond strengthening appeared to be most pronounced in $\text{K}_{12}\text{Mo}_{12}\text{Se}_{56}$ which has the greatest $[\text{Mo}_3\text{Se}_7]^{4+}\cdots\text{Se}_{ap}$ interactions, resulting in shorter average Mo-Mo distance of $2.75(2)\text{\AA}$ while those in $(\text{Me}_4\text{N})_2\text{Mo}_3\text{Se}_{13}$ and $\text{K}_2\text{Mo}_3\text{Se}_{13}$ are $2.784(6)\text{\AA}$ and $2.774(5)\text{\AA}$ respectively. For the same d , the decreases in the Mo(1)-Se(17) and Mo(3)-Se(17) overlap populations are up to 0.051 and 0.073. Other bonds, mainly the $\text{Mo-(}\mu_3\text{-Se)}$, Mo-Se_a , Mo-Se_b , $\text{Mo-Se}_2(\text{terminal})$, and terminal Se-Se bonds, remain almost unaffected.

The calculated electron distribution in $[\text{Mo}_3\text{Se}_{13}]^{2-}$ helps in understanding why an incoming Se_{ap} atom negatively charged tends to form bonds with the trinuclear cluster and why it approaches preferably the doubly bridged Se_2^{2-} rather than other Se atoms in the cluster. Of the five types of selenium atoms present in a $[\text{Mo}_3\text{Se}_{13}]^{2-}$ cluster the terminal diselenides are the most negatively charged. While $\mu_3\text{-Se}$ carries a smaller negative charge, the doubly bridging Se_a atoms are the most electron poor with a calculated 0.185 electron loss. Therefore Se_a becomes the most suitable site for anionic attack by a Se_{ap} atom such as Se^{2-} . Changes in the electron density of individual atoms in the $[\text{Mo}_3\text{Se}_{13}]^{2-}$ model system, as a function of the $\text{Mo}\cdots\text{Se}_{\text{ap}}^{2-}$ distance are given in Figure 2-18, which clearly shows that charge transfer occurs as the $\text{Se}_{\text{ap}}^{2-}$ atom approaches the trinuclear cluster. $\text{Se}_{\text{ap}}^{2-}$ appears to suffer the greatest electron loss of 0.96, going from $d=\infty$ to $d=3.6\text{\AA}$. This electron density ends up largely on the metal atoms and the Se_b atoms, as indicated in the plot. At $d=3.6\text{\AA}$, a total gain of 0.145 electrons for each Mo atom, and 0.284 electrons for Se(5) and Se(7) are calculated. The Se_a atoms, previously charged, have a further loss of 0.150 electrons for Se(8) and Se(10), and 0.083 electron for Se(9).

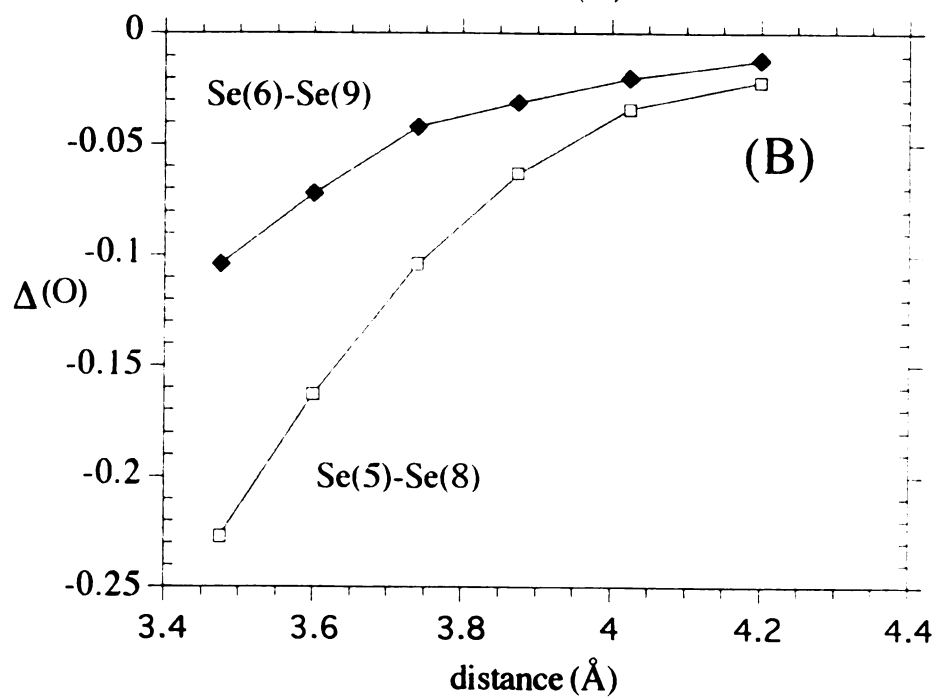
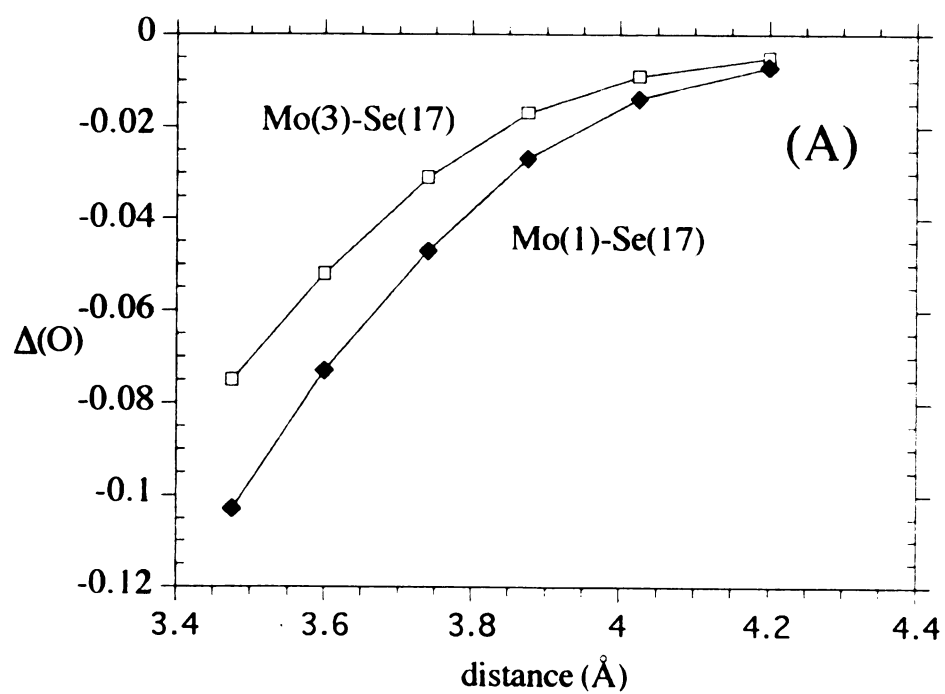
In the above discussion we have showed what happens when an additional ligand, Se_{ap} , interacts with the trinuclear cluster $[\text{Mo}_3\text{Se}_{13}]^{2-}$. To understand the bonding nature of such interactions it is useful to take a closer look at the orbital interaction diagram sketched in Figure 2-19. Outlined in the three boxes are the important frontier molecular orbitals for $d=3.4\text{\AA}$ (left), $3.8\text{\AA}$ (middle) and $4.2\text{\AA}$ (right) respectively. The orbital energies of the two fragments $[\text{Mo}_3\text{Se}_{13}]^{2-}$ and Se^{2-} are drawn on either side of each box. The highest occupied molecular orbitals (HOMO) are #31

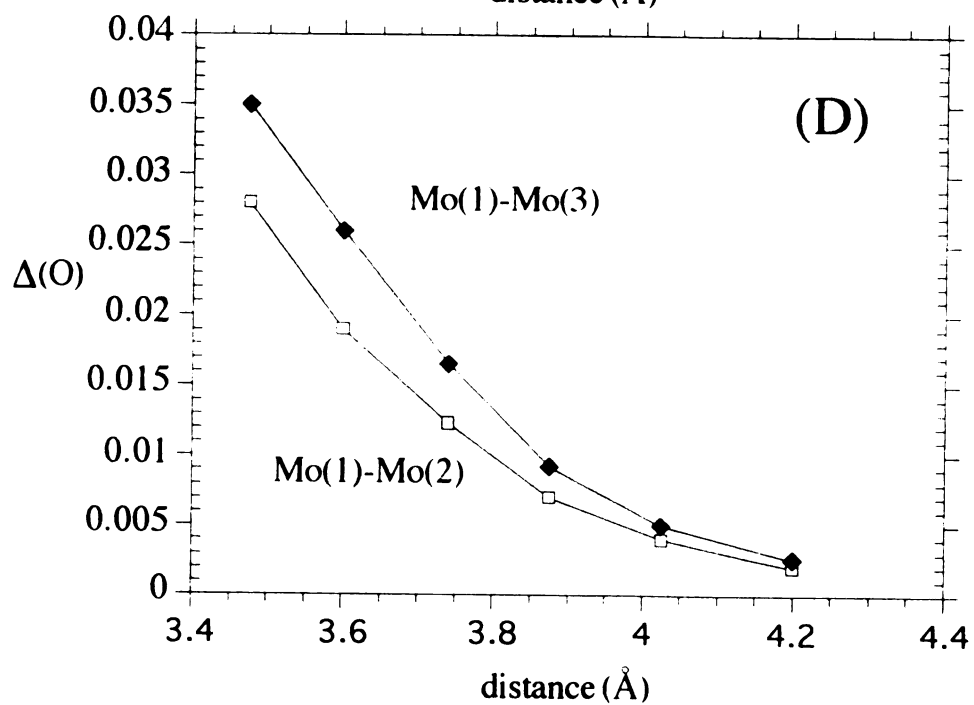
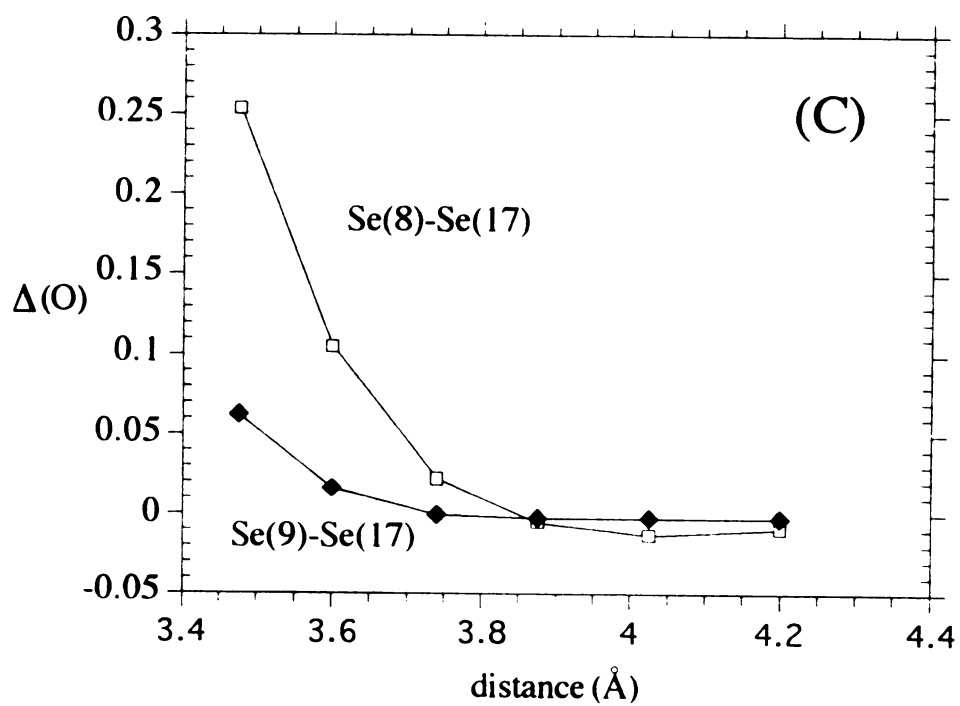
and #32 in all three cases. At large distance between the two fragments, for example $d=3.8\text{\AA}$ and $4.2\text{\AA}$ as in (b) and (c), these orbitals are mostly contributed from the metal 4d orbitals. For smaller d as in (a), however, these metal centered orbitals becomes #33 and #34. The MO 31a" and 32a' in (a), or equivalently the MO 33a'/34a" in (b), and MO 37a'/38a" in (c), contain largely contributions from several high-lying unoccupied $[\text{Mo}_3\text{Se}_{13}]^{2-}$ orbitals, such as #19, #22-24 and #27. Orbital overlap population analysis shows that, in general, these orbitals are *bonding* between the metal atoms (Mo-Mo) and antibonding between the doubly bridging Se_2^{2-} atoms (Se_a and Se_b), and on average, is greater in magnitude for the latter. For example, the fragment molecular orbital (FMO) #19 and #24 of $[\text{Mo}_3\text{Se}_{13}]^{2-}$ contribute an overlap population of 0.022 and 0.031 respectively to both Mo(1)-Mo(2) and Mo(1)-Mo(3) bonds, and -0.043, -0.061 respectively to both Se(5)-Se(8) and Se(6)-Se(9) bonds when occupied by two electrons. Upon the formation of $[\text{Mo}_3\text{Se}_{13}]^{2-}\cdot\text{Se}^{2-}$ aggregate, these orbitals interact with the Se_{ap}^{2-} orbitals in a bonding fashion. When the two fragments interact strongly as in (a), the orbital overlaps are the greatest which lead to a large contribution of these orbitals to the MO 31a" and 32a' that are fully occupied. The FMO #24 and #27, for instance, has a 30% contribution to MO 32a" and 31a' respectively. As the two fragments are pulled apart as in (b) and (c), the orbital overlaps are significantly reduced. Consequently the interactions between the two fragments are much weakened and these vacant high-lying $[\text{Mo}_3\text{Se}_{13}]^{2-}$ fragment orbitals contribute much less to the corresponding molecular orbitals (33a' and 34a" in (b), 37a' and 38a" in (c)). In fact, the fragment orbitals #19, #22-23 and #27 of $[\text{Mo}_3\text{Se}_{13}]^{2-}$ give essentially no contributions to the molecular orbital 37a' and 38a" in case (c). These

FMO contributions are plotted in Figure 2-20 as a function of the distance. Notice that the metal centered molecular orbitals, that is 33a' and 34a" in (a), 31a' and 32a" in both (b) and (c), are essentially the same at all distances.

The conclusion that we may draw from the above analysis is that the extent of the interactions between the two fragments, Se^{2-} and $[\text{Mo}_3\text{Se}_{13}]^{2-}$, determines the amount of the $\text{Se}_a\text{-Se}_b$ antibonding character in the highest occupied molecular orbitals (Se centered). The stronger the interactions between the two, the more the $\text{Se}_a\text{-Se}_b$ bonds are weakened. Correspondingly a less pronounced and opposite effect applies to the Mo-Mo bonds.

Figure 2-17: Changes in the overlap population, $\Delta(O)$, as functions of d , the perpendicular distance between the Se^{2-} and the Mo_3 plane. (A) Mo-Se^{2-} bonds, (B) $\text{Se}_a\text{-Se}_b$ bonds, (C) $\text{Se}^{2-}\text{-Se}_a$ bonds and (D) the Mo-Mo bonds. the Se^{2-} is labeled as $\text{Se}(17)$, Se_a as $\text{Se}(8)$, $\text{Se}(9)$ and Se_b as $\text{Se}(5)$, $\text{Se}(6)$. $\text{Se}(7)$ and $\text{Se}(10)$ are equivalent to $\text{Se}(5)$ and $\text{Se}(8)$ respectively and are not shown in the Figure.





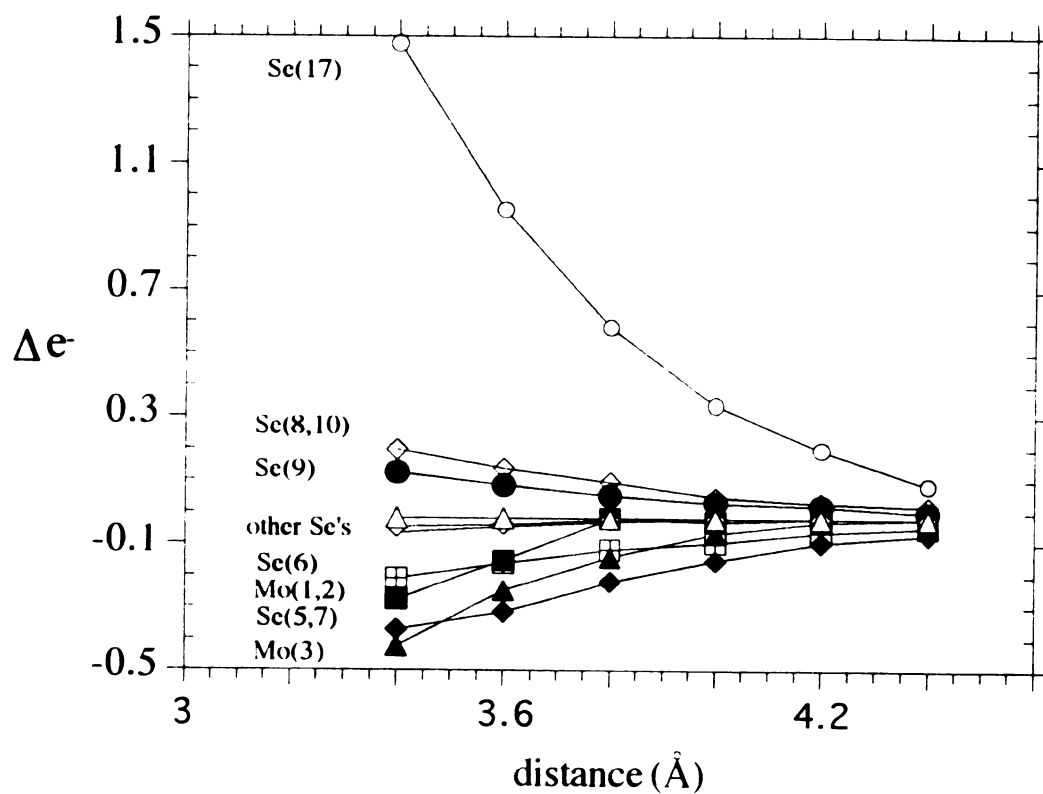
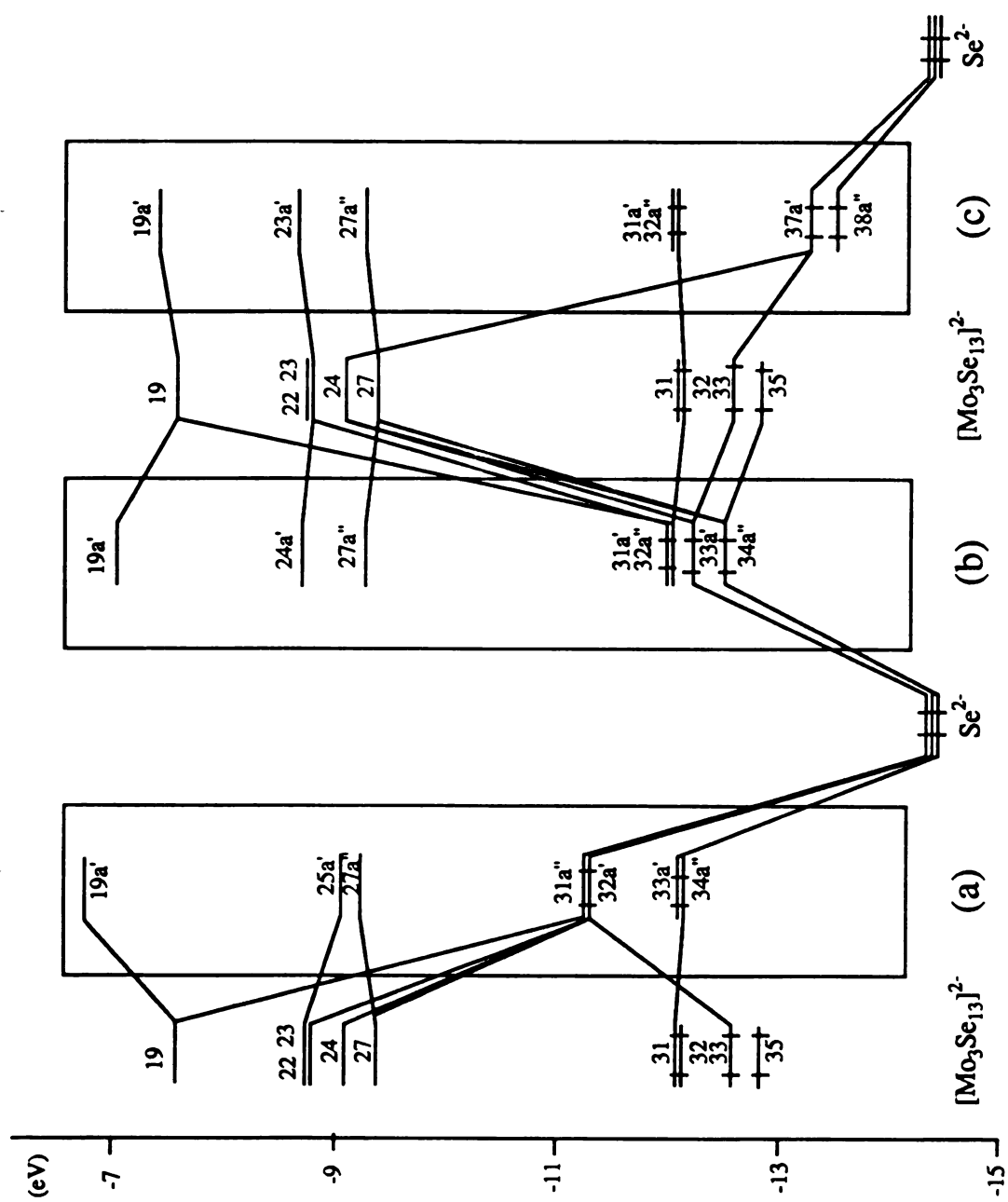


Figure 2-18: Electron density change for all atoms. Δe^- is the difference between the electron density of an atom in $[\text{Mo}_3\text{Se}_{14}]^{4-}$ at various distances and in the extreme case, $d=\infty$.

Figure 2-19: Orbital interaction diagram for the $[\text{Mo}_3\text{Se}_{14}]^{4-}$ model system. Three situations are considered: (a) $d=3.4\text{\AA}$, (b) $d=3.8\text{\AA}$ and (c) $d=4.2\text{\AA}$. The interested molecular orbital levels are sketched in the central area in each case and are outlined within a box. a' and a'' are the symmetry labels for these orbitals. The corresponding fragment orbital energies of $[\text{Mo}_3\text{Se}_{13}]^{2-}$ and Se^{2-} are drawn on either side of each box.



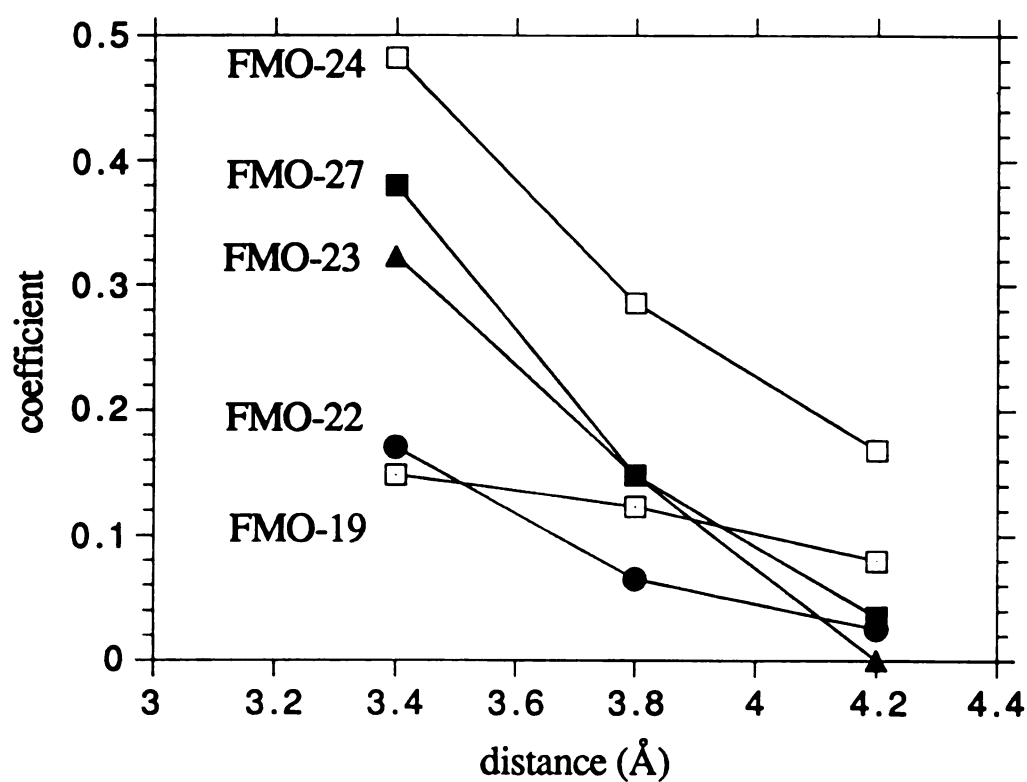


Figure 2-20: Contributions of the fragment molecular orbitals (FMO) of $[\text{Mo}_3\text{Se}_{13}]^{2-}$ to the molecular orbitals (MO) 31a', 32a" ($d=3.4\text{\AA}$), 33a', 34a" ($d=3.8\text{\AA}$) and 37a', 38a" ($d=4.2\text{\AA}$). C is the coefficient of the FMO in the MO.

3.4. Spectroscopy

Vibrational Spectroscopy

The IR spectrum of (I) shows characteristic peaks of tetramethylammonium in the mid-IR region. In the far-IR region, peaks at 451, 370, 333, 308, 279 and 165 cm^{-1} were observed for (I) and peaks at 439, 364, 334, 312, 297, 210, 165 cm^{-1} were observed for (II). We assign the peak at 451 cm^{-1} (I) and 439 cm^{-1} (II) as the vibration of the ($\text{Mo}_3\text{-}\mu_3\text{-Se}$) moiety by comparing to the IR-spectrum of $(\text{NH}_4)_2\text{Mo}_3\text{S}_{13}$, in which the ($\text{Mo}_3\text{-}\mu_3\text{-S}$) vibration is assigned at 459 cm^{-1} . The peak at 165 cm^{-1} ((I) and (II)) can be assigned as a Mo-Mo vibration. The peaks between 210 cm^{-1} and 370 cm^{-1} can be assigned as Mo-Se or Se-Se vibrations. We expect the IR spectrum of (III)~(V) to be similar to those of (I) and (II). The IR spectra of (III)~(V) and the rest of the Mo/Se compounds do not give any peaks in the Far-IR region, even though very concentrated samples were used.

^{77}Se Nuclear Magnetic Resonance Spectroscopy

^{77}Se NMR spectra of $\text{K}_6\text{Mo}_6\text{Se}_{27}\cdot 6\text{H}_2\text{O}$ and $\alpha\text{-K}_8\text{Mo}_9\text{Se}_{40}\cdot 4\text{H}_2\text{O}$ were recorded in several polar solvents. Based on their formula, $(\text{K}_2\text{Mo}_3\text{Se}_{13})_n(\text{K}_2\text{Se})\cdot m\text{H}_2\text{O}$ (where $n=2,3$; $m=6,4$), we simply expected them to dissociate into $[\text{Mo}_3\text{Se}_{13}]^{2-}$, Se^{2-} , K^+ and H_2O in solution. We indeed found that $\text{K}_6\text{Mo}_6\text{Se}_{27}\cdot 6\text{H}_2\text{O}$ and $\alpha\text{-K}_8\text{Mo}_9\text{Se}_{40}\cdot 4\text{H}_2\text{O}$ have identical ^{77}Se NMR spectra. Without counting Se^{2-} , we expect five resonance peaks from the $[\text{Mo}_3\text{Se}_{13}]^{2-}$. However, we found that the $[\text{Mo}_3\text{Se}_{13}]^{2-}$ fragment

does not remain intact in solvents like DMF, DMSO and D₂O. The ⁷⁷Se NMR in D₂O at room temperature gave four peaks at 149 ppm, 143 ppm, -27 ppm and -144 ppm. In DMSO at room temperature, fresh solutions also gave four peaks but at completely different positions, 217 ppm, 123 ppm, 12 ppm and -77 ppm. A peak at -113 ppm grew gradually after 2 weeks, while the relative intensities of the initial peaks decreased. The spectra in DMF at or above room temperature (18°C) show only noisy peaks which cannot be phased properly. This may be due to fast equilibria in DMF. We attempted to slow down the equilibrium by cooling the solution. As shown in Figure 2-21, at 10°C, just 8 degrees below room temperature, we started to see four distinct peaks at 227 ppm, 119 ppm, 11 ppm and -100 ppm probably related to those observed in the spectrum in DMSO. The spectrum at -10 °C and -15°C are practically similar to that at 10 °C. Upon further cooling below -30°C, three extra peaks started to grow at 133 ppm, -105 ppm and -124 ppm, and their relative intensities increased at -50°C. The four initial peaks observed at 10 and -15 °C showed slight downfield or upfield shifts as the temperature was cooling down. It is possible that the terminal ligands are equivalent or the equilibrium exists, shown below:



Based on the synthetic results reported here we believe that at least the [Mo₃Se₇]⁴⁺ core exists in solution, either solvated or ligated by Se_x²⁻.

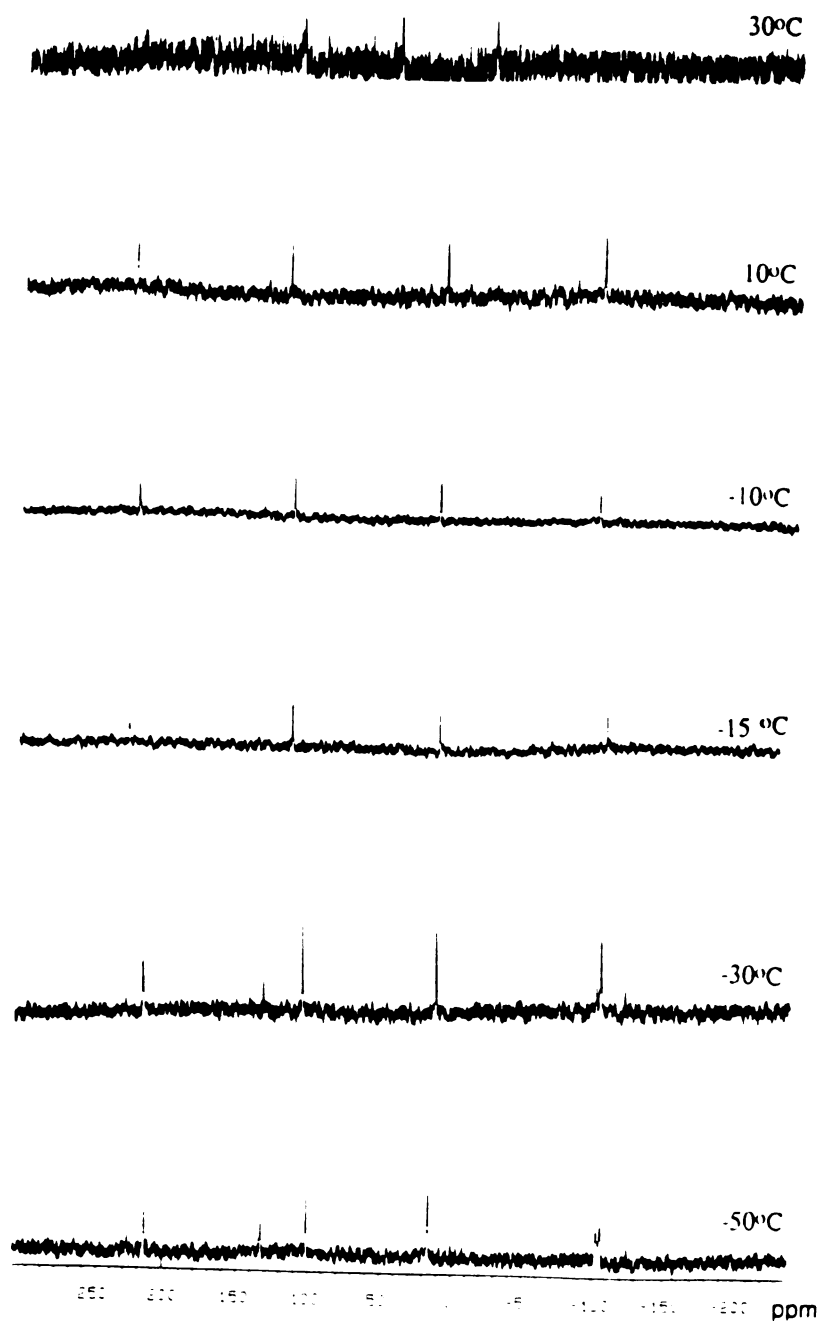


Figure 2-21: Various temperature ^{77}Se NMR spectra of $\alpha\text{-K}_8\text{Mo}_9\text{Se}_{40}\cdot 4\text{H}_2\text{O}$ in DMF.

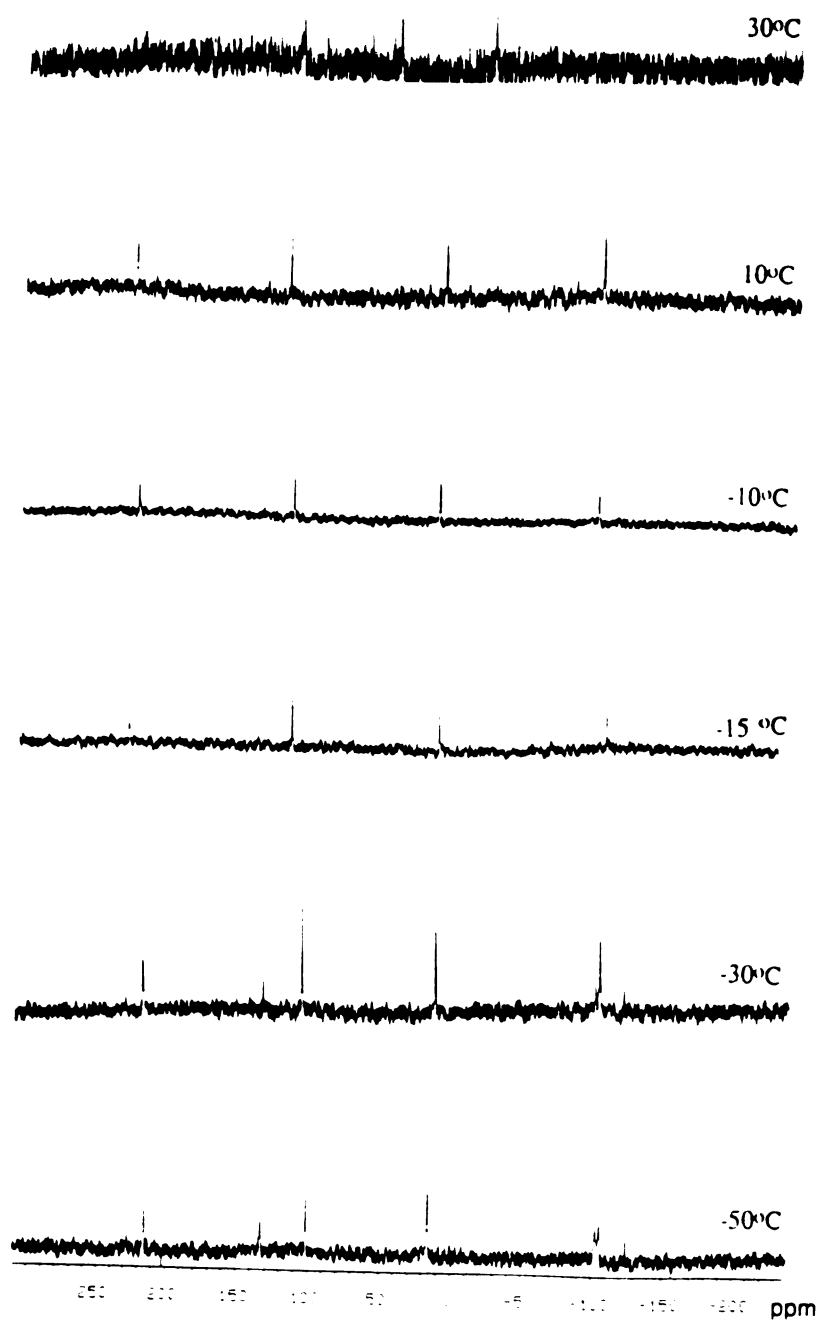


Figure 2-21: Various temperature ^{77}Se NMR spectra of $\alpha\text{-K}_8\text{Mo}_9\text{Se}_{40}\cdot 4\text{H}_2\text{O}$ in DMF.

Electronic Spectroscopy

The UV-Visible spectra of $\text{K}_6\text{Mo}_6\text{Se}_{27}\cdot 6\text{H}_2\text{O}$ were taken in DMF and DMSO. Both solutions prepared in a N_2 glovebox gave reddish brown colors and gave two broad bands at around 405 nm and 480 nm. Since the ^{77}Se NMR data indicate the $[\text{Mo}_3\text{Se}_{13}]^{2-}$ anion does not remain intact in the DMF and DMSO solutions, we are unable to assign the bands. The solid state optical spectrum of $(\text{Me}_4\text{N})_2\text{Mo}_3\text{Se}_{13}$ is shown in Figure 2-22. The peaks between 0.50 eV and 0.56 eV are characteristic absorptions of Me_4N^+ . $(\text{Me}_4\text{N})_2\text{Mo}_3\text{Se}_{13}$ gives absorption bands above 1.6 eV (775 nm) at 1.93 eV (642 nm), 2.31 eV (537 nm), 3.15 eV (394 nm), 3.54 eV (350 nm) and 5.50 eV (225 nm).

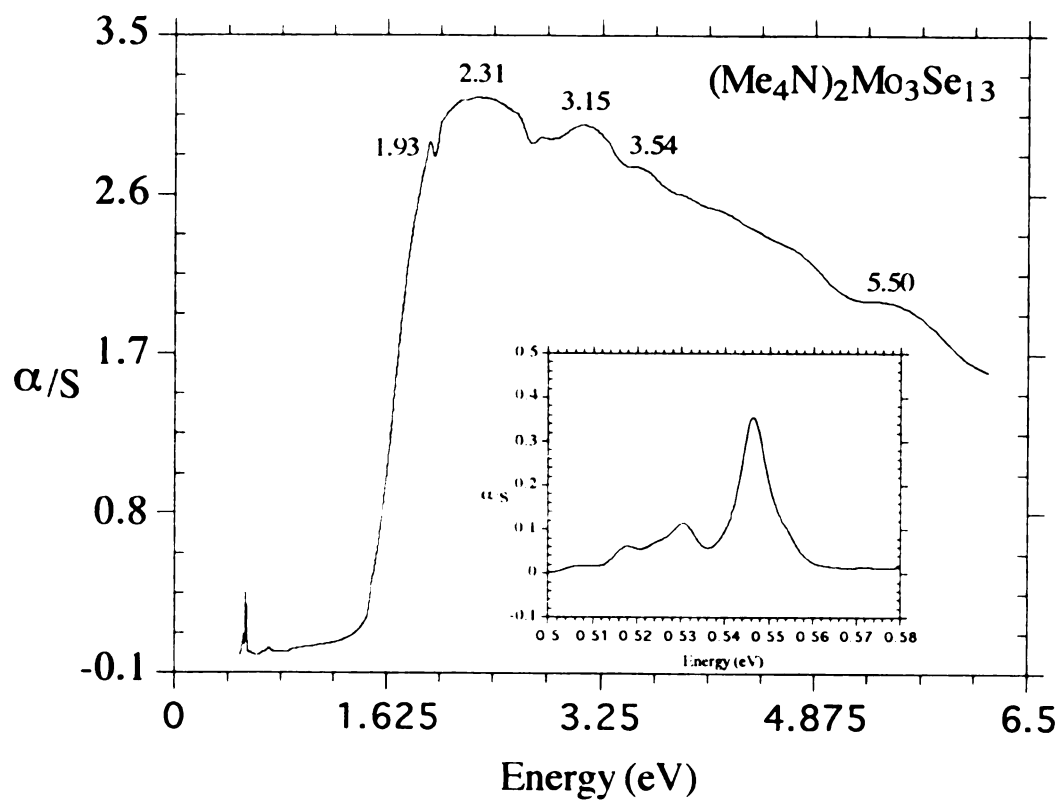


Figure 2-22: Solid state optical spectrum of $(\text{Me}_4\text{N})_2\text{Mo}_3\text{Se}_{13}$.

3.5. Conclusion

Thus far, all Mo/Se phases isolated except (IX) contain recognizable $[\text{Mo}_3(\mu_2\text{-Se}_2)_3\text{Se}]^{4+}$ clusters connected together by bridging selenide or polyselenide ligands. This extraordinarily stable $[\text{Mo}_3(\mu_2\text{-Se}_2)_3\text{Se}]^{4+}$ trinuclear core contains a triangular cavity created by the selenium atoms of the $\mu_2\text{-Se}_2^{2-}$ ligands which have the hitherto unrecognized property of attracting negatively charged species such as Se^{2-} or Se_x^{2-} ligands.

Hydrothermal synthesis with polychalcogenide ligands is a feasible and convenient technique to novel cluster or polymeric phases. Our work in this system alone points to an enormous wealth of new and different K/Mo/Se phases to be discovered. This synthesis is applicable to any cation/metal/chalcogenide system and thus has a very broad scope. We believe that future work in this new area of chalcogenide synthesis will lead to an abundance of novel structure types which may rival, in number, those of zeolites.

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- 27) The atomic parameters for the Mo and Se atoms are taken from Reference 33 and 34. The H_{ij} 's (eV) are -9.66 (5s), -6.36(5p), -12.30(4d) for Mo, and are -20.50(4s), -14.4(4p) for Se. The exponents and coefficients for double-zeta functions are 1.96(5s), 1.90(5p), 4.54, 0.5899(4d), 1.90, 0.5899(4d) for Mo, and are 2.44(4s), 2.07(4p) for Se. The $[Mo_3Se_{13}]^{2-}$ is oriented in such a way that its Mo_3 plane coincides with the xy plane of the cartesian coordinate system, and its three-fold rotation axis is parallel to the z-axis. The Se^{2-} is placed at a perpendicular distance, d, from the Mo_3

plane. Calculations on the model system $[\text{Mo}_3\text{Se}_{14}]^{4-}$ have been carried out at $d=3.4, 3.6, 3.8, 4.0, 4.2$ and $4.4\text{\AA}$, which correspond to an Se(8)-Se(17) interatomic distance of 2.466, 2.598, 2.738, 2.885, 3.038, 3.197 $\text{\AA}$ and an Se(9)-Se(17) distances of 2.690, 2.811, 2.941, 3.223, 3.372 $\text{\AA}$ respectively.

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CHAPTER 3

Hydrothermal Synthesis and Characterization of $(\text{Me}_4\text{N})_4\text{Sn}_4\text{Se}_{10}$ and $(\text{Me}_4\text{N})_2\text{Sn}_3\text{Se}_7 \cdot 2\text{H}_2\text{O}$

1. Introduction

Scheldrick *et al.* have successfully applied the hydrothermal (or solvothermal) technique to prepare a number of alkali metal main group chalcogenides, using alkali metal carbonates as mineralizers.¹ In Chapter 2, we have shown that using polyselenides as mineralizers under hydrothermal conditions, a series of Mo/Se compounds could be synthesized.² Our investigations on (poly)chalcogenides to date conclude that the structure of the anionic complex depends greatly on the counterions used.³ It is also well known that organic templates leads the formation of microporous metal oxides.⁴ Therefore, using the hydrothermal technique we attempted to synthesize chalcogen-based microporous solid state compounds by introduction of organic counterions. In this Chapter, we shall describe the application of hydrothermal synthesis on the Sn/Se system with polyselenides as mineralizers and with organic cations. This synthetic approach resulted in $(\text{Me}_4\text{N})_4\text{Sn}_4\text{Se}_{10}$, a cluster compound, and in $(\text{Me}_4\text{N})_2\text{Sn}_3\text{Se}_7 \cdot 2\text{H}_2\text{O}$, a layered solid state compound.

The alkali metal salts of the former and the Cs^+ salt of the latter have been made by Pohl⁵ and Sheldrick⁶ *et al.*

2. Experimental

2.1. Reagents

Chemicals were used as obtained. Sn metal was purchased from CERAC Inc. ~325 mesh, 99.8%. Selenium powder, -100 mesh, 99.5+%; Tetramethylammonia chloride (Me_4NCl), 97%, Aldrich Chemical Co., Inc., Milwaukee, WI. Potassium metal, Baker analyzed, J. T. Baker, Inc., Phillipsburg, NJ 08865. K_2Se_2 was synthesized by reacting stoichiometric amount of potassium and selenium in liquid ammonia.

2.2. Physical Measurements

The instruments and experimental setups for Infrared measurement and quantitative microprobe analysis on SEM/EDS are the same as those in Section 2.2 in Chapter 2.

Optical diffuse reflectance spectra were measured at room temperature with a Shimadzu UV-3101PC double beam, double monochromated spectrophotometer. The sample was ground into powder and pressed into a thin layer over BaSO_4 on a sample holder. BaSO_4 powder was used as reference. The absorption spectrum was calculated from the reflectance data by using the Kubelka-Munk function⁷: $\alpha/S = (1-R)^2/2R$. R is the reflectance, α is the absorption coefficient and S is the

scattering coefficient which is practically wavelength independent when the particle size is larger than 5 μm .

Thermogravimetric Analysis (TGA) was performed on Shimadzu TGA-50. 8.259 mg of $(\text{Me}_4\text{N})_2\text{Sn}_3\text{Se}_7 \cdot 2\text{H}_2\text{O}$ was loaded in a quartz crucible and heated from room temperature to 500°C at a heating rate of 5°C/min under the flow of nitrogen.

2.3. Synthesis

SnSe₂: A mixture of tin powder (0.594 g, 5.0 mmol), selenium powder (0.790 g, 10.0 mmol) and NH_4Cl (1.070 g, 20.0 mmol) was load in a heavy wall Pyrex tube. (Note: NH_4Cl was used as catalyst in this reaction. In the absence of NH_4Cl , SnSe instead of SnSe₂ will be obtained.) The tube was evacuated and flame sealed at a pressure of $\sim 10^{-3}$ torr. After heating at 400° C for 2 days, quantitative amount of small black thin plate-like crystals was obtained. The product was washed with water to remove remaining NH_4Cl and dried with rinses of acetone and diethylether. The X-ray diffraction powder pattern was identical to that of SnSe₂ reported in the literature.⁸ SEM/EDS semiquantitative analysis also confirmed the stoichiometry of the product to be SnSe_{2.03}.

$(\text{Me}_4\text{N})_4\text{Sn}_4\text{Se}_{10}$ (I) A mixture of SnSe₂ powder (0.138 g, 0.5 mmol), K_2Se_2 powder (0.236 g, 1.0 mmol) and Me_4NCl (0.219g, 2.0 mmol) was loaded in a heavy wall Pyrex tube (~5ml) in which 3-ml degassed water was added. The tube was frozen in liquid N_2 and then flame sealed under a pressure of $\sim 10^{-3}$ torr. After the tube was heated in an oven at 135° C for 1 day, orange crystals of $(\text{Me}_4\text{N})_4\text{Sn}_4\text{Se}_{10}$ were found

deposited on the walls of the tube. The isolation was performed in a glove box under an inert nitrogen atmosphere. The product was washed with H₂O to remove excess Me₄NCl and KCl and washed with methanol and diethylether. Yield: 0.023 g, 12% (based on Sn). The orange crystals are insoluble in water and DMF but degrade slowly in air. SEM/EDS semiquantitative elemental analysis indicated Sn_{1.0}Se_{3.0}. The mid-IR spectrum indicated the presence of tetramethylammonium cations.

(Me₄N)₂Sn₃Se₇·2H₂O (II) The procedure for preparation and isolation of (II) is the same as that given above except that the tube was heated at 135°C for a longer period of time. Red crystals of (Me₄N)₂Sn₃Se₇·2H₂O formed after ~3 days and no new phase was observed after continued heating. Yield: 0.069 g, 38% (based on Sn). The red crystals are insoluble in water and DMF but degrade slowly in air. SEM/EDS semiquantitative elemental analysis indicated Sn_{1.0}Se_{2.4}. The mid-IR spectrum also indicated the presence of tetramethylammonium cations.

Ion Exchange of (Me₄N)₂Sn₃Se₇·2H₂O(II) An amount of 0.118g of (II) was ground into powder (<0.5mm) which was mixed with 5.923 g of Cs(CH₃CO₂) and 25 ml of MeOH in a flask under inert nitrogen atmosphere. The Cs(CH₃CO₂)/MeOH solution was decanted every two days and replaced with the same amount of fresh solution. The same procedure was repeated for two weeks. The final product was washed with water quickly to remove the excess Cs(CH₃CO₂) and then washed with MeOH and diethylether and dried. An amount of 0.086 g of orange crystalline material was obtained. The weight loss was due to the process of decanting.

2.4. X-Ray Crystallography

X-ray powder diffraction patterns were used for the purpose of phase characterization and identification. The X-ray powder diffraction patterns were recorded with a Phillips XRD-3000 controlled by PDP 11 computer and operating at 40 kV/35mA. Graphite monochromated Cu radiation was used. In order to ensure homogeneity, d-spacings obtained from X-ray powder diffraction (XRD) measurements of the products were compared with, and found to be identical, with those calculated from using the atom coordinates determined from the single crystal data. The calculation of d-spacings was performed by using the POWD 10⁹ program. The comparison tables between the calculated and observed d-spacings for these compounds are shown in Tables 3-1 and 3-2.

The single crystal X-ray diffraction data for (I) were collected on P3 Nicolet (Siemens) four circle diffractometer with $\theta/2\theta$ scan mode at -75°C. The data for (II) were collected on a Rigaku AFC6S four-circle diffractometer with $\omega-2\theta$ scan mode at -80°C. Graphite monochromated Mo K α radiation was used. The crystals were mounted at the end of glass fibers. The stability of the experimental setup and crystal intensity were monitored by measuring three standard reflections periodically for every 150 reflections. No significant decay was observed during the data collections. The structures were solved with the Patterson method and were refined by full-matrix least-square methods. The structure refinement was performed with the TEXSAN¹⁰ package of crystallographic programs running on a VAXstation 3100/76 computer. An empirical absorption correction was applied to all the data (based on ψ scans), and equivalent

Table 3-1. Calculated and Observed X-Ray Powder Diffraction Pattern for $(\text{Me}_4\text{N})_4\text{Sn}_4\text{Se}_{10}$

h	k	l	$d_{\text{calc.}}(\text{\AA})$	$d_{\text{obs.}}(\text{\AA})$	%I _{obs.}
2	0	0	10.2640	10.4464	24.12
2	1	0	9.1804	9.3243	84.12
2	1	1	8.3805	8.5032	61.93
2	2	2	5.9259	5.9959	56.47
3	2	0	5.6934	5.7603	26.50
4	0	0	5.1320	5.1842	40.84
4	2	1	4.4796	4.5233	16.19
3	3	2	4.3766	4.4201	38.60
4	2	2	4.1903	4.2309	14.79
4	3	1	4.0259	4.0639	24.12
				4.0145	17.65
4	3	2	3.8120	3.8468	100.00
4	4	0	3.6289	3.6621	17.65
4	3	3	3.5205	3.5520	49.58
4	4	2	3.4213	3.4485	28.99
5	3	2	3.3301	3.3555	23.54
5	4	1	3.1675	3.1224	21.85
6	2	2	3.0947		
5	4	2	3.0601	3.0867	52.11
4	4	4	2.9630	2.9869	61.93
5	4	3	2.9031	2.9285	22.41
6	4	1	2.8197	2.8420	14.34
6	4	2	2.7432	2.7668	10.98
6	4	3	2.6283	2.6292	37.15
6	5	0	2.6283		
6	5	1	2.6071		
5	5	4	2.5268	2.5425	5.89
6	6	2	2.3547	2.3717	31.60
8	3	2	2.3394	2.3391	16.19
7	5	2	2.3243		
7	6	0	2.2266	2.2436	44.71
7	6	1	2.2136	2.2299	64.76
8	5	2	2.1287	2.1412	13.90
9	3	2	2.1173		
8	5	3	2.0736	2.0870	17.16
9	4	1	2.0736	2.0685	39.34
8	6	0	2.0528	2.0581	64.76
9	4	2	2.0426		
8	6	1	2.0426		
7	7	2	2.0326		
8	7	2	1.8978	1.9096	22.41
9	6	0	1.8978	1.8865	16.67
10	3	3	1.8898		
9	6	1	1.8898		
10	4	2	1.8739		

Table 3-2. Calculated and Observed X-Ray Powder Diffraction Pattern for $(\text{Me}_4\text{N})_2\text{Sn}_3\text{Se}_7 \cdot 2\text{H}_2\text{O}$

h	k	l	$d_{\text{calc.}} (\text{\AA})$	$d_{\text{obs.}} (\text{\AA})$	%I _{obs.}
0	1	1	11.4419	11.5023	96.93
0	0	2	10.5723	10.6245	44.23
1	0	-1	8.9529	9.0015	20.65
1	0	1	8.6218	8.6352	100.00
0	1	2	8.3483	8.3468	13.22
1	1	0	7.8740	7.8832	34.81
1	1	2	6.1955	6.2015	10.29
1	0	3	5.5622	5.5702	6.87
2	1	-4	3.5313	3.5421	3.67
0	3	4	3.4421	3.4498	17.54
1	4	2	3.0560	3.0495	12.97
1	3	5	2.9148	2.9245	17.75
3	1	-4	2.7537	2.7540	19.82
1	2	7	2.6230	2.6284	10.28
2	4	3	2.5616	2.5648	10.96
2	4	5	2.2933	2.2869	8.92
4	1	-3	2.2863		9.28
9	5	4	1.8585	1.8494	34.32
10	4	3	1.8361		
8	8	0	1.8144	1.8267	54.71
10	4	4	1.7867	1.7831	13.90
11	3	2	1.7733		
9	7	2	1.7733		
10	5	3	1.7733		
10	6	2	1.7349	1.7407	28.99
10	5	4	1.7288		
11	4	2	1.7288		
11	4	3	1.6989	1.6894	4.79
9	8	2	1.6817		
12	2	2	1.6650		
12	3	1	1.6542	1.6444	9.47
12	3	2	1.6383		
11	5	4	1.6128	1.6213	8.75
10	8	2	1.5838	1.5709	13.03
13	2	0	1.5607		
10	8	3	1.5607		

Table 3-3. Crystal Data for (Me₄N)₄Sn₄Se₁₀ and (Me₄N)₂Sn₃Se₇·2H₂O

	(I)	(II)
formula	Sn ₄ Se ₁₀ N ₄ C ₁₆ H ₄₈	Sn ₃ Se ₇ N ₂ C ₈ H ₂₄ O ₂
fw	1560.94	1089.08
a, Å	20.529(3)	9.667(3)
b, Å	20.529(3)	13.606(4)
c, Å	20.529(3)	21.171(6)
β, deg	90.0	96.86(2)
V, Å ³	8651(4)	2781(3)
Z value	8	4
space group	P-43n	P2 ₁ /n
d _{calc} , g/cm ³	2.397	2.601
crystal size, mm	0.30x0.32x0.36	0.80x0.65x0.50
radiation	Mo Kα (λ=0.71069 Å)	Mo Kα (λ=0.71069 Å)
μ(Mo Kα), cm ⁻¹	106.41	117.63
2θ _{max} , deg	50	50
temperature, °C	-75	-80
scan type	θ/2θ	ω-2θ
scan speed, °/min	2	2
no. of data collected	2022	5447
no. of unique data	2022	5106
no. of observed data (I>3.0σ(I))	507	2846
no. of variables	68	143
final R/R _w , %	6.0/4.4	6.2/8.4

$$* R = \sum ||F_o| - |F_c|| / \sum |F_o| \quad R_w = \{ \sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2 \}^{1/2}$$

Table 3-4. Positional Parameters and Equivalent Isotropic Displacement Values ($\text{\AA}^2$)^a for (Me₄N)₄Sn₄Se₁₀ with Estimated Standard Deviations in Parentheses

atom	x	y	z	B (eq)
Sn (1)	0.3210 (2)	0.4253 (2)	0.0661 (2)	1.1 (2)
Sn (2)	0.0698 (2)	0.0698	0.0698	2.399 (2)
Se (1)	0.3959 (5)	1/2	0	2.4 (5)
Se (2)	0.2477 (5)	0.3566 (3)	-0.0080 (4)	2.8 (4)
Se (3)	0.3849 (3)	0.3514 (4)	0.1344 (4)	3.2 (4)
Se (4)	0	0.1429	0	1.7 (5)
Se (5)	0.1367 (5)	0.1367	0.1367	3.068 (4)
N (1)	0.411 (3)	0.657 (3)	0.160 (3)	3 (1)
N (2)	0.336 (3)	0.3361	0.3361	5 (1)
C (1)	0.454 (2)	0.711 (3)	0.203 (3)	1.4 (8)
C (2)	0.439 (2)	0.662 (2)	0.090 (2)	1 (1)
C (3)	0.436 (3)	0.591 (3)	0.177 (3)	3 (1)
C (4)	0.342 (2)	0.661 (3)	0.174 (2)	1 (1)
C (5)	0.3126	0.4085	0.3116	2.0
C (6)	0.295 (4)	0.2949	0.2949	4 (1)
H (1)	0.4985	0.7029	0.1981	0.9
H (2)	0.4431	0.7525	0.1846	0.9
H (3)	0.4405	0.7088	0.2463	0.9
H (4)	0.4840	0.6610	0.0891	0.3
H (5)	0.4204	0.6295	0.0631	0.3
H (6)	0.4241	0.7043	0.0733	0.3
H (7)	0.4234	0.5803	0.2249	1.3
H (8)	0.4196	0.5562	0.1534	1.3
H (9)	0.4832	0.5876	0.1793	1.3
H (10)	0.3246	0.7030	0.1620	1.8
H (11)	0.3162	0.6286	0.1517	1.8

Table 3-4. (cont'd)

atom	x	y	z	B(eq)
H(12)	0.3322	0.6556	0.2205	1.8
H(13)	0.3474	0.4373	0.3438	10.1
H(14)	0.3308	0.4155	0.2734	10.1
H(15)	0.2767	0.4176	0.3261	10.1
H(16)	0.2523	0.3067	0.3046	5.2
H(17)	0.3067	0.3046	0.2523	5.2
H(18)	0.3046	0.2523	0.3067	5.2

$$^a B(\text{eq}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}].$$

Table 3-5. Positional Parameters and Equivalent Isotropic Displacement Values ($\text{\AA}^2$)^a for $(\text{Me}_4\text{N})_2\text{Sn}_3\text{Se}_7 \cdot 2\text{H}_2\text{O}$ with Estimated Standard Deviations in Parentheses

atom	x	y	z	B (eq)
Sn (1)	0.3064 (2)	0.2057 (1)	0.19592 (8)	0.29 (7)
Sn (2)	0.4329 (2)	0.0287 (1)	0.07771 (8)	0.57 (8)
Sn (3)	0.2868 (2)	-0.0642 (1)	0.22764 (8)	0.26 (7)
Se (1)	0.3403 (3)	0.0905 (2)	0.2918 (1)	0.5 (1)
Se (2)	0.1812 (3)	0.0554 (2)	0.1310 (1)	0.3 (1)
Se (3)	0.6824 (3)	-0.0059 (2)	0.0307 (1)	1.1 (1)
Se (4)	0.5022 (3)	0.2006 (2)	0.1186 (1)	1.1 (1)
Se (5)	0.4389 (3)	0.3452 (2)	0.2670 (1)	0.9 (1)
Se (6)	0.1002 (3)	0.3185 (2)	0.1808 (1)	0.9 (1)
Se (7)	0.4818 (3)	-0.1111 (2)	0.1563 (1)	0.8 (1)
O (1)	0.046 (3)	0.051 (2)	0.539 (1)	3.7 (6)
O (2)	0.852 (5)	0.216 (4)	0.463 (3)	5 (1)
O (3)	-0.067 (4)	0.084 (3)	0.528 (2)	0.9 (7)
N (1)	0.411 (3)	0.245 (2)	0.481 (1)	2.4 (6)
N (2)	0.812 (3)	0.094 (2)	0.278 (1)	2.8 (6)
C (1)	0.483 (5)	0.149 (4)	0.472 (2)	7 (1)
C (2)	0.299 (5)	0.261 (4)	0.436 (2)	6 (1)
C (3)	0.498 (6)	0.334 (4)	0.478 (2)	7 (1)
C (4)	0.356 (6)	0.254 (4)	0.551 (3)	8 (1)
C (5)	0.741 (4)	0.185 (3)	0.281 (2)	4.1 (9)
C (6)	0.962 (4)	0.105 (3)	0.303 (2)	3.9 (9)
C (7)	0.741 (4)	0.013 (3)	0.304 (2)	4.1 (9)
C (8)	0.834 (4)	0.079 (3)	0.200 (2)	4 (1)
H (1)	0.4195	0.0953	0.4801	6.0
H (2)	0.5097	0.1410	0.4291	6.0
H (3)	0.5613	0.1425	0.4997	6.0
H (4)	0.2373	0.3113	0.4494	7.4
H (5)	0.3162	0.2646	0.3949	7.4
H (6)	0.2325	0.1985	0.4389	7.4

Table 3-5. (cont'd)

atom	x	y	z	B(eq)
H(7)	0.5786	0.3281	0.5035	7.2
H(8)	0.5260	0.3426	0.4337	7.2
H(9)	0.4464	0.3898	0.4878	7.2
H(10)	0.3066	0.3029	0.5583	10.5
H(11)	0.3027	0.1889	0.5582	10.5
H(12)	0.4367	0.2436	0.5812	10.5
H(13)	0.7469	0.2085	0.3238	4.1
H(14)	0.7917	0.2319	0.2561	4.1
H(15)	0.6513	0.1801	0.2656	4.1
H(16)	1.0112	0.0459	0.3043	5.1
H(17)	1.0106	0.1537	0.2805	5.1
H(18)	0.9647	0.1300	0.3480	5.1
H(19)	0.7261	0.0255	0.3497	4.3
H(20)	0.6494	0.0052	0.2849	4.3
H(21)	0.7899	-0.0457	0.3019	4.3
H(22)	0.8800	0.0150	0.1891	5.0
H(23)	0.7480	0.0764	0.1724	5.0
H(24)	0.8910	0.1278	0.1800	5.0

$$^a B(\text{eq}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}].$$

reflections were averaged. An additional absorption correction based on the DIFABS¹¹ procedure was applied to the isotropically refined data. Crystallographic data and details of data collection are listed in Table 3-3. Atomic coordinates and equivalent isotropic thermal parameters for (I) and (II) are given in Tables 3-4 and 3-5.

3. Results and Discussion

3.1. Synthesis

(Me₄N)₄Sn₄Se₁₀ (I) and (Me₄N)₂Sn₃Se₇·2H₂O (II) were synthesized by reacting SnSe₂ and two equivalents K₂Se₂ in the presence of excess (four equivalents) Me₄NCl under hydrothermal conditions at 135°C. Orange crystals of (I) grew after the reaction proceeded for 1 day. Upon prolonged heating (> 3 days) at the same temperature, (I) disappeared and red crystals of (II) formed. No other phases were found after further heating of (II). The amount of Me₄NCl used in this reaction appeared to be crucial for the crystallization of products. No crystals formed when only two equivalents of Me₄NCl were used suggesting that Cl⁻ may be an important "mineralizer" in this reaction. The choice of polyselenide starting material is also important in these reactions. The reactions of SnSe₂ and K₂Se₄ gave only crystals of elemental Se which probably came from the self-redox process of Se₄²⁻.



Compound (I) is probably kinetically favored and formed at an earlier stage of the reaction. It is possible that (I) is attacked by excess Se_x²⁻ in

solution forming soluble precursors which then reorganize to form the more thermodynamically stable structure of (II).

3.2. Description of The Structures

3.2.1. Structure of (Me₄N)₄Sn₄Se₁₀

(I) contains two crystallographically distinct adamantine P₄O₁₀-like clusters which have four corner-sharing tetrahedral SnSe₄ forming fused chair-formed six-membered rings. See Figure 3-1. Its alkali metal salt, which belongs to the family of [M₄Q₁₀]⁴⁻, (where M=Ge, Sn; Q=S, Se) was reported by Krebs *et al.*¹² The site symmetry of [Sn₄Se₁₀]⁴⁻ clusters is tetrahedral with four terminal Sn-Se bonds pointed toward the corners of a tetrahedron. Each of the remaining six Se atoms binds to two Sn atoms along the edge of the tetrahedron. Selected bond distances and angles are given in Table 3-6. The average Sn-Sn distance is 4.08(3)Å. The average terminal Sn-Se distance (2.41(5)Å) is shorter than that of bridging Sn-Se distances (2.54(2)Å). The Se-Sn-Se angles are close to those in a perfect tetrahedron. The average (terminal Se)-Sn-(bridging Se) angle (108(1)Å) is slightly smaller than the average (bridging Se)-Sn-(bridging Se) angle (110.6(5)Å).

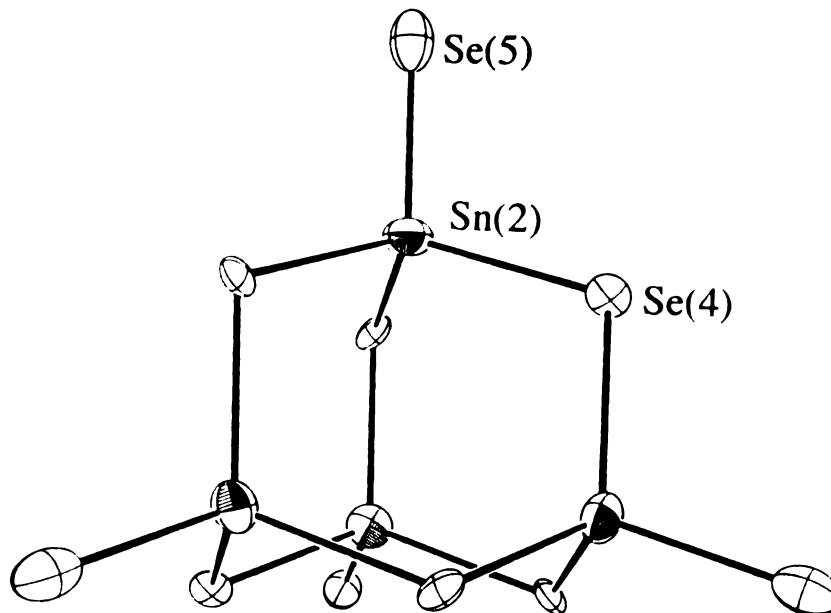
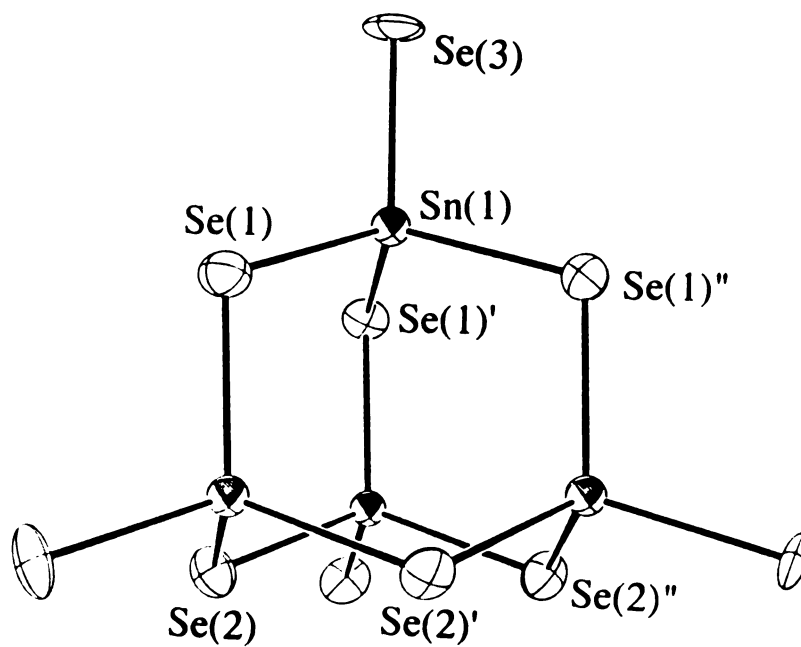


Figure 3-1: ORTEP representation and labeling scheme for two crystallographically independent $[\text{Sn}_4\text{Se}_{10}]^{4+}$ clusters.

Table 3-6. Selected Bond Distances (Å) and Angles (deg) for (Me₄N)₄Sn₄Se₁₀ with Estimated Standard Deviations in Parentheses.

Selected Bond Distances (Å)			
Sn(1)-Se(1)	2.562(7)	C(1)-H(1)	0.932
Sn(1)-Se(2)	2.562(9)	C(1)-H(2)	0.966
Sn(1)-Se(2)	2.525(9)	C(1)-H(3)	0.927
Sn(1)-Se(3)	2.447(9)	C(2)-H(4)	0.926
Sn(2)-Se(5)	2.379(7)	C(2)-H(5)	0.944
Sn(2)-Se(4)	2.521(3)x3	C(2)-H(6)	0.978
mean (Sn-Se)	2.50(6)	C(3)-H(7)	1.040
Sn(1)-Sn(1)	4.098(9)x2	C(3)-H(8)	0.930
Sn(1)-Sn(1)	4.110(8)x2	C(3)-H(9)	0.975
Sn(2)-Sn(2)	4.051(7)x4	C(4)-H(10)	0.970
mean(Sn-Sn)	4.08(3)	C(4)-H(11)	0.973
N(1)-C(1)	1.68(8)	C(4)-H(12)	0.976
N(1)-C(2)	1.55(7)	C(5)-H(13)	1.139
N(1)-C(3)	1.49(8)	C(5)-H(14)	0.881
N(1)-C(4)	1.44(8)	C(5)-H(15)	0.817
N(2)-C(5)	1.64(2)x3	C(6)-H(16)	0.930
N(2)-C(6)	1.47(6)	C(6)-H(17)	0.930
		C(6)-H(18)	0.930
Selected Bond Angles (deg)			
Se(1)-Sn(1)-Se(2)	111.5(3)	H(1)-C(1)-H(2)	109.64
Se(1)-Sn(1)-Se(2)	110.0(3)	H(1)-C(1)-H(3)	113.15
Se(1)-Sn(1)-Se(3)	110.7(3)	H(2)-C(1)-H(3)	110.12
Se(2)-Sn(1)-Se(2)	110.1(2)	H(4)-C(2)-H(5)	112.18
Se(2)-Sn(1)-Se(3)	108.3(3)	H(4)-C(2)-H(6)	109.12
Se(2)-Sn(1)-Se(3)	106.0(3)	H(5)-C(2)-H(6)	107.65
Se(4)-Sn(2)-Se(5)	108.2(1)x3	H(7)-C(3)-H(8)	103.78
Se(4)-Sn(2)-Se(4)	110.7(2)x3	H(7)-C(3)-H(9)	100.66
Sn(1)-Se(1)-Sn(1)	106.2(4)	H(8)-C(3)-H(9)	109.11
Sn(1)-Se(2)-Sn(1)	107.8(3)	H(10)-C(4)-H(11)	105.99
Sn(2)-Se(4)-Sn(2)	106.91(9)	H(10)-C(4)-H(12)	105.71

Table 3-6. (cont'd)

C(1)-N(1)-C(2)	104(4)	H(11)-C(4)-H(12)	105.53
C(1)-N(1)-C(3)	107(4)	H(13)-C(5)-H(14)	99.53
C(1)-N(1)-C(4)	112(4)	H(13)-C(5)-H(15)	103.73
C(2)-N(1)-C(3)	99(4)	H(14)-C(5)-H(15)	131.95
C(2)-N(1)-C(4)	124(4)	H(16)-C(6)-H(17)	113.10
C(3)-N(1)-C(4)	110(5)	H(16)-C(6)-H(18)	113.10
C(5)-N(2)-C(5)	117(2)x3	H(17)-C(6)-H(18)	113.10
C(5)-N(2)-C(6)	100(3)x3		

3.2.2. Structure of $(\text{Me}_4\text{N})_2\text{Sn}_3\text{Se}_7 \cdot 2\text{H}_2\text{O}$

$(\text{Me}_4\text{N})_2\text{Sn}_3\text{Se}_7 \cdot 2\text{H}_2\text{O}$ has a two-dimensional anionic framework which is built up with trigonal bipyramidal SnSe_5 units. Every three SnSe_5 trigonal bipyramids are fused together by sharing their $\text{Se}_{\text{eq}}\text{-Sn-Se}_{\text{ax}}$ edges to form a trimeric $\text{Sn}_3\text{Se}_{10}$ cluster as shown in Figure 3-2. The triply bridging Se atom is the common axial Se of the three SnSe_5 trigonal bipyramids. The $[\text{Sn}_3\text{Se}_4]^{4+}$ cores of these triangular clusters can be viewed as defect cubanes (one Sn center missing) which are further connected by sharing their six terminal selenides. This results in a two-dimensional net-like anionic framework perforated with large holes as shown in Figure 3-3. The charge of the $[\text{Sn}_3\text{Se}_7]_n^{2n-}$ layers is balanced by two equivalents of tetramethylammonium cations located between the layers, as shown in Figure 3-4.

The anionic framework differs conformationally from that of its cesium salt which crystallizes in a different space group. Because of the larger size of tetramethylammonium compared to that of Cs^+ , the total volume of $(\text{Me}_4\text{N})_2\text{Sn}_3\text{Se}_7 \cdot 2\text{H}_2\text{O}$ is ~29% larger than its Cs^+ salt. The change of the volume is mainly achieved by expansion of the interlayer spacing from 6.64 Å in the Cs^+ salt to 8.62 Å. Additional void space is filled by the inclusion of H_2O molecules.

Comparison of the bond distances and bond angles between $(\text{Me}_4\text{N})_2\text{Sn}_3\text{Se}_7 \cdot 2\text{H}_2\text{O}$ and $\text{Cs}_2\text{Sn}_3\text{Se}_7$ are given in Table 3-7. The corresponding bond distances and angles are comparable to each other in their anionic frameworks.

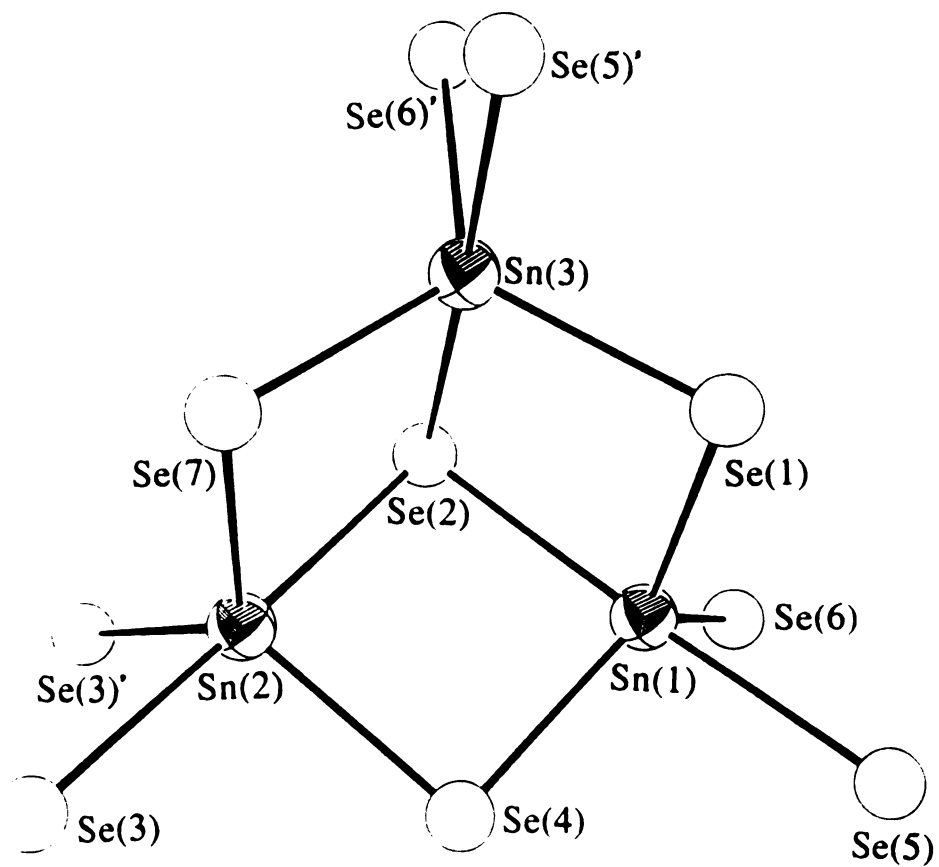


Figure 3-2: ORTEP representation and labeling scheme of a building unit in $(\text{Me}_4\text{N})_2\text{Sn}_3\text{Se}_7 \cdot 2\text{H}_2\text{O}$.

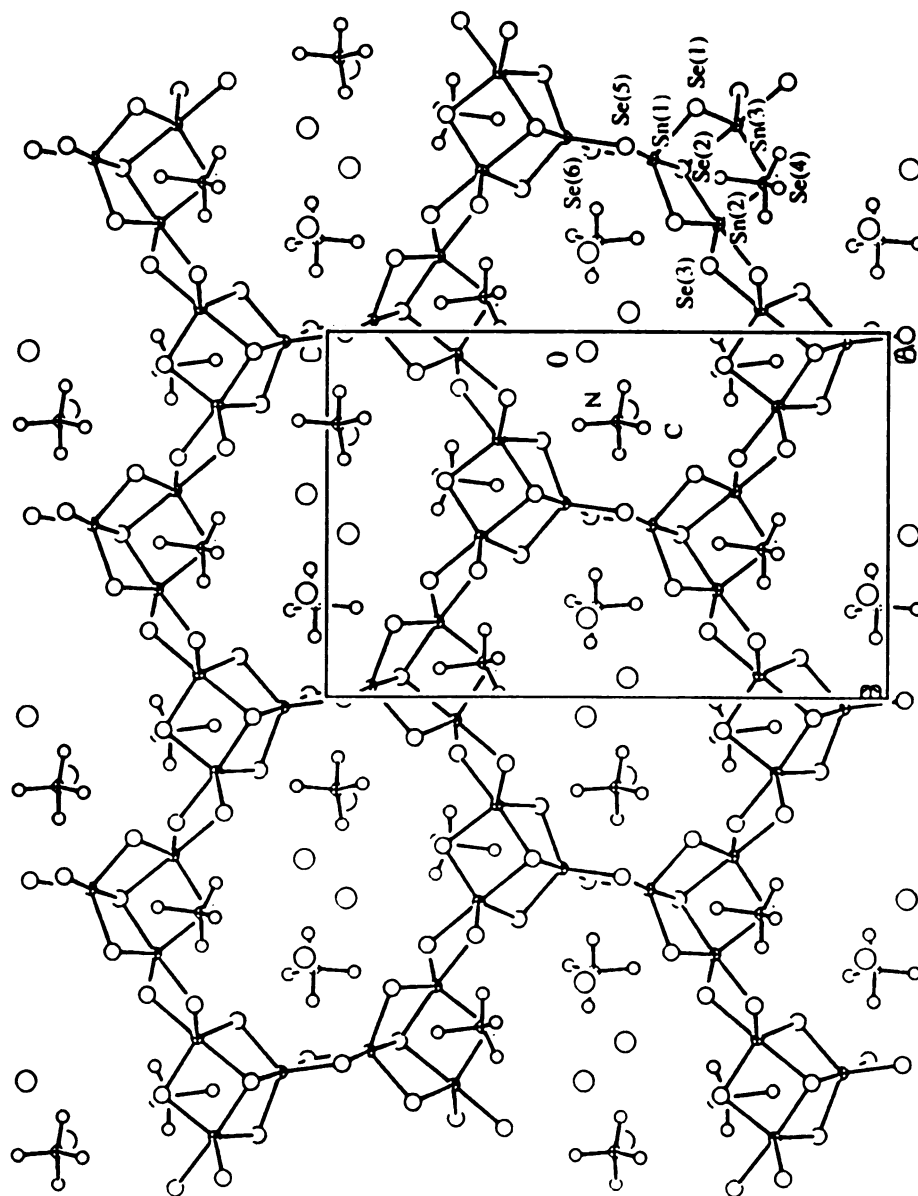


Figure 3-3: ORTEP representation and labeling scheme of a single layer of $(\text{Me}_4\text{N})_2\text{Sn}_3\text{Se}_7 \cdot 2\text{H}_2\text{O}$. View down the a -axis.

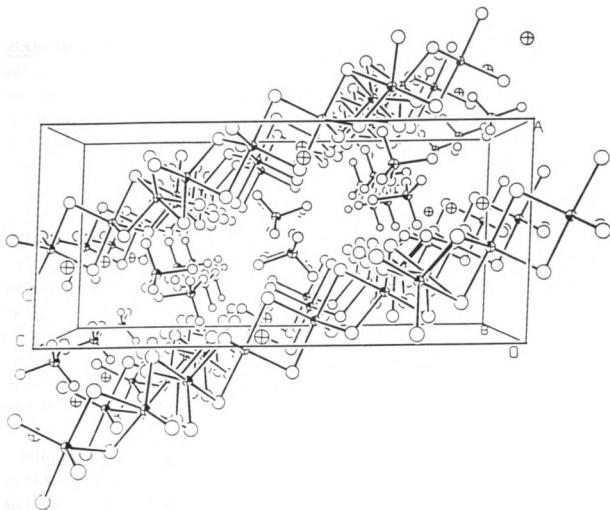


Figure 3-4: The structure of $(\text{Me}_4\text{N})_2\text{Sn}_3\text{Se}_7 \cdot 2\text{H}_2\text{O}$ viewed parallel to the layers. Double layers of Me_4N^+ cations are located between the $[\text{Sn}_3\text{Se}_7]^{2-}$ layers. Water molecules, shown by crossed circles, are located inside the holes of the $[\text{Sn}_3\text{Se}_7]^{2-}$ layers.

Table 3-7. Selected Bond Distances (Å) and Angles (deg) for (Me₄N)₂Sn₃Se₇·2H₂O with Standard Deviations in Parentheses

Selected Bond Distances (Å)			
Sn(1)-Se(1)	2.573(3)	Sn(1)-Sn(2)	3.723(3)
Sn(1)-Se(2)	2.714(3)	Sn(1)-Sn(3)	3.658(3)
Sn(1)-Se(4)	2.565(3)	Sn(1)-Sn(3)	3.739(3)
Sn(1)-Se(5)	2.706(3)	Sn(2)-Sn(2)	3.680(4)
Sn(1)-Se(6)	2.523(3)	Sn(2)-Sn(3)	3.757(3)
Sn(2)-Se(2)	2.757(3)	mean(Sn-Sn)	3.71(4)
Sn(2)-Se(3)	2.696(4)		
Sn(2)-Se(3)	2.520(3)	N(1)-C(1)	1.50(6)
Sn(2)-Se(4)	2.571(4)	N(1)-C(2)	1.42(5)
Sn(2)-Se(7)	2.556(3)	N(1)-C(3)	1.47(6)
Sn(3)-Se(1)	2.544(3)	N(1)-C(4)	1.61(6)
Sn(3)-Se(2)	2.768(3)	N(2)-C(5)	1.42(5)
Sn(3)-Se(5)	2.514(3)	N(2)-C(6)	1.52(4)
Sn(3)-Se(6)	2.700(3)	N(2)-C(7)	1.43(5)
Sn(3)-Se(7)	2.554(3)	N(2)-C(8)	1.69(5)
Selected Bond Angles (deg)			
Se(1)-Sn(1)-Se(2)	88.7(1)	Se(2)-Sn(3)-Se(7)	88.0(1)
Se(1)-Sn(1)-Se(4)	114.7(1)	Se(5)-Sn(3)-Se(6)	89.9(1)
Se(1)-Sn(1)-Se(5)	87.1(1)	Se(5)-Sn(3)-Se(7)	124.9(1)
Se(1)-Sn(1)-Se(6)	122.6(1)	Se(6)-Sn(3)-Se(7)	89.6(1)
Se(2)-Sn(1)-Se(4)	88.9(1)	Sn(1)-Se(1)-Sn(3)	93.9(1)
Se(2)-Sn(1)-Se(5)	175.6(1)	Sn(1)-Se(2)-Sn(2)	85.76(9)
Se(2)-Sn(1)-Se(6)	93.7(1)	Sn(1)-Se(2)-Sn(3)	86.00(9)
Se(4)-Sn(1)-Se(5)	91.7(1)	Sn(2)-Se(2)-Sn(3)	85.68(9)
Se(4)-Sn(1)-Se(6)	122.6(1)	Sn(2)-Se(3)-Sn(2)	89.7(1)
Se(5)-Sn(1)-Se(6)	89.6(1)	Sn(1)-Se(4)-Sn(2)	92.9(1)
Se(2)-Sn(2)-Se(3)	176.6(1)	Sn(1)-Se(5)-Sn(3)	88.9(1)
Se(2)-Sn(2)-Se(3)	91.7(1)	Sn(1)-Se(6)-Sn(3)	88.8(1)
Se(2)-Sn(2)-Se(4)	87.9(1)	Sn(2)-Se(7)-Sn(3)	94.7(1)

Table 3-7. (cont'd)

Se(2)-Sn(2)-Se(7)	88.2(1)	C(1)-N(1)-C(2)	113(3)
Se(3)-Sn(2)-Se(3)	90.3(1)	C(1)-N(1)-C(3)	117(3)
Se(3)-Sn(2)-Se(4)	93.5(1)	C(1)-N(1)-C(4)	111(4)
Se(3)-Sn(2)-Se(7)	88.3(1)	C(2)-N(1)-C(3)	105(3)
Se(3)-Sn(2)-Se(4)	121.0(1)	C(2)-N(1)-C(4)	109(3)
Se(3)-Sn(2)-Se(7)	124.1(1)	C(3)-N(1)-C(4)	101(3)
Se(4)-Sn(2)-Se(7)	114.9(1)	C(5)-N(2)-C(6)	110(3)
Se(1)-Sn(3)-Se(2)	88.1(1)	C(5)-N(2)-C(7)	114(3)
Se(1)-Sn(3)-Se(5)	122.4(1)	C(5)-N(2)-C(8)	103(3)
Se(1)-Sn(3)-Se(6)	92.4(1)	C(6)-N(2)-C(7)	114(3)
Se(1)-Sn(3)-Se(7)	112.7(1)	C(6)-N(2)-C(8)	101(3)
Se(2)-Sn(3)-Se(5)	91.8(1)	C(7)-N(2)-C(8)	112(3)
Se(2)-Sn(3)-Se(6)	177.6(1)		

The average Sn-Sn distance in (II), 3.71(4) Å, is shorter than that in (I). In the three SnSe₅ trigonal bipyramids, the axial Sn-Se distances (average=2.72(3)Å) are longer than the equatorial Sn-Se distances (average=2.55(2)Å). The Se_{ax}-Sn-Se_{ax} angles range from 175.6(1)° to 177.6(1)°, the Se_{ax}-Sn-Se_{eq} angles range from 85.7(1)° to 94.7(1)° and the Se_{eq}-Sn-Se_{eq} angles range from 112.8(1)° to 124.8(1)°. These angles do not show much deviation from the ideal bond angles in trigonal bipyramids.

3.3. Ion Exchange Experiments with (Me₄N)₂Sn₃Se₇·2H₂O

Since the Cs⁺ salt of (II) is known, it is interesting to see whether the cations of the layered (Me₄N)₂Sn₃Se₇ structure are exchangeable. The ion exchange experiment was performed according to the following equation: $(\text{Me}_4\text{N})_2\text{Sn}_3\text{Se}_7 + 2\text{Cs}^+ \rightleftharpoons \text{Cs}_2\text{Sn}_3\text{Se}_7 + 2\text{Me}_4\text{N}^+$. The final product was examined under an optical microscope where the small orange crystalline pieces were found to maintain their original sizes and shapes but with cracks on their surfaces. Its vibration spectrum shows no organic peaks, indicating all the Me₄N⁺ counterions are replaced. Semiquantitative elemental analysis performed on SEM/EDS was done on both the surface of larger pieces (~0.5mm) and the small particles (~1-10 mm) from further grinding, which indicated Cs_{2.0}Sn_{3.0}Se_{7.5} consistently. This confirms that Me₄N⁺ cations are replaced by Cs⁺. The powder X-ray diffraction, however, shows poor product crystallinity with a strong peak at 6.92Å, which corresponds to the interlayer spacing of Cs₂Sn₃Se₇.

3.4. Thermogravimetric Analysis of $(\text{Me}_4\text{N})_2\text{Sn}_3\text{Se}_7 \cdot 2\text{H}_2\text{O}$

$(\text{Me}_4\text{N})_2\text{Sn}_3\text{Se}_7 \cdot 2\text{H}_2\text{O}$ decomposes at $\sim 270^\circ\text{C}$, as shown in Figure 3-5, forming SnSe_2 as a black powder according to its X-ray diffraction powder pattern. The decomposition process is rationalized by the formation of volatile trialkyl amine, dialkyl selenide and water molecules, as shown in the following equation:



The calculated weight loss, 23.8%, is slightly smaller than the observed 27%. This could be attributed to experimental errors or indicate two more equivalents of water molecules may be trapped inside the framework or on the surface of the crystals.

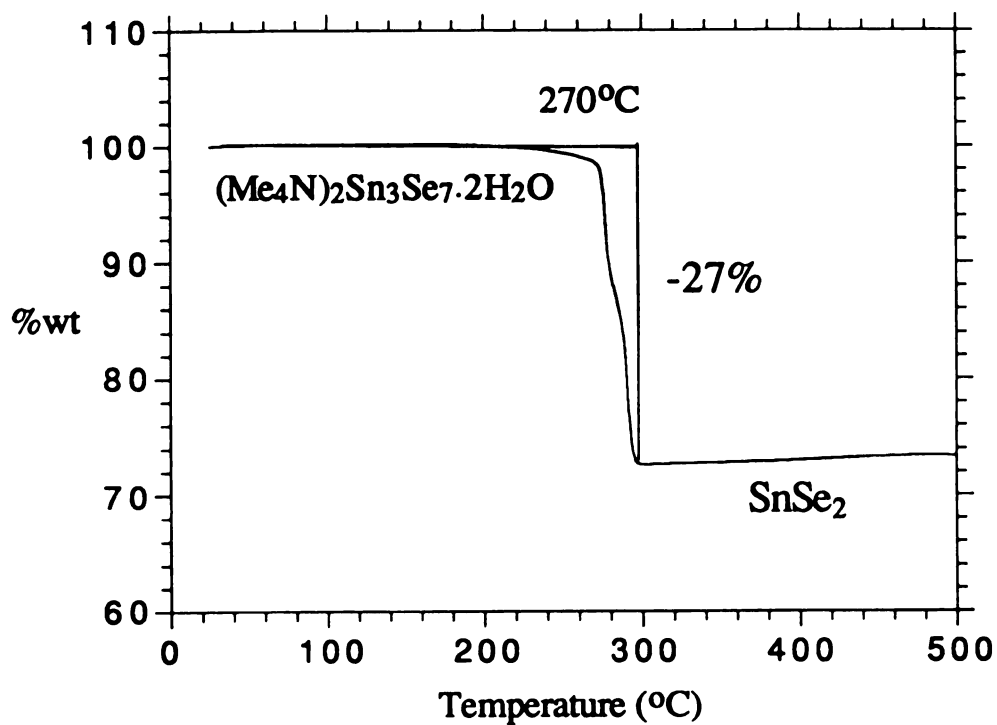


Figure 3-5: Thermogravimetric analysis (TGA) data of $(\text{Me}_4\text{N})_2\text{Sn}_3\text{Se}_7 \cdot 2\text{H}_2\text{O}$. The heating rate was 5 °C/min.

3.5. Spectroscopy

Optical Spectroscopy

The optical absorption spectrum of $(\text{Me}_4\text{N})_2\text{Sn}_3\text{Se}_7 \cdot 2\text{H}_2\text{O}$ is given in Figure 3-6. It indicates the semiconductor nature of the compound with a steep absorption edge and an optical band gap at 2.0 eV which is consistent with the red color of the crystals. The compound also shows four absorption peaks in the near IR region at 0.507, 0.518, 0.532 and 0.548 eV respectively which are due to the presence of Me_4N^+ . The $(\text{Me}_4\text{N})_4\text{Sn}_4\text{Se}_{10}$ contains discrete *molecular* $[\text{Sn}_4\text{Se}_{10}]^{4-}$. Instead, it shows three absorption bands at 218 nm (5.69 eV), 266 nm (4.66 eV), 417 nm (2.97 eV) and a shoulder between 550 nm and 850 nm (1.49~2.25 eV), as shown in Figure 3-7.

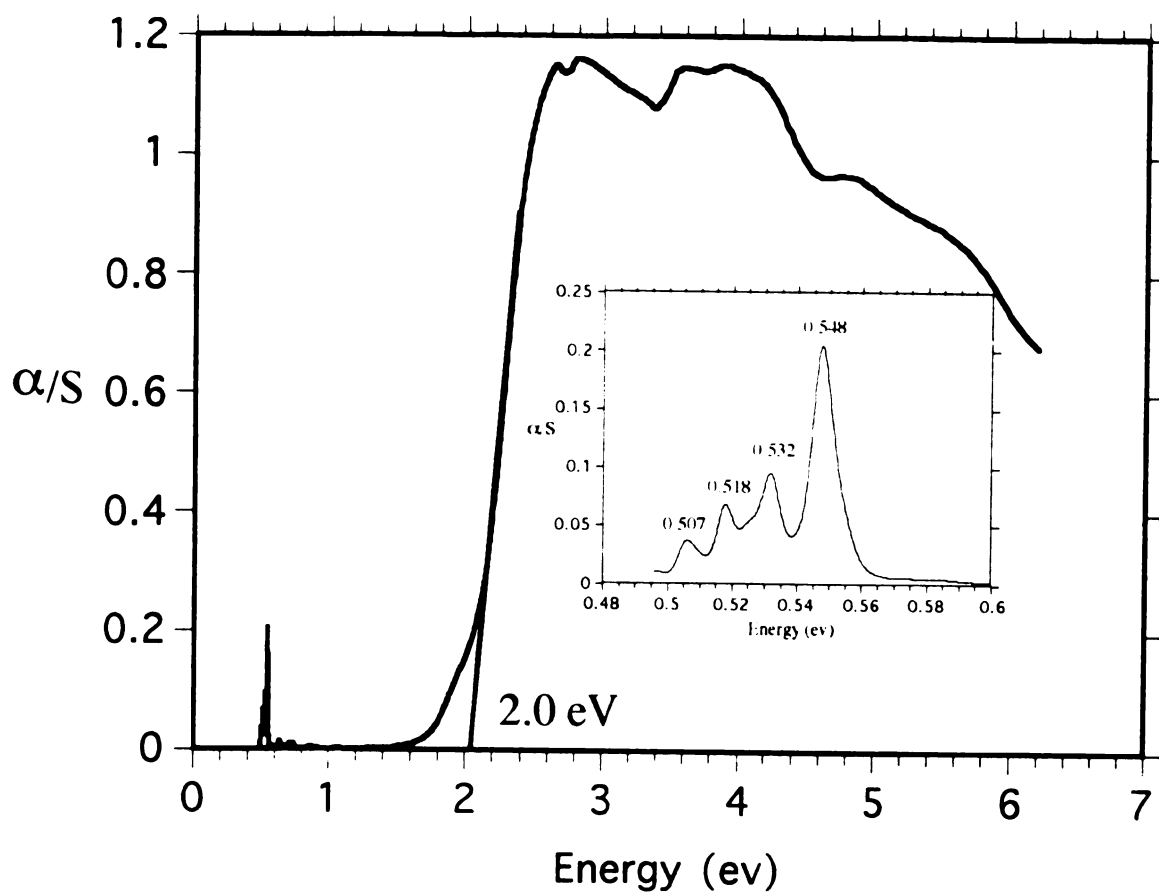


Figure 3-6: Solid state optical spectrum of $(\text{Me}_4\text{N})_2\text{Sn}_3\text{Se}_7 \cdot 2\text{H}_2\text{O}$. The absorptions in the 0.5~0.6 eV region are due to vibrational excitations within the Me_4N^+ molecule.

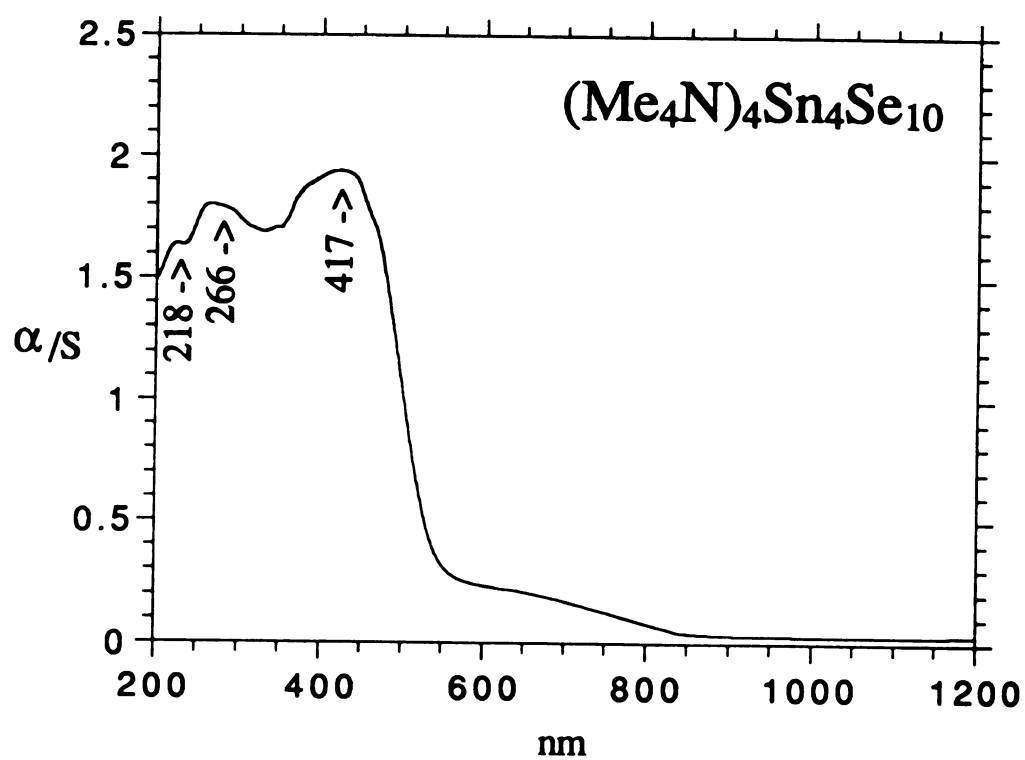


Figure 3-7: Solid state optical spectrum of $(\text{Me}_4\text{N})_4\text{Sn}_4\text{Se}_{10}$.

Vibrational Spectroscopy

The Far-IR spectra of (I) and (II) are shown in Figure 3-8. (I) exhibits vibrations at 452 cm^{-1} , 274 cm^{-1} , 238 cm^{-1} and 192 cm^{-1} , while (II) exhibits vibrations at 262 cm^{-1} , 231 cm^{-1} , 211 cm^{-1} , 202 cm^{-1} , 194 cm^{-1} and 186 cm^{-1} . These peaks represent Sn-Se vibrations. The vibrational spectra of the alkali metals salts of $[\text{Sn}_4\text{Se}_{10}]^{2-}$ and $[\text{Sn}_3\text{Se}_7]^{2-}$ were not reported. For comparison, the Sn-Se vibrations of $\text{Na}_4\text{SnSe}_4 \cdot 16\text{H}_2\text{O}$ ¹³ were reported at 252 cm^{-1} and 195 cm^{-1} .

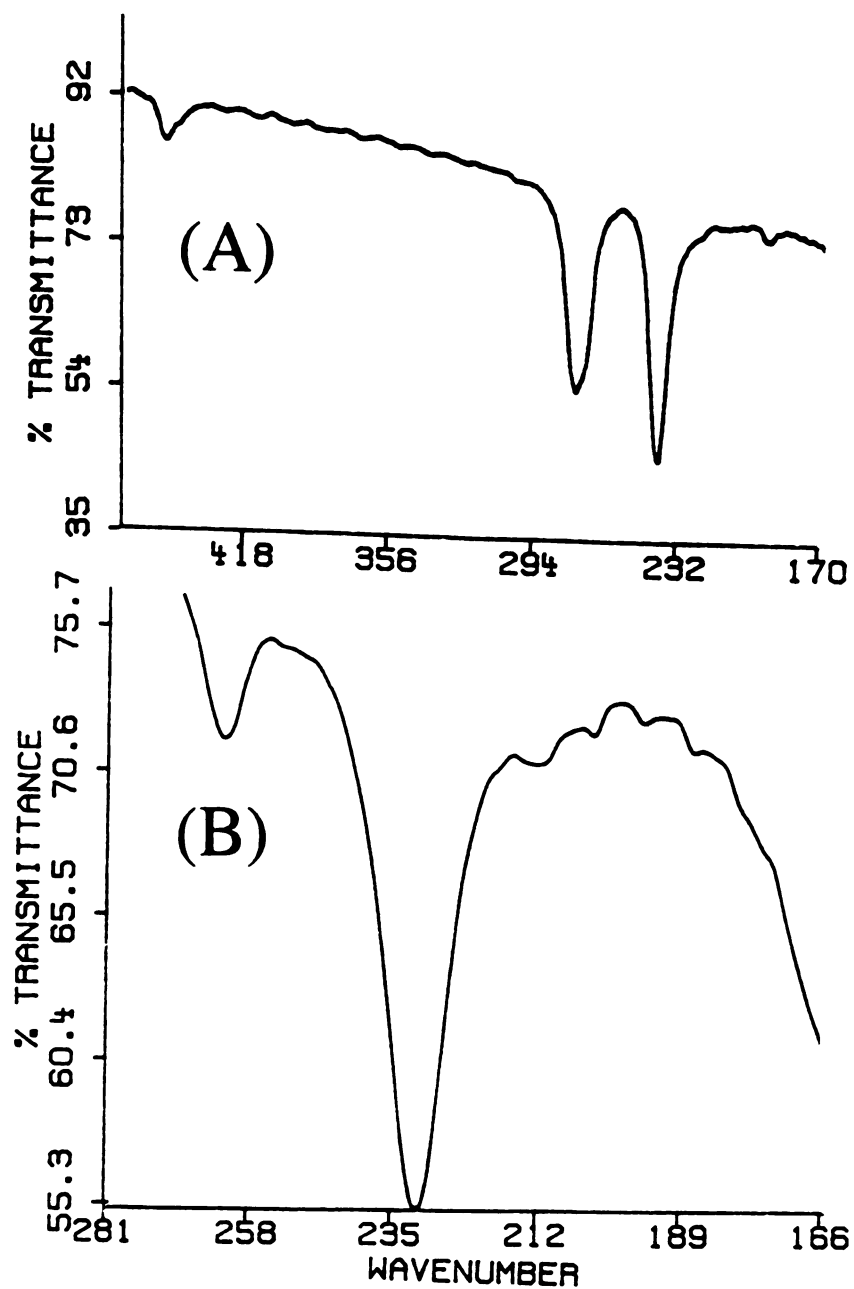


Figure 3-8: Infrared spectra of (A) $(\text{Me}_4\text{N})_4\text{Sn}_4\text{Se}_{10}$ and (B) $(\text{Me}_4\text{N})_2\text{Sn}_3\text{Se}_7 \cdot 2\text{H}_2\text{O}$.

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CHAPTER 4

Methanothermal Synthesis and Characterization of Vanadium, Niobium and Tungsten (Poly)selenides Systems

1. Introduction

Unlike hydrothermal techniques which use hard bases as mineralizers and yield monochalcogenide compounds¹, our approach uses the polychalcogenides themselves as mineralizers often giving rise to polychalcogenide compounds. In Chapter 2, we have shown that the Mo/Se system has produced cluster compounds in which the trimeric $[\text{Mo}_3\text{Se}_7]^{4+}$ core exists as a building block, and the Mo is in the 4+ oxidation state.² Given the known chemical similarity between Mo and V, Nb and W, we extended this technique to these metals to see if the analogous, hitherto unknown, $[\text{M}_3\text{Se}_7]^+$ ($\text{M}=\text{V}(3+)$, $\text{Nb}(3+)$ or $\text{W}(4+)$) clusters could be produced. Although this cluster core was not found, we were able to synthesize and crystallize two new vanadium polyselenide compounds, $\text{K}_4\text{V}_2\text{O}_2\text{Se}_{10}\cdot 2\text{MeOH}$ (I), $\text{K}_4\text{V}_2\text{O}_2\text{Se}_8\cdot 0.65\text{MeOH}$ (II). For Nb and W systems, mixed oxo/seleno $[\text{SO}_4]^{2-}$ type tetrahedral anions were obtained: $[\text{NbOSe}_3]^{3-}$ (III) and $[(\text{WO}_2\text{Se}_2)_{0.5}(\text{WSe}_3)_{0.5}]^{2-}$ (IV). In contrast to the

Mo systems, we found that, due to the stronger affinity of V, Nb and W ions for oxygen, water is not a suitable solvent for these systems, causing product hydrolysis. A weaker Lewis base, methanol, was used to minimize the formation of oxometalates.

2. Experimental Section

2.1. Reagents

Chemicals in this work were used as obtained from commercial sources. All manipulations were carried out in a glove-box under a nitrogen atmosphere. K_2Se_4 was prepared by dissolving the stoichiometric amount of the elements in liquid ammonia.

2.2. Physical Measurements

The instruments and experimental setups for Infrared spectroscopy and SEM/EDS quantitative microprobe analysis are the same as those in previous chapters. UV/Vis spectra were measured on a Hitachi U-2000 spectrometer.

2.3. Synthesis

$K_4V_2O_2Se_{10} \cdot 2MeOH$ (I) An amount of 0.025 g (0.5 mmol) V metal, 0.197 g (0.5 mmol) K_2Se_4 and 0.3 ml (7.37 mmol) of MeOH were mixed in a heavy-wall (2 mm thickness) Pyrex tube of ~5 ml total capacity. The tube was placed in an oven at 135°C for 4 days at the end of which it

afforded black needle-like crystals of $\text{K}_4\text{V}_2\text{O}_2\text{Se}_{10}\cdot 2\text{MeOH}$ in ~20% yield (based on V). Isolation of the product was performed in a nitrogen-filled glove box. The crystals were isolated by filtration and washed with degassed MeOH to remove excess K_2Se_x and then dried with ether. These crystals are soluble in water, DMF, DMSO and slightly soluble in acetonitrile. They degrade slowly in air. Quantitative microprobe analysis on the single crystals gave a composition of $\text{K}_{1.7}\text{V}_{1.0}\text{Se}_{4.9}$.

$\text{K}_4\text{V}_2\text{O}_2\text{Se}_8\cdot 0.65\text{MeOH}$ (II) An amount of 0.125 g (2.5 mmol) V metal, 0.985 g (2.5 mmol) K_2Se_4 and 1.5 ml (36.9 mmol) MeOH were mixed in a Parr bomb of 21 ml total capacity at 135°C for 24 days, giving black plate-like crystals of $\text{K}_4\text{V}_2\text{O}_2\text{Se}_8\cdot 0.65\text{MeOH}$ in ~29 % yield (based on V). The product was isolated with MeOH and dried with ether. The solubility and air-sensitivity of this material are similar to that of (I). SEM/EDS semiquantitative elemental analysis indicated $\text{K}_{1.5}\text{V}_{1.0}\text{Se}_{3.0}$.

K_3NbOSe_3 (III) The reaction of 0.046 g (0.50 mmol) Nb, 0.236 g K_2Se_2 (1.0 mmol) and 0.3-ml (7.92 mmol) MeOH at 135°C for 7 days afforded yellow needle-like crystals of K_3NbOSe_3 in less than 10% yield (based on Nb). The yellow crystals are air sensitive and soluble in water and common polar solvents such as DMF, DMSO and MeOH. The product was isolated and dried with rinses of ether. SEM/EDS semiquantitative elemental analysis indicated $\text{K}_{3.3}\text{Nb}_{1.0}\text{Se}_{3.6}$.

$\text{K}_2[\text{WO}_2\text{Se}_2]_{0.5}(\text{WOSe}_3)_{0.5}$ (IV) The reaction of 0.093 g (0.4 mmol) WO_3 , 0.189 g (0.8mmol) K_2Se_2 and 0.3-ml (7.92 mmol) MeOH at 135°C for 9 days afforded red plate-like crystals of

$\text{K}_2[\text{WO}_2\text{Se}_2]_{0.5}(\text{WSe}_3)_{0.5}$ in ~15 % yield. The red crystals dissolve in MeOH slowly and therefore were isolated with quick rinses of MeOH and then dried with ether. They decompose slowly in air and are soluble in water. SEM/EDS semiquantitative elemental analysis indicated $\text{K}_{0.7}\text{W}_{1.0}\text{Se}_{2.4}$.

2.4. X-Ray Crystallography

X-ray powder diffraction patterns were used for the purpose of phase characterization and identification. The X-ray powder diffraction patterns were recorded with a Phillips XRD-3000 controlled by PDP 11 computer and operating at 40 kV/35mA. Graphite monochromated Cu radiation was used. In order to ensure the homogeneity, d-spacings obtained from X-ray powder diffraction (XRD) measurements of the products were compared with, and found to be identical, with those calculated from using the atom coordinates determined from the single crystal data. The calculation of d-spacings was performed using the POWD 10.³ program. The comparison tables between the calculated and observed d-spacings for these compounds are shown in Tables 4-1~4-4.

Single crystal X-ray diffraction data for (I), (II) and (IV) were collected on a Rigaku AFC6S diffractometer equipped with graphite-monochromated Mo $\text{K}\alpha$ radiation. The data for (III) were collected on a four-circle Nicolet (Siemens) autodiffractometer equipped with graphite-monochromated Mo $\text{K}\alpha$ radiation. Crystals of (I), (II) and (IV) were mounted on the tops of glass fibers and coated with a thin layer of epoxy to

prevent direct exposure to air. The crystal of (III) was sealed inside a thin-walled glass capillary under N₂. Accurate unit cell parameters for all compounds were obtained from the least-squares refinement of the 2θ , ω , χ , ϕ values of 20-25 machine-centered reflections. Three standard reflections were monitored for every 200 reflections for both (I), (II) and (IV) while six standard reflections were used for (III) at the frequency of every 300 reflections. No significant decay was observed during the data collection period. An empirical absorption correction was applied to all data based on ψ scans by using three reflections for (I), (II) and (IV) and six reflections for (III). An additional absorption correction by using the DIFABS⁴ procedure was applied to the isotropically refined data. All the structures except for (IV) were solved with direct methods by using SHELXS-86⁵. The structure of (IV) was solved by the Patterson heavy atom method. All structures were refined with full matrix least-squares techniques by using the TEXSAN⁶ package of crystallographic programs running on a VAXstation 3100/76 computer. Since (I) and (III) crystallize in noncentrosymmetric space groups (Pnc2 and Cmc2₁ respectively), their enantiomorphic models were also refined, but no significant changes in R value or standard deviations of bond distances and angles were observed. In (II), the cocrystallized solvent, MeOH, was found to be disordered, with the occupancy of O atoms being refined to be ~0.65. The position of C and H atoms could not be located. The data collection parameters and details of the structure solution and refinement are given in Table 4-5. The final atomic coordinates, temperature factors and their estimated standard deviations for (I)~(IV) are given in Tables 4-6~4-9.

Table 4-1. Calculated and Observed X-Ray Powder Diffraction Pattern for $K_4V_2O_2Se_{10} \cdot 2MeOH$

h	k	l	d _{calc.} (Å)	d _{obs.} (Å)	%I _{obs.}
1	1	0	12.2575	12.6449	100.00
2	0	0	7.1145	7.2742	27.77
1	1	1	6.0174	6.1259	90.91
3	3	0	4.0858	4.0685	45.48
3	1	1	3.8596	3.9111	18.85
0	0	2	3.4535	3.4967	54.23
2	6	1	3.1232	3.1359	39.41
2	0	2	3.1068	3.0998	89.44
4	2	1	3.0592	3.0449	49.98
3	1	2	2.7733	2.8019	35.63
1	9	0	2.6354	3.6593	86.53
3	7	1	2.5861	2.5994	57.65
2	8	1	2.5770		
5	3	1	2.5009	2.5226	23.10
4	6	1	2.4862	2.4765	23.86
4	4	2	2.2921	2.3049	38.45
2	10	0	2.2857		
2	2	3	2.1553	2.1584	20.93
6	4	1	2.1024	2.1156	18.85
1	9	2	2.0951	2.0810	13.27
6	6	1	1.9590	1.9726	15.02
				1.9467	12.18
3	11	1	1.9135	1.9227	21.62
4	2	3	1.9085	1.8900	20.21
2	10	2	1.9060		
1	7	3	1.8976		

Table 4-2. Calculated and Observed X-Ray Powder Diffraction Pattern for $\text{K}_4\text{V}_2\text{O}_2\text{Se}_8 \cdot 0.65\text{MeOH}$

h	k	l	$d_{\text{calc.}} (\text{\AA})$	$d_{\text{obs.}} (\text{\AA})$	$\%I_{\text{obs.}}$
0	1	2	6.2208	6.2343	42.25
1	0	1	5.7681	5.8044	100.00
1	2	0	5.6246	5.6506	75.69
1	1	1	5.4834	5.4947	47.61
2	1	-1	3.7043	3.6841	28.09
0	4	2	3.6793		
1	4	1	3.5074	3.5140	33.64
1	3	2	3.5039		
1	3	-3	3.4970		
2	2	0	3.3707	3.3818	36.00
2	1	1	3.2400	3.2521	60.84
2	1	-3	3.2313		
1	2	3	3.1729	3.1752	44.89
1	2	-4	3.1657		
0	2	4	3.1104	3.0998	88.36
1	4	2	3.1029		
2	2	1	3.0881		
1	5	1	3.0136	3.0195	19.36
2	3	1	2.8763	2.8797	43.56
2	3	-3	2.8702		
1	5	2	2.7453	2.7490	64.00
1	5	-3	2.7420		
0	6	2	2.6928	2.6967	67.24
1	6	1	2.6231	2.6309	82.81
1	6	-2	2.6214		
2	5	-1	2.5844	2.5894	60.84
2	3	-4	2.5836		
1	3	-5	2.4912	2.4973	26.01
1	5	-4	2.4469	2.4531	25.00
0	3	5	2.4231	2.4234	56.25
1	7	-2	2.3116	2.3146	43.56
2	3	-5	2.2968		
1	1	5	2.2853	2.2897	37.21
3	4	-2	2.1847	2.1855	39.69
2	2	-6	2.1100	2.1015	47.61
0	8	2	2.0962		
3	1	2	2.0914		
1	7	3	2.0268	2.0372	23.04
1	9	0	1.8960	1.8940	42.25
1	9	-1	1.8958		
1	8	3	1.8523	1.8547	34.81
3	3	3	1.8278		
1	6	-6	1.8129	1.8144	30.25
1	5	-7	1.7226	1.7281	29.16
2	0	-8	1.6954	1.6972	24.01
3	7	1	1.6938		
1	2	-8	1.6926		

Table 4-3. Calculated and Observed X-Ray Powder Diffraction Pattern for K₃NbOSe₃

h	k	l	d _{calc.} (Å)	d _{obs.} (Å)	%I _{obs.}
0	2	0	6.7720	6.8823	27.99
2	0	0	5.5070	5.5886	17.59
1	1	1	5.3261	5.3901	55.05
2	2	0	4.2726	4.3169	16.00
2	2	1	3.6194	3.5751	65.04
1	3	1	3.5609		
0	0	2	3.4055	3.4217	100.00
0	4	0	3.3860		
3	1	1	3.1435	3.0546	11.25
0	2	2	3.0425		
0	4	1	3.0320		
2	0	2	2.8964	2.8895	35.23
2	4	0	2.8844		
3	3	0	2.8484		
4	0	0	2.7535	2.7744	29.37
				2.7429	14.98
2	2	2	2.6631	2.6483	17.59
2	4	1	2.6560		
1	5	0	2.6304		
3	3	1	2.6279		
4	2	0	2.5507	2.5770	9.59
3	1	2	2.4554	2.4672	20.40
1	5	1	2.4538		
0	4	2	2.4011	2.4150	19.25
3	3	2	2.1849	2.1925	44.16
3	5	0	2.1797		
5	1	1	2.0713	2.0790	11.25
2	2	3	2.0049	2.0070	12.59
2	6	1	1.9969		
3	5	2	1.8359	1.8436	29.37
6	0	0	1.8357		
3	7	0	1.7117	1.7236	11.25
0	0	4	1.7027	1.7018	12.59

Table 4-4. Calculated and Observed X-Ray Powder Diffraction Pattern for $K_2[(WO_2Se_2)_{0.5}(WOSe_3)_{0.5}]$

h	k	l	d _{calc.} (Å)	d _{obs.} (Å)	%I _{obs.}
1	1	1	6.5919	6.6128	12.03
0	0	2	6.0320	6.0584	18.65
1	0	2	5.3729	5.4035	56.24
0	2	0	5.2745	5.2815	51.44
2	1	0	5.1563	5.1657	72.54
1	1	2	4.7877	4.8018	100.00
2	1	1	4.7414	4.7524	80.21
0	2	2	3.9706	3.9832	35.14
2	1	2	3.9194	3.9205	12.09
1	2	2	3.7639	2.7698	20.14
3	0	2	3.2989	3.3024	69.25
3	1	2	3.1485	3.1502	15.48
1	2	3	3.0870	3.0908	14.64
3	2	1	3.0539	3.0582	38.21
0	0	4	3.0160	3.0156	35.58
2	3	1	2.9314	2.9354	64.52
1	1	4	2.8163	2.8145	22.35
3	0	3	2.8144		
2	2	3	2.8126		
2	3	2	2.7019	2.7029	12.57
0	3	3	2.6471	2.6482	26.54
0	4	0	2.6372		
2	1	4	2.6034	2.6105	15.82
4	2	1	2.5212	2.5267	36.25
3	2	3	2.4831	2.4935	34.25
1	3	4	2.2475	2.2416	24.21
3	4	1	2.1564	2.1564	9.29
5	1	3	2.0011	2.0112	24.67
2	5	0	1.9870		
1	5	2	1.9638	1.9721	24.65
4	4	1	1.9420	1.9395	11.47
5	3	1	1.9365		
3	4	3	1.9244		
2	3	5	1.8855	1.8838	8.69
5	3	2	1.8658		
6	2	1	1.8244	1.8205	17.64
4	3	4	1.8098		
5	3	3	1.7633	1.7658	35.91
4	2	5	1.7617		
0	6	0	1.7582		
1	3	6	1.7267	1.7301	12.99
3	2	6	1.6959	1.7003	4.65
3	6	2	1.5516	1.5546	14.27

Table 4-5. Summary of Crystallographic Data for $K_4V_2O_2Se_{10} \cdot 2MeOH$, $K_4V_2O_2Se_8 \cdot 0.65MeOH$, K_3NbOSe_3 and $K_2[(WO_2Se_2)_{0.5}(WOSe_3)_{0.5}]$

	(I)	(II)
formula	$K_4V_2Se_{10}O_4C_2H_8$	$K_4V_2Se_8O_{0.65}$
fw	1143.96	932.35
a, Å	14.229(3)	7.577(3)
b, Å	24.136(9)	17.672(6)
c, Å	6.907(4)	13.810(5)
β	90.0	105.74(3)
Z, V, Å ³	4, 2372(2)	4, 1780(2)
space group	Pnc2 (#30)	P2 ₁ /n (#14)
d _{calc} , g/cm ³	3.203	3.479
crystal size, mm	0.6x0.6x1.0	0.42x0.3x0.1
temperature, °C	-90.0	23
scan type	ω	ω
scan rate, deg/min	4.0	4.0
radiation	Mo K α ($\lambda=0.71069\text{\AA}$)	Mo K α ($\lambda=0.71069\text{\AA}$)
μ (Mo K α), cm ⁻¹	166.70	181.46
2 θ _{max} , deg	50.0	50.0
no. of data collected	2433	3511
no. of unique data	2433	3511
no. of obs. data ($I > 3\sigma(I)$)	1231	1185
no. of variables	168	150
final R/R _w , %	5.4/6.2	4.9/5.2

$$R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$

$$R_w = \{ \Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2 \}^{1/2}$$

Table 4-5. (cont'd)

	(III)	(IV)
formula	K ₃ NbOSe ₃	K ₄ W ₂ Se ₅ O ₃
fw	231.54	966.89
a, Å	11.014(3)	11.821(5)
b, Å	13.544(4)	10.549(4)
c, Å	6.811(2)	12.064(5)
Z, V, Å ³	8, 1016.0(9)	4, 1504(2)
space group	Cmc2 ₁ (#36)	Pnma (#62)
d _{calc} , g/cm ³	3.027	4.269
crystal size, mm	0.05x0.07x0.52	0.92x0.86x0.88
temperature, °C	20	23
scan type	ω	ω-2θ
scan rate, deg/min	3.0°-35.9° 4°/min 35.9°-45.8° 2°/min 45.8°-56.8° 1°/min	4.0
radiation	Mo Kα (λ=0.71069Å)	Mo Kα (λ=0.71069Å)
μ(Mo Kα), cm ⁻¹	129.4	286.8
2θ _{max} , deg	57	50
no. of data collected	756	2930
no. of unique data	727	1568
no. of obs. data (I>3σ(I))	569	670
no. of variables	43	67
final R/R _w , %	3.7/2.5	6.9/7.3

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$R_w = \{ \sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2 \}^{1/2}$$

Table 4-6. Positional Parameters and Equivalent Isotropic Displacement Values ($\text{\AA}^2$)^a for $\text{K}_4\text{V}_2\text{O}_2\text{Se}_{10}\cdot 2\text{MeOH}$ with Estimated Standard Deviations in Parentheses

atom	x	y	z	B (eq)
Se(1)	-0.1176 (3)	0.0354 (2)	0.8745	1.5 (2)
Se(2)	0.1909 (2)	0.0766 (2)	0.798 (1)	1.6 (2)
Se(3)	0.2240 (3)	0.1760 (2)	0.781 (1)	2.2 (2)
Se(4)	0.1079 (3)	0.2091 (2)	0.992 (1)	2.0 (2)
Se(5)	-0.0173 (2)	0.1504 (2)	0.888 (1)	1.7 (2)
Se(6)	0.6240 (3)	0.0240 (2)	0.361 (1)	1.7 (2)
Se(7)	0.3262 (2)	0.0944 (2)	0.302 (1)	1.8 (2)
Se(8)	0.3234 (3)	0.1947 (2)	0.289 (1)	2.0 (2)
Se(9)	0.4486 (3)	0.2143 (2)	0.498 (1)	2.2 (2)
Se(10)	0.5566 (2)	0.1475 (2)	0.379 (1)	1.6 (2)
V(1)	0.0431 (4)	0.0545 (3)	0.967 (1)	1.2 (3)
V(2)	0.4704 (4)	0.0588 (3)	0.459 (1)	1.1 (3)
K(1)	0.0891 (6)	0.1455 (4)	0.418 (2)	2.6 (5)
K(2)	0.1384 (5)	-0.0303 (4)	0.378 (2)	2.1 (4)
K(3)	0.4492 (6)	0.1472 (4)	-0.071 (2)	2.0 (4)
K(4)	0.6414 (5)	0.0200 (3)	0.867 (2)	1.7 (4)
O(1)	0.053 (2)	0.056 (1)	1.204 (4)	1.5 (5)
O(2)	0.465 (1)	0.061 (1)	0.688 (4)	1.2 (5)
O(3)	0.641 (1)	0.133 (1)	0.831 (4)	1.3 (5)
O(4)	-0.107 (2)	0.139 (1)	0.330 (5)	3.1 (6)
C(1)	0.698 (3)	0.181 (2)	0.87 (1)	5 (1)
C(2)	-0.153 (3)	0.189 (2)	0.393 (9)	4 (1)

^a $B(\text{eq}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table 4-7. Positional Parameters and Equivalent Isotropic Displacement Values ($\text{\AA}^2$)^a for $\text{K}_4\text{V}_2\text{O}_2\text{Se}_{8-0.65}\text{MeOH}$ with Estimated Standard Deviations in Parentheses

atom	x	y	z	B(eq)
Se(1)	-0.0742(4)	0.6655(2)	0.2893(2)	2.0(1)
Se(2)	-0.0849(4)	0.5658(2)	0.4039(2)	2.8(1)
Se(3)	-0.2327(5)	0.6276(2)	0.5096(2)	3.3(2)
Se(4)	-0.0856(4)	0.7533(2)	0.5189(2)	2.4(1)
Se(5)	0.0900(4)	0.8943(2)	0.4735(2)	1.8(1)
Se(6)	0.1016(4)	0.8081(2)	0.2263(2)	2.0(1)
Se(7)	0.2152(4)	0.9971(2)	0.1853(2)	2.3(1)
Se(8)	0.1268(4)	1.0487(2)	0.3225(2)	2.6(1)
V(1)	0.1020(6)	0.7668(3)	0.3983(3)	1.3(2)
V(2)	0.2226(6)	0.9132(3)	0.3343(3)	1.6(2)
K(1)	0.297(1)	1.0175(4)	0.6639(4)	2.9(3)
K(2)	0.5352(8)	0.8366(4)	0.5652(4)	2.4(3)
K(3)	0.1605(9)	0.0933(4)	0.9628(4)	2.8(3)
K(4)	0.989(1)	0.2296(5)	0.1958(5)	4.4(4)
O(1)	0.307(2)	0.731(1)	0.449(1)	1.9(8)
O(2)	0.442(2)	0.901(1)	0.382(1)	2.8(9)
O(3)	-0.174(4)	0.360(2)	0.291(2)	2.7(6)

^a $B(\text{eq}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table 4-8. Positional Parameters and Equivalent Isotropic Displacement Values ($\text{\AA}^2$)^a for K_3NbOSe_3 with Estimated Standard Deviations in Parentheses

atom	x	y	z	B (eq)
Nb	0	0.2071 (1)	0	1.26 (6)
Se (1)	-0.1870 (1)	0.1302 (1)	-0.1145 (3)	2.17 (6)
Se (2)	0	0.3814 (1)	-0.0895 (4)	1.84 (9)
K (1)	0.2012 (3)	0.1187 (2)	0.4043 (7)	2.2 (1)
K (2)	0	0.3798 (3)	-0.5726 (8)	2.3 (2)
O	0	0.200 (1)	0.257 (2)	1.3 (5)

$$^a B(\text{eq}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}].$$

Table 4-9. Positional Parameters and Equivalent Isotropic Displacement Values ($\text{\AA}^2$)^a for $\text{K}_2[(\text{WO}_2\text{Se}_2)_{0.5}(\text{WOSe}_3)_{0.5}]$ with Estimated Standard Deviations in Parentheses

atom	x	y	z	B (eq)
W (1)	0.1730 (2)	3/4	0.8596 (1)	1.00 (8)
W (2)	-0.0500 (1)	1/4	0.6928 (2)	1.10 (8)
Se (1)	0.2656 (4)	3/4	0.6888 (4)	1.5 (2)
Se (2)	0.0612 (3)	0.5709 (4)	0.8724 (3)	2.3 (2)
Se (3)	-0.1144 (3)	0.0707 (5)	0.6006 (3)	2.9 (2)
K (1)	0.2387 (7)	0.4380 (8)	0.6322 (6)	2.5 (3)
K (2)	-0.0156 (8)	3/4	0.620 (1)	2.2 (5)
K (3)	0.1104 (9)	1/4	0.940 (1)	2.7 (6)
O (1)	0.273 (2)	3/4	0.967 (2)	1.9 (6)
O (2)	0.099 (2)	1/4	0.707 (2)	1.6 (6)
O (3)	-0.106 (2)	1/4	0.831 (2)	1.2 (6)

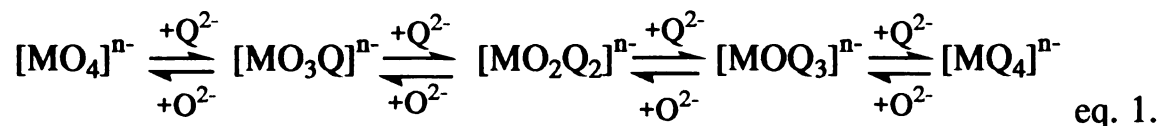
$$^a B(\text{eq}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}].$$

3. Results and Discussion

3.1. Synthesis

In contrast to the Mo/Se compounds described in Chapter 2, all the compounds contain oxygen atoms bonded to the metal centers. Water is therefore not suitable for these systems because oxide will compete with selenide to form oxometalates. For the vanadium system, (I) and (II) were produced in the same V/K₂Se₄ ratio. (II) is not readily reproducible since most of the time (I) was obtained. (I) and (II) differs only in the length of the chelating polyselenides to the [V₂O₂Se₂] core. It is likely that the chelating polyselenides are labile and that (I) and (II) or other species with the general formula, [(Se_x)(V₂O₂Se₂)(Se_y)]⁴⁻, coexist in the polyselenide solution. The more symmetric complex of (I) probably formed a more stable or more insoluble crystal lattice with K⁺ cations than did (II). MeOH or H₂O impurities are the probable oxygen sources of the terminal oxide in (I) and (II).

(III) and (IV) belong to the group of [MO_xQ_{4-x}]ⁿ⁻ (x=0~4; M=V, Nb, Ta, Mo, W and Re; Q=S, Se) which can be made either by reaction in the solid state (x=0) by using stoichiometric amount of constituents or by passing H₂Q gas through a basic aqueous solution of the corresponding oxometalates. The latter method involves an equilibrium between different [MO_xQ_{4-x}]ⁿ⁻ species as shown below.



$[\text{NbSe}_4]^{3-}$ has been made by the solid state method.⁷ No $[\text{NbO}_x\text{Se}_{4-x}]^{3-}$ ($x>1$) have been made in aqueous solution because the oxygen affinity of Nb will shift the equilibrium of eq. 1 to the left. Using Nb metal and a less efficient oxygen donor, MeOH, as solvent, we are able to crystallize K_3NbOSe_3 under methanothermal conditions. In this reaction Nb metal is oxidized to the +5 oxidation state by Se_2^{2-} which itself is reduced to Se^{2-} . Apparently, the basicity or the concentration of Se^{2-} ions is not enough to push the equilibrium to $[\text{NbSe}_4]^{3-}$. $\text{K}_2[(\text{WO}_2\text{Se}_2)_{0.5}(\text{WOSe}_3)_{0.5}]$ forms via the substitution of oxides in $[\text{WO}_4]^{2-}$ anions by Se^{2-} as described in equation 1. There are no redox reactions involved between WO_3 and Se_2^{2-} . Both $[\text{WO}_2\text{Se}_2]^{2-}$ and $[\text{WOSe}_3]^{2-}$,⁹ have been synthesized by passing H_2Se in aqueous $[\text{WO}_4]^{2-}$ solutions. (IV) is the cocrystallization of both anions as a potassium salt.

3.2. Description of Structures

Structures of $\text{K}_4\text{V}_2\text{O}_2\text{Se}_{10} \cdot 2\text{MeOH}$ and $\text{K}_4\text{V}_2\text{O}_2\text{Se}_8 \cdot 0.65\text{MeOH}$.

Compound (I) contains two crystallographically independent but structurally similar anionic molecules, $[\text{V}_2\text{O}_2\text{Se}_{10}]^{4-}$ (I-a, and I-b), while (II) contains a single $[\text{V}_2\text{O}_2\text{Se}_8]^{4-}$ molecule. Both complexes contain the same central $[\text{V}_2\text{O}_2\text{Se}_2]$ core. This core consists of a bent V_2Se_2 rhombus and two cis- terminal oxygen atoms. The latter are presumed to come from methanol. The V atoms in these $[\text{V}_2\text{O}_2\text{Se}_2]$ cores are chelated by two Se_2^{2-} ligands in (I) and one Se_4^{2-} ligand and one Se_2^{2-} ligand in (II). The structures of $[\text{V}_2\text{O}_2\text{Se}_{10}]^{4-}$ and $[\text{V}_2\text{O}_2\text{Se}_2]^{4-}$ are shown in Figure 4-1 and 4-2. There is a C_2 rotation axis passing through the centers of $[\text{V}_2\text{O}_2\text{Se}_{10}]^{4-}$.

All the V-O bonds in the acentric space group of (I) are pointed in the same direction as shown in Figure 4-3. In the contrary, (II) packs centrosymmetrically and its packing diagram is shown in Figure 4-4. $[\text{V}_2\text{O}_2\text{Se}_{10}]^{4-}$ is isostructural to $[\text{Mo}_2\text{O}_2\text{S}_{10}]^{2-}$ and $[\text{W}_2\text{O}_2\text{S}_{10}]^{2-}$, while $[\text{V}_2\text{O}_2\text{Se}_8]^{4-}$ is isostructural to $[\text{Mo}_2\text{O}_2\text{S}_8]^{2-}$ all of which belong to the family of $[\text{M}_2\text{X}_2\text{Q}_2(\text{Q}_x)(\text{Q}_y)]^{2-}$, ¹⁰⁻¹⁸ complexes, where M=Mo, W; X=O, S; Q=S, Se. The V atoms in (I) and (II) have the formal oxidation state of +4 and thus the same d^1 electronic configuration as their Mo^{5+} and W^{5+} analogs. Although the $[\text{M}_2\text{O}_2\text{Q}_2]^{2+}$ (M=Mo, W; Q=S, Se) core has high formation tendency, its isoelectronic analog $[\text{V}_2\text{O}_2\text{Se}_2]$ is reported here for the first time. The only other known vanadium polyselenide anion is $[\text{V}_2\text{Se}_{13}]^{2-}$, ¹⁹ which was synthesized by reducing VO_3^- with bis-(dimethyloctylsilyl)selenide in toluene/acetonitrile solution at room temperature. The structure of $[\text{V}_2\text{Se}_{13}]^{2-}$ is unique, compared to the Mo/W polychalcogenide anions. The lack of previous examples of vanadium analogs $[\text{M}_2\text{X}_2\text{Q}_2(\text{Q}_x)(\text{Q}_y)]^{2-}$ may be attributed to the difficulty in crystallizing the tetra-valent anions by using the typical large organic cations since now four cations instead of two are needed to balance the charge in the crystal lattice. The crystallization problem could be overcome if smaller cations were used (e.g. alkali ions), but such crystallization from DMF or CH_3CN , the typical solvents for classical synthesis, seldom succeed. However, the difficulty can be overcome by the solvothermal method which has been proven useful in promoting crystallization of alkali metal-polyselenide salts.

Selected bond distances and angles for (I) and (II) are given in Table 4-10 and 4-11 respectively. The average V-Se distance in $[\text{V}_2\text{O}_2\text{Se}_{10}]^{4-}$ and $[\text{V}_2\text{O}_2\text{Se}_8]^{4-}$ are 2.48(4)Å and 2.47(4)Å respectively.

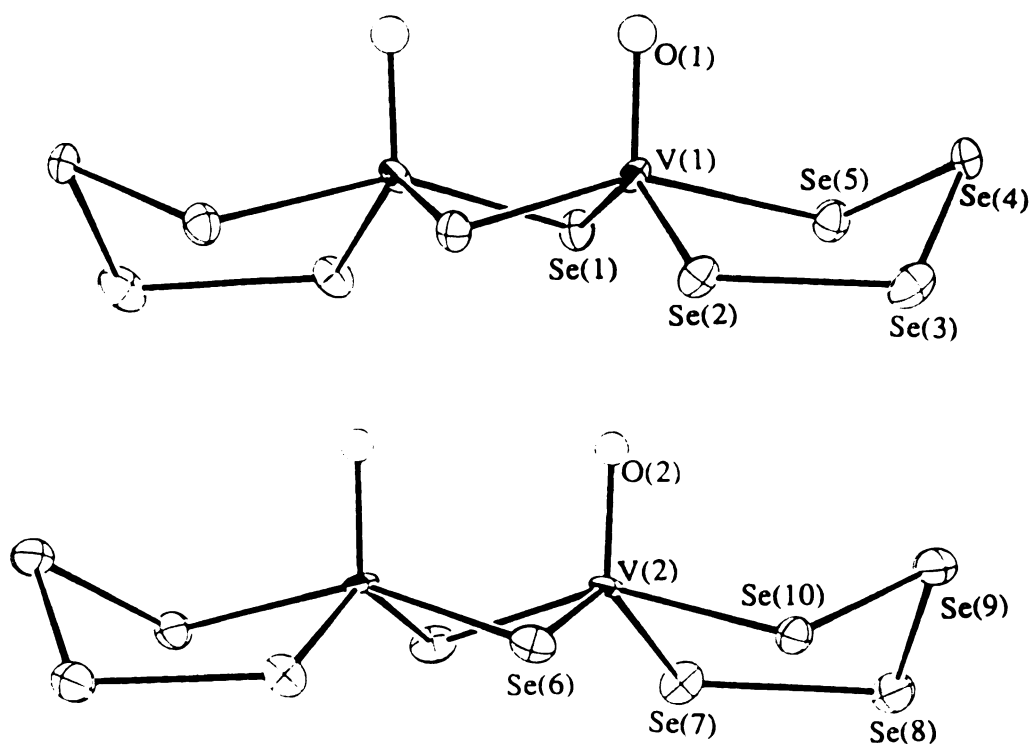


Figure 4-1: ORTEP representation and labeling scheme for two crystallographically independent anions of $[V_2O_2Se_{10}]^{4+}$.

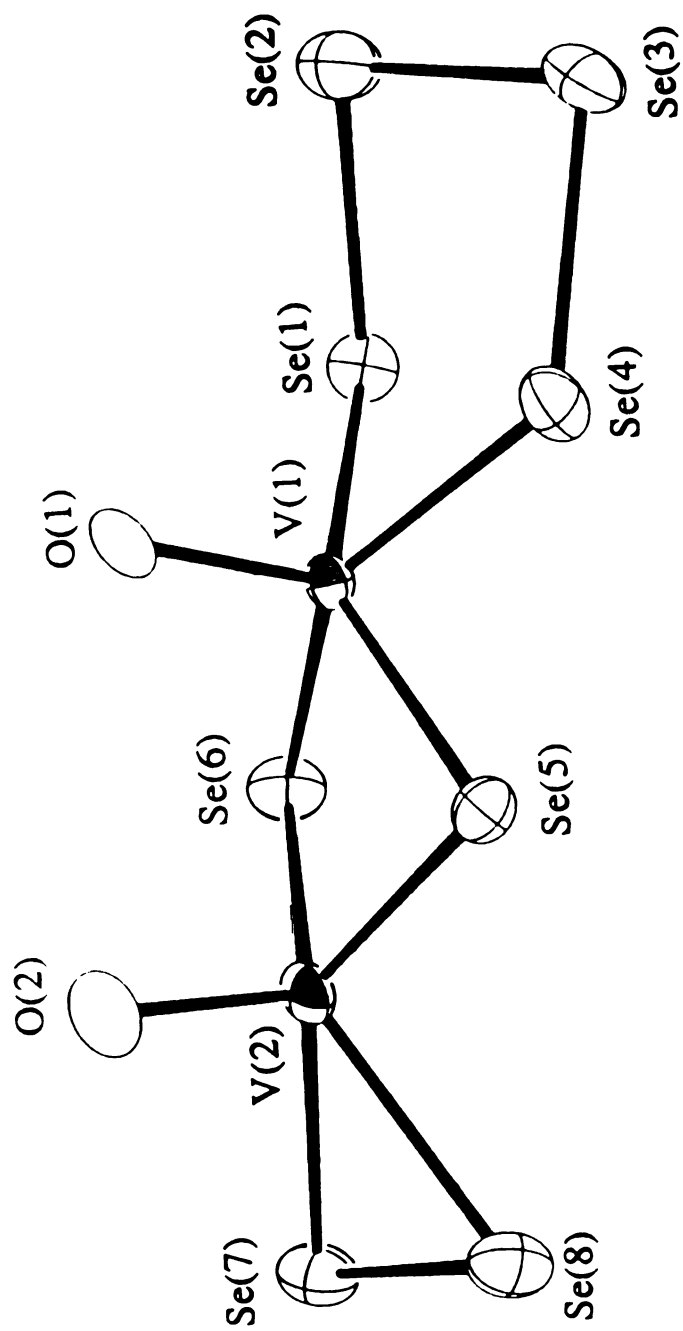


Figure 4-2: ORTEP representation and labeling scheme for $[V_2O_2Se_8]^{4-}$.

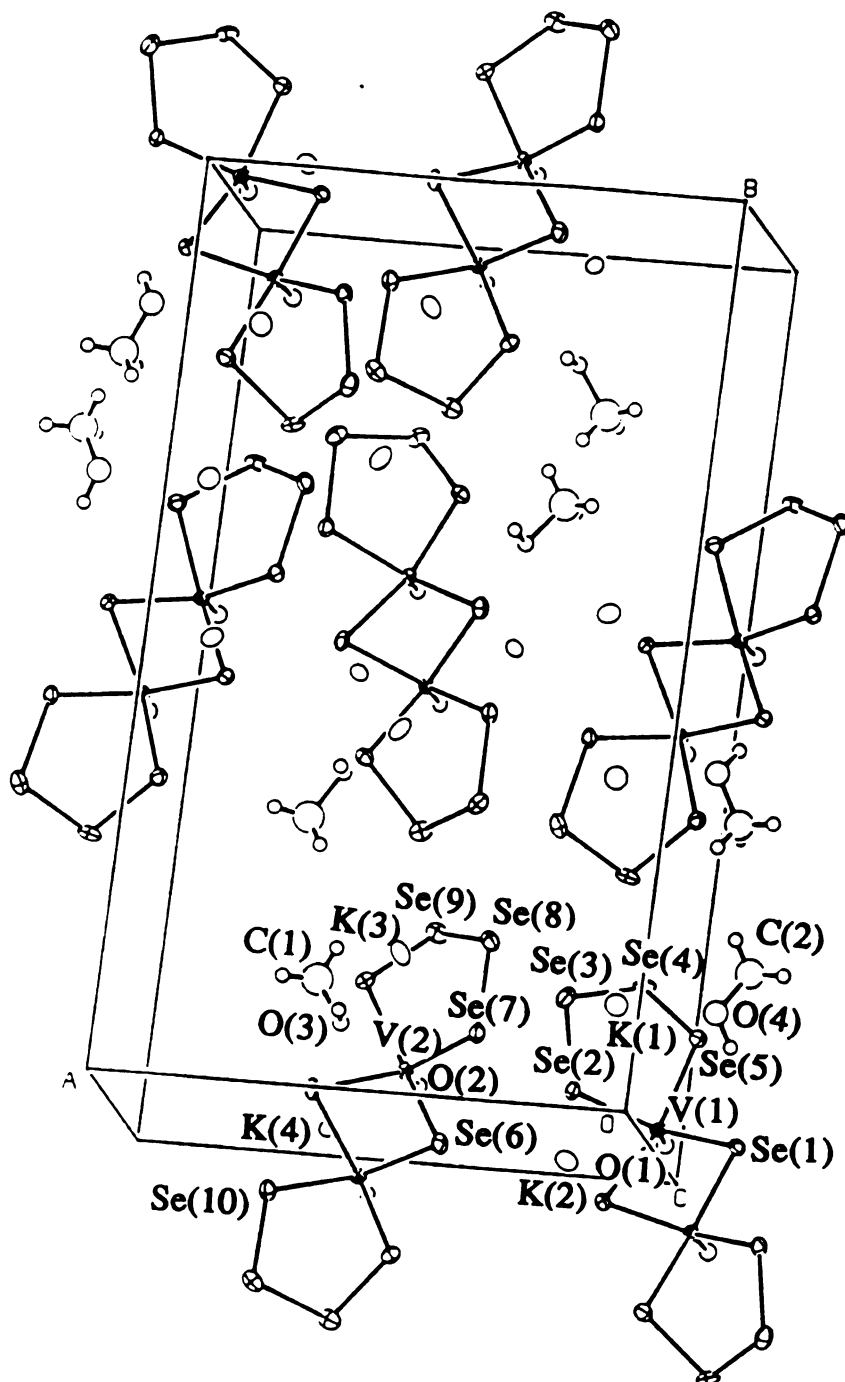


Figure 4-3: Packing diagram for an unit cell of $\text{K}_4[\text{V}_2\text{O}_2\text{Se}_{10}] \cdot 2\text{MeOH}$.

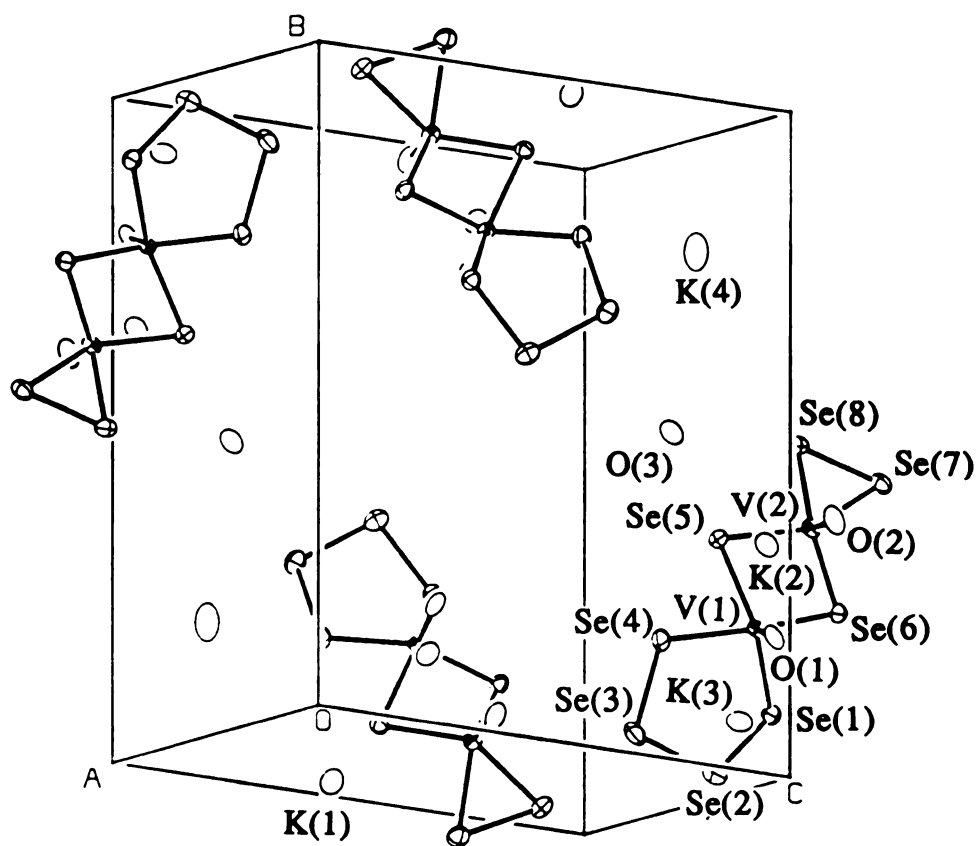


Figure 4-4: Packing diagram for an unit cell of $\text{K}_4[\text{V}_2\text{O}_2\text{Se}_8] \cdot 0.65\text{MeOH}$. The MeOH molecules are omitted.

Table 4-10. Selected Bond Distances(Å) and Angles (deg) for K₄V₂O₂Se₁₀·2MeOH with Standard Deviations in Parentheses

Selected Bond Distances (Å)			
V(1)-O(1)	1.64(3)	V(2)-O(2)	1.59(3)
V(1)-Se(1)	2.418(7)	V(2)-Se(6)	2.439(7)
V(1)-Se(1)	2.497(7)	V(2)-Se(6)	2.502(8)
V(1)-Se(2)	2.465(7)	V(2)-Se(7)	2.474(7)
V(1)-Se(5)	2.529(8)	V(2)-Se(10)	2.528(8)
V(1)-V(1)	2.90(1)	V(2)-V(2)	2.96(1)
Se(2)-Se(3)	2.447(6)	Se(7)-Se(8)	2.424(6)
Se(3)-Se(4)	2.342(7)	Se(8)-Se(9)	2.342(6)
Se(4)-Se(5)	2.385(6)	Se(9)-Se(10)	2.376(6)
O(3)-C(1)	1.46(5)	K(2)-O(4)	2.67(3)
O(4)-C(2)	1.44(5)	K(3)-Se(3)	3.434(9)
K(1)-Se(2)	3.43(1)	K(3)-Se(7)	3.37(1)
K(1)-Se(3)	3.24(1)	K(3)-Se(8)	3.27(1)
K(1)-Se(4)	3.56(1)	K(3)-Se(9)	3.38(1)
K(1)-Se(4)	3.33(1)	K(3)-Se(9)	3.38(1)
K(1)-Se(5)	3.59(1)	K(3)-Se(10)	3.47(1)
K(1)-Se(7)	3.68(1)	K(3)-O(2)	2.68(3)
K(1)-Se(8)	3.65(1)	K(3)-O(3)	2.83(2)
K(1)-O(1)	2.67(3)	K(4)-Se(1)	3.44(9)
K(1)-O(4)	2.86(3)	K(4)-Se(2)	3.36(9)
K(2)-Se(1)	3.44(1)	K(4)-Se(6)	3.51(1)
K(2)-Se(1)	3.49(1)	K(4)-Se(6)	3.42(1)
K(2)-Se(6)	3.386(9)	K(4)-O(2)	2.97(2)
K(2)-O(1)	2.70(3)	K(4)-O(2)	2.76(3)
K(2)-O(1)	3.04(3)	K(4)-O(3)	2.73(2)
Selected Bond Angles (deg)			
Se(1)-V(1)-Se(1)	99.7(3)	Se(6)-V(2)-Se(6)	97.5(3)
Se(1)-V(1)-Se(2)	136.4(4)	Se(6)-V(2)-Se(7)	137.8(3)
Se(1)-V(1)-Se(2)	72.8(2)	Se(6)-V(2)-Se(7)	73.3(2)

Table 4-10. (cont'd)

Se(1)-V(1)-Se(5)	78.3(2)	Se(6)-V(2)-Se(10)	78.2(2)
Se(1)-V(1)-Se(5)	152.3(4)	Se(6)-V(2)-Se(10)	151.3(3)
Se(1)-V(1)-O(1)	110.3(9)	Se(6)-V(2)-O(2)	109.4(9)
Se(5)-V(1)-O(1)	66.4(4)	Se(10)-V(2)-O(2)	66.2(4)
Se(2)-V(1)-Se(5)	89.4(3)	Se(7)-V(2)-Se(10)	90.7(3)
Se(2)-V(1)-O(1)	113.3(9)	Se(7)-V(2)-O(2)	112.8(9)
Se(5)-V(1)-O(1)	103(1)	Se(10)-V(2)-O(2)	103(1)
V(1)-Se(2)-Se(3)	113.5(2)	V(2)-Se(7)-Se(8)	112.2(2)
Se(2)-Se(3)-Se(4)	99.7(2)	Se(7)-Se(8)-Se(9)	99.5(2)
Se(3)-Se(4)-Se(5)	98.0(2)	Se(8)-Se(9)-Se(10)	98.1(2)
Se(4)-Se(5)-V(1)	103.0(2)	Se(9)-Se(10)-V(2)	100.6(2)

Table 4-11. Selected Bond Distances (Å) and Angles (deg) for $K_4V_2O_2Se_8 \cdot 0.65MeOH$ with Standard Deviations in Parentheses

Selected Bond Distances (Å)			
V(1)-O(1)	1.65(2)	V(2)-Se(6)	2.402(5)
V(1)-Se(1)	2.482(5)	V(2)-Se(7)	2.525(5)
V(1)-Se(4)	2.477(5)	V(2)-Se(8)	2.496(6)
V(1)-Se(5)	2.494(5)	Se(1)-Se(2)	2.385(4)
V(1)-Se(6)	2.485(5)	Se(2)-Se(3)	2.338(5)
V(2)-O(2)	1.63(2)	Se(3)-Se(4)	2.473(5)
V(2)-Se(5)	2.421(5)	Se(7)-Se(8)	2.358(4)
V(1)-V(2)	2.958(7)		
Selected Bond Angles (deg)			
O(1)-V(1)-Se(1)	108.7(6)	V(1)-Se(5)-V(2)	74.0(2)
O(1)-V(1)-Se(4)	105.7(6)	V(1)-Se(6)-V(2)	74.5(2)
O(1)-V(1)-Se(5)	107.8(6)	O(2)-V(2)-Se(5)	104.9(6)
O(1)-V(1)-Se(6)	106.2(6)	O(2)-V(2)-Se(6)	109.0(7)
Se(1)-V(1)-Se(4)	91.5(2)	O(2)-V(2)-Se(7)	101.8(7)
Se(1)-V(1)-Se(6)	76.8(1)	O(2)-V(2)-Se(8)	113.6(8)
Se(4)-V(1)-Se(5)	73.4(2)	Se(5)-V(2)-Se(6)	102.5(2)
Se(5)-V(1)-Se(6)	98.1(2)	Se(5)-V(2)-Se(8)	90.4(2)
V(1)-Se(1)-Se(2)	103.9(1)	Se(6)-V(2)-Se(7)	91.6(2)
V(1)-Se(4)-Se(3)	112.6(2)	Se(7)-V(2)-Se(8)	56.0(1)
Se(1)-Se(2)-Se(3)	100.2(2)	V(2)-Se(7)-Se(8)	61.4(1)
Se(2)-Se(3)-Se(4)	89.3(2)	V(2)-Se(8)-Se(7)	62.6(1)

The Se-V-Se angle formed by the diselenide ligand is much smaller than that formed by tetraselenide ligand, $56.0(1)^\circ$ and $91.5(2)^\circ$ respectively. The V-V distances of $2.90(1)\text{\AA}$ in (I-a), $2.96(1)\text{\AA}$ in (I-b) and $2.958(7)\text{\AA}$ in (II) in the $[\text{V}_2\text{O}_2\text{Se}_2]$ unit are longer than the V-V bonds in the $[\text{V}_2(\text{Se}_2)_2]^{4+}$ units of $[\text{V}_2\text{Se}_{13}]^{2-}$ ($2.779(5)\text{\AA}$) and $\text{V}_2\text{Se}_9^{20}$ ($2.842(2)\text{\AA}$) as well as in the $[\text{V}_2(\text{Se}_2)_2(\text{Se})]^{2+}$ unit of $\text{V}_2(\text{C}_2\text{H}_7)_2\text{Se}_5^{22}$ ($2.779(4)\text{\AA}$). The average V=O_t distances in $[\text{V}_2\text{O}_2\text{Se}_{10}]^{4-}$ is $1.62(4)\text{\AA}$, while in $[\text{V}_2\text{O}_2\text{Se}_8]^{4-}$ is $1.64(2)\text{\AA}$. The Se-Se distance in the Se_4^{2-} ligands lie within the normal range but both complexes exhibit Se-Se bond alternation. In both (I) and (II) the average central Se-Se distance is shorter, $2.341(2)$. The average terminal Se-Se distance in the Se_4^{2-} ligands is $2.42(4)\text{\AA}$. This is opposite to the bond alternation observed in the structure of free Se_4^{2-} and consistent with the corresponding lengths observed in the Se_4^{2-} ligand of $[\text{W}_2\text{Se}_{10}]^{2-}$ ^{18,22}. This phenomenon is probably due to the $\text{M}(\text{d}\pi)\text{-Se}(\text{d}\pi)$ interaction which has been proposed in Mo/S system.¹⁶ The Se-Se distance in the Se_2^{2-} ligand is $2.358(4)\text{\AA}$. In retrospect the formation of a $[\text{V}_3\text{Se}_7]^+$ cluster, isoelectronic and isostructural to $[\text{Mo}_3\text{Se}_7]^{4+}$, would be unlikely under the relatively oxidizing conditions employed in view of the difficulty in reducing V^{4+} to V^{3+} .

Structures of K_3NbOSe_3 and $\text{K}_2[(\text{WO}_2\text{Se}_2)_{0.5}(\text{WOSe}_3)_{0.5}]$

Both (III) and (IV) contain tetrahedral anions crystallized as potassium salts as shown in Figure 4-5. The mixed oxo-chalcogeno-metalates, $[\text{MO}_x\text{Q}_{4-x}]^{n-}$, are well known for $\text{M}=\text{V}$, Mo , W and Re .

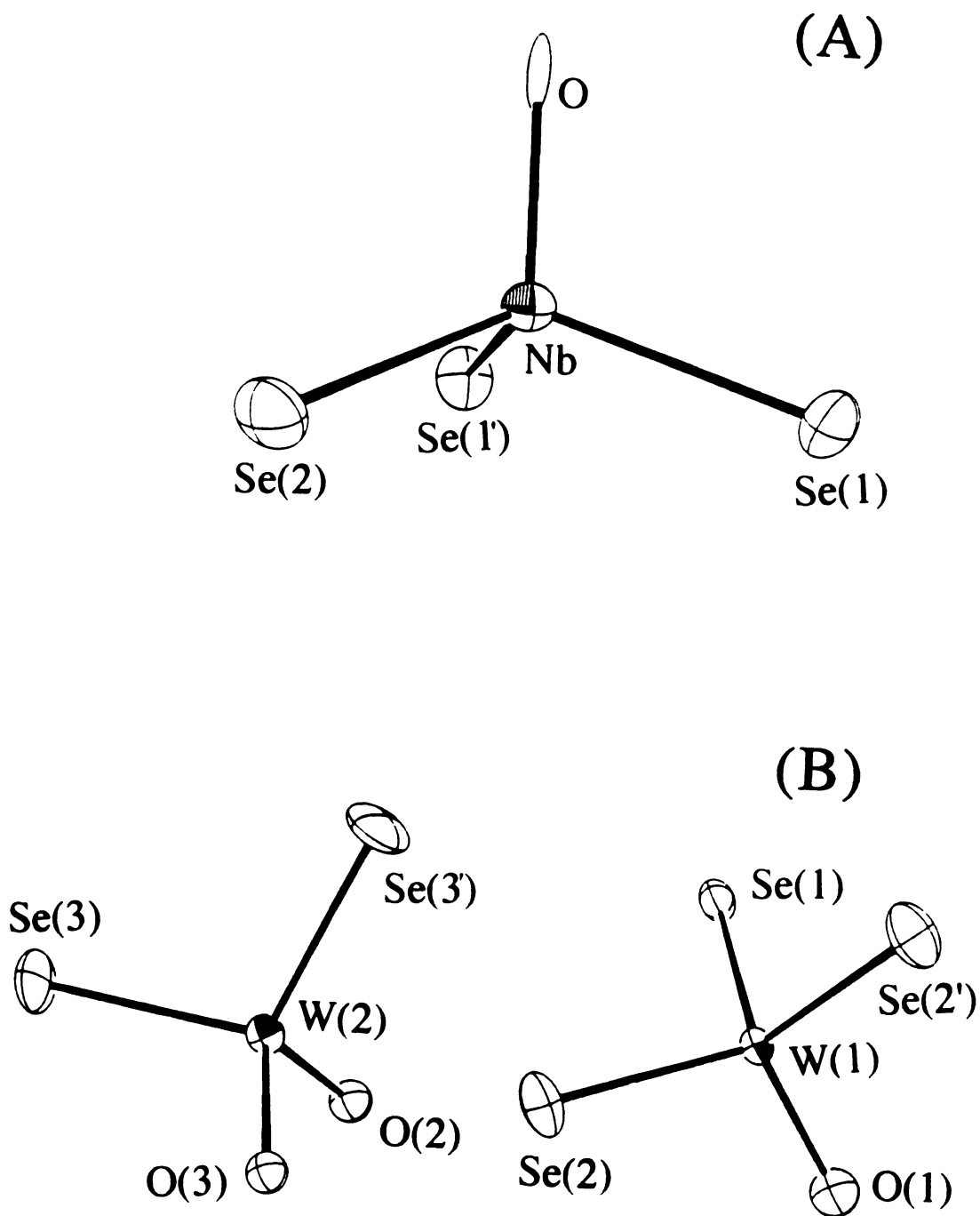


Figure 4-5: ORTEP representation and labeling scheme for (A) $[\text{NbOSe}_3]^{3-}$ and (B) $[(\text{WO}_2\text{Se}_2)(\text{WSe}_3)]^{4-}$.

The crystal structures of $[\text{MS}_4]^{3-}$ and $[\text{MSe}_4]^{3-}$ are also known for $\text{M}=\text{Nb}$ and Ta .⁷ Selected bond distances and angles are given in Table 4-12 and 4-13 are normal comparing to those of the known $[\text{MO}_x\text{Q}_{4-x}]^{n-}$ anions.

Table 4-12. Selected Bond Distances (Å) and Angles (deg) for K_3NbOSe_3 with Standard Deviations in Parentheses

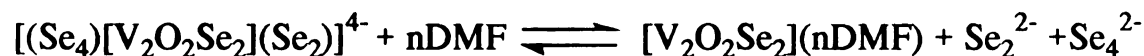
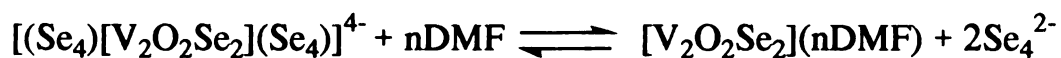
Selected Bond Distances (Å)			
Nb-Se(1)	2.437(2)x2	Se(1)-K(2)	3.461(2)
Nb-Se(2)	2.438(3)	Se(2)-K(2)	3.290(6)
		Se(2)-K(2)	3.521(6)
Nb-O	1.75(1)	Se(2)-K(2)	3.237(5)
Se(1)-K(1)	3.540(5)		
Se(1)-K(1)	3.619(3)	K(1)-O	2.672(9)
Se(1)-K(1)	3.285(5)	K(2)-O	2.70(1)
Se(1)-K(1)	3.377(3)		
Se(2)-K(1)	3.291(3)x2		
Selected Bond Angles (deg)			
Se(1)-Nb-Se(1)	115.4(1)	Se(1)-Nb-O	107.2(2)x2
Se(1)-Nb-Se(2)	109.51(6)x2	Se(2)-Nb-O	107.6(5)

Table 4-13. Selected Bond Distances (Å) and Angles (deg) for $\text{K}_2[(\text{WO}_2\text{Se}_2)_{0.5}(\text{WOSe}_3)_{0.5}]$ with Standard Deviations in Parentheses

Selected Bond Distances (Å)			
W(1)-Se(1)	2.333(5)	Se(2)-K(3)	3.58(1)
W(1)-Se(2)	2.312(4)x2	Se(3)-K(1)	3.465(8)
W(2)-Se(3)	2.323(5)x2	Se(3)-K(2)	3.587(6)
		Se(3)-K(2)	3.61(1)
W(1)-O(1)	1.75(3)	Se(3)-K(3)	3.79(1)
W(2)-O(2)	1.77(3)	Se(3)-K(1)	3.663(8)
W(2)-O(3)	1.80(3)		
		K(1)-O(1)	2.81(2)
Se(1)-K(1)	3.376(9)x2	K(1)-O(2)	2.73(2)
Se(1)-K(2)	3.43(1)	K(1)-O(3)	2.74(2)
Se(1)-K(2)	3.47(1)	K(2)-O(1)	2.71(3)
Se(1)-K(3)	3.34(1)	K(3)-O(2)	2.82(3)
Se(2)-K(2)	3.70(1)	K(3)-O(3)	2.88(3)
Se(2)-K(3)	3.531(5)		
Selected Bond Angles (deg)			
Se(1)-W(1)-Se(2)	109.1(1)	Se(3)-W(2)-Se(3)	109.0(2)
Se(1)-W(1)-Se(2)	109.1(1)	Se(3)-W(2)-O(2)	111.8(5)
Se(1)-W(1)-O(1)	110(1)	Se(3)-W(2)-O(3)	108.9(5)
Se(2)-W(1)-Se(2)	109.7(2)	Se(3)-W(2)-O(2)	111.8(5)
Se(2)-W(1)-O(1)	109.6(5)	Se(3)-W(2)-O(3)	108.9(5)
Se(2)-W(1)-O(1)	109.6(5)		

3.4. Spectroscopy

Infrared spectra of (I) and (II) are shown in Figure 4-6. Both compounds gave no distinguishable peak until the samples were very concentrated in CsI pellets. The spectrum of (I) exhibits peaks at 365 cm⁻¹ (m), 341 cm⁻¹ (sh), 326 cm⁻¹ (sh), 300 cm⁻¹ (sh), 265 cm⁻¹ (sh) and 201 cm⁻¹ (w). The spectrum of (II) exhibits peaks at 363 cm⁻¹ (m), 351 cm⁻¹ (m) and 183 cm⁻¹ (m). These peaks are in the range of M-Se and Se-Se vibrations. The vibrational spectra of [V₂Se₁₃]²⁻, V₂Se₉, V₂(C₆H₇)₂Se₅ and (C₅H₅)₂VSe₅²³ were not reported. The only reported vibrational spectrum of a V/Se system is that of [VSe₄]^{3-,24} which gives peaks at 232 cm⁻¹ and 121 cm⁻¹ in the Raman, 365 cm⁻¹ and 121 cm⁻¹ in the IR spectrum. These peaks are attributed to the vibration modes (ν₁(A₁), ν₂(E), ν₃(F₂) and ν₄(F₂)) of T_d symmetry. The UV-Vis spectra for (I) and (II) in DMF solutions are given in Figure 4-7. The bands at ~430 nm and ~650 nm indicate the presence of Se_x^{-·} radical anions²⁵ which come from the dissociation of (I) and (II) in DMF solutions according to the following possible mechanism:



The polyselenides thus formed further disproportionate into Se_x^{-·} radicals which are responsible for the observed bands in the UV-Vis spectra.

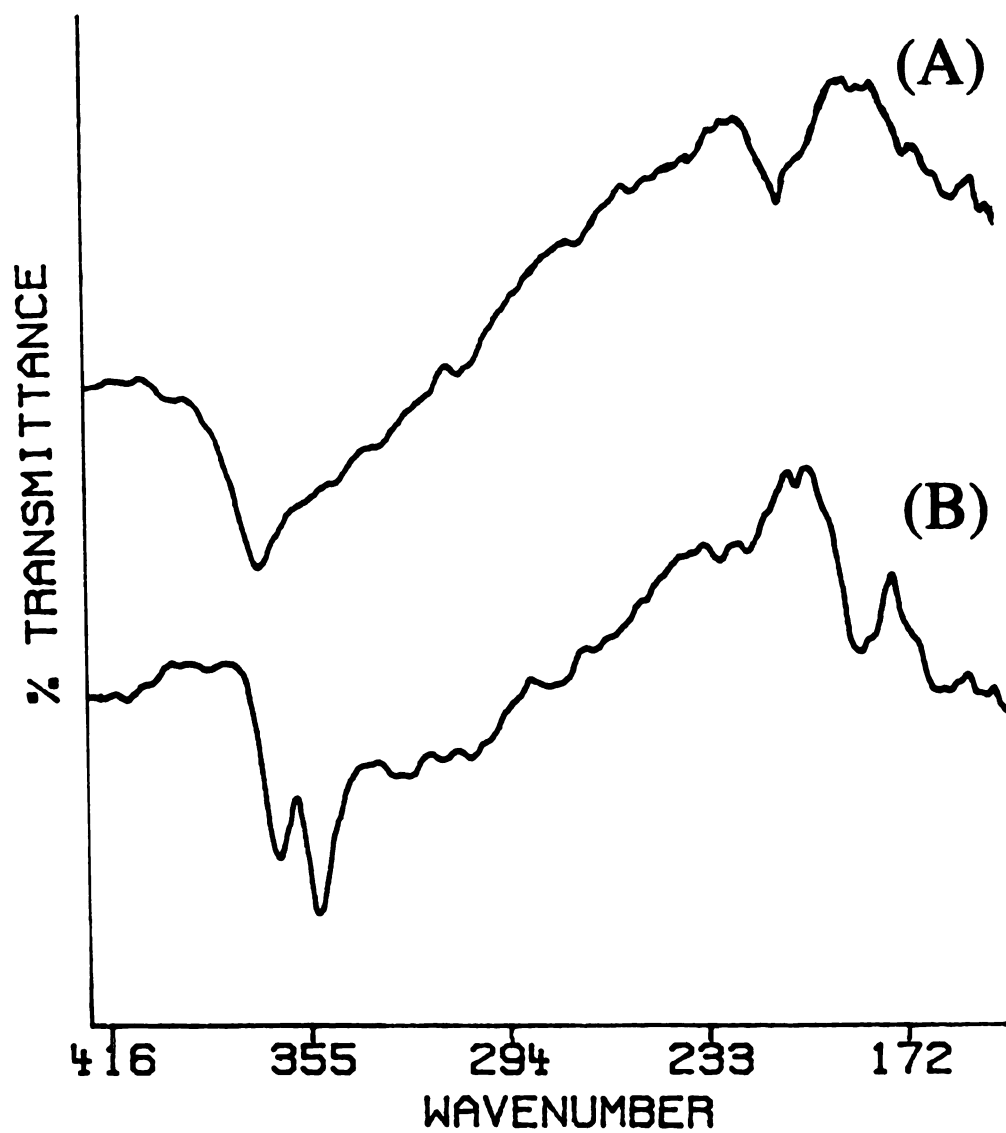


Figure 4-6: Infrared spectra for (A) $\text{K}_4[\text{V}_2\text{O}_2\text{Se}_{10}] \cdot 2\text{MeOH}$ and (B) $\text{K}_4[\text{V}_2\text{O}_2\text{Se}_8] \cdot 0.65\text{MeOH}$.

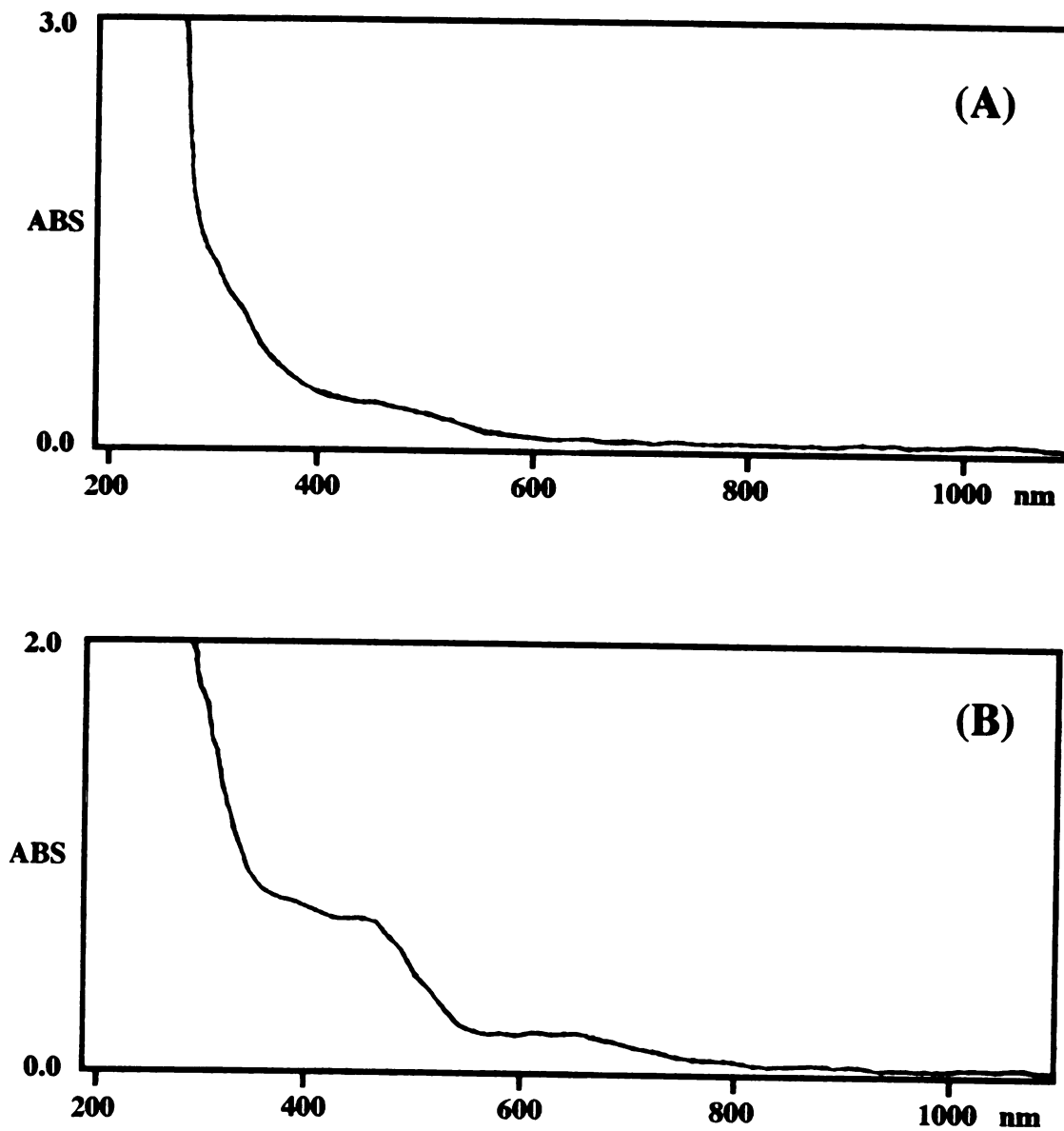


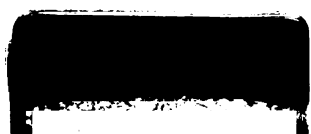
Figure 4-7: UV-Vis spectra for (A) $K_4[V_2O_2Se_{10}] \cdot 2MeOH$ in DMF and (B) $K_4[V_2O_2Se_8] \cdot 0.65MeOH$ in DMF.

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**HYDROTHERMAL (SOLVOTHERMAL) AND MOLTEN
POLYCHALCOGENIDE SALT SYNTHESIS OF TERNARY
AND QUATERNARY CHALCOGENIDES**

Volume II

By

Ju-Hsiou Liao

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CHAPTER 5

Molten Salt Synthesis and Characterization of Ternary Alkali Metal Tin (Poly)chalcogenide System

1. Introduction

Synthesis of new chalcogenide solids can be achieved at intermediate temperatures (200–450°C) by using the molten salt(flux) method. The latter has been proven to be a successful technique in stabilizing and crystallizing interesting new chalcogenides with novel structure types. In recent years, a series of polychalcogenide compounds synthesized by molten salt technique by using intermediate temperatures have been reported including $\text{K}_4\text{Ti}_3\text{S}_{14}$ ^{1,2}, $\alpha\text{-KCuS}_4$, $\beta\text{-KCuS}_4$ ^{3,4}, Na_3AuSe_8 , NaAuSe_2 , KAuSe_2 ⁵, KAuSe_5 , $\text{K}_3\text{AuSe}_{13}$ ^{3,6}, $\text{K}_2\text{Hg}_3\text{Q}_4$ (Q=S, Se), $\text{K}_2\text{Hg}_6\text{S}_7$ ^{3,7} and $\text{K}_2\text{Cu}_5\text{Te}_5$ ⁸. The versatility of polychalcogenide ligands to adopt various binding modes in molecular and polymeric complexes and the ability of the flux method to produce many novel structures has been exploited to form new solid state polychalcogenides. Thus far, transition metals have received the most attention by this technique with main group metals not extensively investigated. The existence of the one dimensional $\text{K}_4\text{Ti}_3\text{S}_{14}$ and the chemical $\text{Ti}^{4+}/\text{Sn}^{4+}$ similarity prompted us to start with Sn as a main group

metal for synthetic investigation. Although several metal tin (poly)sulfides are known, such as the molecular $(\text{Et}_4\text{N})_2[\text{Sn}(\text{S}_4)_3]_{0.4}[\text{Sn}(\text{S}_4)_2(\text{S}_6)]_{0.6}$ ⁹, $\text{Na}_4\text{SnS}_4 \cdot 14\text{H}_2\text{O}$ ¹⁰, $\text{Na}_4\text{Sn}_2\text{S}_6 \cdot 14\text{H}_2\text{O}$ ¹¹, $\text{Na}_6\text{Sn}_2\text{S}_7$ ¹², and the polymeric $\text{K}_2\text{SnS}_3 \cdot 2\text{H}_2\text{O}$ ¹³, $\text{Na}_4\text{Sn}_3\text{S}_8$ ¹⁴, Na_2SnS_3 ¹⁵ and $\text{Cs}_4\text{Sn}_5\text{S}_{12}$ ¹⁶, only $(\text{Et}_4\text{N})_2[\text{Sn}(\text{S}_4)_3]_{0.4}[\text{Sn}(\text{S}_4)_2(\text{S}_6)]_{0.6}$ contains polysulfide ligands. Among these compounds, $\text{Na}_6\text{Sn}_2\text{S}_7$ and $\text{Na}_4\text{Sn}_3\text{S}_8$ were made by heating stoichiometric mixtures of $\text{Sn}/\text{Na}_2\text{S}/\text{S}$ and $\text{SnS}_2/\text{Na}_2\text{S}$ at 450°C and 680°C respectively. $\text{Cs}_4\text{Sn}_5\text{S}_{12}$, was made hydrothermally with SnS_2 and Cs_2CO_3 at 130°C. $(\text{Et}_4\text{N})_2[\text{Sn}(\text{S}_4)_3]_{0.4}[\text{Sn}(\text{S}_4)_2(\text{S}_6)]_{0.6}$ was synthesized from $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and ammonium polysulfide in acetone/methanol solution at 50°C. The rest were synthesized by using SnS_2 or SnCl_4 in reactions with monosulfides in aqueous solutions at ambient temperature. Here we report the first five alkali metal tin polysulfides, $\text{K}_2\text{Sn}_2\text{S}_8$ (I), $\alpha\text{-Rb}_2\text{Sn}_2\text{S}_8$ (II), $\beta\text{-Rb}_2\text{Sn}_2\text{S}_8$ (III), $\text{Cs}_2\text{Sn}_2\text{S}_6$ (V) and $\text{Cs}_2\text{SnS}_{14}$ (VI), one potassium tin sulfide, $\text{K}_2\text{Sn}_2\text{S}_5$ (IV) and one potassium tin telluride, K_2SnTe_5 (VII), to be synthesized by using alkali metal polychalcogenides as reactive fluxes.

2. Experimental Section

2.1 Reagents

Sn metal was purchased from CERAC Inc. ~325 mesh, 99.8%. Sublimed Sulfur was purchased from J. T. Baker Chemical Co. 99.5~100.5%. Tellurium powder, -100 mesh, 99.95% purity, Aldrich Chemical Co., Milwaukee, WI. Potassium metal, analytical reagent, Mallinckrodt Inc., Paris, KY. Cesium metal, 99.98% purity, AESAR,

Johnson Matthey, Seabrook, NH. K_2S , Rb_2S , Cs_2S and K_2Te starting materials were prepared by a modified literature procedure¹⁷. All the reagents are stored under N_2 in a glove box.

2.2 Physical Measurements

The instruments and experimental setups for Infrared spectroscopy, SEM/EDS quantitative microprobe analysis and UV/vis/near-IR optical diffuse spectroscopy are the same as those in previous chapters. Raman spectra were measured by Dr. C. Varotsis in the department of chemistry, Michigan State University. Raman spectra were obtained in backscattering geometry from solid samples in spinning EPR tubes at room temperature. The Raman equipment included a SPEX 1459 Illuminator, a SPEX 1877 triplemate with an EG&G model 1421 diode array detector and an OMA III computer. An Innova 200 Argon-ion laser system was used to provide an excitation wavelength of 514.5 nm and the power incident on the sample was 50 mW. The Raman spectral resolution was approximately 8 cm^{-1} .

2.3. Synthesis

Chemicals were weighed and loaded into Pyrex tubes under a dry nitrogen atmosphere in a Vacuum Atmosphere Dri-Lab glovebox. Isolations were performed by using a standard Schlenk line technique under a dry nitrogen atmosphere.

$\text{K}_2\text{Sn}_2\text{S}_8$ (I) A mixture of Sn metal (0.119 g, 1 mmol), K_2S (0.220 g, 2 mmol) and S (0.256 g, 8 mmol) in 1:2:8 ratio was loaded into

an ~5-ml Pyrex tube in a N₂ glove box. The tube was evacuated and flame sealed at the pressure of $\sim 10^{-3}$ torr. The mixture was heated at 250 or 275 °C for 4-6 days. Upon cooling to room temperature at the rate of 2°C/hr, small orange chunky crystals were formed. The crystals obtained at 275°C are larger in size. The product was washed with water to remove excess K₂S_x flux, and then washed with carbon disulfide to remove unreacted sulfur. The product is obtained in 86% yield (based on Sn metal). The orange crystals are stable in air and insoluble in water and common organic solvents. Semiquantitative elemental analyses were run on a scanning electron microscope (SEM) using an energy dispersive (EDS) microscope technique. EDS indicated K_{2.0}Sn_{2.0}S_{7.9}.

α -Rb₂Sn₂S₈ (II) The preparation and isolation of (II) are similar to that of (I). However, the mixture of Sn metal (0.119 g, 1 mmol), Rb₂S (0.406 g, 2 mmol) and S (0.256 g, 8 mmol) in 1:2:8 ratio at 270°C for 4 days gave only ~38% yield (based on Sn), accompanied with white crystals of Rb₄Sn₂S₆ as an impurity¹⁸. Pure (II) was made and the yield was improved to 89%, when the reaction temperature was increased to 330 °C and the Sn/Rb₂S/S ratio was 1:2:12. Upon cooling at 2°C/hour, larger, well-formed orange needle-like crystals were obtained. The orange crystals are stable in air and insoluble in water and common organic solvents. Semiquantitative elemental analysis on SEM/EDS indicated Rb_{1.4}Sn₂S₉. The Rb content is underestimated due to an artifact of the standardless program used. We found that a correction factor of 1.5 has to be applied.

β -Rb₂Sn₂S₈ (III) The preparation and isolation of (III) are also similar to those outlined above. The mixture of Sn/Rb₂S/S in 1:1:8 ratio

was heated to 450°C for 4 days. Upon cooling at 3°C/hour, orange thin plate-like crystals of β -Rb₂Sn₂S₈ were obtained in the yield of 59% (based on Sn). The orange crystals are also stable in air and insoluble in water and common organic solvents. Semiquantitative elemental analysis on SEM/EDS indicated Rb_{1.4}Sn₂S₉.

K₂Sn₂S₅ (IV) The preparation and isolation of (IV) is the same as for (I) except that the reaction temperature was increased to 320°C. However a cooling rate of 2°C/hr, gave only microcrystals at ~81% yield. In order to grow larger crystals for single crystal X-ray analysis, we increased the reaction temperature to 400°C. At this temperature, the yield of (IV) was very low (less than 10%) and the major product was water-soluble white crystals of K₄Sn₂S₆¹⁹. The yellow crystals are also stable in air and insoluble in water and common organic solvents. Semiquantitative elemental analyses were done by SEM/EDS which indicated K_{2.0}Sn_{2.0}S_{5.7}.

Cs₂Sn₂S₆ (V) Pure yellow thin plate-like crystals of (V) can be obtained under the same reaction conditions used for (VI) but by using less sulfur (Sn:Cs₂S:S=1:3:8). However, crystals obtained at 275°C had poor crystallinity. Crystals suitable for single crystal X-ray diffraction analysis were obtained by heating a mixture of Sn (0.059 g, 0.5 mmol), Cs₂S (0.149 g, 0.5 mmol) and S (0.128 g, 4 mmol) in an evacuated Pyrex tube in 1:1:8 ratio at 400 °C for 4 days by using a cooling rate of 4°C/hr. The product was isolated by washing with DMF to remove excess Cs₂S_x flux followed by washing with ether. The product is insoluble in water and common organic solvents. The reaction gave the product at ~86% yield (based on

Sn). SEM/EDS semiquantitative elemental analysis indicated $\text{Cs}_{2.0}\text{Sn}_{2.0}\text{S}_{7.4}$.

$\text{Cs}_2\text{SnS}_{14}$ (VI) The procedure for the preparation of (VI) is the same as that of (I). Samples of Sn (0.059 g, 0.5 mmol), Cs_2S (0.298 g, 1.0 mmol) were mixed with S in the range of 0.096-0.160 g (3.0-5.0 mmol). The product was washed by methanol under N_2 to remove excess Cs_2S_x flux. All the three sulfur ratios gave mixtures of red crystals of (VI) and the yellow crystalline material of (V). The red crystals of (VI) dissolved slowly in water but are stable in air. Suitable crystals for X-ray diffraction studies were picked manually. Semiquantitative elemental analysis was done also on SEM/EDS which indicated $\text{Cs}_{2.0}\text{Sn}_{1.0}\text{S}_{15}$.

K_2SnTe_5 (VII) A mixture of Sn metal (0.238 g, 2.0 mmol), K_2Te (0.412 g, 0.20 mmol) and Te (1.021 g, 8.0 mmol) in 1:1:4 ratio was loaded into an ~5-ml Pyrex tube in a N_2 glove box. The tube was evacuated and flame sealed at the pressure of $\sim 10^{-3}$ torr. The mixture was heated at 400 °C for 4 days and then cooled to room temperature at 4°C/hr. The product was washed with DMF to remove excess K_2Te_x flux. Black plate-like crystals of (VII) and tellurium powder in ~1:1 ratio were obtained. The black plate-like crystals are stable in air and insoluble in water and common organic solvents. The crystals of (VII) were picked manually for characterization. SEM/EDS semiquantitative elemental analysis indicated $\text{K}_{2.2}\text{Sn}_{1.0}\text{Te}_{5.1}$.

2.4. X-Ray Crystallography

X-ray powder diffraction patterns were used for the purpose of phase characterization and identification. The X-ray powder diffraction patterns were recorded with a Phillips XRD-3000 controlled by PDP 11 computer and operating at 40 kV/35 mA. Graphite monochromated Cu radiation was used. In order to ensure the homogeneity, d-spacing obtained from X-ray powder diffraction (XRD) measurements of the products were compared with, and found to be identical (the crystals of (VI) and (VII) were picked by hand among mixtures.), with those calculated from using the atomic coordinates determined from the single crystal data. The calculation of d-spacings was performed by using the POWD 1020 program. The comparison tables between the calculated and observed d-spacings for these compounds are shown in Tables 5-1~5-7.

Table 5-1. Calculated and Observed X-Ray Powder Diffraction Pattern for $K_2Sn_2S_8$

h	k	l	d _{calc.} (Å)	d _{obs.} (Å)	%I _{obs.}
-1	0	1	8.9232	8.9929	73.8
0	1	1	8.0277	7.8641	49.5
0	0	2	6.7365	6.7503	100.0
1	0	1	6.6614	6.5816	72.6
-1	1	2	5.4122	5.4486	64.0
2	0	0	4.5602	4.5701	28.4
-2	1	1	4.3182	4.3362	16.6
2	1	0	4.1494	4.1924	18.5
1	0	3	3.6104	3.6217	21.8
-2	1	3	3.5834		
2	0	2	3.3307	3.3339	26.89
-2	2	2	3.3296		
-1	1	4	3.3247		
0	3	1	3.2367		
0	1	4	3.1879	3.1653	59.4
1	0	3	3.1318		
-3	1	1	3.0324	3.0163	43.4
-3	1	2	3.0102		
1	3	1	2.9819	2.9574	32.5
0	2	4	2.7910	2.7942	30.1
-2	3	1	2.7362	2.7331	30.1
1	3	2	2.7315		
3	1	1	2.6853	2.6937	31.7
-3	2	1	2.6848		
-3	2	2	2.6694	2.6210	54.9
-2	1	5	2.6142		
-3	1	4	2.6106		
0	1	5	2.5983		
-3	2	3	2.5566	2.5602	14.8
2	3	1	2.5522		
-3	0	5	2.4147	2.4208	64.0
-4	1	1	2.3069	2.3078	38.4
-1	4	3	2.1998	2.1863	47.5
-2	4	2	2.1816		
-4	2	2	2.1591	2.1603	28.44
1	2	5	2.1563		
4	2	0	2.0747	2.0895	37.8
0	2	6	2.0460	2.0445	30.9
3	3	2	1.9994	1.9777	22.0
1	1	6	1.9966		
-2	4	4	1.9746		
-4	0	6	1.9190	1.9179	50.6
-5	1	2	1.8806	1.8791	11.1
-2	5	3	1.7742	1.7719	23.2
-2	5	5	1.6093	1.6101	21.8
-4	0	8	1.6088		
-3	5	4	1.6084		
-6	1	4	1.5589	1.5606	16.0

Table 5-2. Calculated and Observed X-Ray Powder Diffraction Pattern for α -Rb₂Sn₂S₈

h	k	l	d _{calc.} (Å)	d _{obs.} (Å)	%I _{obs.}
1	0	-1	9.0492	8.8404	25.45
0	1	1	8.0772	7.9167	8.31
1	0	1	6.8842	6.7388	100.00
0	0	2	6.8786		
1	1	0	6.8332		
1	1	-2	5.4504	5.3942	19.49
0	2	1	4.6901	4.6611	70.20
2	0	0	4.6886		
1	0	-3	4.6833		
2	0	-2	4.5246	4.5123	23.67
2	1	-1	4.3883	4.3647	43.25
1	2	1	4.0397	4.0149	19.49
1	0	3	3.7201	3.6981	37.53
1	1	3	3.4857	3.4766	68.70
2	0	2	3.4421	3.4224	74.80
1	2	-3	3.4146		
1	1	-4	3.3676	3.3518	91.19
2	2	-2	3.3516		
0	1	4	3.2516	3.2293	73.25
0	3	1	3.2329		
1	3	0	3.1347	3.1210	57.27
3	1	-1	3.0957	3.0783	67.21
3	1	-2	3.0590	3.0411	61.43
1	3	1	2.9948	2.9869	68.70
0	2	4	2.8317	2.8184	26.37
3	1	1	2.7628	2.7437	67.21
1	3	2	2.7546		
2	3	-1	2.7495		
3	2	-1	2.7269		
3	2	-2	2.7017		
0	3	3	2.6924	2.6822	27.30
0	1	5	2.6525		
2	1	-5	2.6428	2.6279	38.64
3	1	-4	2.6389		
2	3	1	2.5815	2.5664	50.65
3	2	-3	2.5813		
1	2	-5	2.4890	2.4773	36.43
1	3	3	2.4795		
3	0	-5	2.4414	2.4323	57.27
1	3	-4	2.4359		
4	1	-1	2.3602	2.3531	25.45
0	4	2	2.3451		
0	1	6	2.2346	2.2733	15.71
				2.2266	23.67

Table 5-2. (cont'd)

h	k	l	d _{calc.} (Å)	d _{obs.} (Å)	%I _{obs.}
1	2	5	2.2040	2.1937	86.11
1	4	-3	2.2017		
4	2	-2	2.1941		
3	2	-5	2.1929		
2	4	-2	2.1845		
2	3	3	2.1816		
4	2	-3	2.1499	2.1446	34.29
4	2	0	2.1217	2.1149	27.30
3	2	3	2.0848	2.0763	33.24
0	2	6	2.0834		
1	1	6	2.0485	2.0398	58.64
4	0	2	2.0470		
1	0	-7	2.0448		
3	3	2	2.0389		
4	2	1	2.0195	2.0143	27.30
0	4	4	2.0193		
3	4	-1	1.9803	1.9766	45.65
2	4	-4	1.9796		
4	0	-6	1.9407	1.9400	30.20
5	1	0	1.8432	1.8411	15.01
4	3	1	1.8398		

Table 5-3. Calculated and Observed X-Ray Powder Diffraction Pattern for β -Rb₂Sn₂S₈

h	k	l	d _{calc.} (Å)	d _{obs.} (Å)	%I _{obs.}
0	2	0	9.8175	9.8974	27.8
1	1	0	8.9010	9.0875	8.16
0	2	1	7.9893	8.0661	11.6
0	0	2	6.8735	6.9024	100.0
1	3	0	5.4740	5.4812	18.8
0	4	1	4.6229	4.7052	22.9
1	3	2	4.2820	4.3014	22.3
1	4	1	4.1951	4.1662	26.1
0	2	3	4.1523		
1	2	3	3.8341	3.8720	8.2
1	5	1	3.5319	3.4940	21.3
0	0	4	3.4367	3.4458	51.8
2	4	1	3.3922		
1	5	2	3.2268	3.2524	25.6
3	1	1	3.1921	3.1919	37.9
1	4	3	3.1758		
1	2	4	3.0851	3.0961	16.1
3	0	2	2.9959	3.0044	25.6
3	3	2	2.7240	2.7297	12.0
3	1	3	2.6681	2.6789	15.2
1	7	1	2.6498	2.6534	22.3
2	6	2	2.5428	2.5499	16.1
0	8	0	2.4544	2.4599	98.9
0	8	1	2.4162	2.4193	13.6
2	8	0	2.2026	2.2021	31.4
1	5	5	2.1971		
4	4	1	2.1967		
2	4	5	2.1622	2.1641	27.3
2	7	3	2.1575		
2	6	4	2.1410	2.1181	15.2
3	1	5	2.1076		
4	4	3	2.0017	1.9885	21.8
0	8	4	1.9973		
4	6	0	1.9849		
2	3	6	1.9844		
0	10	1	1.9438	1.9471	73.5
1	5	6	1.9412		
0	2	7	1.9257	1.9293	22.3

Table 5-4. Calculated and Observed X-Ray Powder Diffraction Pattern for K₂Sn₂S₅

h	k	l	d _{calc.} (Å)	d _{obs.} (Å)	%I _{obs.}
1	1	0	6.2699	6.3705	49.4
-1	1	1	5.9432	6.0396	55.3
0	0	2	5.4757	5.5547	28.4
2	0	0	5.2602	5.3297	6.2
1	1	1	5.0481	5.1122	9.4
-2	0	2	4.5819	4.6214	10.1
0	2	0	3.9040	3.9454	15.4
.1	1	2	3.7872	3.8252	25.0
0	2	1	3.6773	3.7133	15.1
-1	1	3	3.4486	3.4789	47.1
-3	1	1	3.3396	3.3686	65.6
2	0	2	3.3085	3.3346	20.7
3	1	0	3.1990	3.2003	12.1
-2	2	1	3.1756	3.1631	7.7
2	2	1	2.8746	2.8963	100.0
3	1	1	2.8577	2.8364	15.7
-4	0	2	2.7298	2.7472	23.4
-1	1	4	2.7018	2.7184	30.7
0	2	3	2.6663	2.6831	26.7
1	3	0	2.5265	2.5413	62.29
2	2	2	2.5241		
3	1	2	2.4704	2.4831	8.4
-3	1	4	2.4578	2.4361	12.3
1	3	1	2.4205	2.3776	26.3
-1	3	2	2.3631		
1	1	4	2.3524		
-4	0	4	2.2910	2.3036	22.2
-4	2	1	2.2550	2.2669	6.6
1	3	2	2.2308	2.2429	31.1
-5	1	2	2.1277	2.1332	11.2
4	0	2	2.1241		
3	1	3	2.1226		
-5	1	1	2.1162		
-3	3	2	2.0873	2.0989	26.3
-5	1	3	2.0613	2.0715	13.8
4	2	1	2.0397	2.0503	27.1
5	1	0	2.0316	2.0421	22.2
1	1	5	1.9566	1.9664	25.4
0	4	0	1.9520	1.9607	31.6
-5	1	4	1.9374	1.9407	20.3
-1	3	4	1.9309	1.9310	19.9
-2	0	6	1.9219	1.9170	11.2
0	2	5	1.9102	1.9031	10.4
5	1	1	1.8968		
2	2	4	1.8936		
4	2	2	1.8658	1.8730	3.0

Table 5-4. (cont'd)

h	k	l	d _{calc.} (Å)	d _{obs.} (Å)	%I _{obs.}
-3	3	4	1.8357	1.8445	34.4
-4	2	5	1.7980	1.8061	17.4
1	3	4	1.7905	1.7920	11.8
-5	1	5	1.7843	1.7816	25.0
2	4	1	1.7737		
-2	2	6	1.7243	1.7301	6.8
-2	4	3	1.7129	1.7197	9.9
4	2	3	1.6883	1.6956	19.2
2	4	2	1.6812	1.6873	10.9
-6	2	1	1.6520	1.6568	25.4
-6	2	3	1.6491		
5	3	0	1.6362	1.6431	12.3
-2	4	4	1.6048	1.6116	8.1
-4	4	2	1.5894	1.5891	7.44
-5	3	4	1.5859		
5	1	3	1.5825	1.5880	17.8
-7	1	3	1.5441	1.5497	10.3

Table 5-5. Calculated and Observed X-Ray Powder Diffraction Pattern for Cs₂Sn₂S₆

h	k	l	d _{calc.} (Å)	d _{obs.} (Å)	%I _{obs.}
1	0	0	6.5748	6.6196	94.7
0	1	0	6.5620		
0	0	1	5.6133	5.6408	19.9
-1	1	0	5.5818		
1	-1	1	4.0939	4.0875	62.5
-1	1	1	3.8349	3.8583	28.5
0	-2	1	3.7441	3.7700	52.3
-2	0	1	3.5510	3.5730	56.3
-1	2	0	3.3805	3.4002	100.0
1	-2	1	3.3628	3.3593	42.1
2	0	0	3.2874	3.3063	23.7
-2	1	1	3.1520	3.1686	29.2
-2	-1	1	3.0949	3.1122	39.5
-1	-2	2	2.8874	2.98970	7.3
0	0	2	2.8067	2.8204	77.2
-2	2	0	2.7951		
1	2	0	2.6302	2.6388	10.5
1	-1	2	2.5759	2.5661	25.7
2	-2	1	2.5667		
1	-2	2	2.5580		
2	0	1	2.4309	2.4369	23.7
-3	0	1	2.4077	2.4100	32.2
-2	-2	2	2.4049		
0	-3	2	2.3831	2.3747	38.6
-1	-3	1	2.2127	2.1972	47.5
3	0	0	2.1916		
0	3	0	2.1873		
0	-2	3	2.1386	2.1446	10.1
-3	2	1	2.0711	2.0797	18.7
-1	0	3	2.0357	2.0371	10.3
-2	0	3	2.0275	2.0170	22.4
2	1	1	2.0096		
3	-2	1	1.9559	1.9611	13.8
1	-4	1	1.8722	1.8784	33.8
0	-4	1	1.8720		
0	0	3	1.8711		
0	-4	1	1.8358	1.8377	10.1
-3	-2	1	1.8329		
-2	1	3	1.7736	1.7762	7.3
-4	2	1	1.7049	1.7062	14.3
-4	-1	2	1.7045		
-4	2	0	1.6928		
-2	-2	4	1.6731	1.6762	11.4
1	-4	3	1.6418	1.6413	21.7
-4	0	3	1.6096	1.6110	7.3
-4	-1	3	1.6089		
3	2	0	1.6082		
1	3	1	1.5635	1.5672	17.5

Table 5-6. Calculated and Observed X-Ray Powder Diffraction Pattern for Cs₂SnS₁₄. Crystals were manually picked from a mixture of Cs₂Sn₂S₆ and Cs₂SnS₁₄.

h	k	l	d _{calc.} (Å)	d _{obs.} (Å)	%I _{obs.}
1	1	1	5.5912	5.6641	30.6
1	2	1	4.9626	5.0195	8.9
0	3	2	4.7342	4.7921	13.6
1	3	0	4.6111	4.6586	30.6
0	4	1	4.4433	4.4910	15.2
-1	2	3	3.9177	3.9502	56.5
1	0	3	3.6978	3.7395	21.9
0	1	4	3.5822	3.5695	16.9
1	2	3	3.4376	3.4699	26.1
-2	1	1	2.4141	2.4266	26.1
0	5	2	3.3227	3.3120	100.0
1	4	2	3.2899		
1	5	0	3.2792		
-2	1	2	3.2725		
-2	2	2	3.1312	3.1570	42.0
2	2	1	3.0515	3.0765	24.7
1	1	4	2.9869	2.9765	18.7
0	5	3	2.9613		
2	1	2	2.8948	2.8947	33.8
1	2	4	2.8850		
-1	0	5	2.8603	2.8462	37.2
1	6	0	2.8331		
-2	3	3	2.7387	2.7525	35.5
-2	4	3	2.5530	2.5562	26.1
1	0	5	2.5426		
1	4	4	2.5386		
-1	7	1	2.4740	2.4857	15.2
0	0	6	2.4334	2.4483	23.3
1	7	1	2.4263		
0	8	1	2.3326	2.3168	27.5
-3	0	1	2.3214		
2	0	4	2.3203		
-2	6	1	2.3166		
-1	6	4	2.3145		
1	7	2	2.3113		
-2	0	6	2.1584	2.1552	7.7
0	7	4	2.1526		
3	3	0	2.1493		

Table 5-6. (cont'd)

h	k	l	d _{calc.} (Å)	d _{obs.} (Å)	%I _{obs.}
-3	1	4	2.0869	2.0880	25.4
1	8	2	2.0839		
3	3	1	2.0811		
-1	1	7	2.0798		
-2	7	2	2.0795	2.0604	21.9
1	3	6	2.0612		
-3	4	2	2.0590		
-3	0	5	1.9641		
2	3	5	1.9601	1.9089	28.3
-2	1	7	1.9174		
-2	6	5	1.9141		
3	2	3	1.9120		
0	9	3	1.9073	1.8486	11.1
-3	5	3	1.9054		
0	4	7	1.9040		
1	1	7	1.9013		
3	5	1	1.9005	1.8112	10.2
3	6	0	1.8441		
1	9	3	1.8083		
0	10	2	1.8076		
-1	8	5	1.8075	1.7481	12.6
-3	7	1	1.7505		
2	7	4	1.7501		
2	8	3	1.7401		
-3	5	5	1.7381	1.6856	10.6
3	4	4	1.6889		
0	8	6	1.6838		
4	2	1	1.6484		
1	11	0	1.6468	1.6449	14.1
-1	7	7	1.6460		

Table 5-7. Calculated and Observed X-Ray Powder Diffraction Patterns for K₂SnTe₅.

h	k	l	d _{calc.} (Å)	d _{obs.} (Å)	%I _{obs.}
1	1	0	5.9864	5.9989	30.32
2	1	1	3.6760	3.6781	53.11
1	1	4	3.2310	3.2325	5.14
2	1	3	3.0436	3.0470	53.70
2	2	0	2.9932	2.9938	56.10
2	0	4	2.8433	2.8440	100.00
0	0	6	2.5587	2.5595	4.78
2	1	5	2.3848	2.3845	6.10
2	2	4	2.3603	2.3612	5.14
3	2	1	2.3211	2.3175	3.32
3	1	4	2.1958	2.1958	38.37
4	0	0	2.1165	2.1178	4.43
4	1	1	2.0352	2.0377	24.00
				2.0354	17.39
3	3	0	1.9955	1.9973	30.32
0	0	8	1.9190	1.9213	18.77
4	1	3	1.9056	1.9077	31.22
2	1	7	1.8977	1.8940	33.52
4	2	0	1.8931		
4	0	4	1.8534	1.8547	17.73
1	1	8	1.8274	1.8276	5.33
3	3	4	1.7705	1.7701	7.14
4	1	5	1.7068	1.6975	11.02
4	2	4	1.6978		
5	1	0	1.6603	1.6609	12.12
2	2	8	1.6155	1.6160	15.11

Because the orange crystals of $\text{K}_2\text{Sn}_2\text{S}_8$ (I) were small, the X-ray diffraction data were collected by Molecular Structure Corporation (MSC), TX, by using a rotating anode X-ray generator in order to obtain sufficient reflections with reasonable intensity. An orange prismatic crystal was mounted on a glass fiber. All measurements were made on a Rigaku AFC6R diffractometer with graphite monochromated $\text{Mo K}\alpha$ radiation and a 12 KW rotating anode generator. Intensity data for (I) were measured at 23 °C by using the ω -2 θ scan mode. The stability of the experimental setup and crystal intensity were monitored by measuring three standard reflections periodically for every 150 reflections. A decline of ~4.5% was observed, and a linear correction factor was applied to the data. An empirical absorption correction (based on ψ scans) was applied. The equivalent reflections were averaged. The structure of (I) was solved at MSC by direct methods (MITHRIL²¹ and DIRDIF²²) and refined by full-matrix least-square techniques.

The X-ray diffraction data of $\text{Cs}_2\text{SnS}_{14}$ (V) were collected on a P3 Nicolet four-circle diffractometer by using $\theta/2\theta$ scan mode and graphite monochromated $\text{Mo K}\alpha$ radiation. A red crystal of (V) was mounted on the end of a glass fiber. The data were collected at 23 °C and three check reflections were monitored every 100 reflections without evidence of any significant decay during the data collection period. An empirical absorption correction was applied to all the data (based on ψ scans). An additional absorption correction by using the DIFABS²³ procedure was applied to isotropically refined data. The equivalent reflections were averaged. The structure refinement was done with the SDP²⁴ package of crystallographic program running on a VAXstation 2000 computer. The structure of (V)

and (VII) was solved with direct methods (SHELXS-86)²⁵, and they were refined by full-matrix least-square techniques.

The X-ray diffraction data of α -Rb₂Sn₂S₈ (II), β -Rb₂Sn₂S₈ (III), K₂Sn₂S₅ (IV), Cs₂Sn₂S₆ (VI) and K₂SnTe₅ (VII) were collected on a Rigaku AFC6S diffractometer by using ω -2 θ scan mode and graphite monochromated Mo K α radiation at 23°C. Those crystals were mounted on the end of glass fibers. The stability of the experimental setup and crystal intensity were monitored by measuring three standard reflections periodically for every 150 reflections. No significant decay was observed during the data collections. An empirical absorption correction was applied to all the data (based on ψ scans). An additional absorption correction by using the DIFABS procedure was applied to isotropically refined data. The equivalent reflections were averaged. The structure refinement was done with the TEXSAN²⁶ package of crystallographic programs running on a VAXstation 3100/76 computer. The structures of (II), (III), (IV) (VI) and (VII) were solved with direct methods (SHELXS-86), and they were refined by the full-matrix least-square technique available in TEXSAN.

The crystallographic data and detailed information of structure solution and refinement for (I)~(VII) are listed in Table 5-8. Atomic coordinates and equivalent isotropic thermal parameters for (I)~(VII) are given in Tables 5-9~5-15 respectively.

Table 5-8. Summary of Crystallographic Data for K₂Sn₂S₈(I), α-Rb₂Sn₂S₈(II), β-Rb₂Sn₂S₈(III), K₂Sn₂S₅(IV), Cs₂Sn₂S₆(V), Cs₂SnS₁₄(VI) and K₂SnTe₅(VII)

	(I)	(II)	(III)
formula	K ₂ Sn ₂ S ₈	α-Rb ₂ Sn ₂ S ₈	β-Rb ₂ Sn ₂ S ₈
fw	572.06	664.80	664.80
a, Å	9.850(8)	9.788(3)	9.986(4)
b, Å	10.004(5)	9.978(3)	19.635(3)
c, Å	14.131(7)	14.360(2)	13.747(3)
α, deg	90.0	90.0	90.0
β, deg	107.82(6)	106.70(2)	90.0
γ, deg	90.0	90.0	90.0
Z, V, Å ³	4, 1289(3)	4, 1343(1)	8, 2696(2)
space group	P2 ₁ /n	P2 ₁ /n	Pbcn
d _{calc} , g/cm ³	2.947	3.286	3.276
crystal size, mm	0.2x0.1x0.1	0.2x0.2x0.4	0.07x0.09x0.42
radiation	Mo Kα λ=0.71609Å	Mo Kα λ=0.71609Å	Mo Kα λ=0.71609Å
μ(Mo Kα), cm ⁻¹	57.37	118.93	118.54
2θ _{max} , deg	50	50	50
no. of data collected	2565	2686	2721
no. of unique data	2445	2530	2721
no. of obs. data (I>3σ(I))	1325	1693	1301
no. of variables	109	110	110
final R/R _w , %	4.9/5.1	3.0/3.6	3.2/3.5

* At 23°C $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ $R_w = \{ \sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2 \}^{1/2}$

Table 5-8. (cont'd)

	(IV)	(V)
formula	K ₂ Sn ₂ S ₅	Cs ₂ Sn ₂ S ₆
fw	475.88	695.56
a, Å	11.804(3)	7.289(4)
b, Å	7.808(1)	7.597(3)
c, Å	11.538(1)	6.796(3)
α, deg	90.0	114.80(3)
β, deg	108.35(1)	108.56(4)
γ, deg	90.0	97.54(4)
Z, V, Å ³	4, 947.8(5)	1, 308.1(7)
space group	C2/c	P-1
d _{calc} , g/cm ³	3.335	3.784
crystal size, mm	0.4x0.5x0.85	0.8x0.9x1.0
radiation	Mo Kα	Mo Kα
	λ=0.71609Å	λ=0.71609Å
μ(Mo Kα), cm ⁻¹	71.55	107.78
2θ _{max} , deg	50	50
no. of data collected	942	1172
no. of unique data	898	1078
no. of obs. data (I>3σ(I))	687	961
no. of variables	42	46
final R/R _w , %	4.7/6.0	3.1/3.9

* At 23°C $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ $R_w = \{ \sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2 \}^{1/2}$

Table 5-8. (cont'd)

	(VI)	(VII)
formula	Cs ₂ SnS ₁₄	K ₂ SnTe ₅
fw	833.34	834.89
a, Å	6.964(6)	8.466(2)
b, Å	18.66(1)	8.466(2)
c, Å	14.80(1)	15.352(2)
α, deg	90.0	90.0
β, deg	99.39(1)	90.0
γ, deg	90.0	90.0
Z, V, Å ³	4, 1897(5)	4; 1100.3(4)
space group	P2 ₁ /n	I4/mcm
d _{calc} , g/cm ³	2.92	5.04
crystal size, mm	0.12x0.9x0.4	0.3x0.6x0.7
radiation	Mo Kα	Mo Kα
	λ=0.71609Å	λ=0.71609Å
μ(Mo Kα), cm ⁻¹	65.7	160.62
2θ _{max} , deg	45	50
no. of data collected	2918	320
no. of unique data	2345	320
no. of obs. data (I>3σ(I))	1701	226
no. of variables	154	15
final R/R _w , %	4.46/4.95	2.7/4.4

* At 23°C $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ $R_w = \{ \sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2 \}^{1/2}$

Table 5-9. Positional Parameters and Equivalent Isotropic Displacement Values ($\text{\AA}^2$)^a for $\text{K}_2\text{Sn}_2\text{S}_8$ with Estimated Standard Deviations in Parentheses

atom	x	y	z	B (eq)
Sn (1)	0.0325 (1)	0.1710 (1)	0.0178 (1)	1.40 (5)
Sn (2)	0.5940 (1)	0.0001 (1)	0.4050 (1)	1.15 (4)
K (1)	0.3506 (5)	0.3631 (5)	0.2038 (4)	3.0 (2)
K (2)	0.0310 (6)	0.2733 (6)	0.4072 (4)	3.8 (2)
S (1)	0.2196 (5)	0.2742 (5)	-0.0369 (4)	1.6 (2)
S (2)	-0.1670 (5)	0.0428 (5)	-0.0856 (4)	1.9 (2)
S (3)	0.6433 (5)	-0.0983 (5)	0.5783 (3)	1.5 (2)
S (4)	0.5089 (5)	0.0668 (5)	0.2194 (3)	1.6 (2)
S (5)	0.0121 (5)	0.2708 (5)	0.1662 (3)	1.5 (2)
S (6)	0.6924 (6)	0.1425 (5)	0.1947 (4)	2.3 (2)
S (7)	0.6912 (5)	0.3438 (5)	0.2300 (4)	1.8 (2)
S (8)	0.6440 (5)	0.4413 (5)	0.0965 (3)	1.7 (2)

^a $B(\text{eq}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table 5-10. Positional Parameters and Equivalent Isotropic Displacement Values ($\text{\AA}^2$)^a for α -Rb₂Sn₂S₈, with Estimated Standard Deviations in Parentheses

atom	x	y	z	B (eq)
Sn(1)	0.02687 (7)	0.17298 (6)	0.01519 (4)	1.42 (2)
Sn(2)	0.59313 (6)	-0.00021 (6)	0.40486 (4)	1.23 (2)
Rb(1)	0.3511 (1)	0.3664 (1)	0.20466 (8)	2.96 (4)
Rb(2)	0.0292 (1)	0.2751 (1)	0.40894 (8)	3.21 (5)
S(1)	0.2105 (2)	0.2743 (2)	-0.0405 (2)	1.62 (9)
S(2)	-0.1655 (2)	0.0379 (2)	-0.0802 (2)	1.89 (9)
S(3)	0.6379 (2)	-0.0999 (2)	0.5747 (2)	1.40 (8)
S(4)	0.5109 (2)	0.0666 (2)	0.2236 (2)	1.71 (8)
S(5)	0.0078 (2)	0.2702 (2)	0.1628 (2)	1.63 (9)
S(6)	0.6894 (3)	0.1408 (2)	0.1948 (2)	2.1 (1)
S(7)	0.6944 (2)	0.3426 (2)	0.2290 (2)	1.70 (8)
S(8)	0.6514 (2)	0.4418 (2)	0.0987 (2)	1.65 (8)

^a $B(\text{eq}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table 5-11. Positional Parameters and Equivalent Isotropic Displacement Values ($\text{\AA}^2$)^a for β -Rb₂Sn₂S₈ with Estimated Standard Deviations in Parentheses

atom	x	y	z	B (eq)
Sn (1)	0.17289 (7)	0.32611 (4)	0.27038 (6)	1.38 (3)
Sn (2)	1/2	0.41693 (6)	1/4	1.17 (5)
Sn (3)	1/2	0.22879 (6)	1/4	1.23 (5)
Rb (1)	0.2273 (1)	0.42997 (8)	-0.0359 (1)	3.11 (7)
Rb (2)	0.1393 (1)	0.18813 (8)	0.0284 (1)	3.01 (7)
S (1)	0.2778 (3)	0.4240 (2)	0.3385 (2)	1.6 (1)
S (2)	0.0379 (3)	0.3318 (2)	0.1264 (2)	1.9 (1)
S (3)	0.4008 (3)	0.3232 (2)	0.1427 (2)	1.3 (1)
S (4)	0.5637 (3)	0.5084 (2)	0.3775 (2)	1.5 (1)
S (5)	0.2661 (3)	0.2219 (2)	0.3307 (2)	1.5 (1)
S (6)	0.6557 (3)	0.5796 (2)	0.2909 (2)	1.7 (1)
S (7)	0.8589 (3)	0.5604 (2)	0.3018 (3)	2.0 (2)
S (8)	0.4377 (3)	0.1399 (2)	0.1207 (2)	1.8 (1)

^a $B(\text{eq}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table 5-12. Positional Parameters and Equivalent Isotropic Displacement Values ($\text{\AA}^2$)^a for $\text{Cs}_2\text{Sn}_2\text{S}_6$ with Estimated Standard Deviations in Parentheses

atom	x	y	z	B (eq)
Cs (1)	0.1845 (1)	0.8627 (1)	0.2325 (1)	1.87 (2)
Sn	0.5135 (1)	0.4257 (1)	0.2224 (1)	0.67 (2)
S (1)	0.6075 (4)	0.1129 (4)	0.1701 (5)	1.28 (7)
S (2)	0.2345 (4)	0.4348 (4)	0.3383 (5)	1.19 (7)
S (3)	0.6997 (4)	0.7104 (4)	0.2193 (5)	1.35 (7)

^a $B(\text{eq}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table 5-13. Positional Parameters and Equivalent Isotropic Displacement Values ($\text{\AA}^2$)^a for $\text{K}_2\text{Sn}_2\text{S}_5$ with Estimated Standard Deviations in Parentheses

atom	x	y	z	B (eq)
Sn	0.09424 (8)	0.1539 (1)	0.44164 (7)	0.72 (4)
K	-0.2801 (3)	0.1680 (4)	0.3173 (3)	2.1 (1)
S (1)	0.0170 (3)	0.1340 (5)	0.6163 (3)	1.5 (1)
S (2)	0	0.3141 (6)	1/4	1.2 (2)
S (3)	0.3039 (3)	0.0516 (4)	0.4619 (3)	1.0 (1)

^a $B(\text{eq}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table 5-14. Positional Parameters and Equivalent Isotropic Displacement Values ($\text{\AA}^2$)^a for $\text{Cs}_2\text{SnS}_{14}$ with Estimated Standard Deviations in Parentheses

atom	x	y	z	B(eq)
Cs (1)	-0.0858 (2)	0.80160 (6)	0.47666 (8)	4.37 (6)
Cs (2)	0.6252 (2)	0.95164 (6)	-0.16319 (8)	4.38 (6)
Sn	0.0355 (2)	0.82444 (6)	0.16925 (7)	2.77 (5)
S (1)	0.2595 (7)	0.8165 (2)	0.3247 (3)	3.7 (2)
S (2)	0.4119 (8)	0.9090 (3)	0.3562 (3)	4.9 (3)
S (3)	0.267 (1)	0.9672 (3)	0.4438 (3)	5.6 (3)
S (4)	0.0815 (9)	1.0348 (3)	0.3631 (3)	4.7 (3)
S (5)	-0.1502 (8)	0.9730 (2)	0.3083 (3)	4.0 (2)
S (6)	-0.1128 (8)	0.9504 (2)	0.1770 (3)	3.9 (2)
S (7)	0.3328 (7)	0.8643 (2)	0.0983 (3)	3.4 (2)
S (8)	0.2004 (7)	0.9114 (3)	-0.0226 (3)	3.8 (2)
S (9)	0.0152 (8)	0.8311 (3)	-0.0794 (3)	4.0 (2)
S (10)	-0.1810 (7)	0.8260 (3)	0.0104 (3)	3.8 (2)
S (11)	0.1443 (8)	0.6934 (2)	0.1627 (3)	4.3 (2)
S (12)	-0.1178 (9)	0.6430 (3)	0.1328 (3)	4.6 (3)
S (13)	-0.2514 (8)	0.6734 (3)	0.2415 (3)	4.6 (2)
S (14)	-0.2782 (7)	0.7823 (2)	0.2266 (3)	3.6 (2)

^a $B(\text{eq}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table 5-15. Positional Parameters and Equivalent Isotropic Displacement Values ($\text{\AA}^2$)^a for K_2SnTe_5 with Estimated Standard Deviations in Parentheses

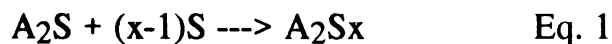
atom	x	y	z	B (eq)
Sn	1/2	0	1/4	1.12 (5)
Te (1)	1/2	0	0	1.43 (5)
Te (2)	0.31840 (9)	0.1816	0.13730 (7)	1.19 (3)
K (1)	0	0	1/4	1.7 (2)
K (2)	0	0	0	2.9 (3)

^a $B(\text{eq}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

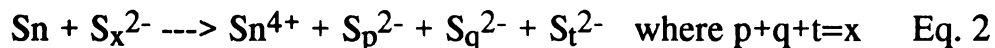
3. Results and Discussion

3.1. Synthesis

All compounds except (VII) were synthesized in A_2S_x fluxes (A=alkali metal). The molten alkali metal polysulfides formed by the *in situ* reaction of alkali metal monosulfide and elemental sulfur, shown in equation 1, serve as reaction media which enhance the mobility of the reacting species by dissolving them and thus help the crystallization of the



final products. In addition, the polysulfide melts are oxidizing agents which oxidize the Sn metal to the 4+ oxidation state as shown in equation 2.



The chelating ability of S_x^{2-} and their diversity of bonding modes are responsible for the great variety of new structures that can be accessed. In the polychalcogenide fluxes, there are equilibria present between the various polychalcogenides. The direction of equilibria can be controlled by the reaction temperature, the nature of the metal and the value of x in S_x^{2-} . In general, higher temperatures promote the crystallization of larger and better crystals, but are generally unfavorable for the stabilization of longer polychalcogenide chains, which tend to break down to shorter chains. In

some cases, more elemental chalcogens can be added to shift the equilibrium.

In the reaction of Sn with alkali metal polysulfides, we found that basic fluxes ($A_2S/S > 3/8$, $A=K, Rb, Cs$), favored formation of molecular compounds of $A_4Sn_2S_6$ ¹⁸. The structure of $[Sn_2S_6]^{4-}$ anions is that of an edge-sharing bi-tetrahedron. On examining the extended structures of (I)~(V), which were formed with $A_2S/S < 3/8$, it appears that they are composed fused $[Sn_2S_6]^{4-}$ units as building blocks linked by polysulfide chains (*vide infra*). Interestingly, the least basic flux of the Cs/Sn/S system afforded Cs_2SnS_{14} which contains the discrete anion $[SnS_{14}]^{2-}$.

$Rb_2Sn_2S_8$ was found in two slightly different phases; the α -form made at lower temperature of 330°C from S_x^{2-} , and the β -form formed at 450°C in a sulfur rich flux. The high temperature promotes the transition from the kinetically stable α - $Rb_2Sn_2S_8$ to the possibly thermodynamically more stable β - $Rb_2Sn_2S_8$. The β -form of $K_2Sn_2S_8$ has not been observed.

Our investigations of the reactions between Sn and potassium polyselenide fluxes at the intermediate range did not come across any new K/Sn/Se structures. $K_4Sn_3Se_8$, which was synthesized earlier under methanothermal conditions²⁷, formed by heating one equivalent of Sn, 1~4 equivalents of K_2Se and 8 equivalents of Se between 280°C~550°C. It is apparently a very thermodynamically stable phase in this temperature regime. Higher reaction temperature synthesis (~800°C) of this system gave rise to $K_2Sn_4Se_8$ ²⁸ and $K_2Sn_2Se_5$ ²⁹; the former is an interesting mixed Sn^{2+}/Sn^{4+} compound while the latter is isostructural to $K_2Sn_2S_5$.

The reaction of (VII) was performed in a K_2Te_x flux which forms by the *in situ* reaction of K_2Te and Te. In this reaction, Sn metal is oxidized to 4+ oxidation state by polytellurides. The central Te atom of the square-

planar $[\text{Te}_5]^{6-}$ fragment is also oxidized by polytelluride to the +2 oxidation state, while the four terminal Te atoms have the oxidation state of 2-. (VII) is a stable phase which is observed in a wide range of $\text{K}_2\text{Te}/\text{Te}$ ratio. However, these reactions gave elemental tellurium as by-product.

3.2. Description of Structures

Structures of $\text{K}_2\text{Sn}_2\text{S}_8$, $\alpha\text{-Rb}_2\text{Sn}_2\text{S}_8$, $\beta\text{-Rb}_2\text{Sn}_2\text{S}_8$

These compounds have unique layered structures and are the first known tin-polysulfide framework solids. The anionic structures of (I) and (II) are identical while that of (III) is a conformational isomer. They all contain two distinct Sn sites, one tetrahedral and one octahedral. These Sn centers are linked via S^{2-} and S_4^{2-} so the layered anionic framework can be expressed by a more descriptive formulation, $[\text{Sn}_2\text{S}_4(\text{S}_4)]^{2-}$. By assigning the formal oxidation states of A^+ ($\text{A} = \text{K}, \text{Rb}$), S^{2-} and S_4^{2-} , the formal oxidation state of Sn atoms at both sites in (I)~(III) is +4. After ACuS_4 , these structures are the only other examples of compounds incorporating tetrasulfides in an extended solid state framework. Based on the chemical similarity of Sn^{4+} and Ti^{4+} , the closest analogs of these compounds may be the Ti^{4+} compounds, $\text{K}_4\text{Ti}_3\text{S}_{14}$ and $\text{Na}_2\text{Ti}_2\text{Se}_8$ ³⁰. These compounds also have been made from polychalcogenide melts in the temperature range of 345~470 °C. Obviously, Sn does not undergo similar chemistry since (I)~(III) are not isostructural to $\text{Na}_2\text{Ti}_2\text{Se}_8$.

The two-dimensional structures of (I) and (II) are shown in Figure 5-1. (I) and (II) crystallize in the same monoclinic space group, the only significant difference being the larger interlayer spacing in (II) due to the

larger size of Rb^+ compared to K^+ . The higher temperature product, (III), has its layers shifted slightly along the [102] crystallographic axis relative to (II) to form a more symmetric orthorhombic lattice as shown in Figure 5-2. The comparison of selected bond distances and angles of (I), (II) and (III) are given in Table 5-16.

The anionic layers of (I)~(III) are formed by a special arrangement of SnS_4 tetrahedra, SnS_6 octahedra and S_4^{2-} ligands. The Sn^{4+} centers are divided into two sets of recognizable dimeric units, one of which involves the tetrahedral centers and the other the octahedral centers, as shown in scheme (A). In the first kind, two distorted SnS_4 tetrahedra share an edge to form a Sn_2S_6 unit with a center of inversion in the middle of the shared edge. In the second kind of dimer, two slightly distorted SnS_6 octahedra also share an edge through two equatorial S atoms to form a Sn_2S_{10} unit that possesses a center of inversion at the middle of the edge. The Sn-Sn vectors in the Sn_2S_{10} units are oriented perpendicular to the

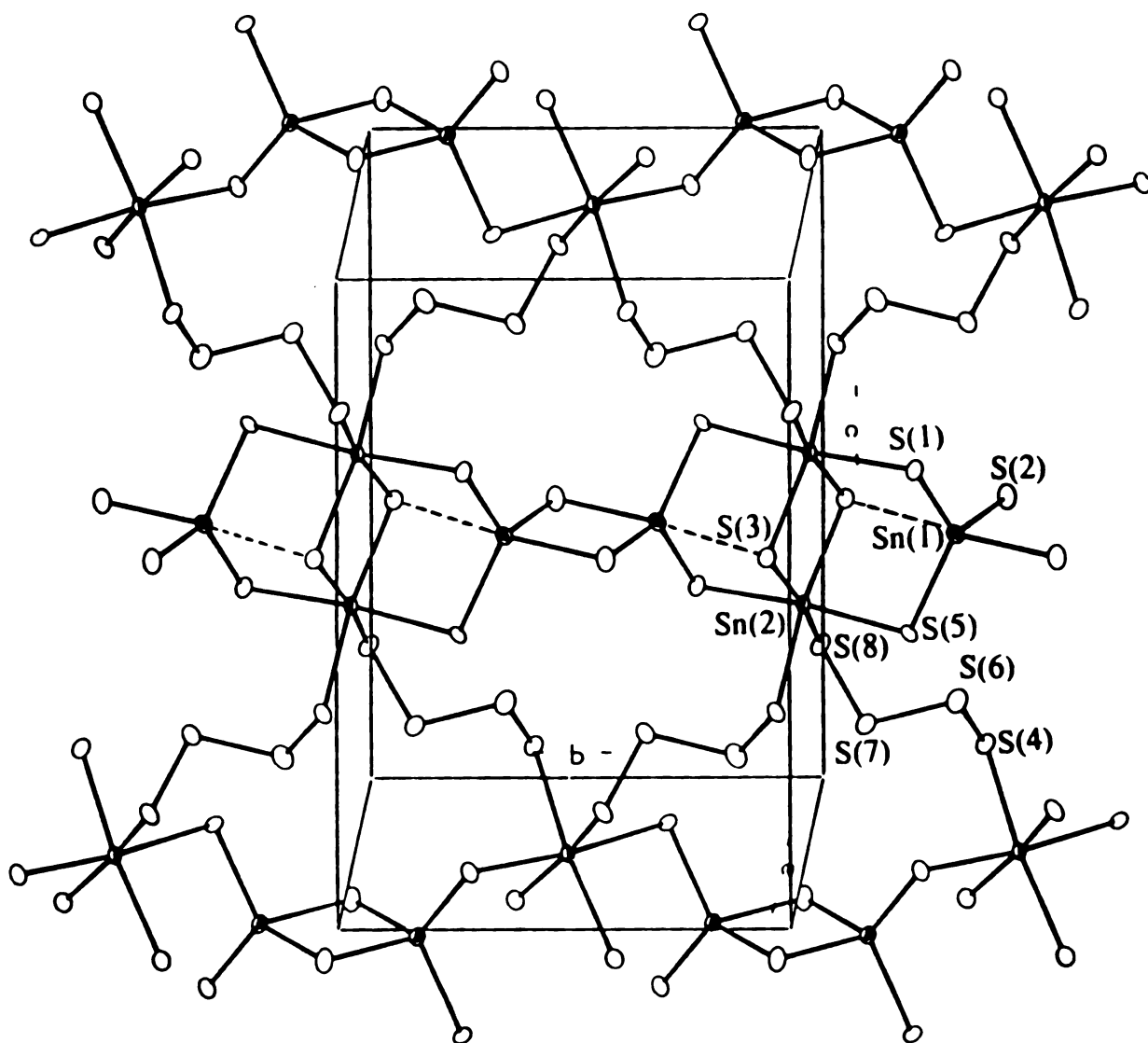


Figure 5-1: ORTEP representation and labeling scheme of the layered structure of $[\text{Sn}_2\text{S}_8]_n^{2n-}$ in (I). The dashed lines indicate the shortest nonbonding $\text{Sn} \cdots \text{S}$ contacts ($2.934(5) \text{ \AA}$).

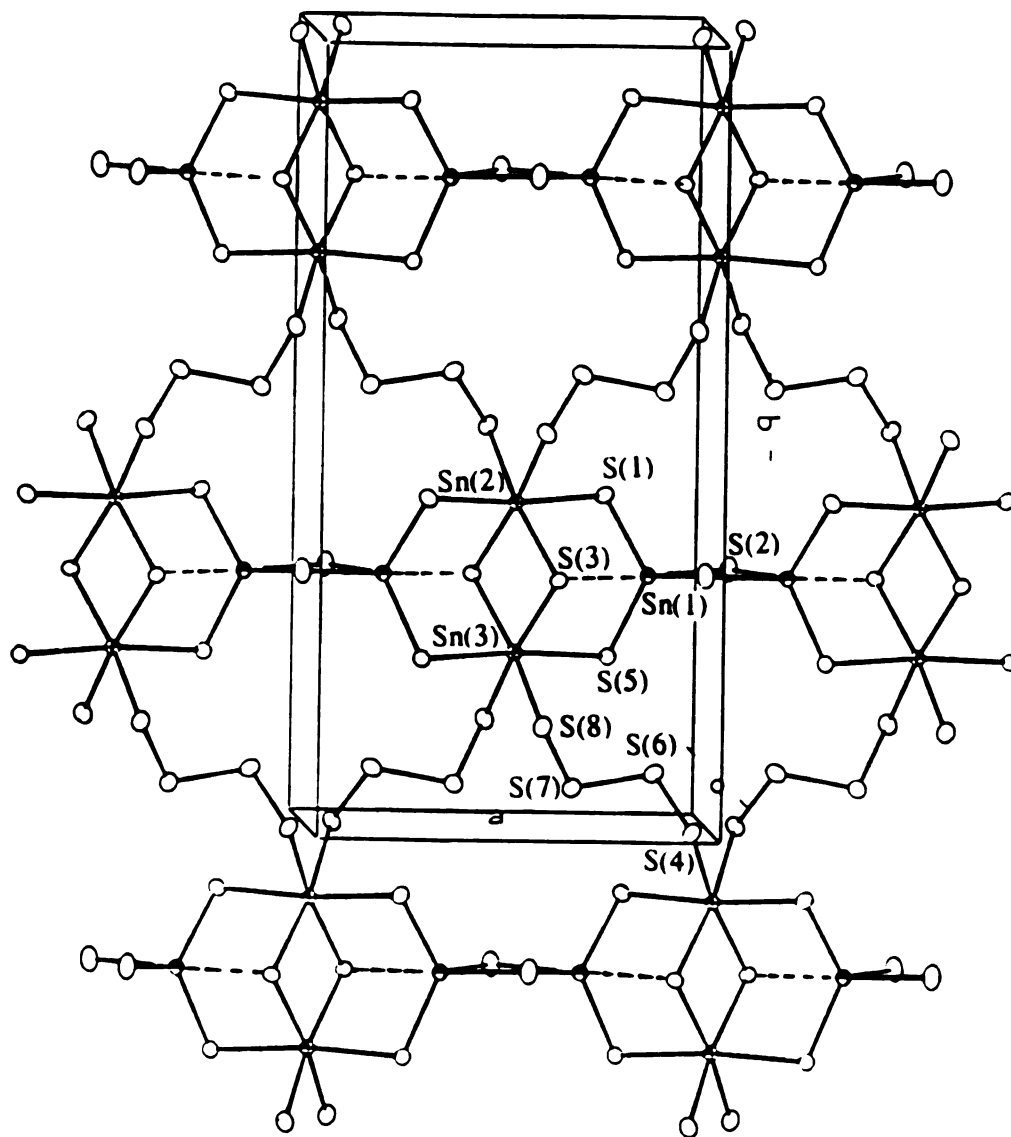


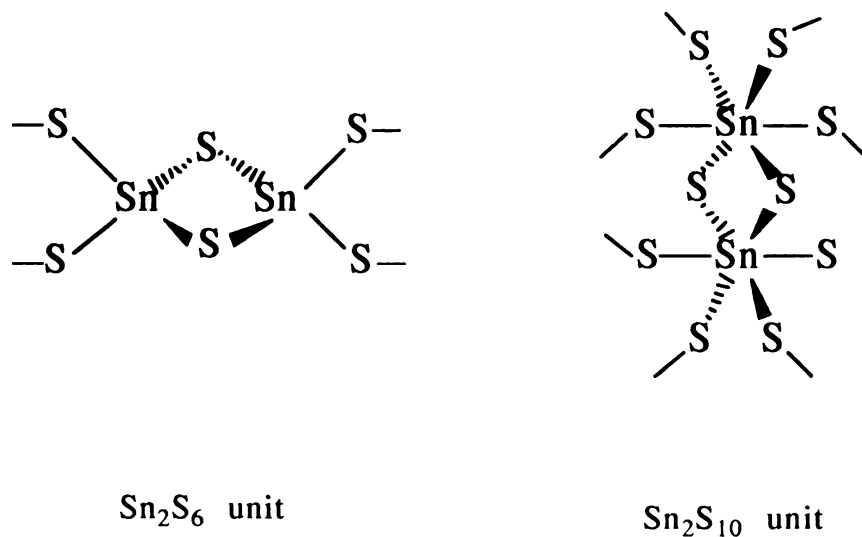
Figure 5-2: ORTEP representation and labeling scheme of the layered structure of $[\text{Sn}_2\text{S}_8]_n^{2n-}$ in (III). The dashed lines indicate the shortest nonbonding Sn...S contacts (2.875(3) Å).

Table 5-16. (cont'd)

	K_2Sn_2Sg (I)	α - Rb_2Sn_2Sg (II)	β - Rb_2Sn_2Sg (III)
S(1)-Sn(1)-S(2)	124.8(2)	126.04(9)	S(1)-Sn(1)-S(2) 122.3(1)
S(1)-Sn(1)-S(2)	98.2(2)	95.76(8)	S(1)-Sn(1)-S(2) 96.3(1)
S(1)-Sn(1)-S(5)	112.0(2)	112.55(8)	S(1)-Sn(1)-S(5) 112.5(1)
S(2)-Sn(1)-S(2)	89.9(2)	89.60(8)	S(2)-Sn(1)-S(2) 89.6(1)
S(2)-Sn(1)-S(5)	119.8(2)	119.12(9)	S(2)-Sn(1)-S(5) 122.9(1)
S(2)-Sn(1)-S(5)	101.0(2)	100.40(8)	S(2)-Sn(1)-S(5) 99.6(1)
S(1)-Sn(2)-S(3)	95.8(2)	96.43(8)	S(1)-Sn(2)-S(3) 95.8(1)
S(1)-Sn(2)-S(3)	88.5(2)	87.41(7)	S(1)-Sn(2)-S(3) 88.7(1)
S(1)-Sn(2)-S(4)	93.9(1)	93.68(8)	S(1)-Sn(2)-S(4) 94.1(1)
S(1)-Sn(2)-S(5)	173.3(2)	173.69(7)	S(1)-Sn(2)-S(1) 173.7(2)
			S(5)-Sn(3)-S(5) 174.0(2)
S(1)-Sn(2)-S(8)	80.9(1)	81.42(7)	S(1)-Sn(2)-S(4) 81.5(1)
S(3)-Sn(2)-S(3)	88.1(1)	87.5(7)	S(3)-Sn(2)-S(3) 88.0(1)
			S(3)-Sn(3)-S(3) 87.6(1)
S(3)-Sn(2)-S(4)	169.8(1)	169.21(7)	S(3)-Sn(2)-S(4) 169.95(9)
S(3)-Sn(2)-S(5)	88.1(1)	87.48(7)	S(3)-Sn(3)-S(5) 86.3(1)
S(3)-Sn(2)-S(8)	91.5(2)	91.74(7)	S(3)-Sn(2)-S(4) 90.8(1)
S(3)-Sn(2)-S(4)	88.9(2)	89.14(7)	S(3)-Sn(3)-S(8) 90.0(1)

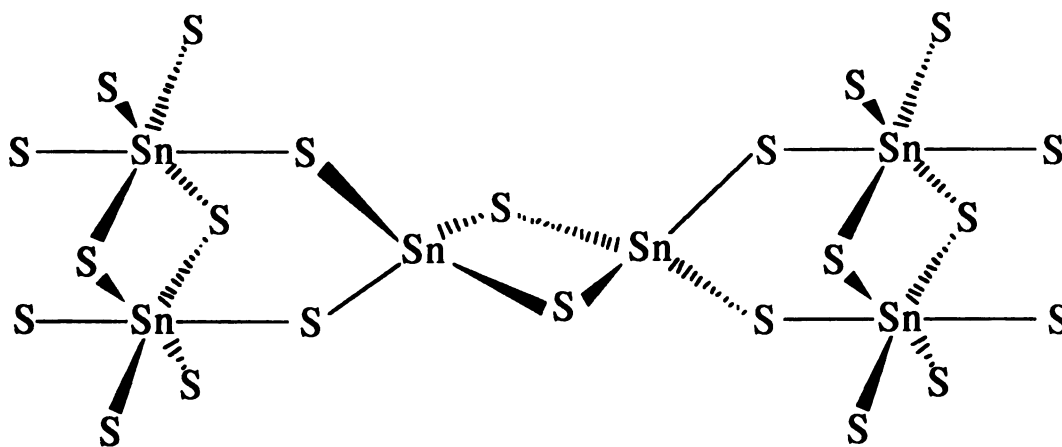
Table 5-16. (cont'd)

S(3)-Sn(2)-S(5)	97.0(2)	97.73(8)	S(3)-Sn(3)-S(5)	98.0(1)
S(3)-Sn(2)-S(8)	169.4(1)	168.6(6)	S(3)-Sn(3)-S(8)	169.1(1)
S(4)-Sn(2)-S(5)	82.5(1)	82.78(7)	S(5)-Sn(3)-S(8)	83.5(1)
S(4)-Sn(2)-S(8)	93.2(2)	93.49(8)	S(4)-Sn(2)-S(4)	92.1(2)
			S(8)-Sn(3)-S(8)	94.3(2)
S(5)-Sn(2)-S(8)	93.6(2)	93.54(8)	S(5)-Sn(3)-S(8)	92.4(1)
Sn(1)-S(1)-Sn(2)	99.2(2)	99.28(8)	Sn(1)-S(1)-Sn(2)	98.7(1)
Sn(1)-S(2)-Sn(1)	90.1(2)	90.40(8)	Sn(1)-S(2)-Sn(1)	90.2(1)
Sn(2)-S(3)-Sn(2)	91.9(1)	92.43(7)	Sn(2)-S(3)-Sn(3)	92.22(9)
Sn(2)-S(4)-S(6)	104.4(2)	105.1(1)	Sn(3)-S(8)-S(7)	104.5(2)
Sn(1)-S(5)-Sn(2)	99.0(2)	98.38(8)	Sn(1)-S(5)-Sn(3)	99.1(1)
S(4)-S(6)-S(7)	104.5(3)	105.5(1)	S(4)-S(6)-S(7)	105.8(2)
S(6)-S(7)-S(8)	105.0(3)	105.6(1)	S(6)-S(7)-S(8)	106.0(2)
Sn(2)-S(8)-S(7)	100.0(2)	100.4(1)	Sn(2)-S(4)-S(6)	100.9(2)



Scheme (A)

corresponding Sn-Sn vectors in the Sn_2S_6 units. The two types of dimeric units are linked together in an alternating fashion by sharing of the tetrahedral edges and the octahedral corners, as shown in scheme (B). This results in a set of parallel linear $[\text{Sn}_4\text{S}_{12}]_n$ chains



Scheme (B)

running in the direction of the b-axis in (I) and (II), and the a-axis in (III). The remaining four equatorial S atoms in the Sn_2S_{10} unit are actually the terminal atoms of S_4^{2-} ligands which link these $[\text{Sn}_4\text{S}_{12}]_n$ chains to form layers which are parallel to [101] crystallographic planes in (I) and (II), and parallel to [001] in (III).

The Sn_2S_6 unit is found in isolated form in $\text{Na}_4\text{Sn}_2\text{S}_6 \cdot 14\text{H}_2\text{O}$ ¹¹. However, in (I)~(III) the two averaged Sn(1)-S(2) distances are significantly different, 2.396(4) Å and 2.534(6) Å, while in $\text{Na}_4\text{Sn}_2\text{S}_6 \cdot 14\text{H}_2\text{O}$, the corresponding Sn-S distances are more equal at 2.452 Å and 2.448 Å respectively. A short contact between the distorted tetrahedral Sn atom and the bridging S(3) atom of the Sn_2S_2 core in the Sn_2S_{10} unit, as shown by the dashed lines in Figures 5-1 and 5-2, is responsible for the asymmetry of the Sn_2S_2 core in the Sn_2S_6 unit. This partial Sn...S bond formation, 2.934(5) Å, 2.865(2) Å and 2.875(3) Å in (I)~(III) respectively, causes the lengthening of Sn-S bond opposite to the Sn...S short contact. The averaged Sn(1)-S(1) and Sn(1)-S(5) distances are 2.396(4) Å and 2.390(6) Å which are expectedly slightly longer than the Sn to terminal sulfide distances in $\text{Na}_4\text{Sn}_2\text{S}_6 \cdot 14\text{H}_2\text{O}$, 2.325 Å and 2.338 Å. This is due to the bridging nature of S(1) and S(5) linking Sn(1) and Sn(2). Bond angles in the Sn_2S_6 unit are similar to those in $\text{Na}_4\text{Sn}_2\text{S}_6 \cdot 14\text{H}_2\text{O}$. The S(2)-Sn(1)-S(2) angles are close to 90 degrees. If the Sn...S short contact is considered to be a bond, the coordination environment around Sn(1) can be viewed as a distorted trigonal bipyramid with an elongated axial Sn-S bond. One of the bridging sulfurs opposite to the Sn...S short contact in the Sn_2S_2 core forms the other axial Sn-S bond in the trigonal bipyramid. The S(axial)-Sn(1)-S(axial) angles in (I)~(III) are 173.9(1)°, 174.9(1)° and

176.1(1)° respectively, while the S(equatorial)-Sn(1)-S(equatorial) angles range from 112.0(2)° to 126.04(9)°.

The average Sn-S distance, 2.57(2) Å in the Sn₂S₁₀ unit is very close to 2.571 Å found in K₂SnS₃·2H₂O¹³, which is in the range of typical Sn-S distances in SnS₆ octahedra. The S-Sn-S angles are close to those of an ideal octahedron. See Table 5-16.

The tetrasulfides linking the Sn₂S₁₀ units possess helical conformation. The dihedral angles between the two outer S-S bonds are similar at 109.4(3)°, 110.4(1)° and 109.8(2)° for (I)~(III) respectively. The S-S distances in the tetrasulfide ligands are in the range of typical S-S distances. See Table 5-16. The averaged central S-S bond distance, 2.070(1) Å, is slightly longer than the averaged terminal S-S bond distance, 2.048(5) Å, while in the free tetrasulfide anion of BaS₄³¹, no significant variation among the S-S distances is observed. The average S-S bond distance in BaS₄ is 2.069(2) Å.

The charge compensating cations are intercalated between layers, as shown in Figure 5-3A and 5-3B. There are two distinct K⁺ or Rb⁺ cations in (I)~(III). In (I) and (II), both K⁺ and Rb⁺ have similar coordination environments. There are two distinct K⁺ or Rb⁺ cations which are surrounded by 7 and 8 S atoms respectively. The coordination environments of the two distinct Rb⁺ cations in (III) is different from those in (I) and (II). These Rb⁺ cations are surrounded by 9 and 6 S atoms respectively. The average K-S distance for (I) is 3.34(11) Å, while the average Rb-S distances are 3.48(15) Å for (II) and 3.48(17) Å for (III).

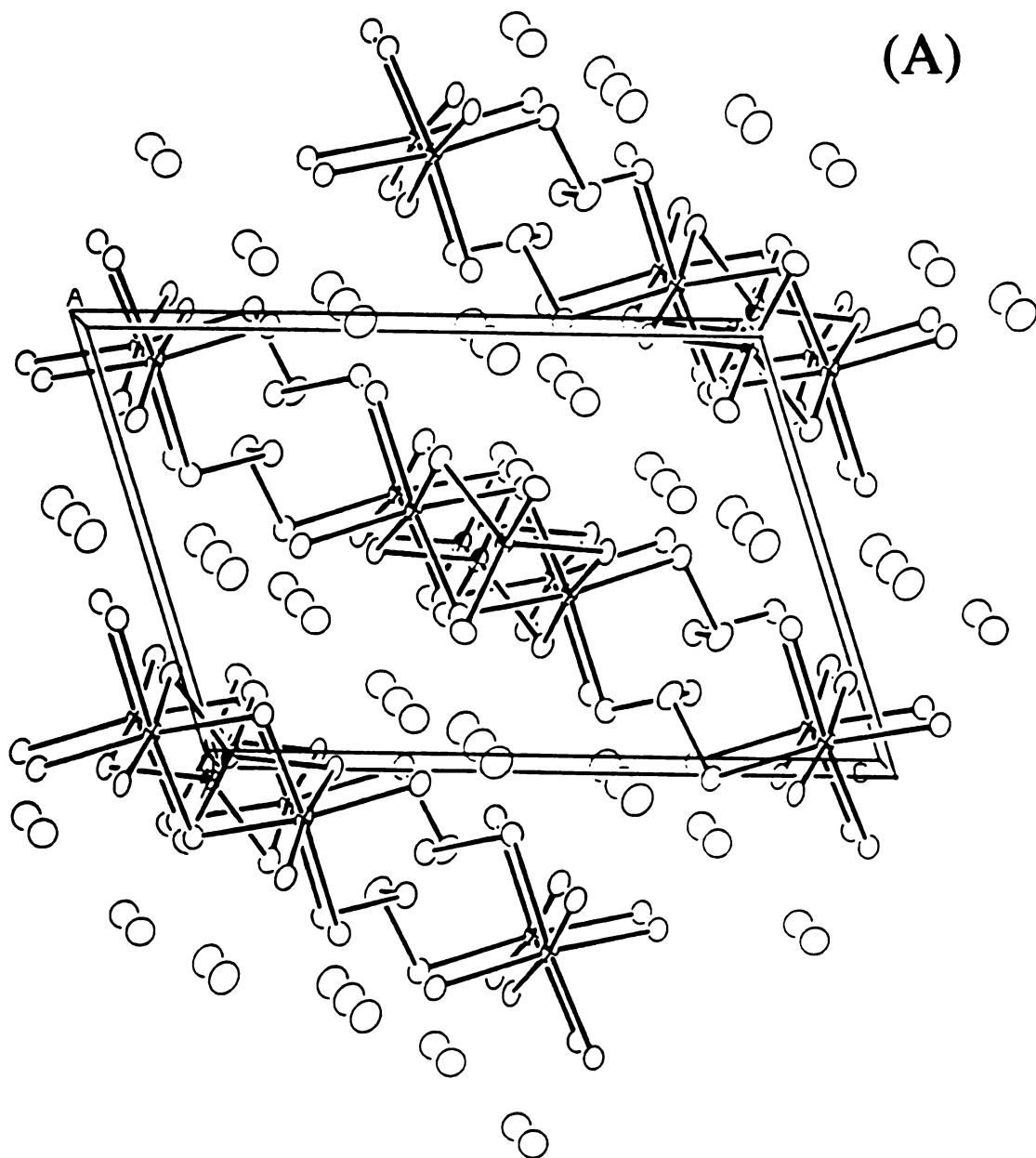
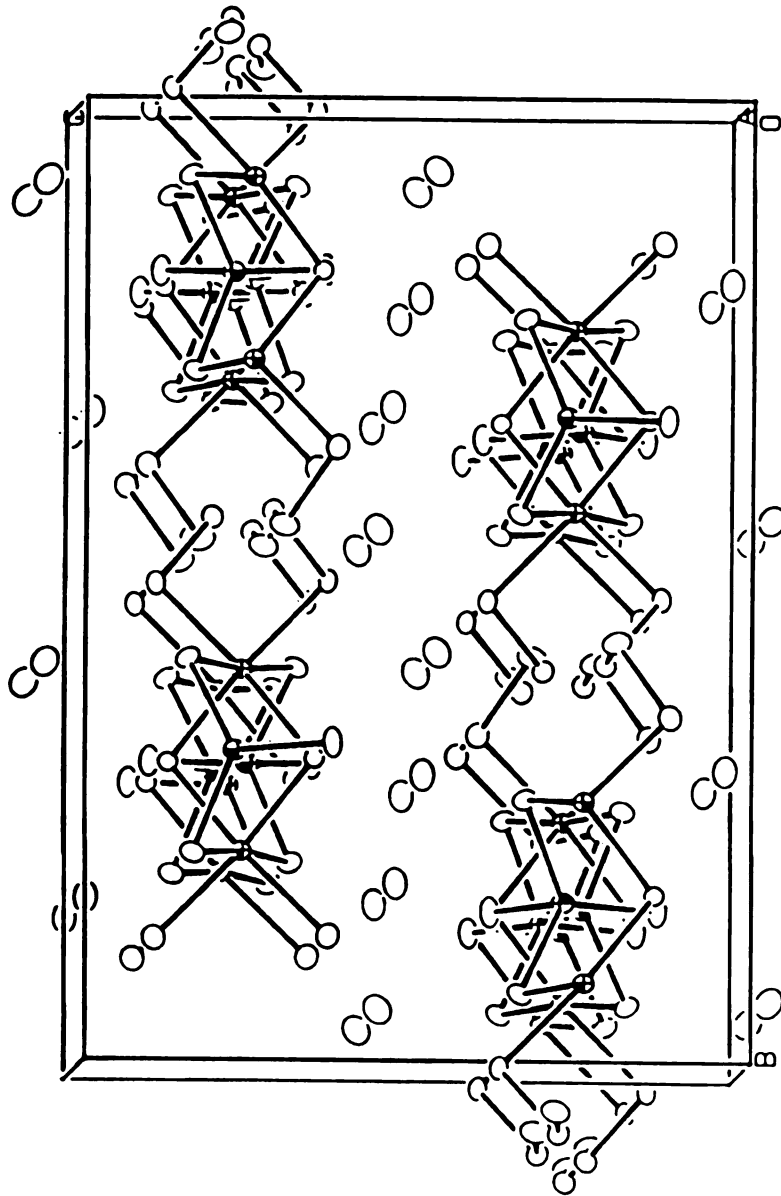


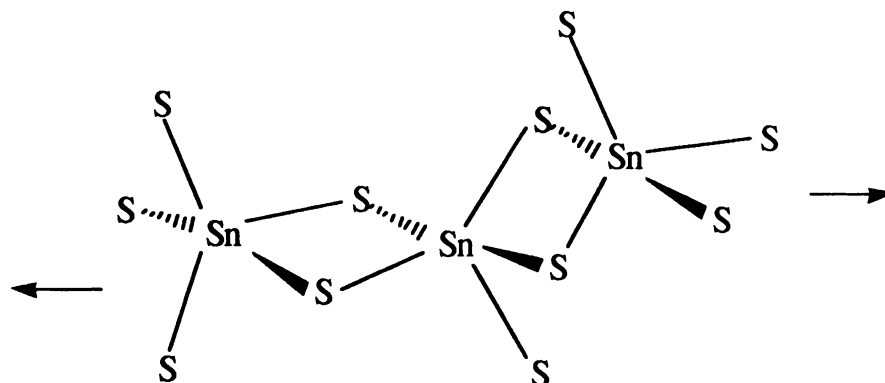
Figure 5-3: Unit cells of (A) $\text{K}_2\text{Sn}_2\text{S}_8$ or $\alpha\text{-Rb}_2\text{Sn}_2\text{S}_8$ (B) $\beta\text{-Rb}_2\text{Sn}_2\text{S}_8$.
Cations located between layers. View down the b-axis.

(B)



The Structure of $\text{K}_2\text{Sn}_2\text{S}_5$

(IV) has a three-dimensional structure which is shown in Figure 5-4. Selected bond distances and angles are given in Table 5-17. This compound is isostructural to the Tl^+ salt, $\text{Tl}_2\text{Sn}_2\text{S}_5$ ³², which has been synthesized by heating a stoichiometric mixture of Tl, Sn and S elements at 300°C. The anionic structure of (IV) and $\text{Tl}_2\text{Sn}_2\text{S}_5$ and the relative positions of Tl^+ and K^+ to S atoms in the anion framework are approximately the same because of the similarity of the ionic radii of Tl^+ and K^+ . The bond distances and angles are almost the same as those in $\text{Tl}_2\text{Sn}_2\text{S}_5$. While this manuscript was in preparation, we learned that (IV) was synthesized by heating the stoichiometric mixture of $\text{K}_2\text{S}/\text{Sn}/\text{S}$ at 1070K²⁹. (IV)'s selenium analog, $\text{K}_2\text{Sn}_2\text{Se}_5$ ²⁹, $\text{Rb}_2\text{Sn}_2\text{Se}_5$ ³³ are also known and have been prepared by high temperature solid state reaction and methanothermal reaction respectively. This suggests that this structure type has considerable thermodynamic stability. Unlike (I)~(III), which feature both four-coordinate and six-coordinate Sn atoms, (IV) features only five coordinate Sn centers. The anionic framework in (IV) has SnS_5 distorted trigonal bipyramids as building blocks which share two of their common edges (formed by an axial S atom and an equatorial S atom) with one another to form $[\text{SnS}_3]_n^{2n-}$ chains (see scheme (C))



Scheme (C)

running in the direction of $[110]$ and $[1-10]$ alternately. The $[\text{SnS}_3]_n^{2-}$ chains are cross-linked by sharing the remaining equatorial S atoms of the trigonal bipyramids to form an extended three-dimensional framework. The S(axial)-Sn-S(axial) angle is $169.4(1)^\circ$; the S(axial)-Sn-S(equatorial) angles range from $83.9(1)^\circ$ to $100.3(1)^\circ$ and the S(equatorial)-Sn-S(equatorial) angles are $112.33(8)^\circ$, $118.8(1)^\circ$ and $128.0(1)^\circ$. The average Sn-S distance is $2.49(9)$ Å. The $(\text{Sn}_2\text{S}_5)^{2-}$ framework features one-dimensional tunnels running parallel to the b-axis. These tunnels contain the K^+ atoms. The K-S distances range from $3.090(5)$ Å to $3.640(5)$ Å with the average of $3.4(2)$ Å and coordination number of 8.

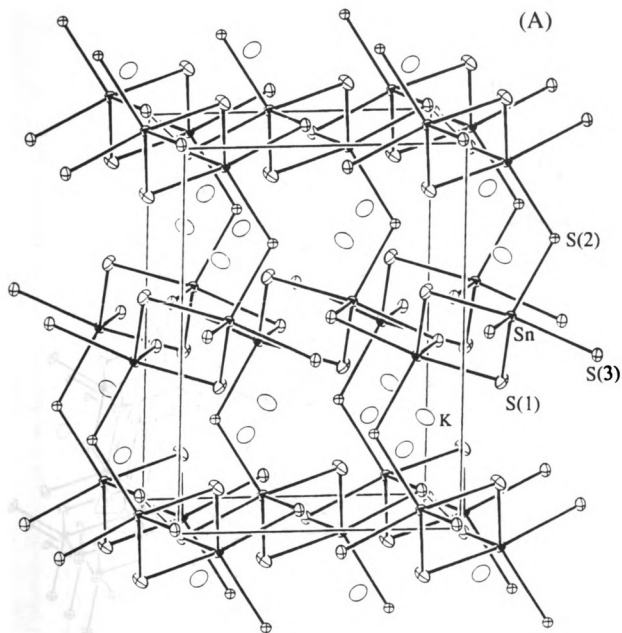


Figure 5-4: Structure and labeling scheme of $\text{K}_2\text{Sn}_2\text{S}_5$: (A) View down the a-axis. (B) View down the b-axis.

(B)

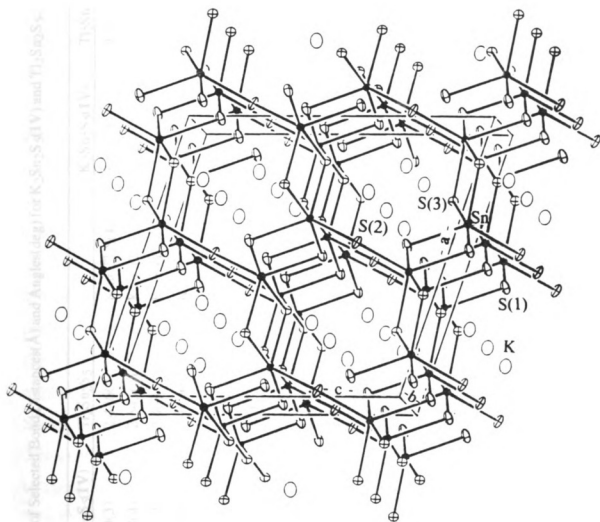


Table 5-17. Comparison of Selected Bond Distances(Å) and Angles(deg) for $K_2Sn_2S_5$ (IV) and $Tl_2Sn_2S_5$.

	$K_2Sn_2S_5$ (IV)	$Tl_2Sn_2S_5$	$K_2Sn_2S_5$ (IV)	$Tl_2Sn_2S_5$
Sn-S(1)	2.430(3)	2.446(4)	K or Tl-S(1)	3.711(4)
Sn-S(1)	2.550(4)	2.543(4)	K or Tl-S(2)	3.615(2)
Sn-S(2)	2.468(2)	2.463(3)	K or Tl-S(2)	3.586(4)
Sn-S(3)	2.398(3)	2.409(4)	K or Tl-S(3)	3.269(4)
Sn-S(3)	2.648(3)	2.623(4)	K or Tl-S(3)	3.339(4)
K or Tl-S(1)	3.090(5)	3.073(4)	K or Tl-S(3)	3.160(4)
K or Tl-S(1)	3.337(5)	3.269(4)		
mean(Sn-S)= 2.50(10)Å, mean(K-S)= 3.39(21)Å				
	$K_2Sn_2S_5$ (IV)	$Tl_2Sn_2S_5$	$K_2Sn_2S_5$ (IV)	$Tl_2Sn_2S_5$
S(1)-Sn-S(1)	83.9(1)	84.1(1)	S(2)-Sn-S(3)	112.5(1)
S(1)-Sn-S(2)	128.0(1)	126.2(1)	S(2)-Sn-S(3)	86.3(1)
S(1)-Sn-S(3)	118.8(1)	120.2(1)	S(3)-Sn-S(3)	88.3(1)
S(1)-Sn-S(3)	85.5(1)	85.1(1)	Sn-S(1)-Sn	95.9(1)
S(1)-Sn-S(2)	100.3(1)	102.0(1)	Sn-S(2)-Sn	117.6(1)
S(1)-Sn-S(3)	96.1(1)	95.1(1)	Sn-S(3)-Sn	91.7(1)
S(1)-Sn-S(3)	169.4(1)	169.0(1)		

The Structure of $\text{Cs}_2\text{Sn}_2\text{S}_6$ and Its Relationship to $\text{K}_2\text{Sn}_2\text{S}_5$

In view of the snug-fit of the K^+ and Tl^+ ions in the $[\text{Sn}_2\text{S}_5]^{2-}$ framework we reasoned that Cs^+ will be too large for its tunnels and may direct the system to a different structure type. Indeed the structure of (V) is different from but closely related to (IV). Its chemical formula can be expressed as $\text{Cs}_2\text{Sn}_2\text{S}_4(\text{S}_2)$. The two-dimensional structure of (V) is shown in Figure 5-5. Selected bond distances and angles are given in Table 5-18. The $[\text{Sn}_2\text{S}_4(\text{S}_2)]^{2-}$ framework contains distorted SnS_5 trigonal bipyramids as building blocks. Similar $[\text{SnS}_3]_n^{2n-}$ chains as found in (IV) formed by trigonal bipyramids sharing two common edges (both contain an axial S atom an equatorial S atom). The $[\text{SnS}_3]_n^{2n-}$ chains in (V) are parallel to the crystallographic a-axis and are cross-linked via S-S bonds formed by connecting the remaining equatorial S atoms of the SnS_5 trigonal bipyramids. This gives rise to a two-dimensional structure whose slabs are perforated by large holes. The holes define 14-member Sn-S rings. In (V), the S(axial)-Sn-S(axial) angle is $173.7(2)^\circ$; the S(axial)-Sn-S(equatorial) angles range from $82.4(2)^\circ$ to $96.1(2)^\circ$ and the three S(equatorial)-Sn-S(equatorial) angles are $110.6(2)^\circ$, $122.8(2)^\circ$ and $126.0(2)^\circ$ respectively. The average Sn-S distance in the SnS_5 trigonal bipyramid of (V) is similar to those in (IV), $2.49(5)\text{\AA}$. The Cs^+ cations are located between the layers. The $\text{Cs}\cdots\text{S}$ distances range from $3.500(5)\text{\AA}$ to $4.042(5)\text{\AA}$ with an average distance of $3.66(17)\text{\AA}$. The coordination number around Cs^+ is 8. The radius of Cs^+ is thus $\sim 0.4\text{\AA}$ larger than that of K^+ , which accounts for the fact that the $[\text{Sn}_2\text{S}_5]^{2-}$ framework is unsuitably small to fit the same number of Cs^+ cations. In order to accommodate Cs^+ , the anionic framework responds by substituting the bridging S^{2-} ligands with S_2^{2-} ligands, thus

increasing the size of the cavities. At the same time, the two sets of parallel $[\text{SnS}_2]^n$ chains which in (IV) oriented along the $[110]$ and $[1-10]$ directions forming a criss-cross pattern, now line up in the same direction, $[100]$ in (V). This is shown in Figure 5-6. In this way, the three-dimensional framework of (IV) breaks up to form a two-dimensional structure which is more flexible especially in the direction perpendicular to the layers. We note that the structure of $\text{Na}_4\text{Sn}_3\text{S}_8$ ¹⁴, whose chemical formula can be expressed as $\text{Na}_2\text{Sn}_2\text{S}_4(\text{Na}_2\text{SnS}_4)$, is somewhat related to that of (IV). This is done by replacing the bridging S^{2-} ligands in (IV) by tetrahedral $[\text{SnS}_4]^{4-}$ ligands. However using $[\text{SnS}_4]^{4-}$ as bridging ligands increases the size of those tunnels even more, which accommodates two more cations and the terminal sulfides of $[\text{SnS}_4]^{4-}$.

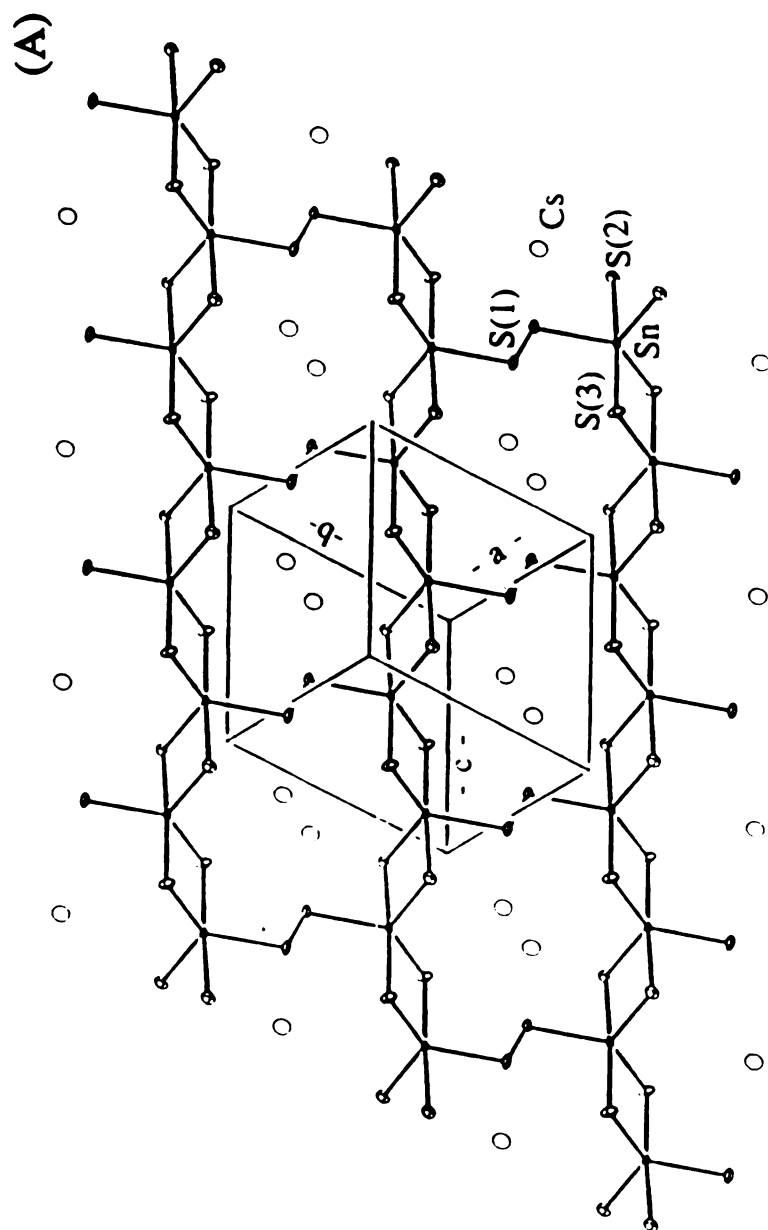
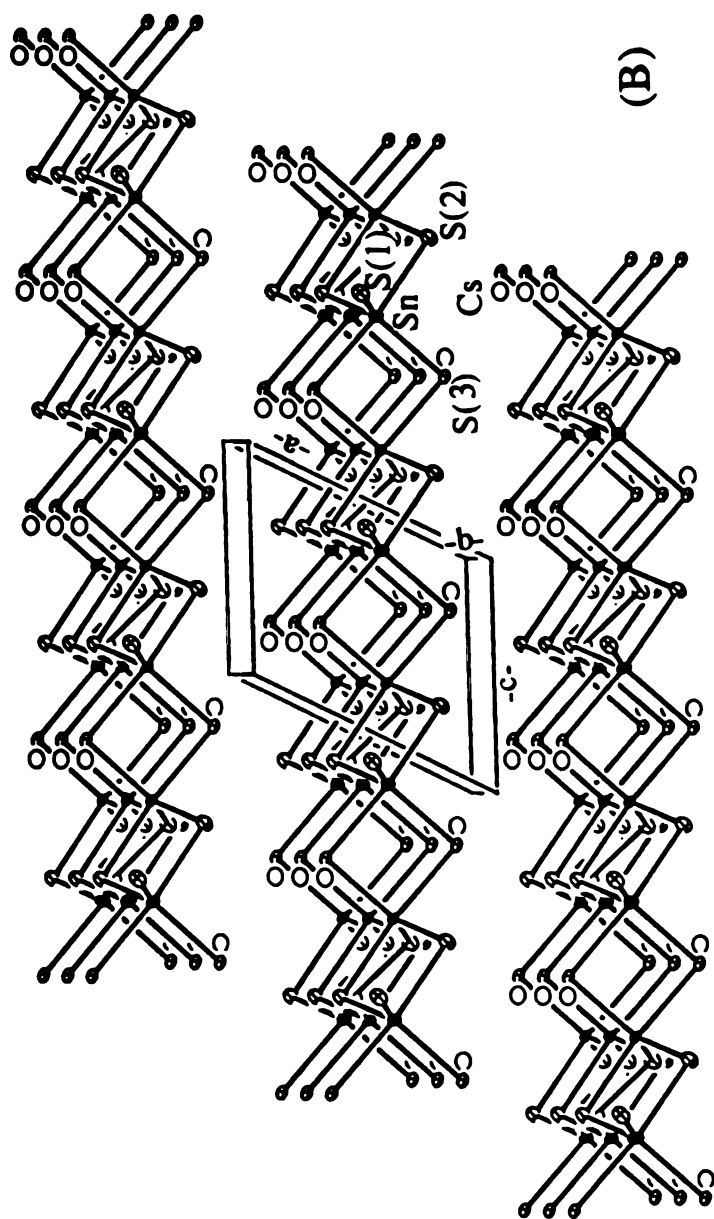
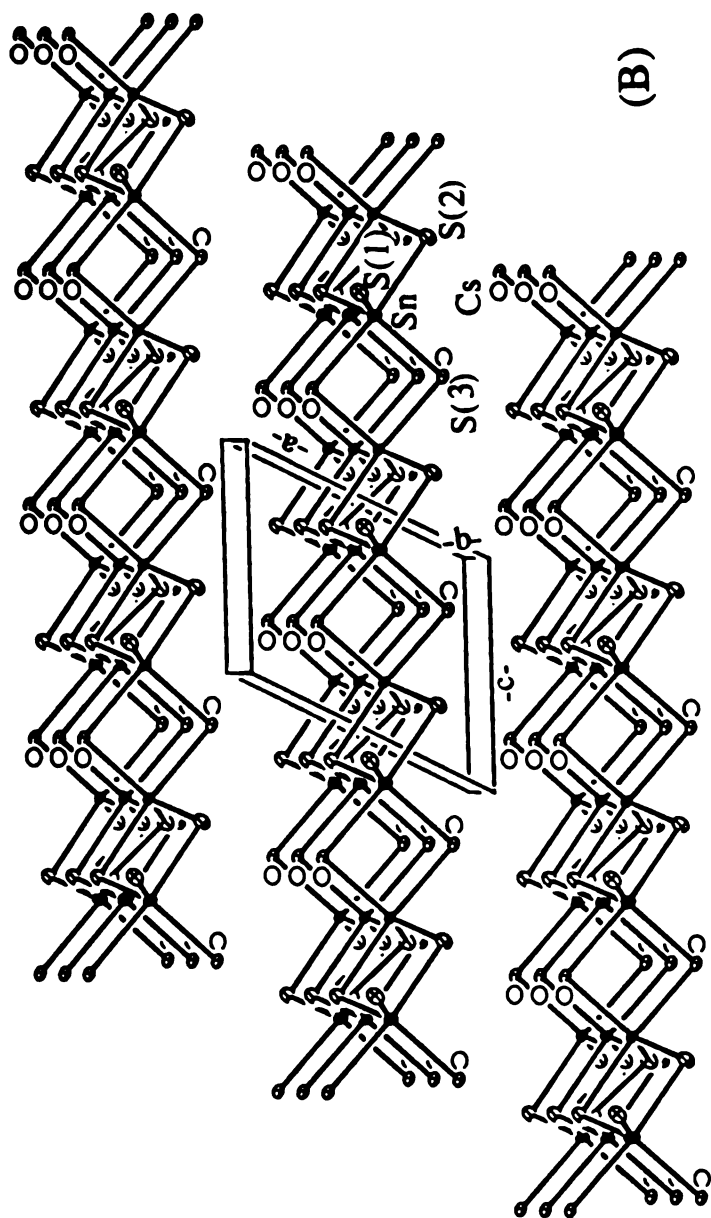


Figure 5-5: (A) ORTEP representation and labeling scheme of $\text{Cs}_2\text{Sn}_2\text{S}_6$ and packing diagram of $\text{Cs}_2\text{Sn}_2\text{S}_6$: (B) View down the b -axis. (C) View down the c -axis.





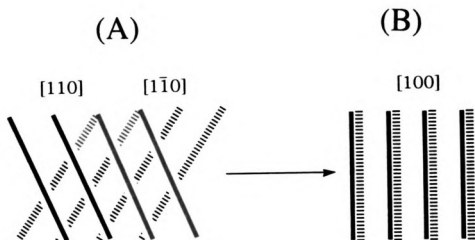


Figure 5-6: Schematic comparison of the orientations of the $(\text{SnS}_2)_n$ chains in $\text{K}_2\text{Sn}_2\text{S}_5$ and $\text{Cs}_2\text{Sn}_2\text{S}_6$. Black solid lines represent the $(\text{SnS}_2)_n$ chains lying above, while the broken lines represent $(\text{SnS}_2)_n$ chains lying below the plane of the paper. (A) shows two parallel sets of $(\text{SnS}_2)_n$ chains in $\text{K}_2\text{Sn}_2\text{S}_5$ oriented along the $[110]$ and $[1\bar{1}0]$ directions, respectively, and linked by S^{2-} . (B) shows parallel sets of $(\text{SnS}_2)_n$ chains in $\text{Cs}_2\text{Sn}_2\text{S}_6$ oriented along the $[100]$ direction and linked by S^{2-} .

Table 5-18. Selected Bond Distances (Å) and Angles (deg) for Cs₂Sn₂S₆ (V) with Standard Deviations in Parentheses

Sn-S(1)	2.474(5)	Cs-S(1)	3.767(5)
Sn-S(2)	2.407(5)	Cs-S(1)	3.645(6)
Sn-S(2)	2.601(5)	Cs-S(2)	3.649(5)
Sn-S(3)	2.412(5)	Cs-S(2)	3.571(6)
Sn-S(3)	2.551(5)	Cs-S(2)	4.042(5)
mean(Sn-S)	2.49(9)	Cs-S(3)	3.527(5)
S(1)-S(1)	2.10(1)	Cs-S(3)	3.500(5)
Cs-S(1)	3.579(5)	mean(Cs-S)	3.66(18)

S(1)-Sn-S(2)	110.6(2)	S(2)-Sn-S(3)	89.6(2)
S(1)-Sn-S(2)	82.4(2)	S(2)-Sn-S(3)	173.7(2)
S(1)-Sn-S(3)	126.0(2)	S(3)-Sn-S(3)	86.9(2)
S(1)-Sn-S(3)	95.5(2)	Sn-S(1)-S(1)	103.9(3)
S(2)-Sn-S(2)	90.2(2)	Sn-S(2)-Sn	89.8(2)
S(2)-Sn-S(3)	122.8(2)	Sn-S(3)-Sn	93.1(2)
S(2)-Sn-S(3)	96.1(2)		

The Structure of $\text{Cs}_2\text{SnS}_{14}$

(VI) is composed of discrete $[\text{SnS}_{14}]^{2-}$ anions and two Cs^+ cations. The structure of a single $[\text{SnS}_{14}]^{2-}$ anion and the packing diagram of the unit cell are shown in Figure 5-7 and Figure 5-8 respectively. The anion features a Sn^{4+} center octahedrally coordinated by two S_4^{2-} and one S_6^{2-} ligands. The tetraethylammonium salt of the anion has been reported to occur cocrystallized with $[\text{Sn}(\text{S}_4)_3]^{2-}$ in a 3:2 ratio⁹. Thus the SnS_6 ring was not well refined. Crystals of (VI) show no such disorder. Interestingly, analogous *molecular* compounds were not isolated from the $\text{Sn}/\text{K}_2\text{S}_x$ and $\text{Sn}/\text{Rb}_2\text{S}_x$ systems perhaps due to high solubility in the solvents used during isolation. A related selenium analog, $(\text{Ph}_4\text{P})_2\text{Sn}(\text{Se}_4)_3$ ^{34, 35}, is known. So far no selenium compound of (VI) has been prepared. Another tetravalent metal center chelated with polysulfides octahedrally is $(\text{NH}_4)_2\text{Pt}(\text{S}_5)_3 \cdot 2\text{H}_2\text{O}$ ^{36, 37}. The tin analog of this compound has not been reported to date either.

Table 5-19 lists the selected bond distances and angles of (VI). The average Sn-S distance in (VI) is 2.575(13) Å, which is typical for octahedrally coordinated Sn^{4+} centers¹⁵. The S-S bond distances are in the normal range from 2.038(8) Å to 2.074(9) Å, compared to the unreasonably 1.84(1) Å obtained before from the disorder data. The S-Sn-S angles are in the range between 80.7(2)° to 101.6(2)° which significantly deviate from 90°, the ideal octahedral geometry. This is probably due to the difference of the Sn-polysulfide ring size. The two five-membered SnS_4 rings adopt an envelope shape with S(8) and S(12) sitting outside the SnS_3 planes respectively. In the seven-membered SnS_6 ring, Sn, S(1), S(3), S(4)

and S(6) are lying in the same plane with S(2) and S(5) sitting above or below the plane. A similar conformation is also observed in a seven-membered HgS_6 ring of $[\text{Hg}(\text{S}_6)_2]^{2-}$,³⁸. The two Cs^+ cations are surrounded by S atoms with coordination number of 6 for Cs(1) and 7 for Cs(2). The average Cs...S distance is 3.65 Å which is about 0.31 Å longer than the average K...S distance in (I). Interestingly, (VI) and (I) are actually synthesized under similar conditions. The size of cations seems to have a dramatic effect on the formation of anions. The layered structure of the $[\text{Sn}_2\text{S}_4(\text{S}_4)]^{2-}$ framework in (I) can not accommodate large Cs^+ cations. By breaking apart into discrete *molecular* anions like (VI), enough room is created for Cs^+ .

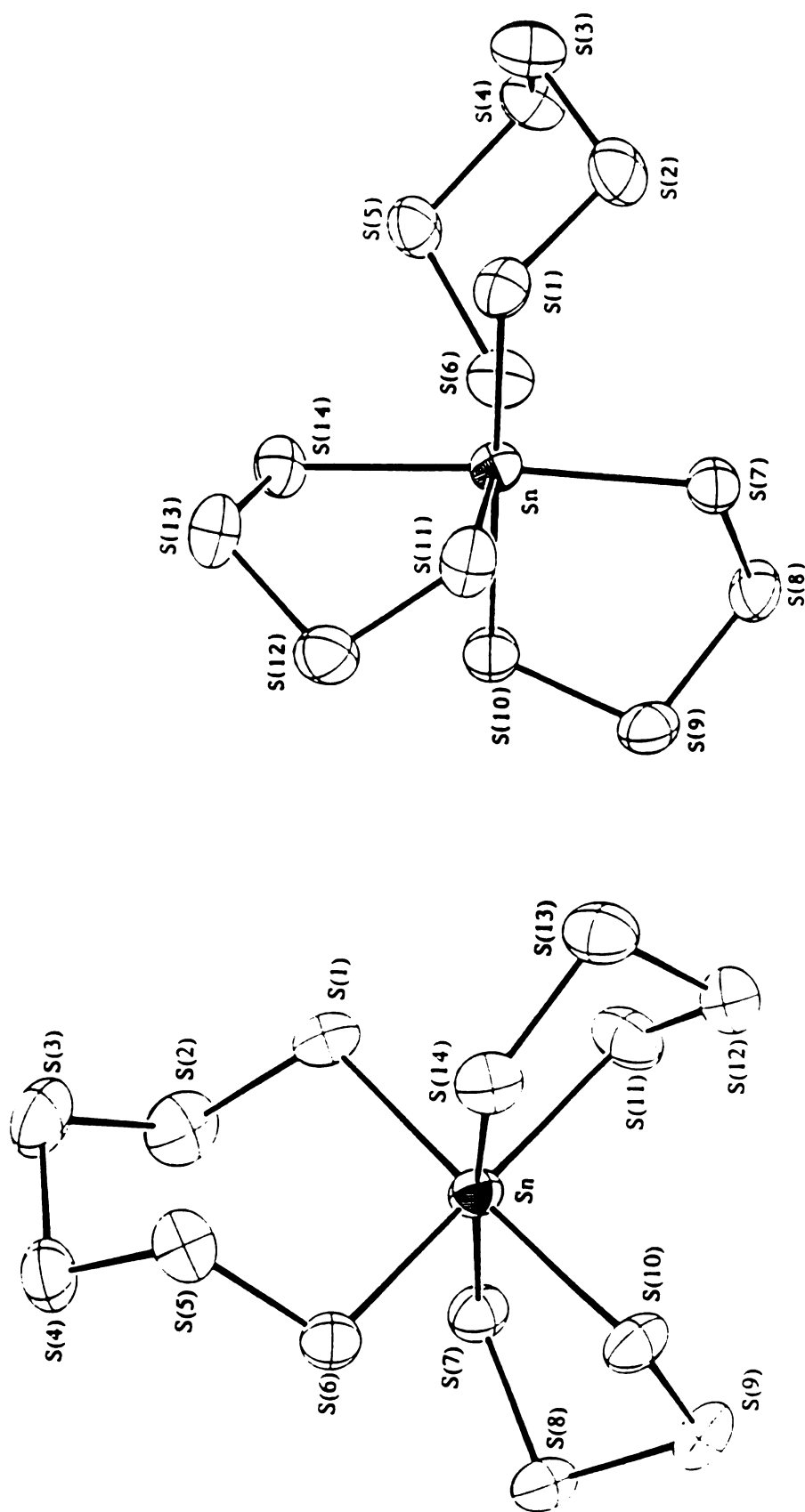


Figure 5-7: Two views and labeling scheme of the $[\text{Sn}(\text{S}_4)_2(\text{S}_6)]^{2-}$ anion.

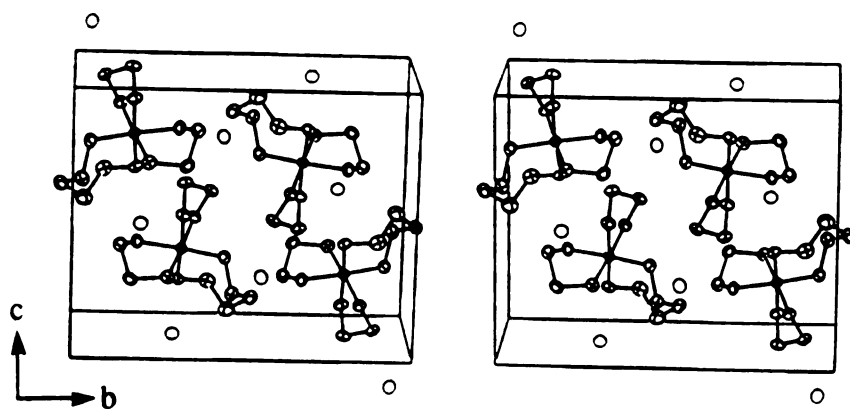


Figure 5-8: The unit cell of $\text{Cs}_2\text{SnS}_{14}$.

Table 5-19. Selected Bond Distances (Å) and Angles (deg) for Cs₂SnS₁₄ (VI) with Standard Deviations in Parentheses

Sn-S(1)	2.555(4)	S(12)-S(13)	2.067(8)
Sn-S(6)	2.580(5)	S(13)-S(14)	2.056(7)
Sn-S(7)	2.576(5)	mean(S-S)	2.054(12)
Sn-S(10)	2.578(4)	Cs(1)-S(1)	3.560(5)
Sn-S(11)	2.567(5)	Cs(1)-S(7)	3.672(5)
Sn-S(14)	2.594(5)	Cs(1)-S(9)	3.715(6)
mean(Sn-S)	2.575(13)	Cs(1)-S(10)	3.664(5)
S(1)-S(2)	2.043(8)	Cs(1)-S(11)	3.577(6)
S(2)-S(3)	2.074(9)	Cs(1)-S(14)	3.739(5)
S(3)-S(4)	2.038(8)	Cs(2)-S(7)	3.568(5)
S(4)-S(5)	2.041(7)	Cs(2)-S(9)	3.587(5)
S(5)-S(6)	2.050(7)	Cs(2)-S(10)	3.574(5)
S(7)-S(8)	2.060(6)	Cs(2)-S(11)	3.752(5)
S(8)-S(9)	2.067(7)	Cs(2)-S(12)	3.665(5)
S(9)-S(10)	2.058(7)	Cs(2)-S(13)	3.618(5)
S(11)-S(12)	2.041(8)	mean(Cs-S)	3.64(7)

S(1)-Sn-S(6)	101.6(2)	Sn-S(1)-S(2)	112.2(2)
S(1)-Sn-S(7)	88.5(2)	Sn-S(6)-S(5)	110.1(2)
S(1)-Sn-S(10)	177.0(2)	Sn-S(7)-S(8)	101.7(2)
S(1)-Sn-S(11)	80.7(2)	Sn-S(10)-S(9)	103.9(2)
S(1)-Sn-S(14)	96.3(2)	Sn-S(11)-S(12)	100.7(3)
S(6)-Sn-S(7)	96.3(2)	Sn-S(14)-S(13)	105.5(3)
S(6)-Sn-S(10)	81.4(2)	S(1)-S(2)-S(3)	107.7(3)
S(6)-Sn-S(11)	173.5(2)	S(2)-S(3)-S(4)	106.5(3)
S(6)-Sn-S(14)	83.9(2)	S(3)-S(4)-S(5)	105.1(3)
S(7)-Sn-S(10)	90.7(2)	S(4)-S(5)-S(6)	106.0(3)
S(7)-Sn-S(11)	89.9(2)	S(7)-S(8)-S(9)	102.0(3)
S(7)-Sn-S(14)	175.1(1)	S(8)-S(9)-S(10)	101.7(3)
S(10)-Sn-S(11)	96.4(2)	S(11)-S(12)-S(13)	101.9(3)
S(10)-Sn-S(14)	84.5(2)	S(12)-S(13)-S(14)	103.5(3)
S(11)-Sn-S(14)	89.8(2)		

The Structure of K_2SnTe_5

Compound (VII) is a one-dimensional structure containing square planar $[\text{Te}_5]^{6-}$ units linked by tetrahedrally coordinated Sn^{4+} ions, as shown in Figure 5-9. There are two distinct Te atoms in the $[\text{Te}_5]^{6-}$ unit. The central Te atom has the formal oxidation state of 2+ while the oxidation state of the terminal Te atoms is 2-. The crystal structures of (VII) and Rb_2SnTe_5 were determined by Schäfer *et al.* earlier with a noncentrosymmetric space group ($I4cm$)^{39,40} Upon reexamining the structures, we observed a center of inversion at the central Te atom of the $[\text{Te}_5]^{6-}$ unit. This inversion center was not identified by these authors who used the space group $I4cm$ to refine the structure. We recollected X-ray diffraction data and refined the structure (VII) with the corresponding centrosymmetric space group ($I4/mcm$). The structure based on the centrosymmetric space group was well refined with much improved standard deviations. The recently reported Tl_2SnTe_5 ⁴¹ and Tl_2GeTe_5 ⁴² were found to be isomorphous to (VII).

Comparison of selected bond distances and angles between (VII) and Tl_2SnTe_5 are given in Table 5-20. There is no significant difference between these two structures.

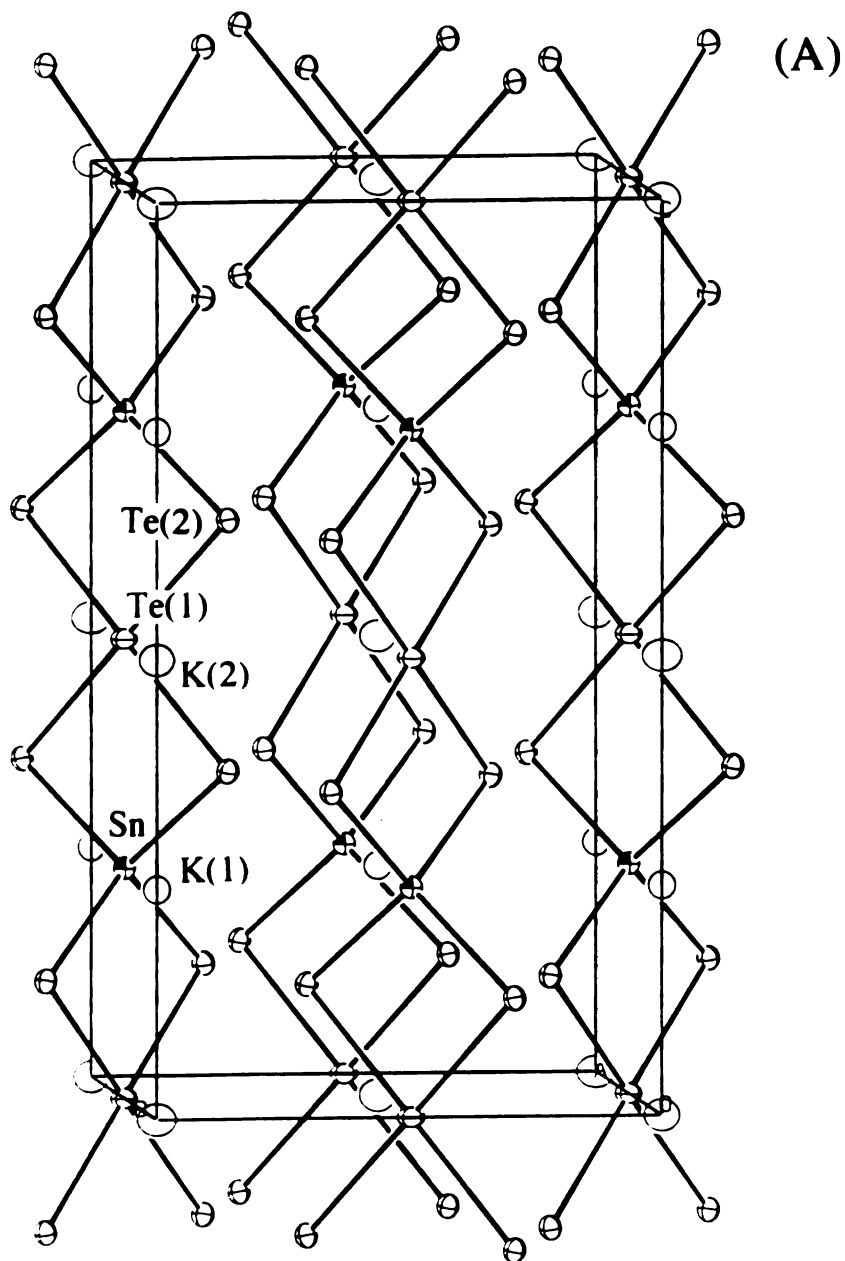


Figure 5-9: ORTEP representation and labeling scheme of K_2SnTe_5 : (A) View down the a-axis. (B) View down the b-axis.

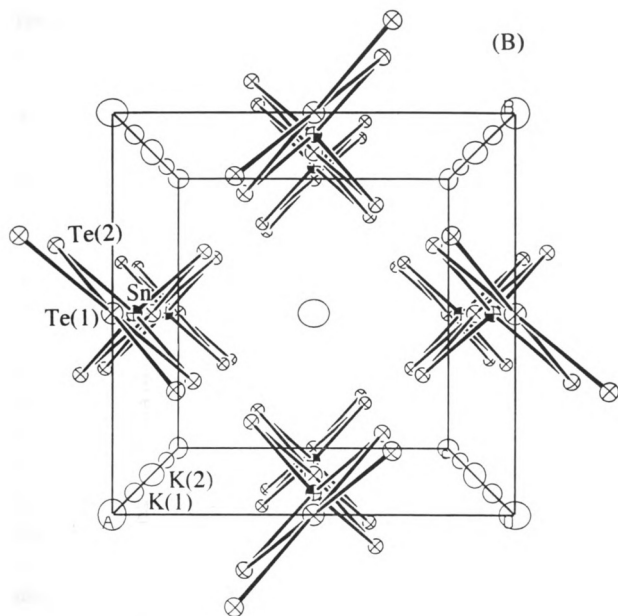


Table 5-20. Comparison of Selected Bond Distances (Å) and Angle (deg) for K_2SnTe_5 and Tl_2SnTe_5 .

Sn-Te(2)	2.778(1)x4	2.792(2)	Te(2)-K(1) or Tl(1)	3.5527(7)x2	3.491(2)
Te(1)-Te(2)	3.028(1)x4	3.004(2)	Te(2)-K(2) or Tl(2)	3.7514(8)x2	3.663(2)
Te(2)-Sn-Te(2)	112.81(2)x4	112.66(3)	Te(2)-Te(1)-Te(2)	88.23(4)x2	86.46(5)
Te(2)-Sn-Te(2)	102.99(4)x2	103.27(5)	Te(2)-Te(1)-Te(2)	91.77(4)x2	93.54(5)

3.3. Spectroscopy

Vibrational Spectroscopy

The Infrared and/or Raman frequencies of $\text{K}_2\text{Sn}_2\text{S}_8$ (I), $\text{K}_2\text{Sn}_2\text{S}_5$ (IV), $\text{Cs}_2\text{Sn}_2\text{S}_6$ (V) and $\text{Cs}_2\text{SnS}_{14}$ (VI) are listed in Table 5-21. The IR spectra of $\alpha\text{-Rb}_2\text{Sn}_2\text{S}_8$ and $\beta\text{-Rb}_2\text{Sn}_2\text{S}_8$ are the same as that of $\text{K}_2\text{Sn}_2\text{S}_8$ (I). Therefore, we did not measure the Raman spectra of $\alpha\text{-Rb}_2\text{Sn}_2\text{S}_8$ (II) and $\beta\text{-Rb}_2\text{Sn}_2\text{S}_8$ (III) because they are expected to be similar to that of $\text{K}_2\text{Sn}_2\text{S}_8$ (I). Since $\text{Cs}_2\text{SnS}_{14}$ (VI) can not be isolated in pure form, no Raman spectrum of this compound was measured. The sample used for the IR spectrum was picked by hand among the mixture.

Representative Raman spectra of $\text{K}_2\text{Sn}_2\text{S}_8$ (I) and $\text{Cs}_2\text{Sn}_2\text{S}_6$ (V) obtained with 514.5 nm excitation are shown in Figure 5-10. Raman spectra were also obtained with 441 and 488 nm excitations (not shown) but gave similar spectra. In Figure 5-10A, the mode at 379 cm^{-1} of $\text{K}_2\text{Sn}_2\text{S}_8$ can be assigned to a Sn-S stretching vibration by analogy to other tin sulfide complexes.^{10,11,12} The vibrations at 483 cm^{-1} and 471 cm^{-1} are assignable to $\nu(\text{S-S})_{\text{sym}}$ and $\nu(\text{S-S})_{\text{asym}}$, respectively.

Figure 5-10B shows the Raman spectrum of $\text{Cs}_2\text{Sn}_2\text{S}_6$ with isolated groups of bands assignable to Sn-S stretchings (382 and 386 cm^{-1}), S-S stretching (469 cm^{-1}) and asymmetric stretching (490 cm^{-1}) vibrations.

The S-S vibrations are not observed in the IR spectrum of $\text{Cs}_2\text{Sn}_2\text{S}_6$ because the S-S bond is sitting at a center of inversion. For an unbranched polysulfide species of n atoms, one may expect $(3n-3)$ vibrational fundamentals, with $(n-1)$ skeletal stretching modes, $(n-3)$ skeletal torsional modes, and $(n-2)$ skeletal bending modes.

Table 5-21. Infrared and Raman Frequencies (cm^{-1}) of $\text{K}_2\text{Sn}_2\text{S}_8$, $\text{K}_2\text{Sn}_2\text{S}_5$, $\text{Cs}_2\text{Sn}_2\text{S}_6$ and $\text{Cs}_2\text{SnS}_{14}$.

$\text{K}_2\text{Sn}_2\text{S}_8(\text{I})$		$\text{K}_2\text{Sn}_2\text{S}_5(\text{IV})$		$\text{Cs}_2\text{Sn}_2\text{S}_6(\text{V})$		$\text{Cs}_2\text{SnS}_{14}(\text{VI})$	
IR	Raman	IR	Raman	IR	Raman	IR	Mode
485	483				490	490	$\nu(\text{S-S})$
	471				469	441	
363		353	367	360	386		$\nu(\text{Sn-S})_{\text{sym}}$
	379	343	346		382	362	
338		334	334	332		327	$\nu(\text{Sn-S})_{\text{asym}}$
		320					
298		274	306	298		288	deformation
277			270	264		277	and
262							torsional
236		224	218	239		226	modes
		201					
195		186				202	
160		156		158		176	
				149		150	

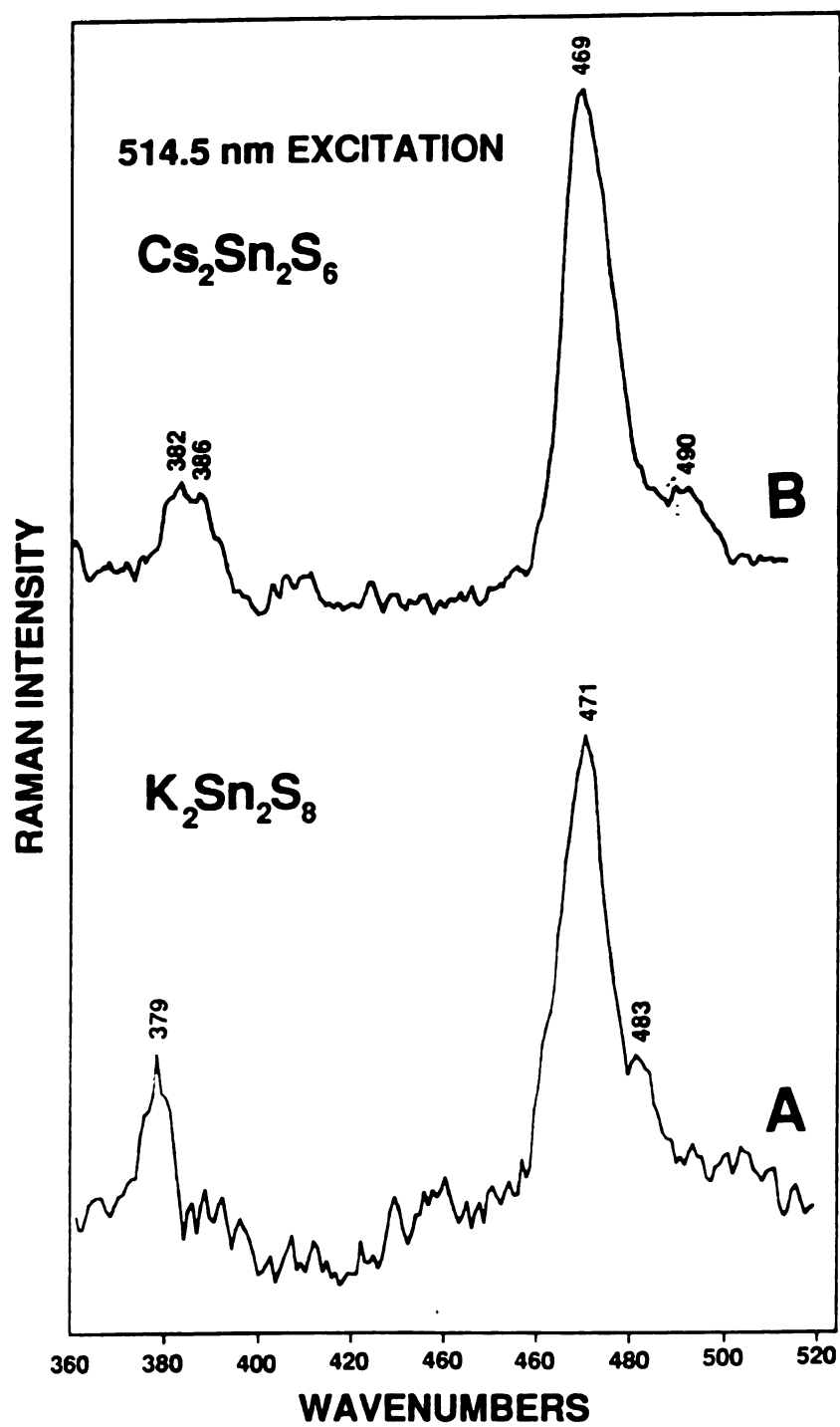


Figure 5-10: (A) Raman spectrum of $\text{K}_2\text{Sn}_2\text{S}_8$ (B) Raman spectrum of $\text{Cs}_2\text{Sn}_2\text{S}_6$

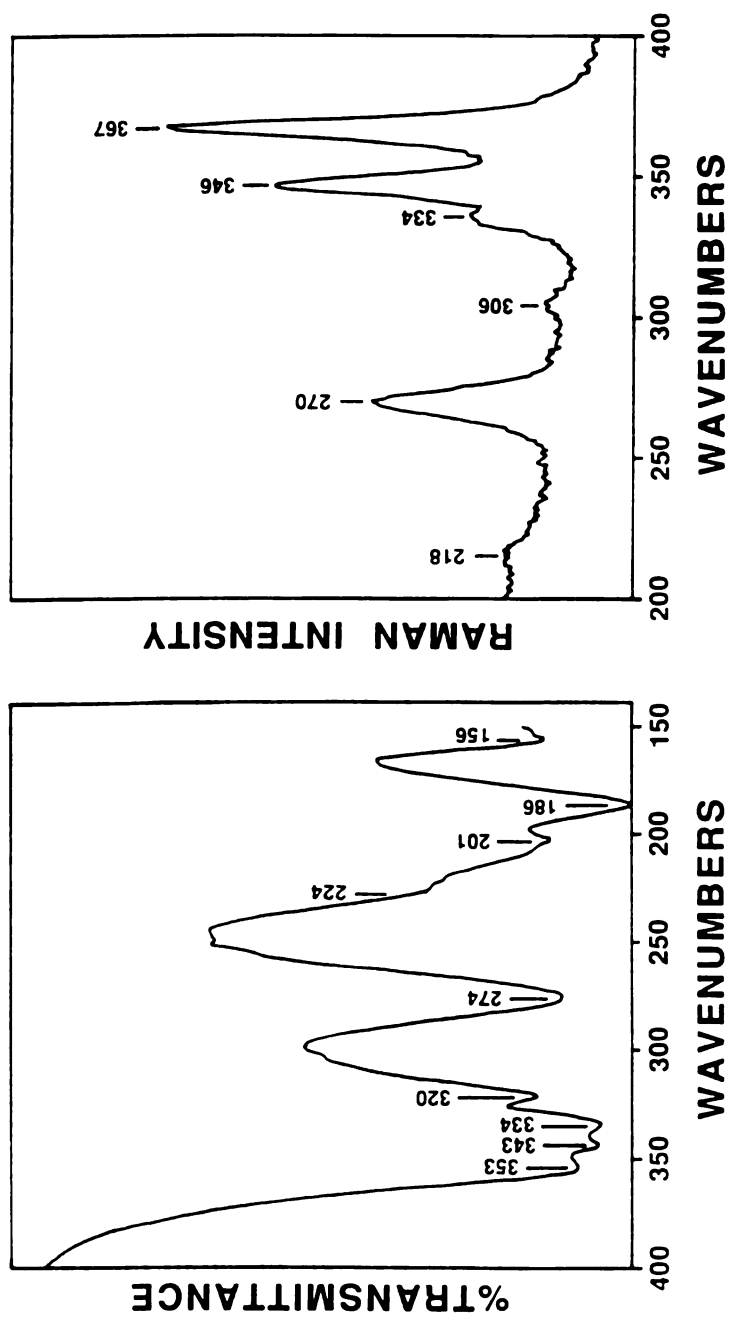


Figure 5-11: Infrared (left) and Raman (right) spectrum of $K_2Sn_2S_5$.

The frequencies for the fundamentals fall in the 400-500 cm^{-1} range¹³. The torsional modes are expected at frequencies below 100 cm^{-1} and are difficult to separate from lattice vibrations. Therefore, more exact assignment of S-S vibrations would require complete polarization data from single-crystal studies.

Figure 5-11 shows the IR and Raman spectra of $\text{K}_2\text{Sn}_2\text{S}_5$ (IV). The vibrations at 353 and 343 cm^{-1} in the IR, and at 367 and 346 cm^{-1} in the Raman spectra are due to $\nu(\text{Sn-S})_{\text{sym}}$. The 334 and 320 cm^{-1} modes (IR) and 335 cm^{-1} (Raman) are assignable to $\nu(\text{Sn-S})_{\text{asym}}$.

UV/Vis/Near-IR Reflectance Spectroscopy

The optical properties of $\text{K}_2\text{Sn}_2\text{S}_8$, $\alpha\text{-Rb}_2\text{Sn}_2\text{S}_8$, $\beta\text{-Rb}_2\text{Sn}_2\text{S}_8$, $\text{K}_2\text{Sn}_2\text{S}_5$ and $\text{Cs}_2\text{Sn}_2\text{S}_6$ were assessed by studying the UV/visible/near-IR reflectance spectra of the materials. The spectra confirm the semiconductor nature by revealing the presence of optical gaps as shown in Figures 5-12 and 5-13. The spectra of all compounds clearly exhibit steep absorption edges from which the band-gap can be assessed at an average of 2.15 eV for (I)~(III) and 2.36 eV for (IV), and 2.44 eV for (V). These transitions are probably charge transfer in character from the primarily S-based valence band to the primarily Sn-based conduction band. Other transitions occur at higher energies, and they are indicated in the spectra in Figure 5-12 and 13. The smaller band gaps of $\text{K}_2\text{Sn}_2\text{S}_8$, $\alpha\text{-Rb}_2\text{Sn}_2\text{S}_8$, $\beta\text{-Rb}_2\text{Sn}_2\text{S}_8$ compared to those of $\text{K}_2\text{Sn}_2\text{S}_5$ and $\text{Cs}_2\text{Sn}_2\text{S}_6$ are consistent with the respective orange and yellow colors of the two groups. By comparison, the corresponding band gap of SnS_2 is 2.16 eV.

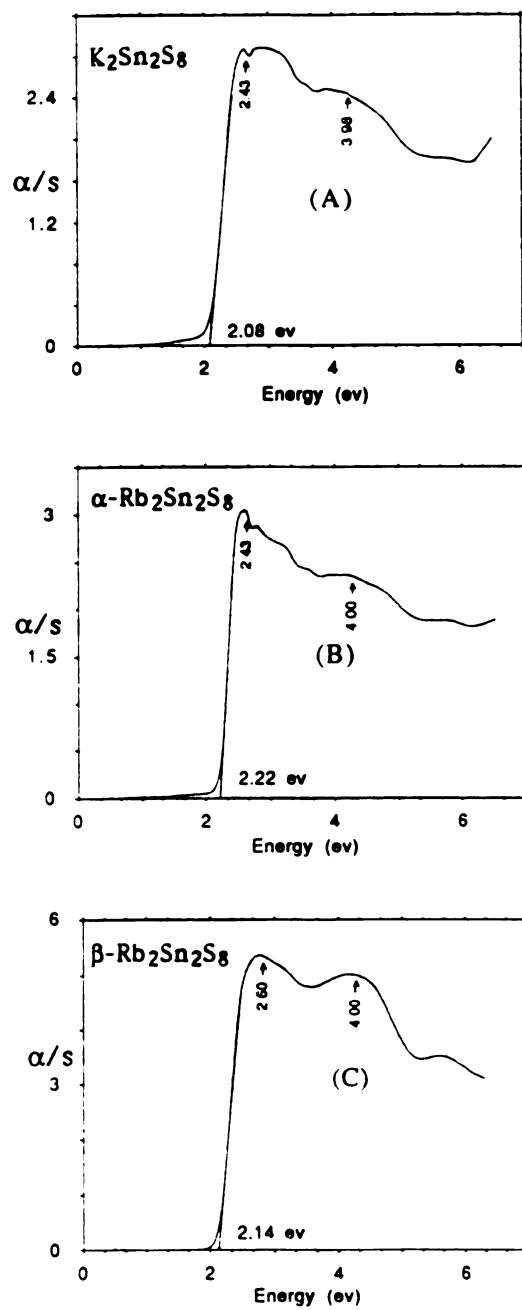


Figure 5-12: Optical absorption spectra of $K_2Sn_2S_8$, $\alpha-Rb_2Sn_2S_8$ and $\beta-Rb_2Sn_2S_8$.

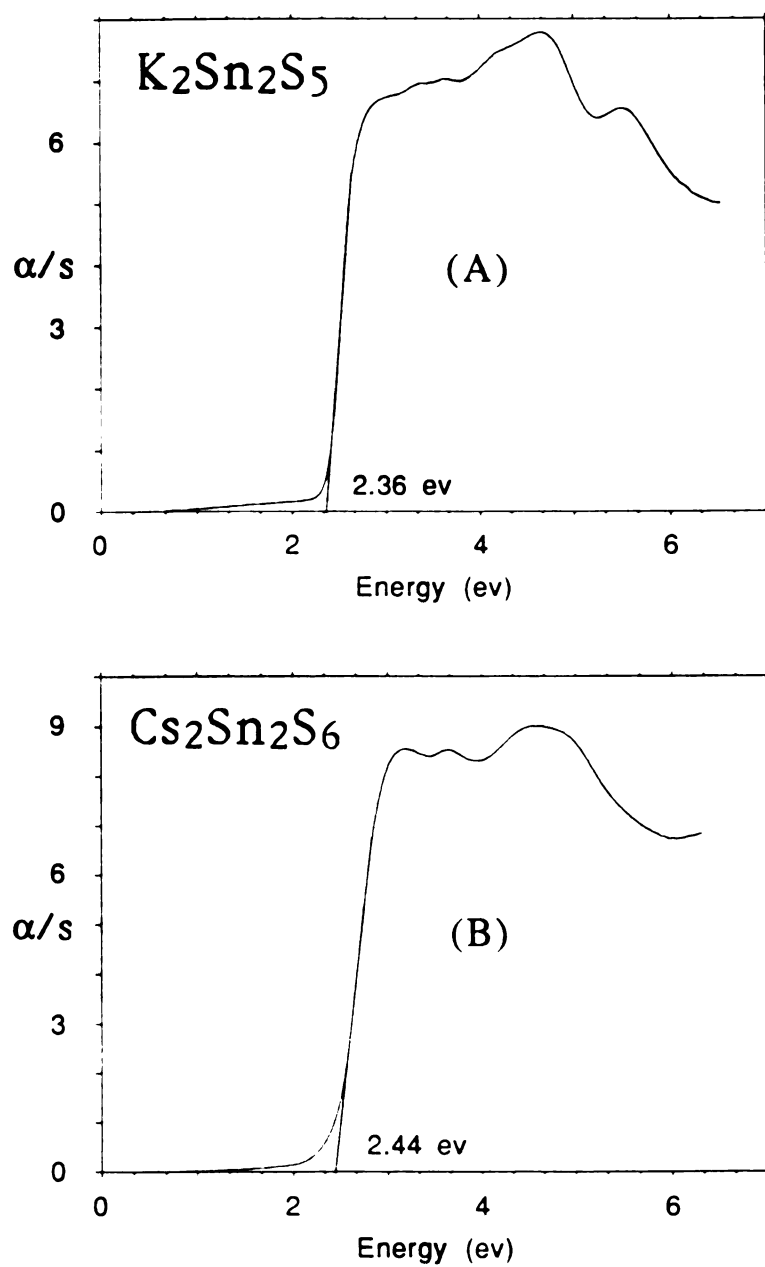


Figure 5-13: Optical absorption spectra of $\text{K}_2\text{Sn}_2\text{S}_5$ and $\text{Cs}_2\text{Sn}_2\text{S}_6$.

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CHAPTER 6

The Quaternary $\text{Rb}_2\text{Cu}_2\text{SnS}_4$, $\text{A}_2\text{Cu}_2\text{Sn}_2\text{S}_6$ ($\text{A}=\text{Na}$, K , Rb , Cs), $\text{A}_2\text{Cu}_2\text{Sn}_2\text{Se}_6$ ($\text{A}=\text{K}$, Rb), $\text{K}_2\text{Au}_2\text{SnS}_4$ and $\text{K}_2\text{Au}_2\text{Sn}_2\text{S}_6$. Syntheses, Structures and Properties of New Solid State Chalcogenides Based on Tetrahedral $[\text{SnS}_4]^{4-}$ Units.

1. Introduction

Chalcogenides of the transition and main group metals exhibit useful physical and chemical properties which are promising for applications in nonlinear optics¹, rechargeable battery cathodes², optical storage³, radiation detection⁴, solar energy conversion⁵ and catalysis⁶. Binary and ternary chalcogenides have been extensively investigated, but relatively little is known about quaternary chalcogenides which may also exhibit interesting properties. Tetrathiometalates, especially $[\text{MoS}_4]^{2-}$ and $[\text{WS}_4]^{2-}$, have been extensively used as building blocks to synthesize heterometallic discrete molecular sulfido-complexes by self-assembly reactions in solution.⁷ A few solid state examples have been reported. One interesting example is the formation of $(\text{NH}_4)\text{CuMoS}_4$ ⁸ which contains linear chains composed of $[\text{MoS}_4]^{2-}$ tetrahedra chelated to Cu^+ ions. Recently, a two-dimensional heterometallic sulfide, Cu_2WS_4 , was reported to form in

powder form by mixing $[\text{WS}_4]^{2-}$ and Cu^+ in DMF solution.⁹ Although these tetrahedral anions work well as ligands in solution they are thermally unstable and cannot be used at higher temperature. Other tetrathiometalates, however, are considerably more stable (e.g. $[\text{SnS}_4]^{4-}$, $[\text{GeS}_4]^{4-}$, $[\text{PS}_4]^{3-}$) and their coordination properties toward other metal ions to form solid state lattices are worthy of investigation. During our studies of ternary alkali metal containing tin (poly)sulfides by using reactive molten salts as solvents, we noticed that $[\text{SnS}_4]^{4-}$ and $[\text{Sn}_2\text{S}_6]^{4-}$ ions are the basic units comprising various anionic frameworks and can actually be isolated, as their alkali metal salts by either increasing the reaction temperatures or adding more A_2S (A =alkali metal) in the polysulfide fluxes.^{10a} These anions have been well known since 1971^{10g-j}. If then $[\text{SnS}_4]^{4-}$ and/or $[\text{Sn}_2\text{S}_6]^{4-}$ exist or are generated in Sn-containing polysulfide melts, they could be used in reactions with other metal ions to form new heterometallic sulfides. Some examples showing the presence of tetrahedral $[\text{SnS}_4]^{4-}$ fragments in solid state quaternary chalcogenides synthesized at high temperatures have been reported.^{11,12} They include $\text{BaAg}_2\text{SnS}_4$, $\text{BaAu}_2\text{SnS}_4$, $\text{BaCu}_2\text{SnS}_4$, $\text{SrCu}_2\text{SnS}_4$, BaHgSnS_4 , BaCdSnS_4 , KGaSnS_4 and $\text{Cu}_2\text{B}^{\text{II}}\text{SnS}_4$ (B^{II} =Mn, Fe, Co, Ni, Zn, Cd or Hg). Here we attempted to exploit three properties associated with Sn-containing polysulfide fluxes: a) the relatively low temperature accessible for synthesis, $T < 500^\circ\text{C}$, and b) the apparent ability of these fluxes to supply the $[\text{SnS}_4]^{4-}$ anion for reaction chemistry and c) the anticipated excellent coordinating ability of the $[\text{SnS}_4]^{4-}$ anion towards transition metals in a similar fashion observed for the $[\text{MoS}_4]^{2-}$ unit.⁷ If the metals, to coordinate to $[\text{SnS}_4]^{4-}$, are chosen to prefer tetrahedral coordination, the products are expected to be based on tetrahedral substructures. Examples of such metals

would be Cu^+ , Zn^{2+} and Cd^{2+} etc. Indeed, quaternary chalcogenides of the $\text{Cu}_2\text{B}^{\text{II}}\text{SnS}_4$ type ($\text{B}^{\text{II}}=\text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Zn}, \text{Cd}$ or Hg)^{12b} adopt structures derived from simple sphalerites or wurtzites. If, on the other hand, metals with other coordination preferences are chosen, such as Au^+ (linear) or Pt^{2+} (square-planar), a departure from the overall tetrahedral motif is expected. By using Cu^+ and Au^+ we explored the partial charge "neutralization" of the $[\text{SnS}_4]^{4-}$ anion in A_2S_x ($\text{A}=\text{alkali metal}$) flux as the reaction medium. To avoid anticipated crystallographic difficulties in distinguishing Sn from Ag the latter element was not chosen for this investigation. Here we report on several new quaternary compounds: $\text{Rb}_2\text{Cu}_2\text{SnS}_4$, $\text{A}_2\text{Cu}_2\text{Sn}_2\text{S}_6$ ($\text{A}=\text{Na}, \text{K}, \text{Rb}, \text{Cs}$), $\text{A}_2\text{Cu}_2\text{Sn}_2\text{Se}_6$, ($\text{A}=\text{K}, \text{Rb}$), $\text{K}_2\text{Au}_2\text{SnS}_4$ and $\text{K}_2\text{Au}_2\text{Sn}_2\text{S}_6$ obtained from the above methodology.

2. Experimental Section

2.1 Reagents

Sn metal, ~325 mesh, 99.8%.purity, CERAC Inc., Milwaukee, WI. Cu metal, electronic dust, purified, Fisher, Scientific Co., Fair Lawn, NJ. Au metal, ~325 mesh, 99.95% purity, CERAC Inc., Milwaukee, WI. Sublimed sulfur was purchased from J. T. Baker Chemical Co. 99.5~100.5%. K_2S and Rb_2S starting materials were prepared as described elsewhere¹³. All reagents were stored under N_2 in a glove box.

2.2. Physical Measurements:

The instruments and experimental setups for Infrared spectroscopy,

SEM/EDS quantitative microprobe analysis and UV/vis/near-IR optical diffuse spectroscopy are the same as those in previous chapters.

2.3. Synthesis

Chemicals were weighed and loaded in Pyrex tubes under a dry nitrogen atmosphere in a Vacuum Atmosphere Dri-Lab glovebox.

Rb₂Cu₂SnS₄ (I) A mixture of Sn powder (0.039 g, 0.33 mmol), Cu powder (0.084 g, 1.32 mmol), Rb₂S (0.267 g, 1.32 mmol) and S (0.171 g, 5.28 mmol) in the ratio of 1:4:4:16 was loaded into an ~5 ml Pyrex tube in a N₂ glove box. The tube was evacuated and sealed at a pressure of ~10⁻³ torr. The mixture was heated slowly from room temperature to 400°C in 12 hours in a furnace programmed by a personal computer. The temperature was kept at 400°C for 4 days, and then was cooled slowly to room temperature at 4°C/hour. Orange plate-like crystals were formed in ~71% yield (based on Sn). The product was washed with degassed DMF to remove excess Rb₂S_x flux by using a standard Schlenk technique, and was dried with acetone and ether. The orange crystals are insoluble in water and common organic solvents, but decompose slowly in air. Semiquantitative elemental analyses performed on a scanning electron microscope (SEM) by using an energy dispersive (EDS) microscopic technique indicated Rb_{2.2}Cu_{3.4}Sn_{1.0}S_{4.2}.

Rb₂Cu₂Sn₂S₆ (II) The procedure for preparation and isolation of (II) is the same as described above except that molar ratios of 1:1~2:4:16 (Sn:Cu:Rb₂S:S) were used. Black crystals of (II) were obtained

in 62% yield (based on Sn). These crystals exhibit mica-like thin layered morphology and are easily separated into very thin sheets. They are stable in air and insoluble in water and common organic solvents. Semiquantitative elemental analysis performed on SEM/EDS indicated $\text{Rb}_{1.0}\text{Cu}_{1.5}\text{Sn}_{1.0}\text{S}_{3.1}$.

Other X-ray isomorphous $\text{A}_2\text{Cu}_2\text{Sn}_2\text{Q}_6$ (A=Na, K, Rb, Cs; Q=S, Se) phases prepared by a similar procedure are: (a) $\text{K}_2\text{Cu}_2\text{Sn}_2\text{S}_6$ (b) $\text{K}_2\text{Cu}_2\text{Sn}_2\text{Se}_6$ (c) $\text{Rb}_2\text{Cu}_2\text{Sn}_2\text{Se}_6$ (d) $\text{Na}_2\text{Cu}_2\text{Sn}_2\text{S}_6$ (e) $\text{Cs}_2\text{Cu}_2\text{Sn}_2\text{S}_6$. All of them are black and exhibit thin-layer morphology. The reactions for (a)~(c) gave good yields (>70%). K^+ and Rb^+ seem to be preferred for the formation of $\text{A}_2\text{Cu}_2\text{Sn}_2\text{Q}_6$ phases. (d) and (e) gave low yields and were present with other binary and ternary products.

$\text{K}_2\text{Au}_2\text{SnS}_4$ (III) A mixture of Sn (0.015 g, 0.13 mmol), Au (0.050 g, 0.25 mmol), K_2S (0.055 g, 0.50 mmol) and S (0.064 g, 2.0 mmol) in a ratio of 1:2:4:16 was loaded into an ~5 ml Pyrex tube in a dry N_2 glove box. The tube was evacuated and flame sealed at a pressure of $\sim 10^{-3}$ torr. The mixture was heated slowly from room temperature to 350°C in 12 hours in a furnace programmed by a personal computer. The temperature was kept at 350°C for 4 days, and then was cooled slowly to room temperature at $4^\circ\text{C}/\text{hour}$. Yellow long parallelepiped crystals of (II) were obtained by removing the excess K_2S_x flux with degassed DMF under N_2 atmosphere. The final product was washed and dried with acetone and ether. Yield: 66% (based on Sn). The yellow crystals are stable in air but break apart into fibers in water and dissolve slowly to form a light yellow solution. The crystals show a fibrous feature when crushed and are hard to grind. SEM/EDS indicated $\text{K}_{1.1}\text{Au}_{1.5}\text{Sn}_{1.0}\text{S}_{3.4}$.

K₂Au₂Sn₂S₆ (IV) The procedure for preparation and isolation was the same as that of (III) except that a molar ratio of 1:1.5:2:16 (Sn: Au: K₂S: S) was used. Orange chunky crystals were obtained in 53% yield (based on Sn). The crystals are stable in air and insoluble in water and common organic solvents. They also split into fibers when crushed and are very hard to grind into fine powder. Semiquantitative elemental analysis performed on SEM/EDS indicated K_{0.9}Au_{1.2}Sn_{1.0}S_{4.0}.

2.4. X-Ray Crystallography

X-ray powder diffraction patterns were used for the purpose of phase characterization and identification. The X-ray powder diffraction patterns were recorded with a Phillips XRD-3000 controlled by PDP 11 computer and operating at 40 kV/35 mA. Graphite monochromated Cu radiation was used. In order to ensure the homogeneity, d-spacings obtained from X-ray powder diffraction (XRD) measurements of the products were compared with, and found to be identical, with those calculated from the atomic coordinates determined from the single crystal data. The calculation of d-spacings was performed by using the POWD 10¹⁴ program. The comparison tables between the calculated and observed d-spacings for these compounds are shown in Tables 6-1~6-4.

The single crystal X-ray diffraction data of (I)~(IV) were collected on a Rigaku AFC6S four-circle diffractometer by using ω -2 θ scan mode. Graphite monochromated Mo K α radiation was used and all data sets were collected at room temperature. The crystals were mounted at the end of glass fibers. The stability of the experimental setup and crystal integrity

were monitored by measuring three standard reflections periodically every 150 reflections. No significant decay was observed during the data collections. (II) tends to grow twinned crystals. A large number of crystals had to be screened before a satisfactory single crystal was found. In order to obtain better refinement, Friedel pairs of (II) were collected and the data were averaged. The structures were solved with direct methods (SHELXS-86)¹⁵, and were refined by a full-matrix least-square technique available in the TEXSAN¹⁶ programs running on a VAXstation 3100/76 computer. An empirical absorption correction was applied to all the data (based on ψ scans). An additional absorption correction by following the DIFABS¹⁷ procedure was applied to isotropically refined data.

The crystallographic data and detailed information of structure solution and refinement are listed in Table 6-5. Atomic coordinates and equivalent isotropic thermal parameters are given in Tables 6-6~6-9 respectively.

Table 6-1. Calculated and Observed X-Ray Powder Diffraction Patterns for $\text{Rb}_2\text{Cu}_2\text{SnS}_4$.

h	k	l	$d_{\text{calc.}}(\text{\AA})$	$d_{\text{obs.}}(\text{\AA})$	% $I_{\text{obs.}}$
0	0	2	6.8500	6.8877	59.71
0	0	4	3.4250	3.4656	100.00
1	3	0	3.1348	3.1587	16.12
1	2	3	2.9967	3.0213	74.59
0	4	2	2.6349	2.6551	20.66
2	0	2	2.5632	2.5801	31.43
1	3	4	2.3125	2.2707	23.51
1	2	5	2.2553		
2	4	0	1.9857	2.0012	19.98
0	4	6	1.7831	1.7940	20.66
2	0	6	1.7604	1.7687	19.98
2	4	4	1.7178	1.7223	26.54
0	0	8	1.7125		

Table 6-2. Calculated and Observed X-Ray Powder Diffraction Patterns for $\text{Rb}_2\text{Cu}_2\text{Sn}_2\text{S}_6$.

h	k	l	$d_{\text{calc.}}$	$d_{\text{obs.}}$	% $I_{\text{obs.}}$
0	0	2	10.0558	10.1093	17.79
0	0	4	5.0279	5.0458	53.27
2	2	0	3.8789	3.9005	11.01
2	2	-1	3.8788		
2	2	1	3.7424	3.7621	8.91
2	2	-2	3.7420		
2	2	2	3.5074	3.5263	17.19
2	2	-3	3.5069		
0	0	6	3.3519	3.3664	27.18
2	2	4	2.9375	2.9398	100.00
2	2	-5	2.9370		
0	4	7	1.9884	1.9908	17.00
4	4	-1	1.9485	1.9528	24.76
4	0	8	1.7361	1.7404	31.81
4	0	-10	1.7357		
0	4	9	1.7354		
6	2	3	1.6242	1.6250	14.02
6	2	-6	1.6239		
2	6	4	1.6234		
2	6	-5	1.6233		

Table 6-3. Calculated and Observed X-Ray Powder Diffraction Patterns for K₂Au₂SnS₄.

h	k	l	d _{calc.} (Å)	d _{obs.} (Å)	%I _{obs.}
0	0	1	6.7916	6.8917	55.49
1	0	-1	6.1626	6.2463	49.57
1	1	1	4.0947	4.1336	25.00
1	2	-1	4.0740		
2	1	-1	3.9822		
2	0	0	3.6607	3.6955	64.98
0	2	1	3.6115	3.6422	46.74
0	1	-2	3.1883	3.2057	100.00
2	1	-2	3.1741		
1	2	-2	3.0205	3.0437	27.08
2	2	-2	2.8886	2.9092	41.33
0	3	0	2.8872		
2	0	1	2.8362	2.8579	30.36
2	3	-1	2.7465	2.7648	23.99
0	3	-1	2.6809	2.7018	63.35
2	3	0	2.6593	2.6540	42.65
0	2	2	2.6409		
2	2	1	2.6366		
3	0	-1	2.6032	2.5916	25.00
1	-2	-2	2.5670		
3	1	-2	2.5346	2.5236	55.49
2	-2	-1	2.5099		
2	-2	0	2.4739	2.4819	28.15
1	-3	0	2.4602		
1	2	2	2.4090	2.4149	32.65
1	1	-3	2.3993		
3	3	-1	2.3234	2.3377	25.00
0	3	-2	2.2268	2.2160	23.00
3	1	-3	2.1262	2.1378	29.25
2	2	2	2.0473	2.0600	43.99
2	-1	2	2.0131	2.0199	29.25
3	-2	-1	1.9774	1.9884	26.03
3	-2	-2	1.8883	1.8989	40.02
2	-3	1	1.8413	1.8463	25.00
1	2	3	1.8368		
4	3	0	1.7900	1.8034	19.25
4	1	1	1.6786	1.6808	12.04
5	1	-2	1.6213	1.6186	10.66
2	-1	3	1.6173		

Table 6-4. Calculated and Observed X-Ray Powder Diffraction Patterns for $\text{K}_2\text{Au}_2\text{Sn}_2\text{S}_6$.

h	k	l	$d_{\text{calc.}}(\text{\AA})$	$d_{\text{obs.}}(\text{\AA})$	%I _{obs.}
1	0	0	7.9680	8.1947	15.43
1	1	0	5.6342	5.7668	100.00
2	0	0	3.9840	4.0630	40.41
2	1	0	3.5634	3.6330	31.84
2	1	2	3.3407	3.3951	33.47
2	1	4	2.8612	2.8952	11.27
2	2	2	2.7031	2.7368	40.41
3	0	0	2.6560	2.6890	30.25
3	0	2	2.5598	2.5894	27.94
2	0	6	2.4949	2.5157	24.29
3	1	2	2.4372	2.4605	29.47
2	2	4	2.4296		
2	1	6	2.3809	2.3510	8.16
3	0	4	2.3240		
3	1	4	2.2310	2.2550	7.37
3	0	6	2.0437	2.0118	25.72
3	3	2	1.8431	1.8597	22.22
3	0	8	1.7807	1.7992	11.27
4	2	2	1.7518	1.7658	25.00
3	3	4	1.7490		
4	0	6	1.6911	1.7082	10.80
2	1	10	1.6903		
2	2	10	1.5866	1.5758	25.72
5	1	0	1.5627		

Table 6-5. Summary of Crystallographic Data for Rb₂SnCu₂S₄, Rb₂Sn₂Cu₂S₆, K₂Au₂SnS₄ and K₂Au₂Sn₂S₆.

	(I)	(II)
formula	Rb ₂ SnCu ₂ S ₄	Rb ₂ Sn ₂ Cu ₂ S ₆
fw	544.96	727.77
a, Å	5.528(4)	11.026(2)
b, Å	11.418(6)	11.019(3)
c, Å	13.700(6)	20.299(4)
α	90.0	90.0
β	90.0	97.79(2)
γ	90.0	90.0
Z, V, Å ³	4, 865(2)	8, 2441(1)
space group	Ibam	C2/c
d _{calc} , g/cm ³	4.185	3.956
crystal size, mm	0.30x0.40x0.04	0.82x0.73x0.31
radiation	Mo Kα	Mo Kα
μ(Mo Kα), cm ⁻¹	195.02	161.51
2θ _{max} , deg	50.0	60
no. of data collected	468	11691
no. of unique data	468	3736
no. of observed data (I>3.0σ(I))	221	1756
no. of variables	23	23
final R/R _w , %	6.9/8.1	6.3/6.4

* $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ $R_w = \{ \sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2 \}^{1/2}$

Table 6-5. (cont'd)

	(III)	(IV)
formula	K ₂ Au ₂ SnS ₄	K ₂ Au ₂ Sn ₂ S ₆
fw	719.06	901.87
a, Å	8.212(4)	7.968(2)
b, Å	9.110(4)	7.968(2)
c, Å	7.314(2)	19.200(6)
α	97.82(3)	90.0
β	111.72(2)	90.0
γ	72.00(3)	90.0
Z, V, Å ³	2, 483.2(7)	4, 1219(1)
space group	P-1	P4/mcc
d _{calc} , g/cm ³	4.941	4.914
crystal size, mm	0.40x0.54x0.53	0.20x0.20x0.33
radiation	Mo Kα	Mo Kα
μ(Mo Kα), cm ⁻¹	343.92	296.20
2θ _{max} , deg	50.0	55.0
no. of data collected	1832	911
no. of unique data	1700	911
no. of observed data (I>3.0σ(I))	1447	459
no. of variables	83	34
final R/R _w , %	4.8/6.0	4.1/3.9
* $R = \sum F_o - F_c / \sum F_o $ $R_w = \{ \sum w(F_o - F_c)^2 / \sum w F_o ^2 \}^{1/2}$		

Table 6-6. Positional Parameters and Equivalent Isotropic Displacement Values ($\text{\AA}^2$)^a for $\text{Rb}_2\text{Cu}_2\text{SnS}_4$ with Estimated Standard Deviations in Parentheses.

atom	x	y	z	B (eq)
Sn	0	0	0.25	1.5 (2)
Rb	0.2725 (7)	0.1252 (4)	0.5	2.2 (2)
Cu	0	0.2811 (5)	0.25	3.1 (4)
S	0.227 (1)	0.1275 (7)	0.1462 (5)	1.6 (3)

^a $B(\text{eq}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table 6-7. Positional Parameters and Equivalent Isotropic Displacement Values ($\text{\AA}^2$)^a for $\text{Rb}_2\text{Cu}_2\text{Sn}_2\text{S}_6$ with Estimated Standard Deviations in Parentheses.

atom	x	y	z	B (eq)
Sn (1)	0.96959 (7)	0.18745 (7)	0.62863 (5)	0.68 (3)
Sn (2)	0.71978 (7)	-0.06244 (7)	0.62961 (5)	0.68 (3)
Rb (1)	1.3347 (1)	0.0630 (1)	0.58767 (9)	1.56 (5)
Rb (2)	0.9160 (1)	0.1881 (1)	0.41243 (8)	1.45 (5)
Cu (1)	1.0000	0.4322 (2)	3/4	0.66 (8)
Cu (2)	1.2478 (1)	0.1933 (3)	0.7499 (1)	2.0 (1)
Cu (3)	1.0000	-0.0643 (2)	3/4	0.65 (8)
S (1)	0.8660 (3)	-0.1958 (3)	0.6853 (2)	0.8 (1)
S (2)	0.6022 (3)	0.0694 (3)	0.6869 (2)	0.9 (1)
S (3)	1.1158 (3)	0.0553 (3)	0.6855 (2)	1.0 (1)
S (4)	0.8511 (3)	0.3184 (3)	0.6839 (2)	1.0 (1)
S (5)	1.0762 (3)	0.3130 (3)	0.5516 (2)	1.6 (1)
S (6)	0.8247 (3)	0.0621 (3)	0.5522 (2)	1.2 (1)

^a $B(\text{eq}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table 6-8. Positional Parameters and Equivalent Isotropic Displacement Values ($\text{\AA}^2$)^a for $\text{K}_2\text{Au}_2\text{SnS}_4$ with Estimated Standard Deviations in Parentheses.

atom	x	y	z	B (eq)
Au (1)	0.3306 (1)	0.42189 (9)	0.2678 (1)	1.25 (4)
Au (2)	0.7123 (1)	0.8297 (1)	0.4683 (1)	1.25 (4)
Sn	0.7245 (2)	0.1941 (2)	0.6254 (2)	0.96 (6)
K (1)	0.2549 (6)	0.0792 (6)	0.9707 (7)	1.8 (2)
K (2)	0.1860 (7)	0.5796 (6)	0.783 (1)	2.8 (3)
S (1)	0.5829 (7)	0.2189 (6)	0.2774 (7)	1.3 (2)
S (2)	0.0852 (7)	0.6343 (6)	0.240 (1)	2.2 (3)
S (3)	0.9194 (7)	0.9375 (6)	0.7084 (8)	1.4 (2)
S (4)	0.4964 (7)	0.7443 (6)	0.2133 (8)	1.5 (2)

^a $B(\text{eq}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table 6-9. Positional Parameters and Equivalent Isotropic Displacement Values ($\text{\AA}^2$)^a for $\text{K}_2\text{Au}_2\text{Sn}_2\text{S}_6$ with Estimated Standard Deviations in Parentheses.

atom	x	y	z	B (eq)
Au	0.6889 (1)	0	0.25	0.98 (4)
Sn	0.5	0	0.41157 (8)	0.66 (6)
K (1)	0	0	0.0966 (6)	1.9 (2)
K (2)	0.5	0.5	0.25	4.3 (6)
K (3)	0.5	0.5	0.0499	2.9 (5)
S (1)	0.662 (1)	0.149 (1)	0.5	0.8 (3)
S (2)	0.3227 (7)	0.1772 (8)	0.3453 (2)	0.9 (2)

^a $B(\text{eq}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

3. Results and Discussion

3.1. Synthesis

The syntheses and crystallization of (I)~(IV) were accomplished in A_2S_x (A=K or Rb) fluxes which were formed by the *in situ* reaction of A_2S and S in various ratios. The polysulfide melts serve as oxidation agents as well as reaction media, enhance the mobility of the reactants, and help crystallization of the products. The mere result of quaternary phase formation in A_2S_x fluxes suggests that the reactions occur in a homogenized medium in which good mixing of Cu and Sn, and Au and Sn is achieved, probably through soluble sulfide precursor complexes. Such mixing is critical since Cu, Au and Sn alone can form stable ternary A/M/S compounds.¹⁸

$Rb_2Cu_2SnS_4$ (I) was synthesized by heating Sn and Cu powder in a Rb_2S_5 flux at 400°C. A Cu rich ratio (Sn:Cu=1:4) was used to obtain (I) in pure form. The ratio of Sn:Cu=1:2 gave $Rb_2Cu_2Sn_2S_6$ (II) while the ratio of 1:3 gave a mixture of (I) and (II). The $Rb_2Cu_2Sn_2S_6$ phase dominates when Cu:Sn=1:1. The Se analog was prepared in an analogous manner. All alkali salts from Na^+ to Cs^+ form isomorphous sulfide phases. However, only K^+ and Rb^+ stabilized the selenide version.

$K_2Au_2SnS_4$ (III) was synthesized by heating Au and Sn powder in a ratio of 2:1 in a K_2S_5 flux at 350°C, while $K_2Au_2Sn_2S_6$ (IV) was prepared by heating Au and Sn powder in a ratio of 1.5:1 in a K_2S_9 flux at 350°C. (IV) which contains $[Sn_2S_2]^{4-}$ fragments was synthesized under a sulfur-rich flux. This suggests that $[Sn_2S_6]^{4-}$, rather than $[SnS_4]^{4-}$, ions are favored in a more oxidizing sulfur-rich polysulfide flux. While this may

seem counterintuitive, we point out that a sulfur-rich flux is less basic than a sulfide-rich (sulfur-poor) flux which breaks the $[\text{Sn}_2\text{S}_6]^{4-}$ dimers further into single $[\text{SnS}_4]^{4-}$ tetrahedra. It should be noted the Sn:Au ratio (1:1.5) used in the reaction is not consistent with the chemical formula of $\text{K}_2\text{Au}_2\text{Sn}_2\text{S}_6$. Using the exact Sn:Au ratio (1:1) under the same reaction conditions gave a mixture of $\text{K}_2\text{Au}_2\text{Sn}_2\text{S}_6$ and reddish orange crystals of $\text{K}_2\text{Sn}_2\text{S}_8$ ^{10a}. Only by increasing the Au content were we able to avoid the competitive side product. However, no ternary K/Au/S phase was observed, indicating that the excess Au forms soluble complexes which are removed during the isolation process.

3.2. Description of Structures

Structure of $\text{Rb}_2\text{Cu}_2\text{SnS}_4$ (I)

The $\text{Rb}_2\text{Cu}_2\text{SnS}_2$ is a layered compound. SnS_4 and CuS_4 tetrahedra in the ratio of 1:2 are the building blocks of the two-dimensional $[\text{Cu}_2\text{SnS}_4]_n^{2n-}$ framework, shown in Figure 6-1. The structure type of the two-dimensional anionic framework can be viewed as an ordered defect anti-PbO¹⁹ structure in which sulfur atoms occupy the lead sites, tin and copper atoms occupy the oxygen sites, but with one half of the tin atoms missing. We note that some ternary metal chalcogenides such as $\text{Rb}_2\text{Mn}_3\text{S}_4$, $\text{Cs}_2\text{Mn}_3\text{S}_4$, $\text{Rb}_2\text{Co}_3\text{S}_4$, $\text{Cs}_2\text{Co}_3\text{S}_4$, $\text{Cs}_2\text{Zn}_3\text{S}_4$ and $\text{Rb}_2\text{Zn}_3\text{S}_4$ ²⁰ are structurally related. In all these compounds the tetrahedral metal centers occupy 3/4 of the O-sites in the PbO lattice. In the $[\text{Cu}_2\text{SnS}_2]_n^{2n-}$ framework, the CuS_4 tetrahedra share two opposite edges to form parallel infinite linear $[\text{CuS}_2]_n^{3n-}$ chains which are related to the $[\text{FeS}_2]^-$ chains in

KFeS_2^{21} . These chains are cross-linked by tetrahedral Sn^{4+} via sulfide ions in the $[\text{CuS}_2]_{n^{3n-}}$ chains. This arrangement leaves tetrahedral holes in the layers.

Selected bond distances and bond angles are given in Table 6-10. There are three mutually perpendicular crystallographic 2-fold rotational axes passing through the Sn atoms. Therefore, all Sn-S distances are equal at $2.390(8)\text{\AA}$. Three pairs of S-Sn-S angles deviate from those in a perfect tetrahedron with $107.0(3)^\circ$, $104.9(4)^\circ$ and $116.7(3)^\circ$ respectively. There is a 2-fold axis passing through the CuS_4 tetrahedra which exhibit significant distortion from the ideal tetrahedron. The Cu...Cu distance is $2.854(4)\text{\AA}$. Two pairs of Cu-S distances are $2.582(8)\text{\AA}$ and $2.322(7)\text{\AA}$. The significant difference of Cu-S bond distances is due to the difference in S-Cu-S bond angles. The S-Cu-S angle between the two shorter Cu-S bonds is a wide $126.6(5)^\circ$; the S-Cu-S angle between two longer Cu-S bonds is very narrow at $94.5(4)^\circ$. The other two pairs of S-Cu-S angles are $106.3(2)^\circ$ and $109.1(2)^\circ$.

The rubidium cations are located between the anionic layers to balance the charge, as shown in Figure 6-2. The Rb^+ cations are sitting on a crystallographic mirror plane and are coordinated by 8 sulfur atoms with an average $\text{Rb}\cdots\text{S}$ distance of $3.45(5)\text{\AA}$.

$\text{SrC}_2\text{SnS}_4^{11d}$, $\text{BaCu}_2\text{SnS}_4^{11e}$ and $\text{BaAg}_2\text{SnS}_4^{11b}$ are related to (I) in their anionic stoichiometries but differ in structure. All of them are three-dimensional modified ZnS-type compounds formed by vertex-sharing CuS_4 and MS_4 (M=Cu or Ag) tetrahedra.

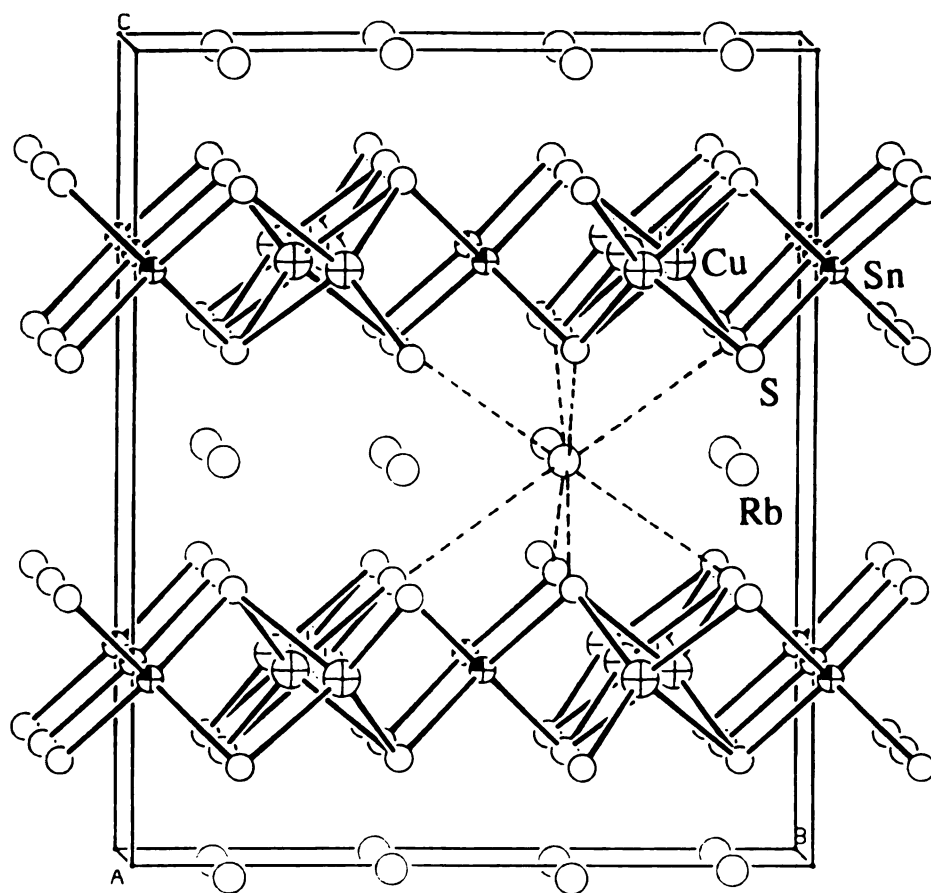


Figure 6-2: The structure of $\text{Rb}_2\text{Cu}_2\text{SnS}_4$ viewed parallel to the layers. A monolayer of rubidium cations is located between layers. Dash lines show the coordination environment of the Rb^+ cations.

The two-dimensional anionic framework of (I) can be compared to that of KCu_2NbS_4 ²² which consists of edge sharing NbS_4 and CuS_4 tetrahedra. Despite the similarity of their anionic formulae, the two frameworks differ in their arrangement of the MS_4 tetrathiometalate units. While the $[\text{Cu}_2\text{SnS}_4]^{2-}$ sheets are flat, those in KCu_2NbS_4 are highly corrugated. The conformational change from corrugated to flat is necessary to minimize the lattice energy because the number of cations is doubled in $\text{Rb}_2\text{Cu}_2\text{SnS}_4$. The defect anti-PbO structure of $\text{Rb}_2\text{Cu}_2\text{SnS}_4$ suggests that Cu^+ ion transport through the material might be possible via a hopping mechanism from the filled to the vacant sites.

Table 6-10. Selected Bond Distances (Å) and Bond Angles(deg) of $\text{Rb}_2\text{Cu}_2\text{SnS}_4$ with Standard Deviations in Parentheses

Selected Bond Distances (Å)			
Sn-S	2.390(8)	Rb-S	3.411(8)
Cu-S	2.583(8)	Rb-S	3.522(8)
Cu-S'	2.322(7)	Rb-S	3.462(8)
Cu-Cu	2.854(4)	Rb-S	3.417(8)
Selected Bond Angles (deg)			
S-Sn-S	107.0(3)	S-Cu-S'	106.5(3)
S-Sn-S	104.9(4)	S'-Cu-S'	126.6(5)
S-Sn-S	116.7(3)	Sn-S-Cu	80.3(2)
S-Cu-S	94.5(4)	Sn-S'-Cu	104.5(3)
S-Cu-S'	109.1(2)	Cu-S-Cu	70.9(2)

The Structure of $\text{Rb}_2\text{Cu}_2\text{Sn}_6$ (II)

$\text{Rb}_2\text{Cu}_2\text{Sn}_2\text{S}_6$ (II) has a two-dimensional structure containing corner-sharing tetrahedral CuS_4 and SnS_4 units, as shown in Figure 6-3. This is a derivative of the three-dimensional zinc blende adamantine type structure of the ternary parent compound Cu_2SnS_3 ²³ The replacement of an alkali metal ion for a Cu atom reduces the dimensionality of the Cu_2SnS_3 framework due to the interruption of covalent bonding throughout the structure. Each anionic slab, thus formed, contains three metal layers with a Cu layer sandwiched by two Sn layers in which one half of the Sn sites are missing forming parallel grooves which run perpendicularly above and below the slabs. The Rb^+ cations are located inside the grooves as shown in Figure 6-4 and therefore are an integral part of the slabs. Thus, a true van der Waals gap exists between the $\text{Rb}_2\text{Cu}_2\text{Sn}_2\text{S}_6$ layers which must be stabilized partially by interlayer $\text{S}\cdots\text{S}$ interactions. Nevertheless, $\text{Rb}\cdots\text{S}$ interactions with adjacent layers also exist. This explains the material's thin-layer crystal morphology and tendency to cleave easily into very thin mica-like sheets.

Two, crystallographically distinct, Rb^+ cations are situated within the anionic layers. Both are surrounded by six S atoms with an average $\text{Rb}\cdots\text{S}$ distance of 3.35(5) Å. Their coordination environments are similar, forming pseudo- C_{2v} symmetry as shown in Figure 6-5. The polyhedron of Rb^+ , however, is best described as trigonal prismatic. Each Rb^+ cation is coordinated by four S atoms (S(1)~S(4)) from the $[\text{Cu}_2\text{Sn}_2\text{S}_6]^{2-}$ slab where it is situated and by two more S atoms (S(5), S(6)) from the adjacent layer.

Selected bond distances and angles of (II) are given in Table 6-11. The average Sn-S distance (2.42(8) Å) and the average Cu-S distance

(2.35(2) Å) are normal. There are two types of sulfur atoms: S(1)~S(4) are triply bridging to two Cu atoms and one Sn atom while S(5)~S(6) are doubly bridging between two Sn atoms. The average Sn to S(1)~(4) distance (2.492(5) Å) is significantly longer than that of Sn to S(5)~S(6) distance (2.350(11) Å). Due to the stronger electronic repulsion between the shorter Sn-S bonds, the corresponding S-Sn-S bond angles are wider at 122.5(1)° and 122.3(1)°, whereas the S-Sn-S angle between the two longer Sn-S bonds is smaller at 103.5(1)°. The remaining S-Sn-S angles and S-Cu-S angles do not show much deviation from that of an ideal tetrahedron.

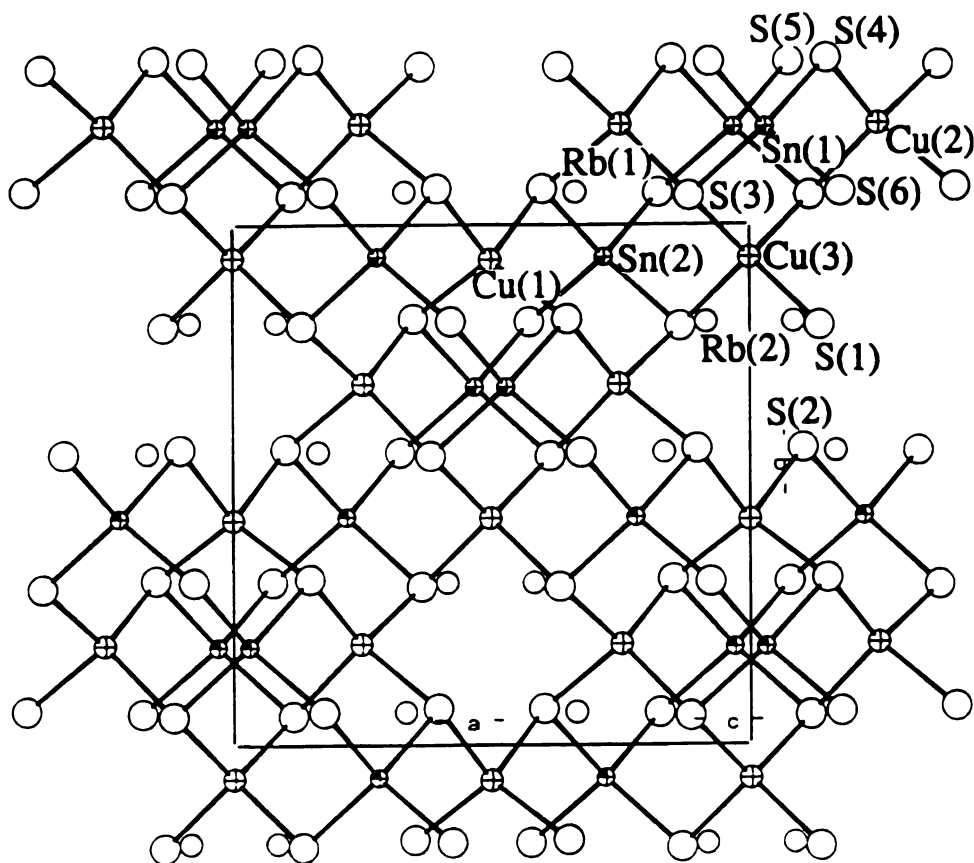


Figure 6-3: ORTEP representation and labeling scheme of the layered structure of $\text{Rb}_2\text{Cu}_2\text{Sn}_2\text{S}_6$. View down the c-axis.

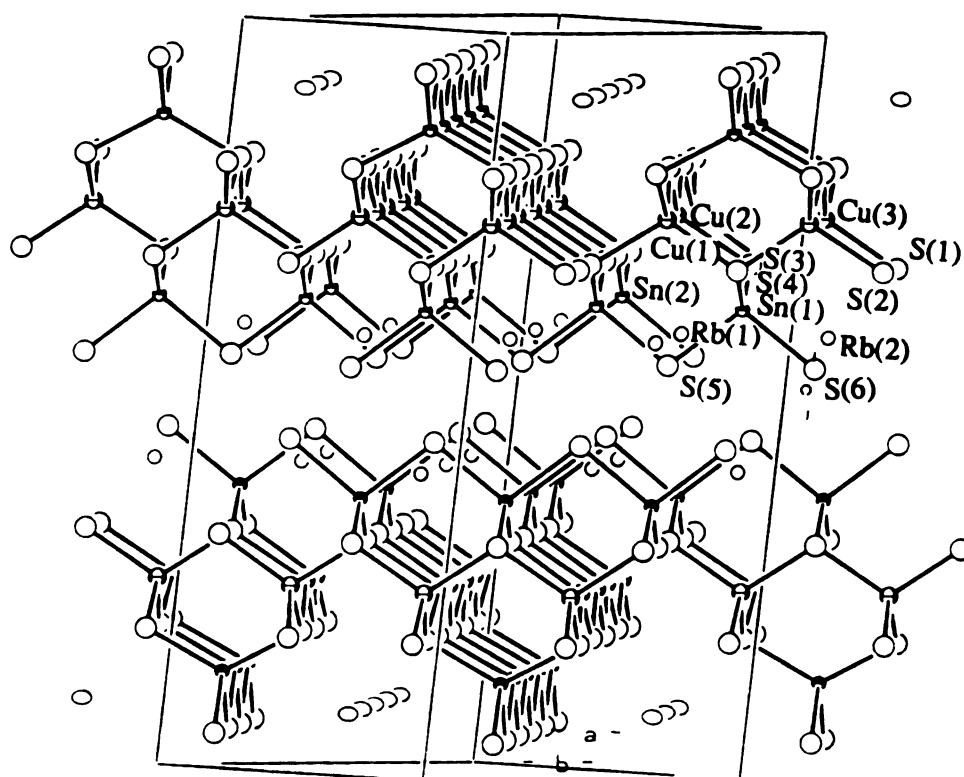


Figure 6-4: The structure of $\text{Rb}_2\text{Cu}_2\text{Sn}_2\text{S}_6$ viewed parallel to the layers.

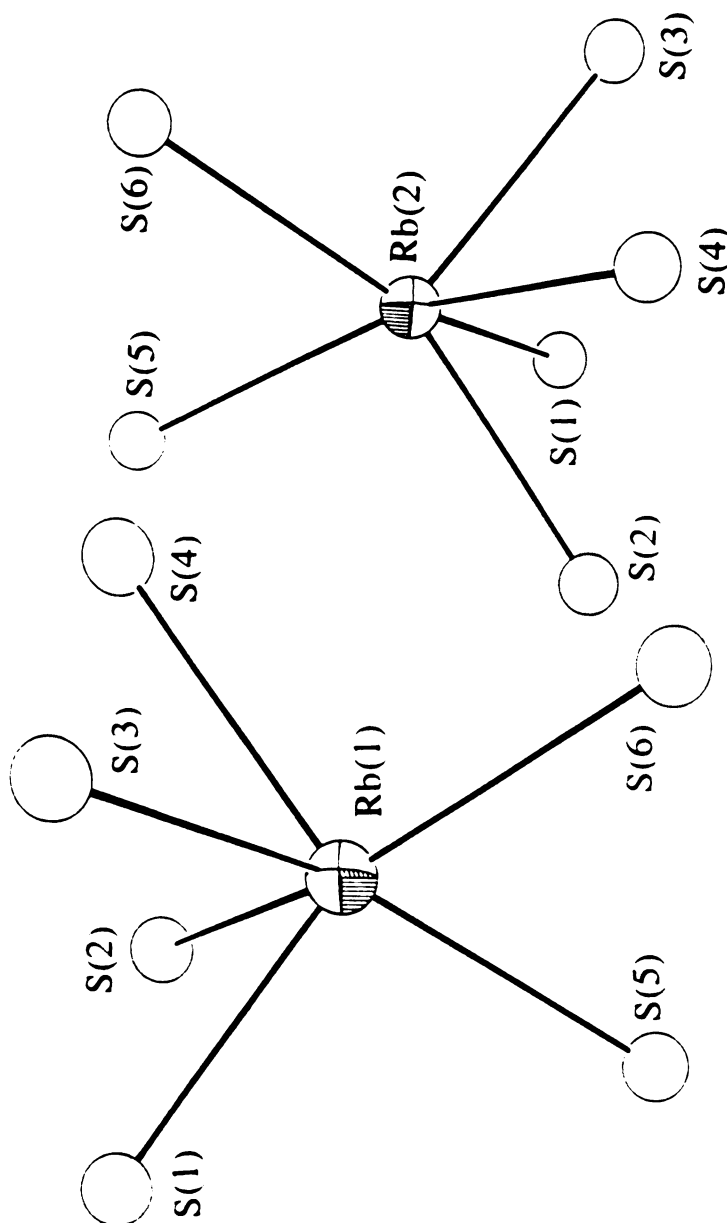


Figure 6-5: The coordination environment for Rb(1) and Rb(2). While S(1), S(2), S(3) and S(4) belong to the $[\text{Cu}_2\text{Sn}_2\text{S}_6]^{2-}$ slab which hosts the Rb^+ cations, S(5) and S(6) belong to another $[\text{Cu}_2\text{Sn}_2\text{S}_6]^{2-}$ slab.

Table 6-11. Selected Bond Distances (Å) and Angles (deg) for Rb₂Cu₂Sn₂S₆ with Standard Deviations in Parentheses

Selected Bond Distances (Å)			
Sn(1)-S(3)	2.355(4)	Cu(3)-S(3)	2.353(4)x2
Sn(1)-S(4)	2.334(4)	mean(Cu-S)	2.35(2)
Sn(1)-S(5)	2.498(4)	Rb(1)-S(1)	3.305(4)
Sn(1)-S(6)	2.490(4)	Rb(1)-S(2)	3.339(4)
Sn(2)-S(1)	2.354(4)	Rb(1)-S(3)	3.328(4)
Sn(2)-S(2)	2.356(4)	Rb(1)-S(4)	3.319(4)
Sn(2)-S(5)	2.494(4)	Rb(1)-S(5)	3.403(5)
Sn(2)-S(6)	2.487(4)	Rb(1)-S(6)	3.419(4)
mean(Sn-S)	2.42(8)	Rb(2)-S(1)	3.318(4)
Cu(1)-S(2)	2.365(4)x2	Rb(2)-S(2)	3.337(4)
Cu(1)-S(4)	2.339(4)x2	Rb(2)-S(3)	3.329(4)
Cu(2)-S(1)	2.318(4)	Rb(2)-S(4)	3.308(4)
Cu(2)-S(2)	2.382(4)	Rb(2)-S(5)	3.412(4)
Cu(2)-S(3)	2.372(4)	Rb(2)-S(6)	3.430(4)
Cu(2)-S(4)	2.300(5)	mean(Rb-S)	3.35(5)
Cu(3)-S(1)	2.342(4)x2		
Selected Bond Angles (deg)			
S(3)-Sn(1)-S(4)	122.5(1)	S(2)-Cu(2)-S(4)	112.2(1)
S(3)-Sn(1)-S(5)	107.5(1)	S(3)-Cu(2)-S(4)	113.7(1)
S(3)-Sn(1)-S(6)	107.5(1)	S(1)-Cu(3)-S(1)	103.5(2)
S(4)-Sn(1)-S(5)	107.5(1)	S(1)-Cu(3)-S(3)	112.5(1)x2
S(4)-Sn(1)-S(6)	106.8(1)	S(1)-Cu(3)-S(3)	108.1(1)x2
S(5)-Sn(1)-S(6)	103.5(1)	S(3)-Cu(3)-S(3)	111.9(2)
S(1)-Sn(2)-S(2)	122.3(1)	Sn(2)-S(1)-Cu(2)	101.5(1)
S(1)-Sn(2)-S(5)	107.2(1)	Sn(2)-S(1)-Cu(3)	102.8(1)
S(1)-Sn(2)-S(6)	107.5(1)	Cu(2)-S(1)-Cu(3)	111.7(2)
S(2)-Sn(2)-S(5)	108.0(1)	Sn(2)-S(2)-Cu(1)	102.0(1)
S(2)-Sn(2)-S(6)	107.8(1)	Sn(2)-S(2)-Cu(2)	103.4(1)

Table 6-11. (cont'd)

S(5)-Sn(2)-S(6)	102.2(1)	Cu(1)-S(2)-Cu(2)	114.9(2)
S(2)-Cu(1)-S(2)	100.5(2)	Sn(1)-S(3)-Cu(2)	101.6(1)
S(2)-Cu(1)-S(4)	112.4(1)x2	Sn(1)-S(3)-Cu(3)	103.4(1)
S(2)-Cu(1)-S(4)	107.7(1)x2	Cu(2)-S(3)-Cu(3)	113.0(2)
S(4)-Cu(1)-S(4)	115.2(2)	Sn(1)-S(4)-Cu(1)	102.2(1)
S(1)-Cu(2)-S(2)	101.8(1)	Sn(1)-S(4)-Cu(2)	104.5(2)
S(1)-Cu(2)-S(3)	112.1(1)	Cu(1)-S(4)-Cu(2)	109.7(2)
S(1)-Cu(2)-S(4)	111.2(2)	Sn(1)-S(5)-Sn(2)	102.7(2)
S(2)-Cu(2)-S(3)	105.0(2)	Sn(1)-S(6)-Sn(2)	103.1(1)

Structures $\text{K}_2\text{Au}_2\text{SnS}_4$ (III) and $\text{K}_2\text{Au}_2\text{Sn}_2\text{S}_6$ (IV)

The one-dimensional anionic structure of (III) is constructed from SnS_4 tetrahedra and linear AuS_2 dumbbell units in the ratio of 1:2. Even though the stoichiometry of (III) is the same as that of (I), the preferred linear coordination of Au^+ forces a dramatic structural change from that of (I). The edges of two SnS_4 tetrahedra are connected by two Au^+ ions to form $\text{Sn}(\text{SAuS})_2\text{Sn}$ eight-membered rings which extend in one-dimension by sharing the Sn atoms at their two ends, as shown in Figure 6-6. These chains run along the crystallographic b-axis and are parallel to one another, separated by charge balancing K^+ cations.

Selected bond distances and bond angles are given in Table 6-12. The average Sn-S distance is $2.396(12)\text{\AA}$ and the SnS_4 tetrahedra are slightly distorted with S-Sn-S angles ranging from $106.7(2)^\circ$ to $111.9(2)^\circ$ (average value = $109.4(21)^\circ$) which are comparable to those in the discrete $[\text{SnS}_4]^{4-}$ ion^{10h-j}. The average Au-S distance, $2.295(4)\text{\AA}$, is normal for linear AuS_2 fragments²⁴. The average S-Au-S angle, $174.9(6)^\circ$, is close to 180° . The linear AuS_2 fragments in the $\text{Sn}(\text{SAuS})_2\text{Sn}$ eight-membered rings are nearly parallel but the $\text{Au}\cdots\text{Au}$ distances are long at $3.929(2)\text{\AA}$ and $4.014(3)\text{\AA}$. An interesting feature of the compounds is the presence of weak intrachain $\text{Au}\cdots\text{Au}$ short contacts of $3.363(2)\text{\AA}$ between two Au^+ ions in two adjacent $\text{Sn}(\text{SAuS})_2\text{Sn}$ eight-membered rings as shown by the dashed lines in Figure 6-6. Interchain $\text{Au}\cdots\text{Au}$ short contacts were reported earlier, KAuS_5 ^{24,25}, which contains chains with two-coordinated Au^+ ions bridged with pentasulfides. No such contacts are observed in (III). Two distinct K^+ cations are surrounded by 7 and 4 S atoms respectively. The

average K...S distance is 3.31(13)Å. Regardless of the larger size of Au, the Au...K distances (3.546(5)Å, 3.634(5)Å and 3.644(6)Å) are shorter than the Sn...K distances (larger than 4 Å) and K...K distances (larger than 3.7Å). Alkali metal...Au interactions were observed before²⁶. The short K⁺...Au distance suggests an attractive interaction of the d¹⁰ electron pairs on Au⁺ ions and the positive charges on alkali metal cations. The short contact may be accounted for by the relatively large electronegativity of Au, 2.4, which is remarkably close to those of Se(2.4) and Te(2.1).²⁷ An extreme case of alkali metal...Au interaction is found in KAu₅²⁸ in which K...Au distances range from 3.27Å to 3.61Å.

We note that in BaAu₂SnS₄ (V)^{11a} the [Au₂SnS₄]²⁻ chains contain the same building blocks as in (III) but adopt a different conformation, as shown in Figure 6-7. In BaAu₂SnS₄, all Sn atoms lie in a straight line, while in (III) the Sn-Sn vectors in the Sn(SAuS)₂Sn eight-membered rings proceed in a zigzag fashion with the angle between two Sn-Sn vectors at 107.46(6)°. The conformational change is clearly due to packing effects and can be explained by the difference in size and number of the counterions between (III) and (V). Zigzag chains are better able to accommodate a double row of K⁺ cations. The straight chains of the Ba²⁺ salt provide enough space for a single row of Ba²⁺ cations. This is illustrated by comparing Figures 6-8A and 6-8B. The structures of K₂Au₂SnS₄ and BaAu₂SnS₄ are also closely related to those of K₂Hg₃S₄, K₂Hg₃Se₄ and Cs₂Hg₃Se₄²⁹ (which can be written as A₂Hg₂Hg'Q₄ (A=alkali metal; Q=S, Se) for a more obvious comparison). These compounds feature straight [Hg₃Q₄]²⁻ chains in which [HgS₄]⁶⁻ tetrahedra are connected via linear Hg²⁺ centers.

The [Au₂Sn₂S₆]²⁻ fragment in (IV) is also one-dimensional, featuring

edge-sharing bitetrahedral $[\text{Sn}_2\text{S}_6]$ units connected by linear Au^+ atoms to form infinite chains. The chains are fully extended by comparison to the zigzag motif exhibited in (III). The unit cell of $\text{K}_2\text{Au}_2\text{Sn}_2\text{S}_6$ is shown in Figure 6-9. The structure of (IV) is also related to that of fully extended $\text{BaAu}_2\text{SnS}_4$. (IV) contains longer $[\text{Sn}_2\text{S}_6]^{4-}$ units so that the chains can accommodate one more equivalent of K^+ cations. The $[\text{Au}_2\text{Sn}_2\text{S}_6]^{2-}$ chains lie parallel to the crystallographic c-axis and are separated by potassium cations.

Selected bond distances and angles for (IV) are given in Table 6-13. The average Sn-S distances is $2.41(4)\text{\AA}$ and the S-Sn-S angles range from $91.9(3)^\circ$ to $115.0(2)^\circ$, which are comparable to those in discrete $[\text{Sn}_2\text{S}_6]^{4-}$ ions^{11g}. The Au-S distances and S-Au-S angles are comparable to those in (III) at $2.313(5)\text{\AA}$ and $175.4(3)^\circ$. There is also a Au...Au short contact at $3.010(2)\text{\AA}$. The Au...Au short contact occurs inside the $\text{Sn}(\text{SAuS})_2\text{Sn}$ eight-membered ring in contrast with (III) in which inter-ring Au...Au are found. The Au...Au short contacts are classical d^{10} - d^{10} interactions³⁰ which were also observed in $\text{BaAu}_2\text{SnS}_4$ and KAuS_5 . The two linear AuS_2 fragments in the $\text{Sn}(\text{SAuS})_2\text{Sn}$ eight-membered rings are not parallel but form a S-Au...Au-S dihedral angle of 75.3° .

There are three distinct potassium cations. K(1) and K(2) are coordinated by 8 and 10 S atoms respectively, while K(3) is found to be disordered evenly between (0.5, 0.5, 0.049) and (0.5, 0.5 -0.049). At either site, K(3) is coordinated by 8 S atoms. The average K...S distance is $3.39(16)\text{\AA}$. The K...Au distances at $3.850(8)\text{\AA}$ are longer than those in (III). We note that the K^+ cations are surrounded by more S atoms in (IV), and, as a result, a fewer number of K...Au interactions are observed.

Although gold and copper belong to the same group in the periodic

table, they behave quite differently in their coordination modes. Tetrahedral coordination is the most common for Cu^+ chalcogenides although three and two coordinated Cu^+ are known. Au^+ prefers linear coordination because of the very large (4.63 eV) 6s-6p energy separation which makes mixing and hybridization of these orbitals more difficult.³¹ The less common Au^{3+} square-planar centers were formed in the ternary AAuSe_2 (A=Na, K), Na_3AuSe_8 and $\text{K}_3\text{AuSe}_{13}$ ^{24,29c,19} systems, and appear to be more stable in a selenide rather than sulfide environment. Extension of the studies reported here into the Se_x^{2-} fluxes may also stabilize Au^{3+} centers which, in conjunction with Sn and alkali metals, should form different structures from those described here.

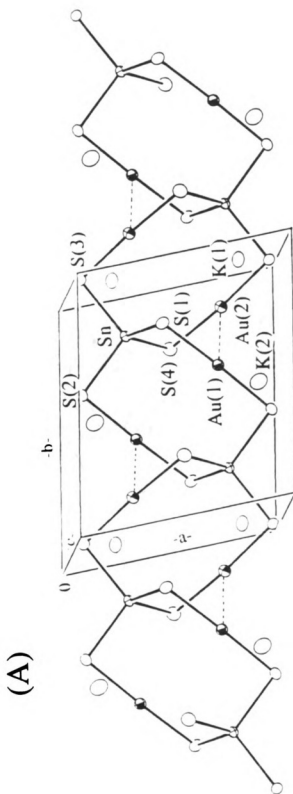
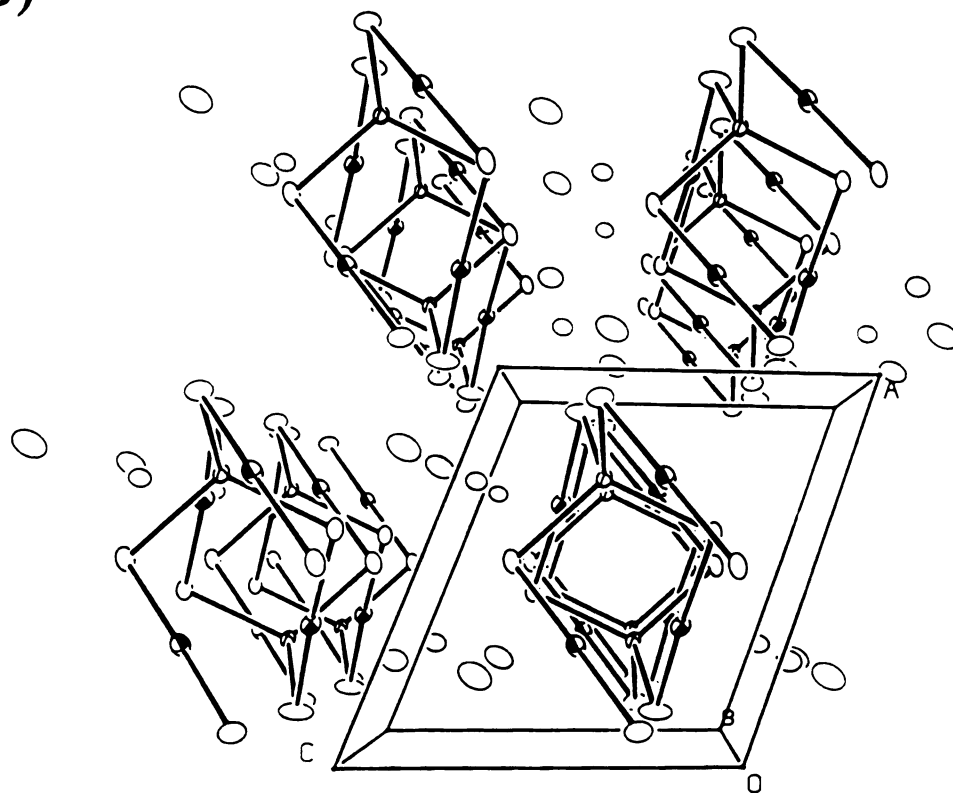


Figure 6-6: ORTEP representation and labeling scheme of (A) a single chain of $K_2Au_2SnS_4$. $Au \cdots Au$ short contacts are shown by dashed lines (B) view down the b -axis.

(B)



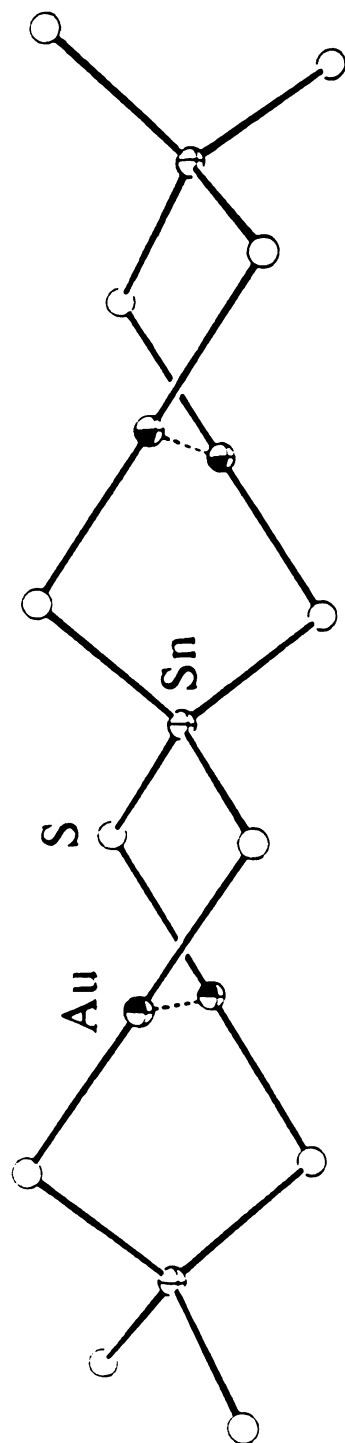


Figure 6-7: ORTEP representation of the anionic structure of BaAu₂SnS₄ (adapted from reference 11a).

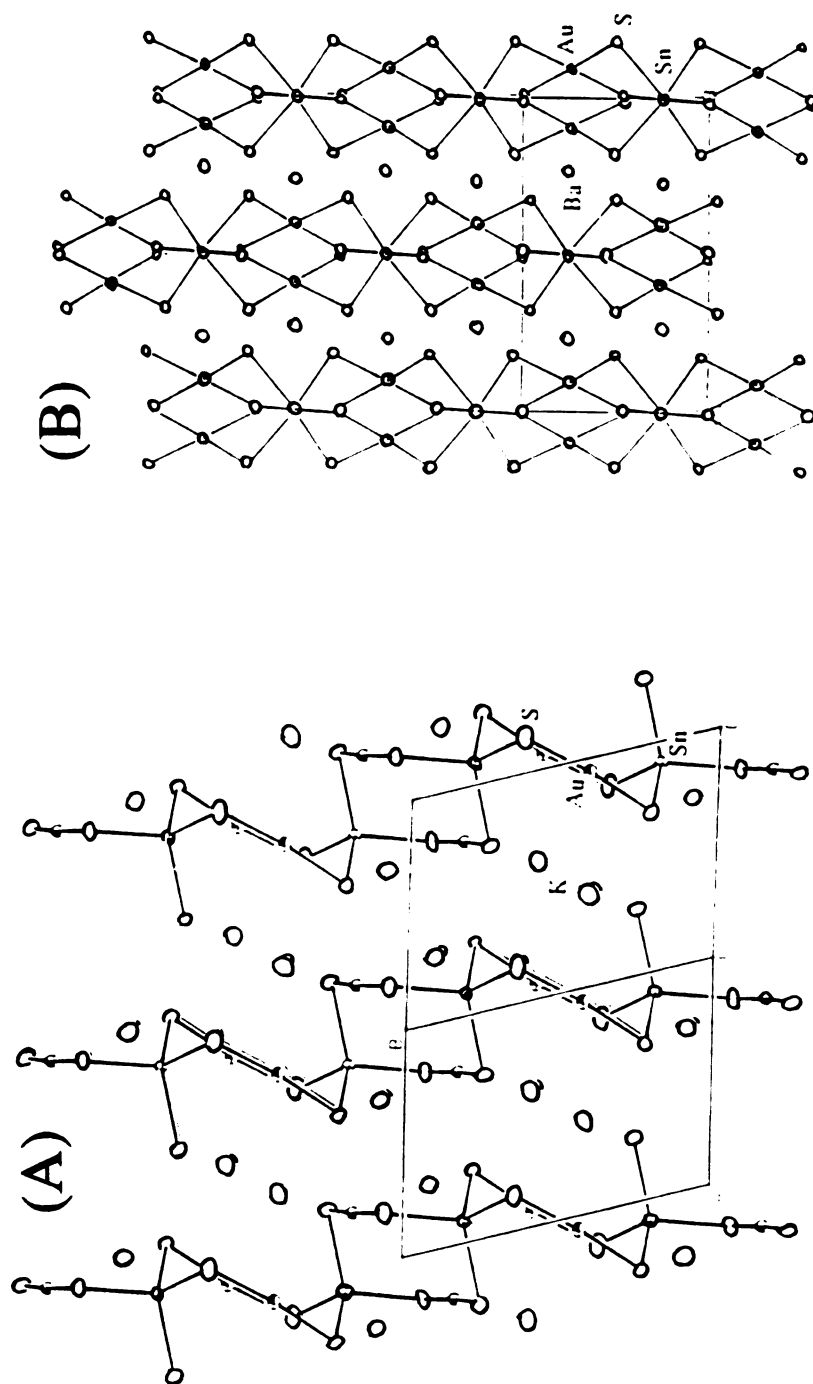


Figure 6-8: Comparison between the unit cells of (A) $\text{K}_2\text{Au}_2\text{SnS}_4$ viewed down the $\langle 101 \rangle$ axis. (B) $\text{BaAu}_2\text{SnS}_4$ viewed down the $\langle 010 \rangle$ axis.

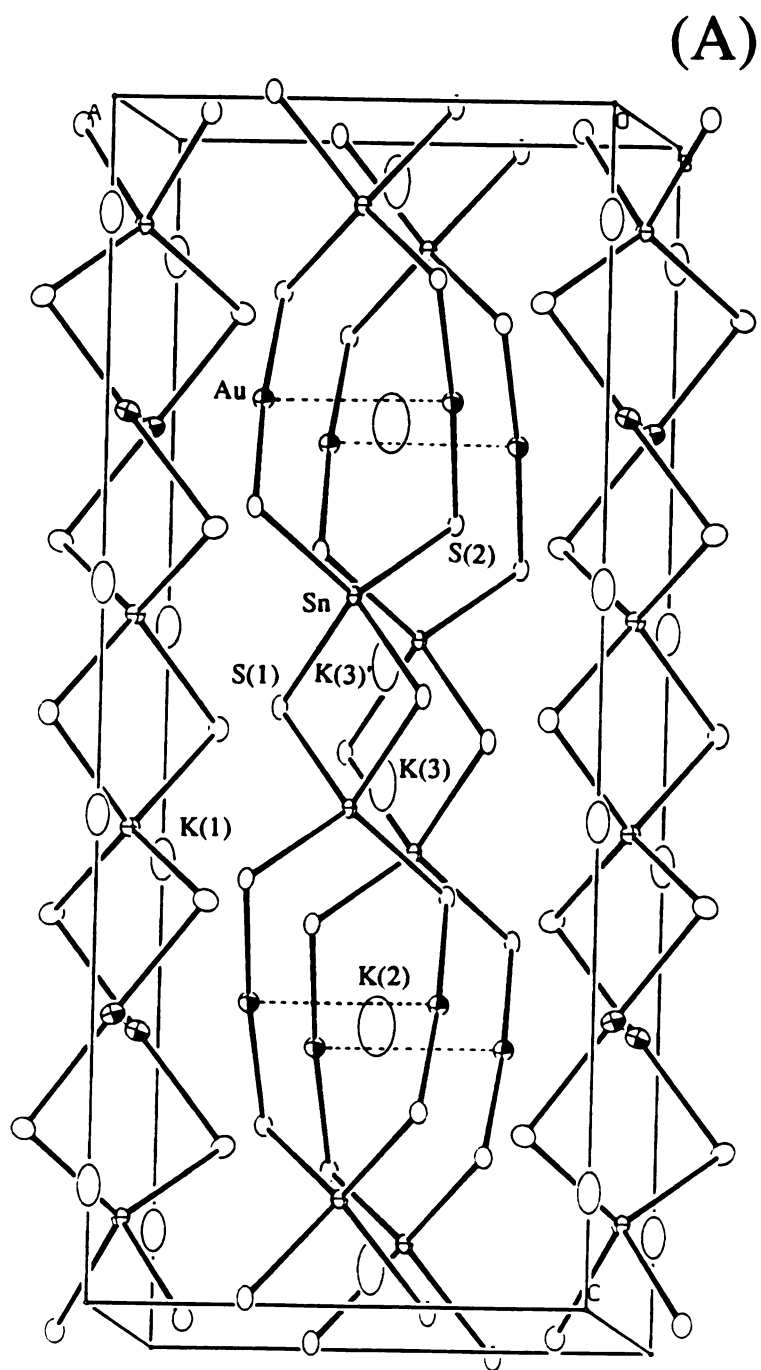


Figure 6-9: ORTEP representation and labeling scheme of $K_2Au_2Sn_2S_6$. $Au \cdots Au$ short contacts are shown by dashed lines. (A) view down the b-axis. (B) view down the c-axis.

(B)

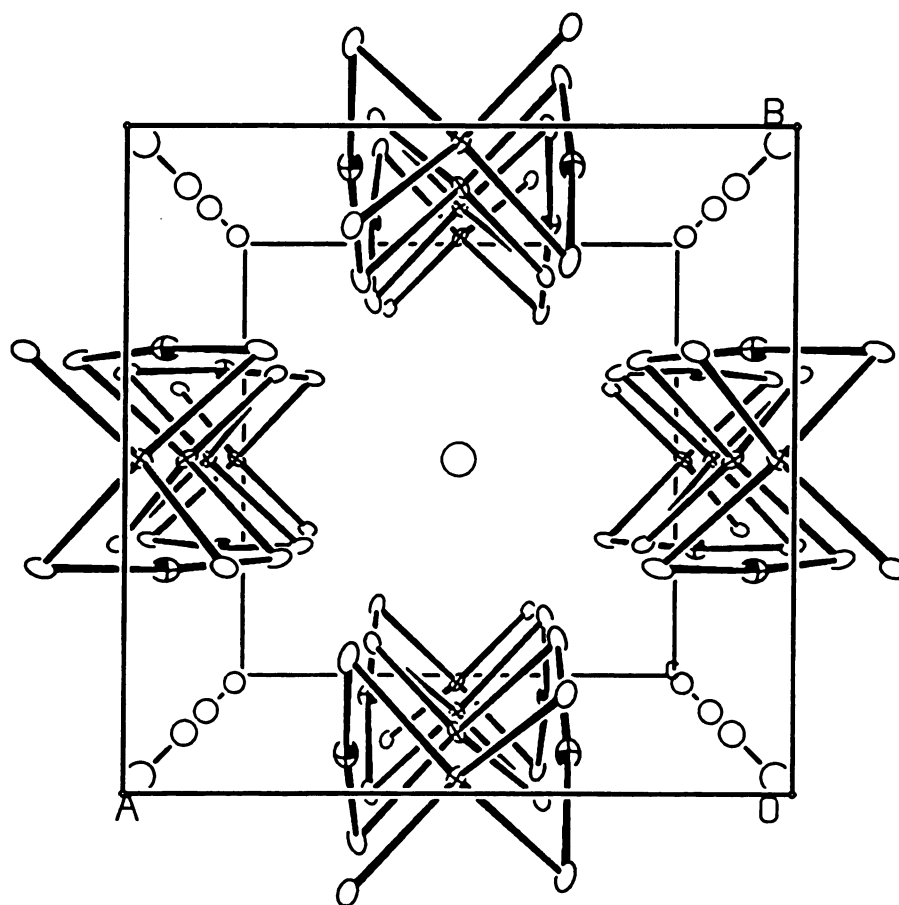


Table 6-12. Selected Bond Distances (Å) and Bond Angles (deg) of K₂Au₂SnS₄ with Standard Deviations in Parentheses

Selected Bond Distances (Å)			
Au(1)-S(1)	2.297(5)	Sn-S(1)	2.384(5)
Au(1)-S(2)	2.290(6)	Sn-S(2)	2.410(5)
Au(2)-S(3)	2.300(5)	Sn-S(3)	2.398(5)
Au(2)-S(4)	2.293(5)	Sn-S(4)	2.401(6)
mean(Au-S)	2.295(4)	mean(Sn-S)	2.398(11)
Au(1)-Au(2)	3.363(2)	K(1)-S(1)	3.264(7)
Au(2)-Au(2)	4.015(3)	K(1)-S(2)	3.224(8)
Au(1)-Au(1)	3.929(2)	K(1)-S(3)	3.248(7)
Au(1)-K(1)	3.634(5)	K(1)-S(3)	3.209(8)
Au(1)-K(2)	3.644(6)	K(1)-S(4)	3.401(8)
Au(2)-K(2)	3.865(6)	K(1)-S(4)	3.642(7)
Au(2)-K(2)	3.914(6)	K(2)-S(1)	3.186(8)
Au(2)-K(1)	3.546(5)	K(2)-S(2)	3.332(8)
Au(2)-K(1)	3.999(5)	K(2)-S(3)	3.303(7)
mean(Au-S)	3.77(18)	K(2)-S(4)	3.269(8)
K(1)-S(1)	3.283(7)	mean(K-S)	3.31(12)
Selected Bond Angles (deg)			
S(1)-Sn-S(2)	110.5(2)	S(1)-Au(1)-S(2)	175.1(2)
S(1)-Sn-S(3)	110.9(2)	S(3)-Au(2)-S(4)	174.6(2)
S(1)-Sn-S(4)	111.9(2)	Au(2)-S(3)-Sn	92.0(2)
S(2)-Sn-S(3)	106.7(2)	Au(1)-S(1)-Sn	99.0(2)
S(2)-Sn-S(4)	107.4(2)	Au(2)-S(4)-Sn	95.1(2)
S(3)-Sn-S(4)	109.2(2)	Au(1)-S(2)-Sn	92.8(2)

Table 6-13. Selected Bond Distances (Å) and Angles (deg) for K₂Au₂Sn₂S₆ with Standard Deviations in Parentheses

Selected Bond Distances (Å)

Au-Au	3.010(2)	K(1)-S(1)	3.477(9)
Au-S(2)	2.313(5)	K(1)-S(2)	3.138(7)
Sn-S(1)	2.443(7)	K(2)-S(2)	3.459(6)
Sn-S(2)	2.368(6)	K(3)-S(1)	3.226(9)
mean(Sn-S)	2.41(5)	K(3)-S(2)	3.559(6)
Au-K(1)	3.850(8)	mean(K-S)	3.39(16)

Selected Bond Angles (deg)

Au-Au-S(2)	87.7(1)	S(2)-Au-S(2)	175.4(3)
Au-Au-S(2)	87.7(1)	S(1)-Sn-S(2)	110.3(2)
S(1)-Sn-S(1)	91.9(3)	S(1)-Sn-S(2)	113.5(2)
S(1)-Sn-S(2)	113.5(2)	S(2)-Sn-S(2)	115.0(2)
S(1)-Sn-S(2)	110.3(2)	Sn-S(1)-Sn	88.1(3)

3.3. Spectroscopy

Optical Spectroscopy

The UV-Vis-near IR spectra of all compounds reported here exhibit steep absorption edges from which optical band gaps can be unequivocally derived. $(\alpha h\nu)^2$ vs. E plots appear quite linear suggesting the band gaps are direct in character. Table 6-14 summarizes the results. Typical absorption spectra are shown in Figures 6-10 and 6-11. The band gap values are consistent with the colors of the samples. These results suggest that all compounds are semiconductors, as predicted by the electron precise nature of their chemical formulas. The spectrum of $\text{Rb}_2\text{Cu}_2\text{SnS}_4$ also reveals other electronic transitions at higher energy (2.58 eV, 2.78 eV and 3.56 eV) above the absorption edge.

The selenide analogs $\text{K}_2\text{Cu}_2\text{Sn}_2\text{Se}_6$ and $\text{Rb}_2\text{Cu}_2\text{Sn}_2\text{Se}_6$ show absorption edges at lower energy, as expected, giving band gaps in the neighborhood of 1.04 eV, see Figure 6-10C. The band gaps of $\text{A}_2\text{Cu}_2\text{Sn}_2\text{S}_6$ and $\text{A}_2\text{Cu}_2\text{Sn}_2\text{Se}_6$ are relatively low and comparable to those of the structurally related chalcopyrites, CuInS_2 (1.55 eV) and CuInSe_2 (1.0 eV). These values suggest that these compounds are suitable for efficient absorption of most of the solar radiation, making them potential candidates for solar cell applications. In CuInQ_2 , the optical band-gap transition originates from a valence band, composed of hybridized orbitals $\text{Cu}(3d)/\text{Q}(3 \text{ or } 4p)$ to a $\text{Cu}(4s)$ conduction band.³² A similar assignment is proposed for $\text{A}_2\text{Cu}_2\text{Sn}_2\text{Q}_6$. The small band-gaps exhibited by $\text{A}_2\text{Cu}_2\text{Sn}_2\text{Q}_6$

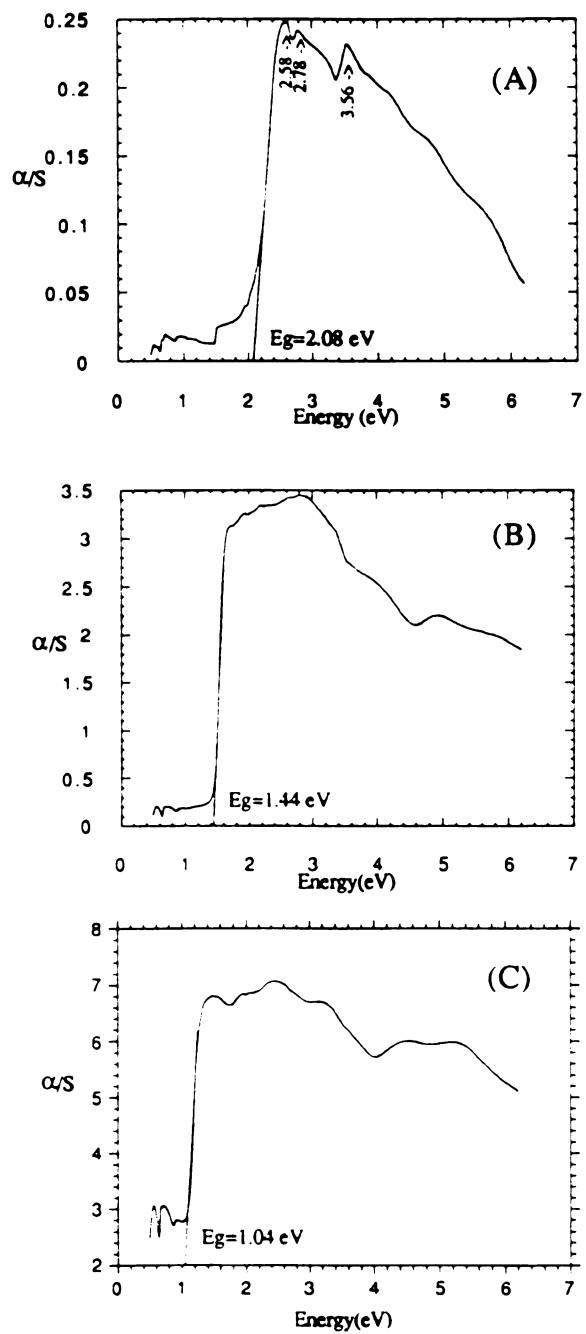


Figure 6-10: Optical absorption spectra of (A) $\text{Rb}_2\text{Cu}_2\text{SnS}_4$ (B) $\text{Rb}_2\text{Cu}_2\text{Sn}_2\text{S}_6$ (C) $\text{K}_2\text{Cu}_2\text{Sn}_2\text{Se}_6$

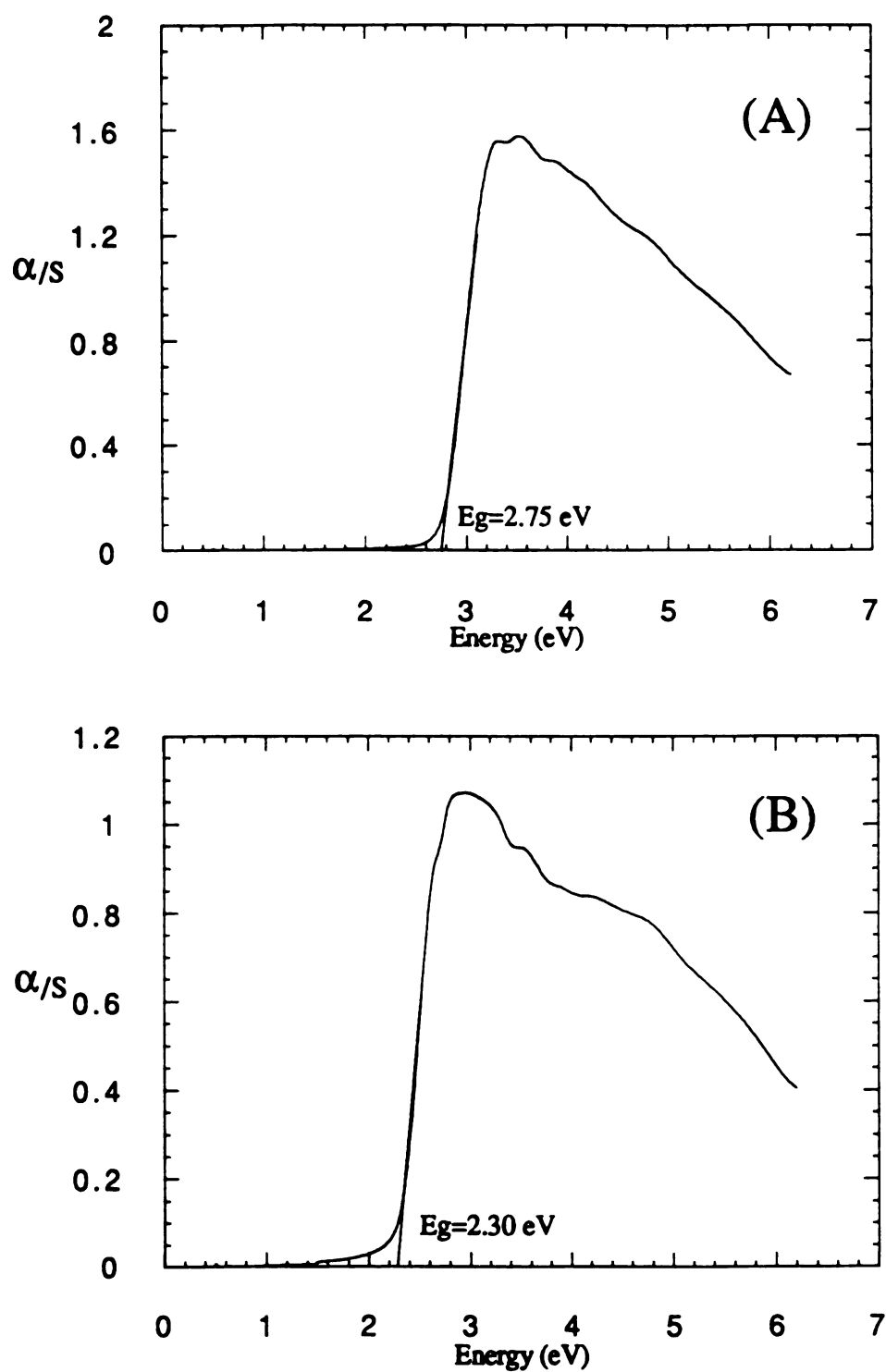


Figure 6-11: Optical absorption spectra of (A) $K_2Au_2SnS_4$ (B) $K_2Au_2Sn_2S_6$.

Table 6-14. Summary of the Optical Band-Gaps (eV) for $\text{Rb}_2\text{Cu}_2\text{SnS}_4$, $\text{A}_2\text{Cu}_2\text{Sn}_2\text{S}_6$ (A=K, Rb), $\text{A}_2\text{Cu}_2\text{Sn}_2\text{Se}_6$ (A=K, Rb), $\text{K}_2\text{Au}_2\text{SnS}_4$ and $\text{K}_2\text{Au}_2\text{Sn}_2\text{S}_6$.

Compound	$E_g(\text{eV})$	Compound	$E_g(\text{eV})$
$\text{Rb}_2\text{Cu}_2\text{SnS}_4$	2.08	$\text{K}_2\text{Cu}_2\text{Sn}_2\text{Se}_6$	1.04
$\text{K}_2\text{Cu}_2\text{Sn}_2\text{S}_6$	1.47	$\text{R}_2\text{Cu}_2\text{Sn}_2\text{Se}_6$	1.04
$\text{Rb}_2\text{Cu}_2\text{Sn}_2\text{S}_6$	1.44	$\text{K}_2\text{Au}_2\text{SnS}_4$	2.75
		$\text{K}_2\text{Au}_2\text{Sn}_2\text{S}_6$	2.30

Table 6-15. Frequencies (cm^{-1}) of Spectral Absorptions for (I)~(IV)

$\text{Rb}_2\text{Cu}_2\text{SnS}_4(\text{I})$	$\text{Rb}_2\text{Cu}_2\text{Sn}_2\text{S}_6(\text{II})$	$\text{K}_2\text{Au}_2\text{SnS}_4(\text{III})$	$\text{K}_2\text{Au}_2\text{Sn}_2\text{S}_6(\text{IV})$
353 (s)	392 (s)	368 (m)	359 (m)
329 (sh)	369 (m)	349 (sh)	337 (m)
223 (w)	349 (m)	339 (s)	320 (m)
152 (w)	305 (m)	328 (sh)	311 (w)
	264 (s)	302 (sh)	298 (s)
	232 (s)	153 (m)	189 (m)
	198 (m)		178 (sh)
			171 (w)
			158 (m)
			151 (m)
			140 (w)
			131 (w)

^a (s) strong; (m) medium; (w) weak; (sh) shoulder

are also comparable to those of CdTe (1.5 eV), GaAs (1.4 eV) and Si (1.1eV) which, together with CuInQ₂, are highly efficient photovoltaic materials.³³

Vibrational Spectroscopy

(I)~(IV) exhibit spectral absorptions due to Cu-S and/or Sn-S and/or Au-S vibrations as shown in Figure 6-12. The observed absorption frequencies are given in Table 6-15. In general, the lighter metal atoms and stronger M-S bonds exhibit higher vibrational frequencies. However, peaks in the range between 400 cm⁻¹ to 150 cm⁻¹ could be attributed to either of the Cu-S, Sn-S and Au-S vibrations. This makes the assignment of the peaks nearly impossible. (I) has a more symmetric structure which could account for its small number of absorption bands. There is only one intense peak at 353 cm⁻¹ with a shoulder at 329 cm⁻¹; the former could be assigned as Cu-S stretching and the latter could be assigned as Sn-S stretching which is less intense because Sn atoms are sitting at more symmetric sites than Cu atoms. (II) has more peaks and could be divided into two set of absorptions due to Cu-S and Sn-S vibrations respectively because the bonding environment of Sn and Cu is similar. However, except that the most left peak could be assigned as Cu-S stretching, it is difficult to assign the rest of peaks. (III) and (IV) exhibit even more complicated overlaps which make the assignment impossible.

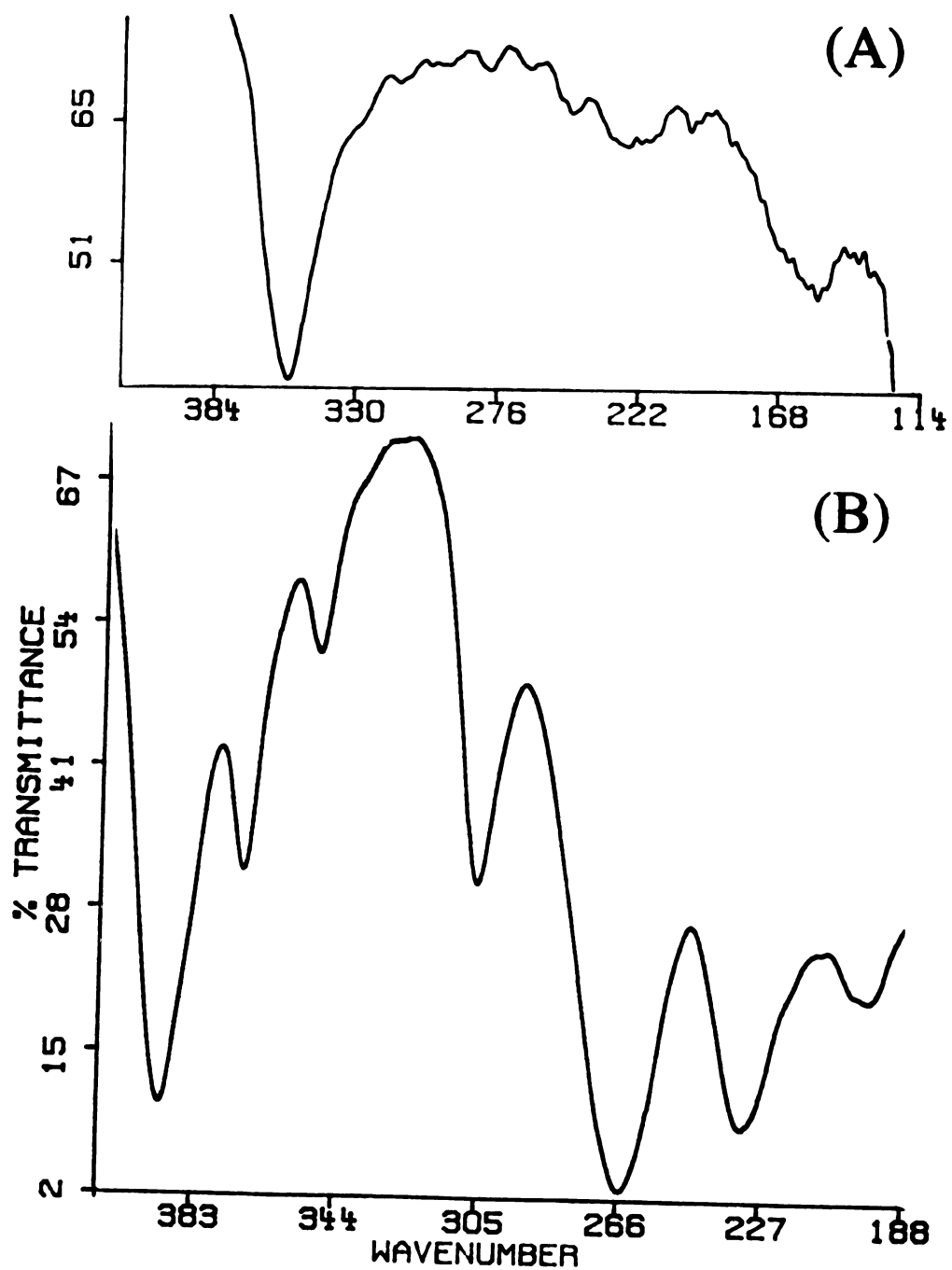
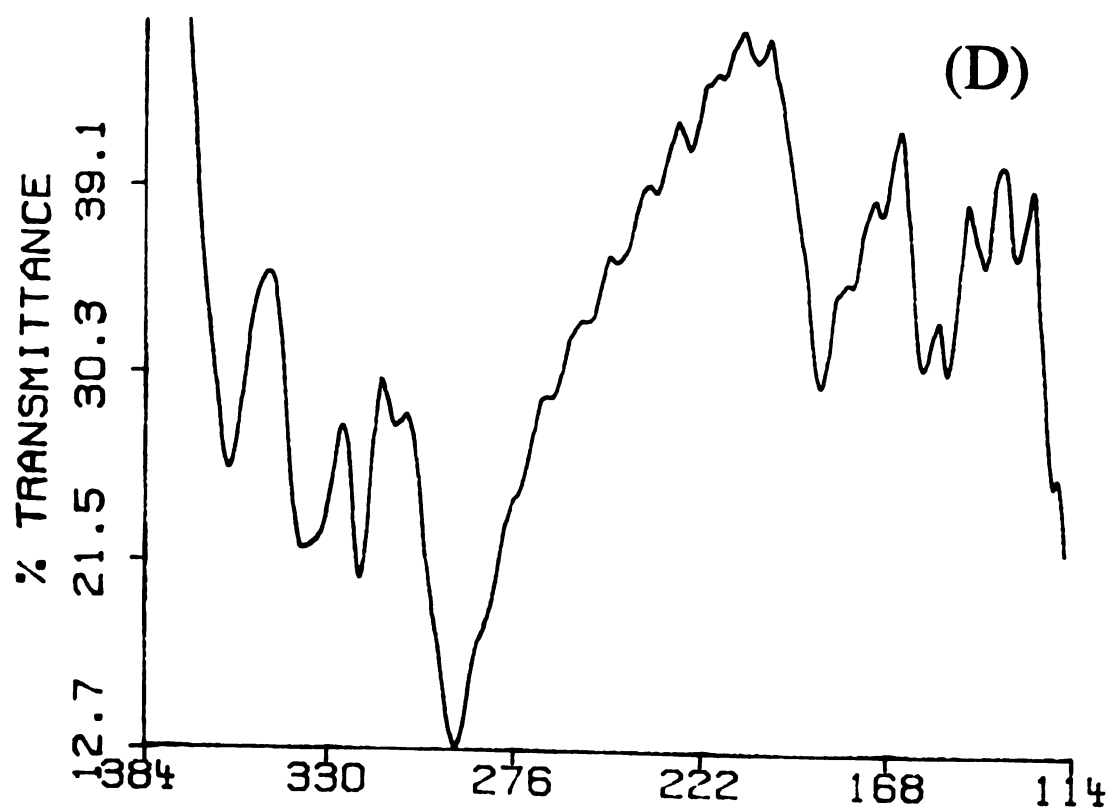
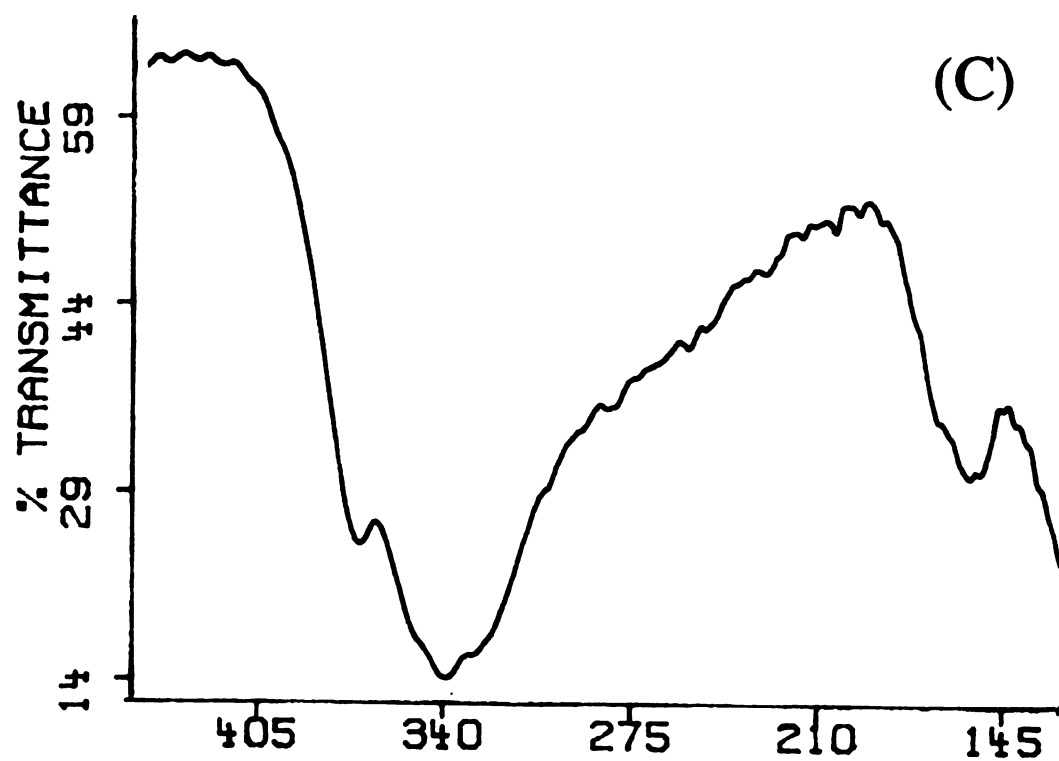


Figure 6-12: Infrared spectra of (A) $\text{Rb}_2\text{Cu}_2\text{SnS}_4$ (B) $\text{Rb}_2\text{Cu}_2\text{Sn}_2\text{S}_6$ (C) $\text{K}_2\text{Au}_2\text{SnS}_4$ (D) $\text{K}_2\text{Au}_2\text{Sn}_2\text{S}_6$.



Conclusion

The results reported here show that the $[\text{SnS}_4]^{4-}$ and $[\text{Sn}_2\text{S}_6]^{4-}$ anions are excellent building blocks which can be linked to other metal ions to form various extended quaternary structures. The ability of the $[\text{SnS}_4]^{4-}$ and $[\text{Sn}_2\text{S}_6]^{4-}$ ligands to coordinate to M^{n+} ions in solid state structures may parallel or exceed that of the versatile $[\text{MoS}_4]^{2-}$ exhibited in discrete complexes, and thus it points to a promising new synthetic avenue in which tetrathiometalates play a central role. Alkali polysulfide fluxes are convenient *in-situ* sources for these anions. ..

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CHAPTER 7

Molten Salt Synthesis and Characterization of Quaternary Chalcogenides Containing Main Group and Transition Metals

1. Introduction

From the structural point of view, quaternary chalcogenides are interesting due to their structural varieties resulting from the combination of two kinds of metal centers with different ratio, size, coordination preference and arrangement. Alkaline earth metal containing quaternary chalcogenides have been extensively investigated by high temperature solid state synthesis.¹ Recently molten alkali metal salts have proved to be convenient reaction media for chalcogenide synthesis at a lower temperature regime (<500°C). So far, most of the research has focused on ternary systems.² Relatively less efforts³ have been put on quaternary chalcogenides where the chemistry could be even richer.

In Chapter 6, we reported a series of alkali metal mixed Sn/Cu or Au quaternary chalcogenides.⁴ We have shown that molten salt techniques are promising for synthesizing quaternary chalcogenides. $[\text{SnS}_4]^{4-}$ and/or $[\text{Sn}_2\text{S}_6]^{4-}$, whose alkali metal salts have been characterized⁵ and were found

available in Sn containing polysulfide fluxes as mentioned in Chapter 3, appear to be excellent building blocks to combine with other metal ions. Their germanium analogs are also well known⁶ and have been found as building blocks in the structures of KInGeS_4 , KGaGeS_4 ^{3d} and $\text{BaAg}_2\text{GeS}_4$.¹ⁱ To further investigate the synthesis of quaternary compounds by using molten salt techniques, we expanded to mixed metal systems of divalent metals (Zn, Cd, Hg, Mn) and main group metals (In, Ge, Sn). Some characteristics of the divalent metals we employed are: Mn is magnetic; Mn, Zn, and Cd prefer tetrahedral coordination but have different ionic size; Hg prefers both tetrahedral and linear coordination. We have synthesized and characterized eleven new quaternary chalcogenides, $\text{K}_2\text{HgSn}_2\text{S}_6$, $\text{K}_2\text{GeIn}_2\text{S}_6$, $\text{K}_2\text{Hg}_3\text{Sn}_2\text{S}_8$, $\text{K}_2\text{Hg}_3\text{Ge}_2\text{S}_8$, $\text{K}_6\text{Zn}_4\text{Sn}_5\text{S}_{17}$, $\text{Rb}_2\text{ZnSn}_2\text{S}_6$, $\text{Cs}_2\text{MnSn}_2\text{S}_6$, K_2MnSnS_4 , $\text{Cs}_2\text{In}_2\text{Ge}_2\text{S}_8$, $\text{Cs}_2\text{MnSn}_3\text{Se}_8$ and $\text{Rb}_2\text{CdGe}_2\text{S}_6$. All the metal centers retain the structural features found in their binary and ternary forms but combine with another metal center with different geometry preference and size to form either novel or known structure types.

2. Experimental Section

2.1. Reagents

Sn metal: ~325 mesh, 99.8% purity; Cd metal: -325 mesh, 99.5% purity; In metal: -325 mesh, 99.999% purity; CERAC Inc., Milwaukee, WI. Ge metal: -100 mesh, 99.99% purity; Mn metal: 99.9% purity, -50 mesh, Aldrich Chemical Company, Inc., Milwaukee, WI. Sublimed sulfur:

99.5~100.5%; Zn powder: purified; HgS powder; J. T. Baker Inc., Phillipsburg, NJ. A_2Q ($A=K, Rb, Cs$; $Q=S, Se$) starting materials were prepared as described elsewhere.⁷

2.2. Physical Measurements

The instruments and experimental setups for Infrared spectroscopy, SEM/EDS quantitative microprobe analysis and UV/vis/near-IR optical diffuse spectroscopy are the same as those described in previous chapters.

Magnetic susceptibility data were collected on a Quantum Design SQUID system. 34.98 mg (0.0466 mmol) of $Cs_2MnSn_2S_6$ and 43.93 mg (0.11 mmol) of K_2MnSnS_4 were loaded in plastic bags respectively and purged with He gas before measurements. The samples of these two compounds include small amount MnS impurity (<1%) which does not significantly influence the results. The diamagnetic contribution of the plastic bags was relatively small and was ignored during data processing. Measurements of magnetization versus applied magnetic field were performed from 50 Gauss to 5000 Gauss at both 5 K and 300 K for $Cs_2MnSn_2S_6$ and from 50 Gauss to 6000 Gauss at 300 K, 50 Gauss $\rightarrow$ 6000 Gauss $\rightarrow$ -6000 Gauss $\rightarrow$ 6000 Gauss at 5 K for K_2MnSnS_4 . Variable temperature magnetic susceptibility data were collected at a magnetic field of 5000 Gauss with an ascending temperature ramp from 5 K to 300 K for both compounds and an additional measurement at 1000 Gauss was performed for K_2MnSnS_4 within the same temperature range.

2.3. Synthesis

K₂HgSn₂S₆ (I) A mixture of Sn (0.030 g, 0.25 mmol), HgS (0.058 g, 0.25 mmol), K₂S (0.055 g, 0.50 mmol) and S (0.128 g, 4.0 mmol) was load into an ~5-ml Pyrex tube in a N₂ glovebox. The tube was evacuated and flame sealed at the pressure of $\sim 10^{-3}$ torr. The mixture was heated slowly to 350°C in 12 hours inside a furnace programmed by a personal computer. The reaction temperature was kept at 350°C for 4 days and was then cooled slowly to room temperature at 4°/hour. The product was washed with degassed DMF to remove excess K₂S_x flux by using a standard Schlenk technique and was dried with acetone and ether. A mixture of orange brown square planar crystals and small amount of yellow needlelike crystals of (I) was obtained. The orange brown crystals are isostructural to K₂MnSnS₄ (VIII), KInSe₂⁸ and TlGaSe₂⁹ based on powder X-ray diffraction. Both the yellow and orange brown crystals are stable in air and insoluble in water and common organic solvents such as DMF, DMSO, MeOH and acetonitrile. The yellow crystals were picked by hand among the mixture for structural characterization. SEM/EDS semiquantitative elemental analysis on yellow crystals indicated K_{1.6}Hg_{1.0}Sn_{1.6}S_{6.0}.

K₂GeIn₂S₆ (II) A mixture of Ge (0.022 g, 0.3 mmol), In (0.034 g, 0.3 mmol), K₂S (0.066 g, 0.6 mmol) and S (0.154 g, 4.8 mmol) was heated at 400°C for 4 days and was then cooled to room temperature at 4°C/hour. The product was washed with degassed DMF and was dried with acetone and ether. The air stable white crystals of (II) were obtained with air-sensitive white crystals (SEM/EDS indicated the air sensitive crystals are K₄GeS₄) which can be removed by washing with water. The yield of

(II) is very low (less than 5%) and most of the product is K_4GeS_4 . SEM/EDS semiquantitative elemental analyses performed on the crystals of (II) indicated $\text{K}_{1.0}\text{Sn}_{1.0}\text{Hg}_{1.9}\text{S}_{6.7}$.

$\text{K}_2\text{Hg}_3\text{Sn}_2\text{S}_8$ (III) A mixture of Sn powder (0.030 g, 0.25 mmol), HgS powder (0.116 g, 0.499 mmol), K_2S (0.055g, 0.50 mmol) and S (0.128 g, 4.00 mmol) was heated at 400°C for 4 days and was then cooled to room temperature at 4°C/hour. The product was washed with degassed DMF, then dried with acetone and ether. Yellow crystals of (III) and small amount of orange brown square planar crystals and red HgS crystals (less than 5%) were obtained. The yield of yellow crystals was 0.101g (69%, based on Sn). The yellow crystals are insoluble in water and common organic solvents. SEM/EDS semiquantitative elemental analyses indicated $\text{K}_{1.0}\text{Sn}_{1.0}\text{Hg}_{1.9}\text{S}_{6.7}$.

$\text{K}_2\text{Hg}_3\text{Ge}_2\text{S}_8$ (IV) The reaction of Ge (0.018 g, 0.25 mmol), HgS (0.087 g, 0.38 mmol), K_2S (0.055 g, 0.50 mmol) and S (0.128 g, 4.00 mmol) at 400°C for 4 days upon cooling at a rate of 4°C/hour afforded yellow crystals of (IV) and very small amount of HgS crystals. The yield of (IV) was 0.083 g (64 %, based on Ge). The product is stable in air and insoluble in water and common organic solvents. SEM/EDS indicated $\text{K}_{0.76}\text{Hg}_{1.0}\text{Ge}_{0.29}\text{S}_{4.97}$.

$\text{K}_6\text{Zn}_4\text{Sn}_5\text{S}_{17}$ (V) The reaction of Sn (0.059 g, 0.5 mmol), Zn (0.033 g, 0.5 mmol), K_2S (0.110 g, 1.0 mmol) and S (0.256 g, 8.0 mmol) at 400°C for 4 days upon cooling at a rate of 4°C/hour afforded 0.068 g yellowish white crystals in ~33% yield (based on Sn). The product was

washed with degassed DMF and was dried with acetone and ether. The yield can be increased by adding more Sn metal in the reactions. The ratio of 6/5:4/5:2:16 (Sn:Zn:K₂S:S) under the same reaction condition gave a yield of ~80%. However this reaction also gave a small amount of yellowish orange crystals of K₂Sn₂S₅ and reddish orange crystals of K₂Sn₂S₈ as by-products. The yellowish white crystals of (V) are stable in air and insoluble in water and common organic solvents. SEM/EDS semiquantitative elemental analysis indicated K_{2.3}Zn_{1.0}Sn_{1.75}S_{7.38}.

Rb₂ZnSn₂S₆ (VI) The reaction of Sn (0.119 g, 1.00 mmol), Zn (0.033 g, 0.50 mmol), Rb₂S (0.406 g, 1.00 mmol) and S (0.512 g, 8.00 mmol) at 400°C for 4 days upon cooling at a rate of 4°C/hour afforded 0.131-g brownish orange crystals of (VI) in ~40% yield (based on Sn). The product was washed with degassed DMF was dried with acetone and ether. The brownish white crystals are insoluble in water and common organic solvents. SEM/EDS semiquantitative elemental analysis indicated Rb_{1.1}Zn_{1.0}Sn_{1.9}S_{6.0}.

Cs₂MnSn₂S₆ (VII) The reaction of Sn powder (0.072 g, 0.61 mmol), Mn powder (0.016 g, 0.29 mmol), Cs₂S (0.358 g, 1.20 mmol) and S (0.154 g, 4.81 mmol) at 400°C for 4 days upon cooling at a rate of 4°C/hour gave 0.083-g brownish white crystals of (VII) and very small amount of MnS powder. The yield of (VII) was ~38% yield (based on Sn). The product was washed with degassed DMF and was dried with acetone and ether. The brownish white crystals are insoluble in water and common organic solvents. SEM/EDS semiquantitative elemental analysis indicated Cs_{2.6}Mn_{1.0}Sn_{2.8}S_{10.2}.

K₂MnSnS₄ (VIII) The reaction of Sn powder (0.059 g, 0.50 mmol), Mn powder (0.027 g, 0.50 mmol), K₂S (0.220 g, 2.00 mmol) and S (0.256 g, 8.0 mmol) at 400°C for 4 days upon cooling at a rate of 4°C/hour afforded 0.129-g orange crystals of (VIII) in ~70% yield (based on Sn). The product was washed with degassed DMF and was dried with acetone and ether. The orange crystals are insoluble in water and common organic solvents. SEM/EDS semiquantitative elemental analysis indicated K_{2.0}Mn_{1.0}Sn_{1.3}S_{4.8}.

Cs₂Ge₂In₂S₈ (IX) The reaction of Ge (0.022 g, 0.30 mmol), In (0.034 g, 0.30 mmol), Cs₂S (0.197 g, 0.60 mmol) and S (0.154 g, 4.8 mmol) at 500°C for 5 days upon cooling at a rate of 5°C/hr afforded light brownish white crystals of (IX) in 49.7 % yield (0.0669 g). The product was washed with degassed DMF and was dried with acetone and ether. The brownish white crystals are stable in air and insoluble in water and common organic solvents. SEM/EDS indicated Cs_{1.4}Ge_{1.0}In_{1.3}S_{6.4}.

Cs₂MnSn₃Se₈ (X) The reaction of Sn (0.036 g, 0.30 mmol), Mn (0.016 g, 0.30 mmol), Cs₂Se (0.207 g, 0.60 mmol) and Se (0.379 g, 4.8 mmol) at 400°C for 4 days upon cooling at a rate of 4°C/hr afforded a mixture of small amount of dark red crystal (X) and black Se powder. The product was washed with degassed DMF and was dried with acetone and ether. The dark red crystals are stable in air and insoluble in water and common organic solvents. The yield of (X) is very low (less than 10%). Crystals were picked by hand for further characterization. SEM/EDS indicated Cs_{1.8}Mn_{1.0}Sn_{2.3}Se_{5.8}.

Rb₂CdGe₂S₆ (XI) The reaction of Ge (0.036 g, 0.50 mmol), Cd (0.056 g, 0.50 mmol), Rb₂S (0.203 g, 1.0 mmol) and S (0.256 g, 8.0 mmol) at 460°C for 4 days upon cooling at a rate of 4°C/hr afforded brownish white chunky crystals of (XI) and air-sensitive white crystals (SEM/EDS indicated the air-sensitive white crystals are Rb₄GeS₄). The product was washed with MeOH and was dried ether. Rb₄GeS₄ can be removed by further washing with water. Around 0.036-g crystals of (XI) were obtained in 23% yield (based on Cd). The brownish white crystals are stable in air and insoluble in water and common organic solvents. SEM/EDS indicated Rb_{1.8}Cd_{1.0}Ge_{1.3}S_{8.4}.

2.4. X-Ray Crystallography

X-ray powder diffraction patterns were used for the purpose of phase characterization and identification. The X-ray powder diffraction patterns were recorded with a Phillips XRD-3000 controlled by PDP 11 computer and operating at 40 kV/35 mA. Graphite monochromated Cu radiation was used. In order to ensure the homogeneity, d-spacings obtained from X-ray powder diffraction (XRD) measurements of the products were compared with, and found to be identical to those calculated from the atomic coordinates determined from the single crystal data. The calculation of d-spacings was performed by using the POWD 10¹⁰ program. The comparison tables between the calculated and observed d-spacings for these compounds are shown in Tables 7-1~7-8.

The single crystal X-ray diffraction data of (I), (II), (IV), (V), (VI), (X) and (XI) were collected on a Rigaku AFC6S four-circle diffractometer while the data for (III), (VII), (VIII) and (IX) were collected on a Niclolet P3 diffractometer. Graphite monochromated Mo K α radiation was used. All the crystals were mounted at the end of glass fibers. The stability of the experimental setup and crystal integrity were monitored by measuring three standard reflections periodically every 150 reflections for all the data sets except for (III) which was monitored every 300 reflections. No significant decay was observed during the data collections. The structures were solved with direct methods (SHELXS-86)¹¹, and were refined by a full-matrix least-square technique available in the TEXSAN¹² programs running on a VAXstation 3100/76 computer. An empirical absorption correction was applied to all the data (based on ψ scans). An additional absorption correction following the DIFABS¹³ procedure was applied to isotropically refined data. Since (II), (III), (IV), (V), (VI), (VII) and (X) crystallize in acentric space groups, their enantiomorphs were checked. The refinement of the enantiomorphous models of (II), (VII) and (X) did not show significant improvement while the R/Rw values for (III), (IV), (V) and (VI) dropped from 5.1/5.1 to 3.9/4.2, from 4.9/6.6 to 4.3/5.9, from 4.3/5.4 to 3.6/4.6 and from 3.6/4.7 to 2.7/3.4 respectively. The models with lower R/Rw values and smaller standard deviation of bond distances and angles are reported.

The crystallographic data and detailed information of structure solution and refinement are listed in Table 7-9. Atomic coordinates and equivalent isotropic thermal parameters are given in Tables 7-10~7-20 respectively.

Table 7-1. Calculated and Observed X-Ray Powder Diffraction Patterns for $K_2Hg_3Sn_2S_8$.

h	k	l	$d_{calc.} (\text{\AA})$	$d_{obs.} (\text{\AA})$	%I _{obs.}
2	0	0	9.7610	9.8671	8.60
1	1	1	6.0824	6.1322	46.81
2	1	1	5.3527	5.3950	34.39
3	1	1	4.5633	4.5953	22.44
2	0	2	3.8700	3.8959	51.02
4	2	0	3.4640	3.4863	45.79
0	2	2	3.2005	3.2176	100.00
4	0	2	3.1902	3.1766	29.31
1	2	2	3.1583		
2	2	2	3.0412	3.0603	59.98
2	3	1	2.9159	2.9102	5.79
6	1	1	2.9005		
3	3	1	2.7658	2.7781	13.57
6	0	2	2.5757	2.5887	18.37
7	1	1	2.5567		
0	4	0	2.4588	2.4526	56.53
8	0	0	2.4402		
1	4	0	2.4395		
6	2	2	2.2817	2.2934	19.02
1	3	3	2.1210	2.1337	14.70
2	4	2	2.0753	2.0876	19.02
2	0	4	2.0603		
3	4	2	2.0191	2.0299	24.63
4	4	2	1.9475	1.9490	39.89
8	2	2	1.9405		
0	2	4	1.9373		
4	0	4	1.9350		
1	5	1	1.9064	1.9120	19.02
2	2	4	1.9002		
5	4	2	1.8657	1.8738	15.88
6	4	2	1.7785	1.7779	12.49
10	0	2	1.7715		
6	0	4	1.7690		
8	4	0	1.7320	1.7428	8.16
10	2	2	1.6666	1.6748	21.73
6	2	4	1.6646		
3	6	0	1.5895	1.5873	15.29

Table 7-2. Calculated and Observed X-Ray Powder Diffraction Patterns for $K_2Hg_3Ge_2S_8$.

h	k	l	d _{calc.} (Å)	d _{obs.} (Å)	%I _{obs.}
2	0	0	9.5940	9.8260	15.17
1	1	1	5.9821	6.0799	23.85
2	1	1	5.2637	5.4787	16.56
0	2	0	4.8090	4.8625	27.38
4	0	0	4.7970	3.7645	5.96
3	1	1	4.4868	4.5376	7.15
3	2	0	3.8437	3.8662	54.52
4	2	0	3.3962	3.3862	20.57
5	1	1	3.2768	3.2997	8.12
6	0	0	3.1980	3.1760	100.00
0	2	2	3.1479	3.1331	23.85
4	0	2	3.1445		
1	2	2	3.1064	3.0667	26.18
5	2	0	2.9996	3.0163	42.40
2	2	2	2.9910		
1	3	1	2.9562	2.9706	16.56
2	3	1	2.8563	2.8868	29.87
6	1	1	2.8512		
6	0	2	2.5363	2.5576	12.17
0	4	0	2.4045	2.4152	44.70
8	0	0	2.3985		
1	4	0	2.3858		
3	4	0	2.2507	2.2571	18.01
6	2	2	2.2434		
5	1	3	2.1901	2.2033	9.86
1	3	3	2.0862	2.0892	17.04
2	4	2	2.0349	2.0473	18.51
2	0	4	2.0346		
3	4	2	1.9800	1.9915	19.52
0	2	4	1.9106	1.9207	27.99
4	4	2	1.9101		
8	2	2	1.9078		
2	2	4	1.8738	1.8760	10.98
5	4	2	1.8302	1.8387	8.79
7	4	0	1.8076	1.8114	9.14
4	2	4	1.7750	1.7766	10.23
9	2	2	1.7652		
6	3	3	1.7546	1.7519	10.98
6	0	4	1.7448		
10	0	2	1.7427		
8	4	0	1.6981	1.6886	11.37
5	5	1	1.6841		
6	2	4	1.6402	1.6469	10.23
10	2	2	1.6384		
8	0	4	1.5723	1.5776	8.79
1	4	4	1.5687		
3	6	0	1.5549	1.5602	9.86
2	4	4	1.5532		

Table 7-3. Calculated and Observed X-Ray Powder Diffraction Patterns for $K_6Zn_4Sn_5S_{17}$.

h	k	l	$d_{calc.} (\text{\AA})$	$d_{obs.} (\text{\AA})$	%I _{obs.}
1	1	0	9.7552	9.9671	29.22
1	0	1	7.8689	8.0369	81.16
2	0	0	6.8980	7.0378	9.94
2	2	0	4.8776	4.9289	91.19
0	0	2	4.7900		
3	1	0	4.3627	4.4093	17.93
3	0	1	4.1458	4.1968	35.35
2	0	2	3.9344	4.0212	23.67
3	2	1	3.5534	3.5897	28.25
4	0	0	3.4490	3.4779	81.16
2	2	2	3.4176		
3	3	0	3.2517	3.2765	79.55
3	1	2	3.2254	3.1869	100.00
4	1	1	3.1589		
2	1	3	2.8360	2.8334	43.25
4	0	2	2.7989		
3	3	2	2.6904	2.6709	94.67
4	3	1	2.6514		
5	2	1	2.4749	2.4516	67.21
3	2	3	2.4517		
4	4	0	2.4388	2.4105	23.67
0	0	4	2.3950		
1	1	4	2.3259	2.3399	10.52
4	1	3	2.3101	2.3110	23.67
6	0	0	2.2993		
3	1	4	2.0994	2.1150	53.25
4	3	3	2.0878		
5	0	3	2.0878		
5	2	3	1.9983	1.9971	38.64
6	2	2	1.9852		
4	0	4	1.9672		
7	0	1	1.9304	1.9394	24.55
4	2	4	1.8918	1.9039	17.93
7	2	1	1.8590	1.8661	19.49
2	1	5	1.8298	1.8180	18.70
7	3	0	1.8115		
7	1	2	1.8069	1.8031	32.21
6	5	1	1.7371	1.7316	54.57
8	0	0	1.7245		
4	4	4	1.7088	1.7033	35.35
7	3	2	1.6944	1.6929	51.93
7	4	1	1.6845		
5	0	5	1.5738	1.5829	18.70
4	3	5	1.5738		

Table 7-4. Calculated and Observed X-Ray Powder Diffraction Patterns for $\text{Rb}_2\text{ZnSn}_2\text{S}_6$.

h	k	l	$d_{\text{calc.}} (\text{\AA})$	$d_{\text{obs.}} (\text{\AA})$	% $I_{\text{obs.}}$
0	2	0	6.7285	6.8059	22.80
0	0	1	6.7003		
1	0	0	6.3213	6.4246	23.28
0	1	1	5.9979	6.0882	18.49
1	0	-1	5.8962	5.9798	26.78
1	1	0	5.7215	5.8138	36.30
0	2	1	4.7477	4.8027	8.85
1	0	1	3.8973	3.9441	10.24
1	1	1	3.7435	3.7866	62.81
0	3	1	3.7275	3.6970	48.30
1	3	0	3.6582		
1	0	-2	3.6025	3.6378	62.81
1	3	-1	3.5700	3.5130	47.60
1	1	-2	3.4800	3.4619	100.00
2	0	-1	3.4238		
1	2	1	3.3724	3.3824	47.96
0	4	0	3.3643		
0	0	2	3.3501	3.3515	40.96
2	1	-1	3.3181	3.2803	25.76
0	1	2	3.2509		
1	2	-2	3.1759	3.1967	17.64
2	1	0	3.0769	3.1096	37.82
0	4	1	3.0065	3.0275	40.01
0	2	2	2.9990	2.9955	17.85
1	4	0	2.9698	2.9733	21.86
1	3	1	2.9420	2.9462	19.14
1	4	-1	2.9221		
2	2	0	2.8608	2.8886	45.90
1	3	-2	2.8088	2.8319	6.13
2	3	-1	2.7216	2.7236	6.63
2	2	-2	2.7003	2.7050	7.98
0	3	2	2.6842		
2	3	0	2.5837	2.6079	6.76
1	4	1	2.5467	2.5479	26.78
1	1	2	2.5260	2.5284	31.64
1	5	0	2.4763	2.4846	18.06
2	3	-2	2.4637		
1	2	2	2.4022	2.4054	9.15
0	4	2	2.3739	2.3683	17.43
2	2	1	2.3470		
0	0	3	2.2334	2.2496	62.41
1	5	-2	2.1561	2.1766	8.70
1	3	-3	2.1340	2.1489	8.41
0	6	1	2.1268	2.1253	38.44
3	2	-2	2.1072	2.1003	30.25
2	3	-3	2.0453	2.0519	20.25
3	3	-1	2.0345	2.0261	10.89

Table 7-4. (cont'd)

3	3	-2	1.9888	2.0035	15.41
3	0	-3	1.9654	1.9797	28.09
1	6	1	1.9439	1.9438	9.15
2	1	2	1.9285	1.9224	13.51
3	3	0	1.9072	1.9032	16.20
1	6	-2	1.9040		
3	4	-1	1.8890	1.8865	41.60
2	6	-1	1.8761	1.8856	30.80
2	2	2	1.8717		
0	4	3	1.8607	1.8594	12.43
3	4	-2	1.8523		
0	7	1	1.8479	1.8468	11.90
2	5	1	1.8334		
2	6	0	1.8291	1.8279	11.56
1	2	3	1.8161	1.8147	35.70
3	1	1	1.8000	1.7963	50.41
2	3	2	1.7873		
3	4	0	1.7858	1.7669	15.21
2	1	-4	1.7853		
3	2	1	1.7536	1.7508	17.85
1	2	-4	1.7424		
1	7	1	1.7241	1.7236	9.00
3	5	-2	1.7121	1.7110	27.56
4	1	-2	1.6982	1.7059	22.33
1	6	2	1.6903	1.6934	34.52
2	4	2	1.6862		
2	3	-4	1.6715	1.6712	24.01
0	7	2	1.6674	1.6701	12.08
3	5	0	1.6591	1.6514	5.41
4	2	-2	1.6591		
2	7	0	1.6425		
0	8	1	1.6315	1.6319	4.31
1	8	0	1.6256		
2	6	-3	1.6051	1.6097	5.64
3	6	-1	1.5999		
4	3	-2	1.5994	1.5976	10.24
1	4	-4	1.5898		

Table 7-5. Calculated and Observed X-Ray Powder Diffraction Patterns for Cs₂MnSn₂S₆.

h	k	l	d _{calc.} (Å)	d _{obs.} (Å)	%I _{obs.}
1	1	0	5.9140	5.9778	39.97
1	1	1	3.8665	3.9048	91.02
0	3	1	3.8074	3.7826	39.97
1	3	0	3.7518		
1	0	-2	3.6746	3.7042	91.02
1	3	-1	3.6466		
1	1	-2	3.5497	3.5709	95.46
2	0	-1	3.5304		
0	4	0	3.4320	3.4530	100.00
2	1	-1	3.4192		
0	1	2	3.3293	3.3518	29.18
1	2	-2	3.2396	3.2148	26.75
2	1	0	3.1871		
0	4	1	3.0696	3.0917	64.74
0	2	2	3.0695		
1	4	0	3.0403		
1	4	-1	2.9835	2.9796	84.56
2	2	0	2.9570		
1	4	1	2.6128	2.6116	29.18
1	1	2	2.6025		
2	3	-2	2.5195	2.4927	34.36
1	2	2	2.4726		
2	2	1	2.4273	2.4447	25.58
0	4	2	2.4267		
0	0	3	2.2878	2.3017	88.84
1	5	1	2.2690		
1	5	-2	2.1995	2.2011	35.72
2	5	-1	2.1673	2.1758	55.82
3	2	-2	2.1653		
3	3	-2	2.0420	2.0228	44.44
3	0	-3	2.0121		
3	3	0	1.9713	1.9858	34.36
3	4	-1	1.9444	1.9514	22.21
1	6	-2	1.9423		
2	5	1	1.8859	1.8773	27.96
0	7	1	1.8857		
2	3	2	1.8440	1.8523	39.97
2	1	-4	1.8211	1.8294	54.12
1	6	2	1.7320	1.7194	35.72
4	2	-2	1.7096		
1	8	-1	1.6506	1.6484	13.53
1	4	-4	1.6232		
2	2	3	1.5659	1.5748	13.53

Table 7-6. Calculated and Observed X-Ray Powder Diffraction Patterns for K₂MnSnS₄.

h	k	l	d _{calc.} (Å)	d _{obs.} (Å)	%I _{obs.}
1	1	0	7.5915	7.5737	14.27
0	0	2	7.3815		
1	1	1	6.4243	6.5974	2.78
1	1	-2	5.6681	5.7949	3.67
0	2	0	5.4120		
0	2	1	5.0813	5.0773	2.73
2	2	0	3.7958	3.8472	17.94
2	2	-1	3.7955		
0	0	4	3.6907	3.7434	33.70
2	2	1	3.5675	3.6141	51.76
2	2	-2	3.5668		
3	1	-1	3.4179	3.4606	13.24
1	3	0	3.4172	3.4156	6.25
1	3	2	3.0349	3.0737	3.21
3	1	-3	3.0349		
3	1	2	2.8871	2.9199	7.72
1	3	-3	2.8860		
1	1	-5	2.8794	2.8678	100.00
2	2	3	2.8348		
2	2	-4	2.8341		
1	3	3	2.7338	2.7631	6.25
3	1	-4	2.7336		
1	1	5	2.6397	2.6358	6.46
0	2	5	2.5919	2.6114	4.00
3	1	3	2.5839		
1	3	-4	2.5829		
3	3	-2	2.4939	2.4640	1.82
3	3	1	2.4425		
1	3	4	2.4383		
3	1	-5	2.4380		
4	2	-2	2.3888		
3	3	-3	2.3779	2.3992	1.39
5	1	-1	2.1220	2.1389	7.64
1	5	0	2.1214		
1	1	-7	2.1028		
2	4	3	2.0995	2.0730	3.57
3	1	5	2.0544		
1	3	-6	2.0538		
5	1	1	2.0204		
1	5	2	2.0198	2.0114	44.82
4	0	4	1.9956		
0	4	5	1.9949		
4	0	-6	1.9948		
5	1	-4	1.9742	1.9709	8.92
1	5	-3	1.9740		
3	3	4	1.9724		
1	1	7	1.9680		
2	2	6	1.9534		
5	1	2	1.9238	1.9277	43.16

Table 7-7. Calculated and Observed X-Ray Powder Diffraction Pattern for Cs₂In₂Ge₂S₈.

h	k	l	d _{calc.} (Å)	d _{obs.} (Å)	%I _{obs.}
0	0	2	6.2095	6.2420	100.00
0	1	1	6.1290		
2	1	2	4.1140	4.1963	13.05
2	0	3	3.7433	3.7656	44.25
3	1	2	3.6430	3.7042	26.11
0	1	3	3.5694	3.6315	31.30
3	0	3	3.3781	3.3993	20.19
2	2	0	3.2693	3.2997	45.43
2	2	1	3.1616	3.1320	22.22
0	2	2	3.0645	3.0713	43.08
1	0	4	3.0572		
5	0	2	3.0534		
5	1	1	3.0437		
3	2	1	2.9322	2.9391	12.42
2	0	4	2.9266		
6	0	0	2.9222		
6	0	1	2.8445	2.8504	5.87
1	2	3	2.6523	2.6561	5.25
6	0	2	2.6440		
6	1	1	2.6377		
0	2	4	2.3294	2.3451	7.7
4	2	3	2.2884	2.2991	13.69
3	0	5	2.2859		
6	0	4	2.1279	2.1321	9.24
4	2	4	2.0570	2.0869	10.63
3	3	2	2.0565		
5	2	4	1.9403	1.9555	9.78
4	2	5	1.8421	1.8538	16.43
8	2	1	1.8404		

Table 7-8. Calculated and Observed X-Ray Powder Diffraction Patterns for $\text{Rb}_2\text{CdGe}_2\text{S}_6$.

h	k	l	$d_{\text{calc.}} (\text{\AA})$	$d_{\text{obs.}} (\text{\AA})$	% $I_{\text{obs.}}$
0	0	2	6.5932	6.7337	9.75
1	1	0	6.3193	6.5549	9.20
1	1	-2	5.1272	5.3433	9.75
1	1	2	4.1504	4.1973	19.75
1	1	-3	4.0229	4.0690	23.67
0	2	3	3.5597	3.5653	16.44
1	3	-1	3.5332		
1	1	3	3.3003	3.3257	37.53
1	1	-4	3.2101	3.2348	100.00
2	2	-2	3.1135	3.1361	14.78
0	4	1	2.9567	3.9632	25.76
2	2	1	2.9371	2.9213	14.55
0	2	4	2.8967		
0	4	2	2.7562	2.7819	3.93
1	1	4	2.7010	2.7196	12.34
2	2	2	2.6428	2.6586	7.97
0	4	3	2.4969	2.5127	12.77
3	1	0	2.4179	2.4295	11.52
3	1	-3	2.3716	2.3877	17.17
1	1	5	2.2714	2.2843	71.21
2	2	-5	2.2709		
3	3	-1	2.1511	2.1406	21.95
2	0	-6	2.1320		
2	2	4	2.0752	2.0872	39.02
0	2	6	2.0664	2.0725	60.49
1	5	3	1.9812	1.9894	4.55
1	1	6	1.9533	1.9616	27.93
1	1	-7	1.9180	1.9164	8.84
3	1	-6	1.8633	1.8691	5.92
4	2	-2	1.8192	1.8068	18.44
0	2	7	1.7991		
2	6	0	1.7749		
3	5	-1	1.7548	1.7587	17.42
1	3	-7	1.7511		
2	4	-6	1.7444		
4	2	-4	1.7377		
3	5	-3	1.7131	1.7177	19.49
1	7	-1	1.6862	1.6855	17.17
4	0	2	1.6782	1.6707	38.64
1	5	5	1.6742		
2	0	-8	1.6643		
1	5	-6	1.6552	1.6551	26.37
4	4	-1	1.6087	1.6068	10.52
1	7	-3	1.6060		
1	3	7	1.5887	1.5938	12.56

Table 7-9. Summary of Crystallographic Data for K₂HgSn₂S₆(I), K₂GeIn₂S₆(II), K₂Hg₃Sn₂S₈(III), K₂Hg₃Ge₂S₈(IV), K₆Zn₄Sn₅S₁₇(V), Rb₂ZnSn₂S₆(VI), Cs₂MnSn₂S₆(VII) , K₂MnSn₄(VIII), Cs₂Ge₂In₂S₈(IX), Cs₂MnSn₃Se₈(X) and Rb₂CdGe₂S₆(XI).

	(I)	(II)
formula	K ₂ HgSn ₂ S ₆	K ₂ GeIn ₂ S ₆
fw	708.53	572.79
a, Å	7.519(2)	16.251(4)
b, Å	16.009(4)	9.986(2)
c, Å	10.222(2)	7.408(3)
α	90.0	90.0
β	91.92(2)	90.0
γ	90.0	90.0
Z, V, Å ³	4, 1229.8(9)	4, 1202(1)
space group	P2 ₁ /n (# 14)	P2 ₁ 2 ₁ 2 ₁ (#18)
d _{calc} , g/cm ³	3.826	3.164
crystal size, mm	0.64x0.72x0.84	0.9x0.8x0.7
temperature (°C)	23	23
radiation	Mo Kα	Mo Kα
μ(Mo Kα), cm ⁻¹	181.06	78.43
2θ _{max} , deg	50	50
scan mode	ω-2θ	ω-2θ
scan speed, °/min	4	8
no. of data collected	2426	1264
no. of unique data	2249	1264
no. of observed data	1776	943
(I>3.0σ(I))		
no. of variables	101	102
final R/R _w , %	3.9/5.7	3.8/5.9

Table 7-9. (cont'd)

	(III)	(IV)	(V)
formula	K ₂ Hg ₃ Sn ₂ S ₈	K ₂ Hg ₃ Ge ₂ S ₈	K ₆ Zn ₄ Sn ₅ S ₁₇
fw	1173.83	1081.63	1634.58
a, Å	19.522(5)	19.188(3)	13.796(2)
b, Å	9.835(3)	9.618(2)	13.796(2)
c, Å	8.431(2)	8.328(5)	9.580(2)
α	90.0	90.0	90.0
β	90.0	90.0	90.0
γ	90.0	90.0	90.0
Z, V, Å ³	4, 1618.7(9)	4, 1537(1)	2, 1823.3(6)
space group	Aba2 (# 41)	Aba2(# 41)	I $\bar{4}$ m2 (#119)
d _{calc} , g/cm ³	4.816	4.674	2.977
crystal size, mm	0.23x0.30x0.31	0.16x0.30x0.50	0.26x0.44x0.52
temperature (°C)	20	23	23
radiation	Mo Kα	Mo Kα	Mo Kα
μ(Mo Kα), cm ⁻¹	328.89	352.34	76.59
scan mode	ω	ω-2θ	ω-2θ
scan speed, °/min	2θ=3~43° 4°/min 2θ=43~55° 2°/min	2	4
2θ _{max} , deg	55	50	50.0
no. of data collected	1087	801	497
no. of unique data	999	795	497
no. of observed data (I>3.0σ(I))	882	632	456
no. of variables	69	69	46
final R/R _w , %	3.9/4.2	4.3/5.9	3.6/4.6

Table 7-9. (cont'd)

	(VI)	(VII)	(VIII)
formula	Rb ₂ ZnSn ₂ S ₆	Cs ₂ MnSn ₂ S ₆	K ₂ MnSnS ₄
fw	666.06	750.49	380.06
a, Å	6.873(2)	7.098(1)	10.827(3)
b, Å	13.456(4)	13.729(3)	10.824(4)
c, Å	7.285(2)	7.434(1)	15.008(5)
α	90.0	90.0	90.0
β	113.12(2)	112.57(1)	100.37(2)
γ	90.0	90.0	90.0
Z, V, Å ³	2, 619.7(3)	2, 668.9(4)	4, 1730.1(9)
space group	P2 ₁ (#4)	P2 ₁ (#4)	C2/c (#15)
d _{calc} , g/cm ³	3.569	3.726	2.918
crystal size, mm	0.42x0.40x0.14	0.43x0.42x0.15	0.12x0.33x0.36
temperature (°C)	-90	-95	-90
radiation	Mo K α	Mo K α	Mo K α
μ (Mo K α), cm ⁻¹	145.04	107.99	61.054
scan mode	ω -2 θ	ω -2 θ	ω -2 θ
scan speed, °/min	8	4	4
2 θ _{max} , deg	50.0	55.0	50
no. of data collected	1247	1737	1709
no. of unique data	1154	1619	1615
no. of observed data (I>3.0 σ (I))	1044	1560	715
no. of variables	100	100	74
final R/R _w , %	2.7/3.4	6.29/8.36	8.08/8.66

Table 7-9. (cont'd)

	(IX)	(X)	(XI)
formula	Cs ₂ Ge ₂ In ₂ S ₈	Cs ₂ MnSn ₃ Se ₈	Rb ₂ CdGe ₂ S ₆
fw	897.11	1308.50	620.89
a, Å	17.533(4)	12.732(3)	7.633(3)
b, Å	7.409(2)	18.503(4)	12.136(2)
c, Å	12.419(4)	7.898(3)	13.598(2)
α	90.0	90.0	90.0
β	90.0	90.0	90.0
γ	90.0	90.0	90.0
Z, V, Å ³	4, 1613(2)	4, 1861(2)	4, 1221.4(5)
space group	Pnma (#62)	P2 ₁ 2 ₁ 2 ₁ (#19)	C2/c
d _{calc} , g/cm ³	3.693	4.671	3.376
crystal size, mm	0.18x0.25x0.44	0.2x0.38x0.21	0.8x0.48x0.29
temperature (°C)	-95	23	23
radiation	Mo K α	Mo K α	Mo K α
μ (Mo K α), cm ⁻¹	118.09	239.43	151.90
scan mode	ω -2 θ	ω -2 θ	ω -2 θ
scan speed	4	2	4
2 θ _{max} , deg	50	50	50
no. of data collected	1675	1919	1235
no. of unique data	1675	1919	1141
no. of observed data (I>3.0 σ (I))	1063	1122	858
no. of variables	77	128	52
final R/R _w , %	6.6/7.0	4.5/6.0	2.5/3.4

Table 7-10. Positional Parameters and Equivalent Isotropic Displacement Values ($\text{\AA}^2$)^a for $\text{K}_2\text{HgSn}_2\text{S}_6$ with Estimated Standard Deviations in Parentheses

atom	x	y	z	B (eq)
Hg	1.08176 (8)	0.88041 (4)	0.26731 (6)	1.56 (3)
Sn(1)	0.5809 (1)	0.88537 (6)	0.1904 (1)	0.82 (4)
Sn(2)	0.7831 (1)	0.76581 (7)	0.4912 (1)	0.89 (4)
K(1)	0.1614 (5)	1.1079 (3)	0.1564 (4)	2.4 (2)
K(2)	0.3118 (5)	0.9103 (3)	0.6197 (4)	2.1 (2)
S(1)	0.8361 (5)	0.9642 (3)	0.1423 (4)	1.4 (2)
S(2)	0.3699 (5)	0.9592 (3)	0.3128 (4)	1.4 (2)
S(3)	0.6256 (5)	0.7473 (3)	0.2809 (4)	1.3 (2)
S(4)	0.4606 (5)	0.8582 (3)	-0.0264 (4)	1.6 (2)
S(5)	1.0895 (6)	0.7384 (3)	0.1669 (4)	2.0 (2)
S(6)	0.9270 (5)	0.8952 (3)	0.4913 (4)	1.4 (2)

^a $B(\text{eq}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table 7-11 Positional Parameters and Equivalent Isotropic Displacement Values ($\text{\AA}^2$)^a for $\text{K}_2\text{GeIn}_2\text{S}_6$ with Standard Deviations in Parentheses

atom	x	y	z	B (eq)
In (1)	0.3687 (1)	0.7179 (2)	0.3324 (2)	0.97 (8)
In (2)	0.3697 (1)	0.7857 (2)	0.8270 (3)	1.20 (8)
Ge (1)	0.5	0.5	0.0487 (5)	1.2 (2)
Ge (2)	0.5	1.0000	0.5420 (5)	0.8 (2)
K (1)	0.1425 (4)	0.6410 (6)	0.9020 (8)	1.8 (3)
K (2)	0.3477 (4)	0.3528 (5)	0.583 (1)	2.2 (3)
S (1)	0.3896 (5)	0.4829 (6)	0.2097 (8)	1.6 (3)
S (2)	0.2903 (5)	0.6619 (7)	0.609 (1)	1.9 (3)
S (3)	0.5061 (7)	0.8176 (7)	0.3725 (9)	1.7 (3)
S (4)	0.2884 (4)	0.8319 (6)	0.0952 (9)	0.9 (3)
S (5)	0.3811 (5)	1.0054 (6)	0.6924 (8)	1.3 (3)
S (6)	0.5061 (7)	0.6877 (7)	0.8859 (9)	1.8 (3)

^a $B(\text{eq}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table 7-12. Positional Parameters and Equivalent Isotropic Displacement Values ($\text{\AA}^2$)^a for $\text{K}_2\text{Hg}_3\text{Sn}_2\text{S}_8$ with Estimated Standard Deviations in Parentheses

atom	x	y	z	B (eq)
Hg(1)	0.5	1.0000	0.4894 (2)	1.06 (4)
Hg(2)	0.25473 (5)	0.5396 (1)	0.6491	1.47 (3)
Sn	0.36675 (7)	0.7856 (2)	0.3366 (2)	0.39 (5)
K	0.3835 (3)	0.7960 (7)	0.8424 (9)	1.7 (2)
S(1)	0.2674 (2)	0.7891 (6)	0.4952 (9)	1.1 (2)
S(2)	0.4697 (3)	0.7709 (6)	0.4967 (9)	0.9 (2)
S(3)	0.3751 (3)	0.4894 (6)	0.6835 (8)	0.9 (2)
S(4)	0.1330 (2)	0.5843 (6)	0.6806 (7)	0.6 (2)

$$^a B(\text{eq}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}].$$

Table 7-13. Positional Parameters and Equivalent Isotropic Displacement Values ($\text{\AA}^2$)^a for $\text{K}_2\text{Hg}_3\text{Ge}_2\text{S}_8$ with Estimated Standard Deviations in Parentheses

atom	x	y	z	B (eq)
Hg(1)	0.5	0	0.5251 (5)	1.51 (8)
Hg(2)	0.74494 (8)	0.4552 (1)	0.3587	1.95 (6)
Ge	0.6351 (2)	0.2110 (4)	0.6719 (5)	0.9 (2)
K	0.6125 (5)	0.198 (1)	0.161 (1)	2.2 (4)
S(1)	0.7298 (5)	0.2079 (8)	0.527 (2)	1.6 (4)
S(2)	0.5388 (5)	0.2330 (8)	0.520 (2)	1.6 (4)
S(3)	0.6234 (5)	0.518 (1)	0.314 (1)	1.2 (4)
S(4)	0.8681 (4)	0.4026 (9)	0.322 (1)	1.0 (3)

$$^a B(\text{eq}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}].$$

Table 7-14. Positional Parameters and Equivalent Isotropic Displacement Values ($\text{\AA}^2$)^a for $\text{K}_6\text{Zn}_4\text{Sn}_5\text{S}_{17}$ with Estimated Standard Deviations in Parentheses

atom	x	y	z	B (eq)
Sn (1)	1/2	1/2	0	1.50 (7)
Sn (2)	0.7756 (1)	1/2	-0.0260 (1)	1.53 (6)
Zn	1.0000	0.3611 (2)	-0.1095 (2)	1.4 (1)
K (1)	1.0000	1/2	1/4	2.9 (3)
K (2)	0.7585 (4)	1.2585	-1/4	3.8 (2)
K (3)	1/2	1/2	1/2	29 (3)
S (1)	1.0000	1/2	-1/4	1.1 (2)
S (2)	0.7174 (4)	1/2	-0.2589 (6)	2.3 (2)
S (3)	0.8628 (2)	0.3578 (3)	0.0326 (4)	1.9 (1)
S (4)	0.6428 (4)	1/2	0.1434 (6)	2.9 (3)

^a $B(\text{eq}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table 7-15 Positional Parameters and Equivalent Isotropic Displacement Values ($\text{\AA}^2$)^a for $\text{Rb}_2\text{ZnSn}_2\text{S}_6$ with Estimated Standard Deviations in Parentheses

atom	x	y	z	B (eq)
Sn (1)	0.3925 (1)	0.2663	0.3662 (1)	0.59 (3)
Sn (2)	0.2806 (1)	-0.0123 (1)	0.3020 (1)	0.62 (3)
Rb (1)	0.0580 (2)	0.2402 (1)	0.7341 (2)	1.89 (6)
Rb (2)	0.6596 (2)	0.0824 (1)	0.0081 (2)	1.60 (6)
Zn	0.8413 (2)	0.3966 (2)	0.2470 (2)	0.79 (6)
S (1)	0.4872 (5)	0.3414 (3)	0.1226 (5)	1.1 (1)
S (2)	0.5523 (6)	0.3307 (3)	0.7017 (5)	1.2 (1)
S (3)	0.1305 (5)	0.0271 (3)	-0.0431 (5)	0.9 (1)
S (4)	0.0233 (5)	0.2481 (3)	0.2507 (6)	1.1 (1)
S (5)	0.9758 (5)	0.4756 (3)	0.5606 (5)	1.3 (1)
S (6)	0.5611 (6)	0.1038 (3)	0.4693 (6)	1.2 (1)

Table 7-16. Positional Parameters and Equivalent Isotropic Displacement Values ($\text{\AA}^2$)^a for $\text{Cs}_2\text{MnSn}_2\text{S}_6$ with Estimated Standard Deviations in Parentheses

atom	x	y	z	B (eq)
Sn (1)	0.3966 (3)	0.2663	0.3626 (3)	0.53 (6)
Sn (2)	0.2862 (3)	-0.0082 (2)	0.3222 (3)	0.50 (6)
Cs (1)	0.0544 (3)	0.2358 (2)	0.7311 (3)	1.45 (7)
Cs (2)	0.6606 (3)	0.0778 (2)	0.0209 (3)	1.32 (7)
Mn	0.8412 (7)	0.3933 (4)	0.2286 (7)	0.7 (1)
S (1)	0.495 (1)	0.3300 (7)	0.118 (1)	1.2 (3)
S (2)	0.542 (1)	0.3419 (6)	0.681 (1)	1.2 (3)
S (3)	0.138 (1)	0.0257 (6)	-0.015 (1)	1.0 (2)
S (4)	0.041 (1)	0.2498 (6)	0.249 (1)	1.0 (3)
S (5)	0.958 (1)	0.4841 (7)	0.537 (1)	1.2 (3)
S (6)	0.554 (1)	0.1088 (6)	0.481 (1)	1.0 (2)

^a $B(\text{eq}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table 7-17. Positional Parameters and Equivalent Isotropic Displacement Values ($\text{\AA}^2$)^a for K_2MnSnS_4 with Estimated Standard Deviations in Parentheses

atom	x	y	z	B (eq)
Sn (1)	0.1004 (2)	0.1886 (3)	0.6550 (2)	0.38 (7)
Sn (2)	0.3523 (2)	-0.0631 (3)	0.6554 (2)	1.49 (8)
Mn (1)	0.1004	0.1886	0.6550	0.5
Mn (2)	0.3523	-0.0631	0.6554	1.9
K (1)	0.5329 (7)	0.3131 (7)	0.8825 (5)	2.4 (3)
K (2)	0.2843 (6)	0.0628 (7)	0.8887 (5)	2.4 (3)
S (1)	0.2038 (8)	0.0638 (8)	0.5656 (7)	2.6 (3)
S (2)	0.2554 (5)	0.320 (1)	0.7491 (4)	0.9 (3)
S (3)	-0.0490 (8)	0.311 (1)	0.5525 (5)	2.5 (3)
S (4)	0	0.049 (1)	3/4	0.9 (4)
S (5)	1/2	0.061 (1)	3/4	1.4 (4)

^a $B(\text{eq}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table 7-18 Positional Parameters and Equivalent Isotropic Displacement Values ($\text{\AA}^2$)^a for $\text{Cs}_2\text{In}_2\text{Ge}_2\text{S}_8$ with Standard Deviations in Parentheses

atom	x	y	z	B (eq)
Cs (1)	0.3499 (2)	1/4	-0.0651 (2)	2.3 (1)
Cs (2)	0.4435 (1)	1/4	-0.3853 (2)	1.9 (1)
In (1)	0.1792 (2)	1/4	0.1991 (3)	1.2 (1)
In (2)	0.5177 (2)	1/4	0.1927 (3)	1.3 (1)
In (3)	0.3474 (1)	-0.0025 (3)	0.2567 (2)	1.60 (8)
Ge (1)	0.1792	1/4	0.1991	1.5
Ge (2)	0.5177	1/4	0.1927	1.7
Ge (3)	0.3474	-0.0025	0.2567	1.9
S (1)	0.4571 (4)	-0.006 (1)	0.1436 (6)	2.5 (4)
S (2)	0.2394 (5)	-0.011 (1)	0.1425 (7)	2.8 (4)
S (3)	0.3515 (7)	-1/4	0.377 (1)	2.8 (5)
S (4)	0.3420 (7)	1/4	0.370 (1)	2.9 (6)
S (5)	0.1360 (7)	1/4	0.380 (1)	2.5 (5)
S (6)	0.0528 (6)	1/4	0.1293 (8)	1.8 (5)

^a $B(\text{eq}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table 7-19. Positional Parameters and Equivalent Isotropic Displacement Values ($\text{\AA}^2$)^a for $\text{Cs}_2\text{MnSn}_3\text{Se}_8$ with Estimated Standard Deviations in Parentheses

atom	x	y	z	B (eq)
Cs (1)	0.1295 (2)	0.5530 (1)	-0.2482 (7)	3.0 (1)
Cs (2)	0.3172 (2)	0.8444 (2)	0.2424 (7)	3.4 (1)
Sn (1)	0.0517 (2)	0.6803 (1)	0.2411 (7)	2.0 (1)
Sn (2)	-0.0707 (2)	0.5151 (1)	0.2647 (6)	1.8 (1)
Sn (3)	0.0158 (3)	0.3495 (2)	0.0031 (5)	2.1 (2)
Se (1)	0.1140 (7)	0.7340 (4)	-0.027 (1)	3.2 (3)
Se (2)	0.1104 (5)	0.7381 (3)	0.515 (1)	2.0 (3)
Se (3)	-0.1428 (3)	0.6442 (2)	0.249 (1)	2.5 (2)
Se (4)	0.1232 (3)	0.5503 (2)	0.257 (1)	2.2 (2)
Se (5)	-0.1162 (5)	0.4506 (3)	-0.011 (1)	2.4 (3)
Se (6)	-0.1251 (5)	0.4587 (3)	0.5335 (9)	2.2 (3)
Se (7)	0.3773 (3)	0.6572 (2)	-0.2345 (8)	2.2 (2)
Se (8)	0.1347 (3)	0.3515 (2)	-0.2467 (8)	2.0 (2)
Mn (1)	-0.0017 (5)	0.8448 (4)	-0.014 (1)	1.4 (3)

Table 7-20. Positional Parameters and Equivalent Isotropic Displacement Values ($\text{\AA}^2$)^a for $\text{Rb}_2\text{CdGe}_2\text{S}_6$ with Estimated Standard Deviations in Parentheses

atom	x	y	z	B (eq)
Cd	0.0	0.45945 (6)	0.25	1.57 (3)
Rb	-0.2985 (1)	0.57618 (7)	0.43436 (6)	2.57 (3)
Ge	0.1917 (1)	0.74572 (6)	0.31351 (6)	1.20 (3)
S (1)	0.0742 (2)	0.7839 (2)	0.1467 (1)	1.74 (7)
S (2)	0.0804 (2)	0.3458 (2)	0.1101 (1)	2.06 (7)
S (3)	-0.2699 (2)	0.5728 (1)	0.1649 (2)	2.00 (7)

^a $B(\text{eq}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

3. Results and Discussion

3.1. Synthesis

The molten salt synthetic techniques have been described extensively in Chapter 1, 5 and 6. Following Chapter 6, here we add more examples to prove the feasibility of by using molten salts as synthetic tools for new quaternary compounds. This suggests molten salts provide good homogeneous reaction media for mixed metal systems. In Chapter 6, we discussed that $[\text{Sn}_2\text{S}_6]^{4-}$ and $[\text{SnS}_4]^{4-}$, which can be isolated as separate anions from the A_2S_x fluxes, are potentially good building blocks to construct quaternary structures. It is interesting to note that in this chapter, all the compounds also contain $[\text{MS}_4]^{4-}$ ($\text{M}=\text{Sn}$ or Ge) or $[\text{Sn}_2\text{Se}_6]^{4-}$ linked by linear HgS_2 or tetrahedral MQ_4 units ($\text{M}=\text{Hg}$, Zn , Mn , Cd , In ; $\text{Q}=\text{S}$, Se).

The formation of $\text{K}_2\text{Hg}_3\text{Sn}_2\text{S}_8$ (III) and $\text{K}_2\text{Hg}_3\text{Ge}_2\text{S}_8$ (IV) is an example of the fact that Sn and Ge often undergo similar chemistry since they belong to the same group in the periodic table. Other examples are the formation of discrete anions such as $[\text{MQ}_4]^{4-}$, $[\text{M}_2\text{Q}_6]^{4-}$, and $[\text{M}_4\text{Q}_{10}]^{4-}$,^{5,6} where $\text{M}=\text{Ge}$, Sn ; $\text{Q}=\text{S}$, Se . The size of Sn^{4+} is about 0.2 Å larger than that of Ge^{4+} . The three-dimensional structures of (III) and (IV) must be flexible enough to tolerate the large size difference between Ge and Sn . In contrast to (III) and (IV), the Ge analog of $\text{K}_2\text{HgSn}_2\text{S}_6$ (I) was not observed. Thus far, (I) could not be synthesized in pure form. (I) was made by reacting Sn and Hg in 1:1 ratio in a K_2S_9 flux. In this reaction, the dominant product is K_2HgSnS_4 , a KInSe_2 type structure. $\text{Sn}:\text{Hg}=2:1$ in a K_2S_9 flux produces no (I) but a mixture of K_2HgSnS_4 (~2/3) and $\text{K}_2\text{Sn}_2\text{S}_5$

($\sim 1/3$), while, in the other direction, Sn:Hg=1:2 in the same K_2S_9 flux (III) was obtained. $K_2GeIn_2S_6$ (II) was also made in very low yield. The dominant products are moisture-sensitive K_4GeS_4 and/or $K_4Ge_2S_6$ which, compared to their Sn analogs, have larger tendency to form even in low basicity K_2S_x fluxes such as K_2S_9 . In fact, all the quaternary compounds in this Chapter were synthesized in fluxes of relatively low basicity, i.e. K_2Q_x ($x \geq 5$), to avoid the competition of A_4MQ_4 and/or $A_4M_2Q_6$ ($A=K, Rb, Cs$; $M=Ge, Sn$; $Q=S, Se$).

As in Chapters 5 and 6, here we also see the size of the counterions exclusively directing the formation of $K_2GeIn_2S_6$ and $Cs_2In_2Ge_2S_8$, $K_6Zn_4Sn_5S_{17}$ and $Rb_2ZnSn_2S_6$, K_2MnSnS_4 and $Cs_2MnSn_2S_6$. In addition, the relative size difference of metal ions plays an important role in determining how the MQ_4 tetrahedra are arranged in the quaternary structures. This perhaps explains why $K_2HgSn_2S_6$, $K_2GeIn_2S_6$, $Rb_2ZnSn_2S_6$, $Cs_2MnSn_2S_6$ and $Rb_2CdGe_2S_6$ all have the same stoichiometry but adopt different structures.

3.2. Description of Structures

Structure of $K_2HgSn_2S_6$ (I)

Compound (I) has a two-dimensional structure which is composed of corner-sharing $[SnS_4]^{4-}$ and $[HgS_4]^{6-}$ tetrahedra in 2:1 ratio. As shown in Figure 7-1, the anionic layer of (I) is constructed by parallel $[SnS_3]_n^{2n-}$ chains cross-linked by HgS_4 tetrahedra unsymmetrically at every two Sn sites. The $[SnS_3]_n^{2n-}$ chains, running along the crystallographic a-axis, are made up by linking SnS_4 tetrahedra in a corner-sharing fashion. This two-

dimensional network features 12-membered rings separated by $[\text{HgSn}_2\text{S}_3]$ six-membered rings. The charge balancing K^+ cations are situated between the corrugated layers as shown in Figure 7-2.

Selected bond distances and bond angles of (I) are given in Table 7-21. The average Hg-S distance is normal at $2.56(5)\text{\AA}$, slightly longer than $2.51(2)\text{\AA}$ of a typical tetrahedral $[\text{HgS}_4]^{6-}$ ion in K_6HgS_4 .¹⁴ The average Sn-S distances is $2.39(4)\text{\AA}$ which is comparable to $2.39(6)\text{\AA}$ of the separate $[\text{SnS}_3]_n^{2n-}$ chains in $\text{K}_2\text{SnS}_3 \cdot 2\text{H}_2\text{O}$.¹⁵ Both S-Hg-S and S-Sn-S angles deviate from those of a perfect tetrahedron, ranging from $93.1(1)^\circ$ to $119.8(1)^\circ$ and from $95.1(1)^\circ$ to $118.3(2)^\circ$ respectively. There are two crystallographically distinct K^+ cations. Both are surrounded by six S atoms with an average $\text{K}^+ \cdots \text{S}$ distance of $3.26(7)\text{\AA}$.

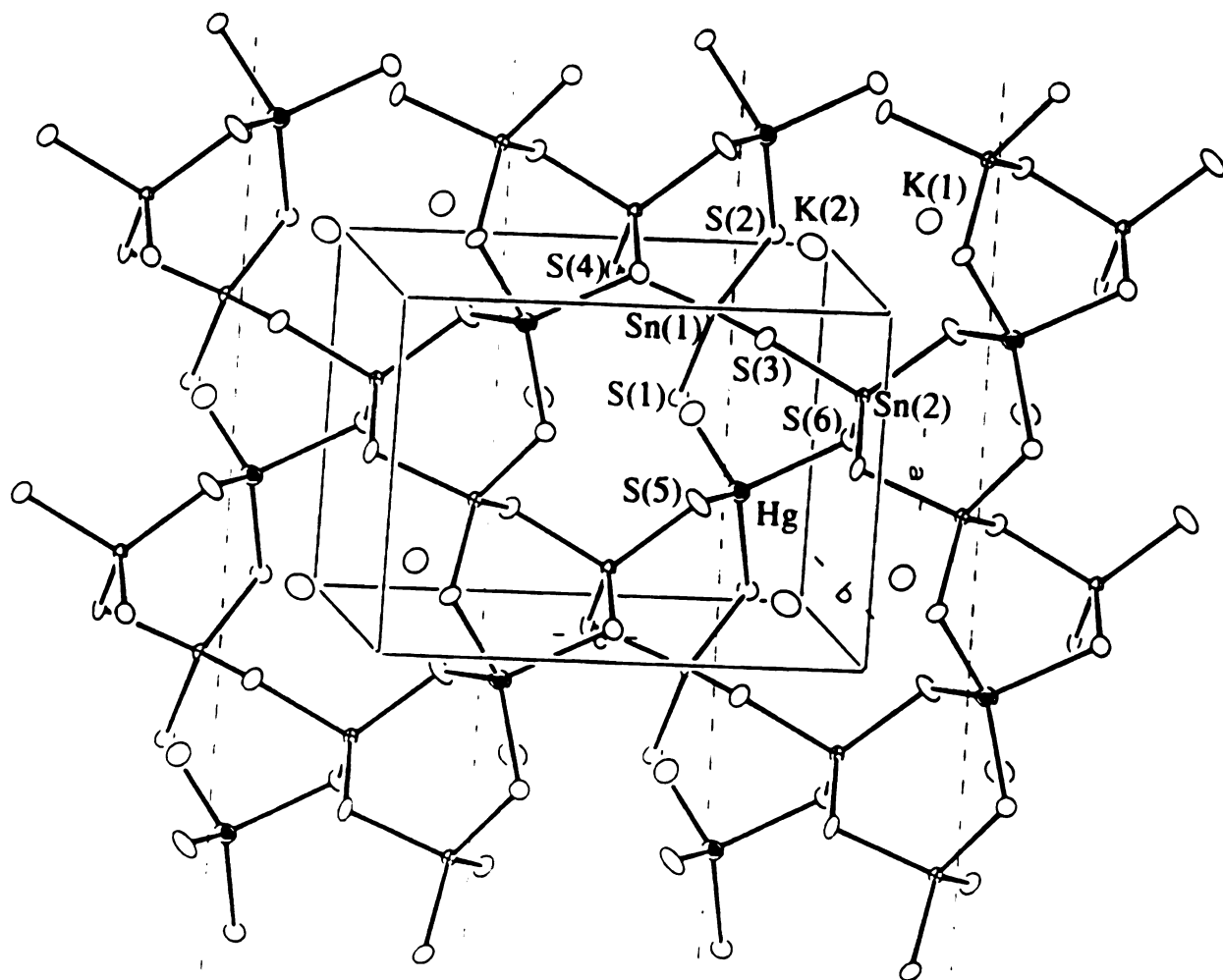


Figure 7-1: ORTEP representation and labeling scheme of the layered structure of $K_2HgSn_2S_6$. View down the b-axis. The dashed lines represent the way $[HgSn_2S_6]^{2-}$ layers are folded.

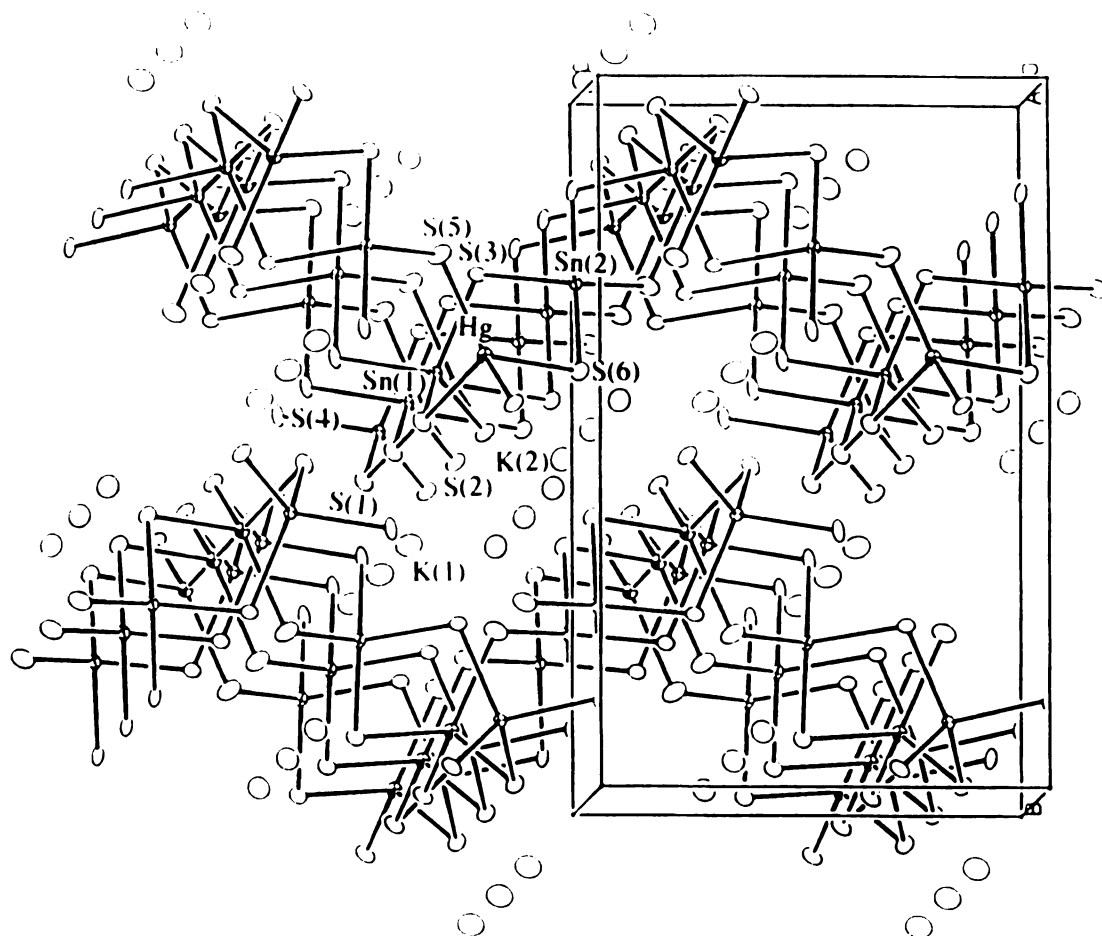


Figure 7-2: The structure of $\text{K}_2\text{HgSn}_2\text{S}_6$ viewed parallel to the layers. A monolayer of potassium cations is located between layers.

Table 7-21. Selected Bond Distances (Å) and Angles (deg) for K₂HgSn₂S₆ with Standard Deviations in Parentheses

Selected Bond Distances (Å)			
Hg-S(1)	2.586(4)	K(1)-S(1)	3.358(6)
Hg-S(2)	2.536(4)	K(1)-S(1)	3.264(6)
Hg-S(5)	2.496(4)	K(1)-S(2)	3.243(6)
Hg-S(6)	2.614(4)	K(1)-S(3)	3.184(6)
mean(Hg-S)	2.56(5)	K(1)-S(4)	3.223(6)
Sn(1)-S(1)	2.362(4)	K(1)-S(5)	3.303(7)
Sn(1)-S(2)	2.368(4)	K(2)-S(1)	3.373(6)
Sn(1)-S(3)	2.416(4)	K(2)-S(2)	3.277(6)
Sn(1)-S(4)	2.405(4)	K(2)-S(2)	3.234(5)
Sn(2)-S(3)	2.438(4)	K(2)-S(3)	3.346(6)
Sn(2)-S(4)	2.403(4)	K(2)-S(5)	3.193(6)
Sn(2)-S(5)	2.351(4)	K(2)-S(6)	3.146(6)
Sn(2)-S(6)	2.337(4)	mean(K-S)	3.26(7)
mean(Sn-S)	2.39(4)		
Selected Bond Angles (deg)			
S(1)-Hg-S(2)	115.1(1)	S(3)-Sn(2)-S(4)	95.1(1)
S(1)-Hg-S(5)	107.2(1)	S(3)-Sn(2)-S(5)	112.0(2)
S(1)-Hg-S(6)	93.1(1)	S(3)-Sn(2)-S(6)	108.6(1)
S(2)-Hg-S(5)	119.8(1)	S(4)-Sn(2)-S(5)	113.1(2)
S(2)-Hg-S(6)	101.4(1)	S(4)-Sn(2)-S(6)	118.3(2)
S(5)-Hg-S(6)	117.4(1)	S(5)-Sn(2)-S(6)	108.9(2)
S(1)-Sn(1)-S(2)	114.0(1)	Hg-S(1)-Sn(1)	101.1(1)
S(1)-Sn(1)-S(3)	117.7(1)	Hg-S(2)-Sn(1)	103.8(1)
S(1)-Sn(1)-S(4)	100.8(1)	Sn(1)-S(3)-Sn(2)	106.5(2)
S(2)-Sn(1)-S(3)	110.0(1)	Sn(1)-S(4)-Sn(2)	105.8(1)
S(2)-Sn(1)-S(4)	109.8(1)	Hg-S(5)-Sn(2)	111.3(2)
S(3)-Sn(1)-S(4)	103.3(1)	Hg-S(6)-Sn(2)	98.0(1)

Structure of $\text{K}_2\text{GeIn}_2\text{S}_6$ (II) and Comparison with $\text{K}_2\text{HgSn}_2\text{S}_6$ (I)

Compound (II) is also a two-dimensional structure which is similar to, but different from that of (I). By comparing the chemical formula between (II) and (I), parallel $[\text{InS}_3]_n^{3n-}$ chains, corresponding to $[\text{SnS}_3]_n^{2n-}$ chains in (I), can be readily recognized in Figure 7-3. These $[\text{InS}_3]_n^{3n-}$ chains are then cross-linked by $[\text{GeS}_4]^{4-}$ tetrahedra in the same manner as are $[\text{HgS}_4]^{6-}$ tetrahedra in (I). However, (II) is not isomorphous to (I) as one might expect. Surprisingly, (II) crystallizes in a noncentrosymmetric space group ($\text{P2}_1\text{2}_1\text{2}_1$, #18), while (I) crystallizes in a centrosymmetric space group ($\text{P2}_1/\text{n}$, #14). The centro- and noncentro- symmetry of (I) and (II) can be illustrated in Figure 7-2 and 7-4 respectively. Centers of inversion can only be found between the layers in the packing diagram of (I). The difference comes from the ways the layers are folded into corrugated forms, as shown by the dashed lines in Figure 7-1 and 7-3. According to the folding of the layers, it would be helpful to rewrite the formula of (I) as $\text{K}_2\text{Sn}(\text{SnHg})\text{S}_6$ so that (I) can be viewed as $[(\text{SnHg})\text{S}_6]_n^{6n-}$ chains cross-linked by $[\text{SnS}_4]^{4-}$ tetrahedra. The spatial rearrangement of atoms causes the change of symmetry between (I) and (II). Interestingly, the folding of anionic layers in both (I) and (II) occurs along the rows of smaller metal centers (Sn in (I); Ge in (II))

Selected bond distances and bond angles of (II) are given in Table 7-22. Both In and Ge are in a good tetrahedral environment without much deviation. The average In-S distance (2.46 Å) and Ge-S distance (2.21(3) Å) are normal compared to 2.46 Å in $\beta\text{-In}_2\text{S}_3$ ¹⁶ and 2.20 Å in Pb_2GeS_4 ^{6a}. Two, crystallographically distinct, potassium cations are both surrounded by seven sulfur atoms with an average $\text{K}^+\cdots\text{S}$ distance of 3.29(15) Å.

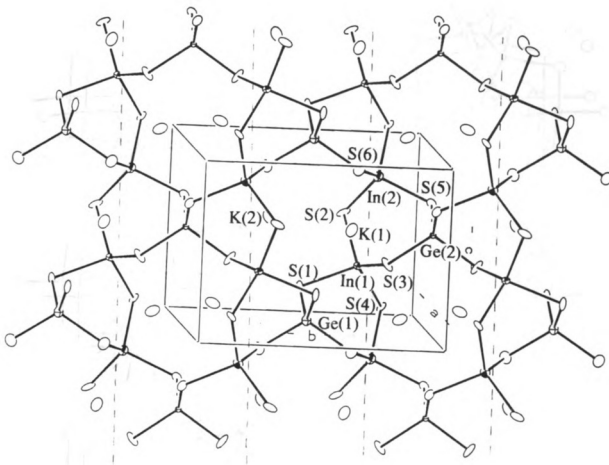


Figure 7-3: ORTEP representation and labeling scheme of the layered structure of $K_2GeIn_2S_6$. View down the *a*-axis. The dashed lines represent the way $[GeIn_2S_6]^{2-}$ layers are folded.

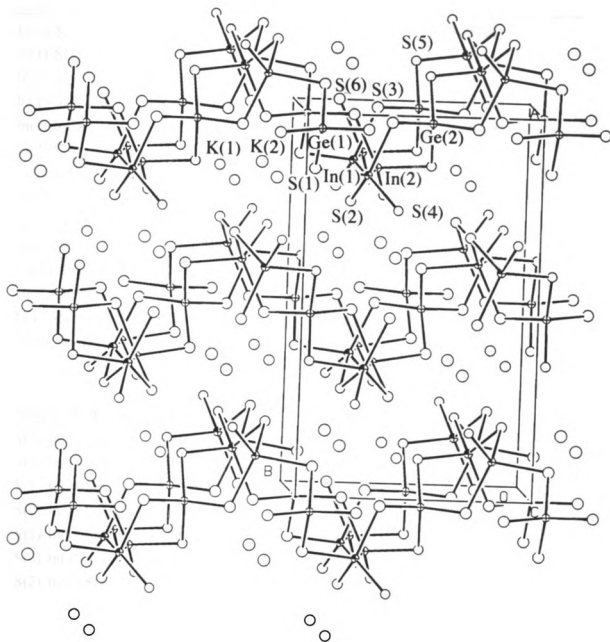


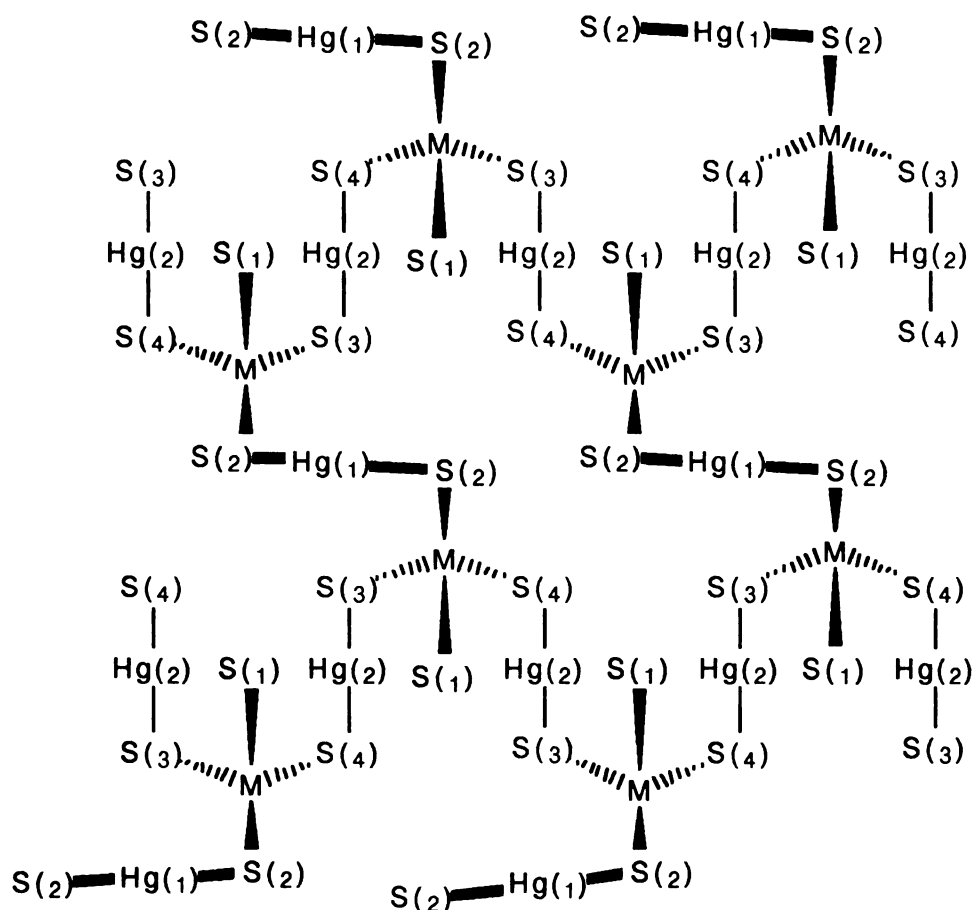
Figure 7-4: The structure of $K_2GeIn_2S_6$ viewed parallel to the layers. A monolayer of potassium cations is located between layers.

Table 7-22 Selected Bond Distances(Å) and Angles(deg) for K₂GeIn₂S₆ with Standard Deviations in Parentheses

Selected Bond Distances (Å)			
In(1)-S(1)	2.539(6)	K(1)-S(1)	3.552(8)
In(1)-S(2)	2.474(8)	K(1)-S(2)	3.25(1)
In(1)-S(3)	2.46(1)	K(1)-S(3)	3.04(1)
In(1)-S(4)	2.467(7)	K(1)-S(4)	3.284(8)
In(2)-S(2)	2.410(8)	K(1)-S(4)	3.363(9)
In(2)-S(4)	2.431(7)	K(1)-S(5)	3.317(8)
In(2)-S(5)	2.417(6)	K(1)-S(6)	3.21(1)
In(2)-S(6)	2.46(1)	K(2)-S(1)	3.130(9)
mean(In-S)	2.46(4)	K(2)-S(2)	3.231(9)
Ge(1)-S(1)	2.162(7)x2	K(2)-S(2)	3.27(1)
Ge(1)-S(6)	2.231(7)x2	K(2)-S(3)	3.31(1)
Ge(2)-S(3)	2.215(7)x2	K(2)-S(4)	3.26(1)
Ge(2)-S(5)	2.232(7)x2	K(2)-S(5)	3.604(8)
mean(Ge-S)	2.21(3)	K(2)-S(6)	3.29(1)
		mean(K-S)	3.29(15)
Selected Bond Angles (deg)			
S(1)-In(1)-S(2)	99.0(2)	S(1)-Ge(1)-S(6)	113.7(3)x2
S(1)-In(1)-S(3)	107.2(3)	S(1)-Ge(1)-S(6)	101.2(3)x2
S(1)-In(1)-S(4)	104.0(2)	S(6)-Ge(1)-S(6)	114.6(4)
S(2)-In(1)-S(3)	117.3(3)	S(3)-Ge(2)-S(3)	110.9(4)
S(2)-In(1)-S(4)	114.9(2)	S(3)-Ge(2)-S(5)	110.0(3)x2
S(3)-In(1)-S(4)	112.2(3)	S(3)-Ge(2)-S(5)	103.0(3)x2
S(2)-In(2)-S(4)	110.8(2)	S(5)-Ge(2)-S(5)	120.1(4)
S(2)-In(2)-S(5)	103.3(2)	In(1)-S(1)-Ge(1)	103.6(2)
S(2)-In(2)-S(6)	113.4(3)	In(1)-S(2)-In(2)	99.4(3)
S(4)-In(2)-S(5)	101.9(2)	In(1)-S(3)-Ge(2)	111.1(4)
S(4)-In(2)-S(6)	114.8(2)	In(1)-S(4)-In(2)	102.0(2)
S(5)-In(2)-S(6)	111.4(3)	In(2)-S(5)-Ge(2)	104.5(3)
S(1)-Ge(1)-S(1)	113.0(4)	In(2)-S(6)-Ge(1)	112.9(4)

Structures of $\text{K}_2\text{Hg}_3\text{Sn}_2\text{S}_8$ (III) and $\text{K}_2\text{Hg}_3\text{Ge}_2\text{S}_8$ (IV)

Compounds (III) and (IV) are isostructural with Sn and Ge occupying the same metal sites. They have complicated three-dimensional structures made up with tetrahedral MS_4 ($\text{M}=\text{Sn}$ in (I) and Ge in (II)), linear HgS_2 and "saddle-like" HgS_4 which contains two short and two long Hg-S bonds. The structure of (III) or (IV) is shown in Figure 7-5. The structures of (III) and (IV) are noncentrosymmetric. This can be readily seen by the fact that all $\text{S}(1)\text{-Hg}(2)\text{-S}(1)$ and $\text{S}(3)\text{-M-S}(4)$ ($\text{M}=\text{Sn}$ or Ge) angles are pointed to the same direction, $\langle 001 \rangle$, see Figure 7-5. If the two long $\text{Hg}(2)\text{-S}(1)$ bonds of the saddle-like HgS_4 units are not considered as bonds, the complicated three-dimensional framework can be simplified to a two-dimensional sheet, as shown in Scheme I.



Scheme I

The two-dimensional sheet is constructed by rows of parallel $S(3)\text{-Hg}(2)\text{-S}(4)$ fragments linked alternately by MS_4 ($M = \text{Sn}$ or Ge) tetrahedra in a corner-sharing fashion to form wave-like chains running in a sequence of $S(3)\text{-Hg}(2)\text{-S}(4)\text{-M-S}(3)\text{-Hg}(2)$. These parallel wave-like chains are then extended to $[\text{Hg}_3\text{M}_2\text{S}_8]^{2-}$ sheets by connecting the $S(2)$ atoms of MS_4 tetrahedra through linear $S(2)\text{-Hg}(1)\text{-S}(2)$ units. These two-dimensional sheets are further expanded to three-dimensional networks via weak $\text{Hg}(2)\text{-S}(1)$ bondings between two adjacent $[\text{Hg}_3\text{M}_2\text{S}_8]^{2-}$ sheets. This forms parallel tunnels, enclosed by edge-sharing 20-membered rings which contains edges of four MS_4 tetrahedra, two linear HgS_2 and four saddle-

like HgS_4 units, running along the $\langle 01\bar{1} \rangle$ crystallographic direction. K^+ cations are located in the tunnels, as shown in Figure 7-6.

A comparison of the selected bond distances and bond angles between (III) and (IV) are given in Table 7-23. The average Sn-S distance is $2.39(3)\text{\AA}$ while the average Ge-S distance is shorter at $2.22(3)\text{\AA}$. The S-M-S angles are close to those of a perfect tetrahedron. There are two distinct Hg atoms. Hg(1) adopts linear coordination with the Hg(1)-S(2) distances at $2.331(6)\text{\AA}$ and $2.361(8)\text{\AA}$, the S(2)-Hg(1)-S(2) angles at $177.0(4)^\circ$ and $177.8(7)^\circ$ for (III) and (IV) respectively. The linear geometry of HgS_2 is common for thiomercurates and has been found in $\text{HgS}(\text{cinnabar})^{17}$, BaHgS_2^{18} $\text{A}_2\text{Hg}_3\text{S}_4$ ($\text{A}=\text{Na}, \text{K}$) and $\text{K}_2\text{Hg}_6\text{S}_7$.^{2g} The Hg-S distances and S-Hg-S angles found in (III) and (IV) are comparable to those found in these compounds. Hg(2) is four coordinated and adopts a saddle-like geometry which has two short and two long Hg-S bonds, the former averaging $2.426(9)\text{\AA}$ and $2.436(9)\text{\AA}$, the latter averaging $2.80(2)\text{\AA}$ and $2.81(5)\text{\AA}$ for (I) and (II) respectively. This coordination type of HgS_4 is novel and has not been observed in other thiomercurates. The angles between the two short Hg-S bonds in (III) and (IV) are $166.8(2)^\circ$ and $163.8(3)^\circ$ respectively, still showing some character of linearity. The deviations from perfect linearity are caused by the formation of two long Hg-S bonds between Hg(2) and S(1) atoms which are actually shared with tetrahedral MS_4 ($\text{M}=\text{Sn}$ or Ge). The two short Hg-S bond distances fall between those in normal linear HgS_2 (ca. $2.35\text{\AA}$) and tetrahedral HgS_4 (ca. $2.55\text{\AA}$). Therefore, the coordination geometry of Hg(2) may be considered as intermediate between tetrahedral HgS_4 and linear HgS_2 having short contacts with two S atoms.

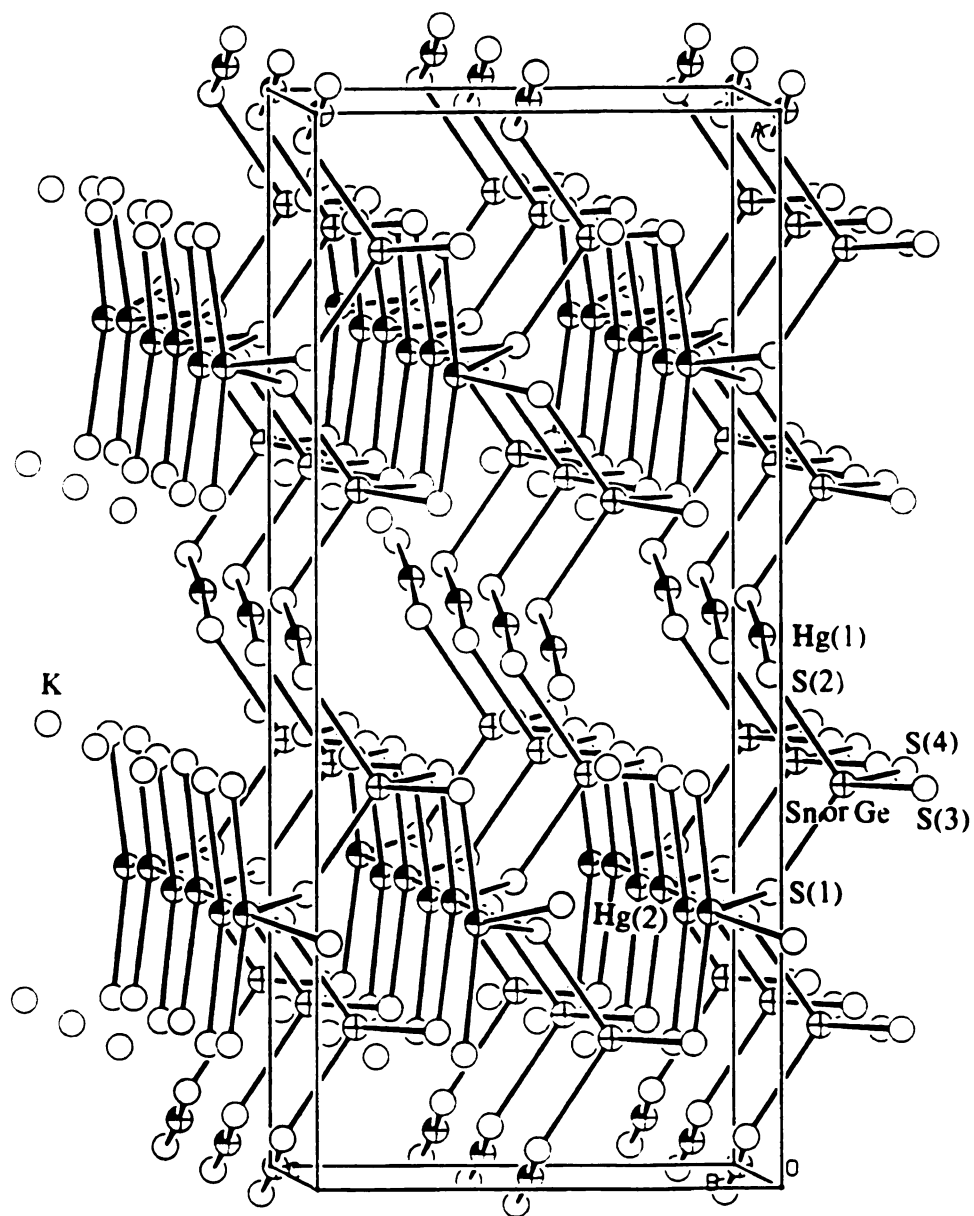


Figure 7-5: ORTEP representation and labeling scheme of $K_2Hg_3Sn_2S_8$ or $K_2Hg_3Ge_2S_8$. View down the b-axis.

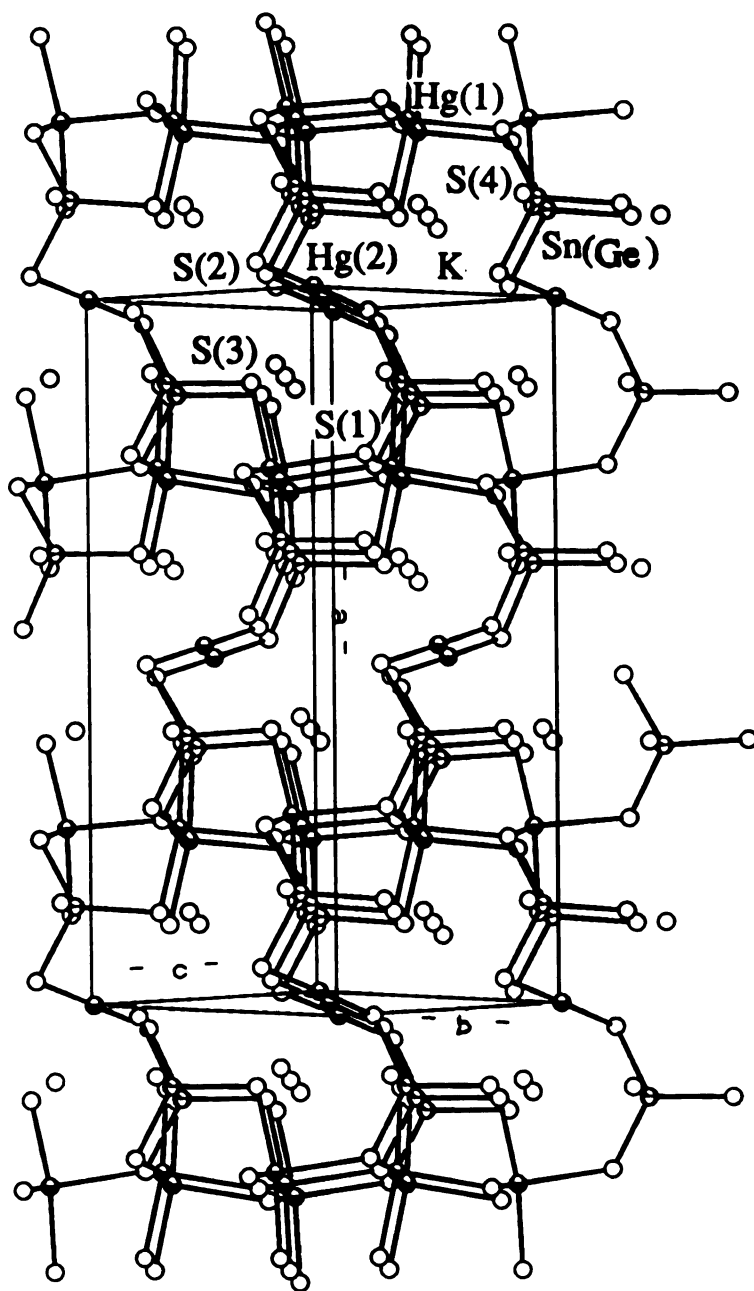


Figure 7-6: ORTEP representation and labeling scheme of $K_2Hg_3Sn_2S_8$ or $K_2Hg_3Ge_2S_8$. View down the $\langle 110 \rangle$ direction.

Table 7-23. Comparison of Selected Bond Distances (Å) and Angles (deg) of K₂Hg₃Sn₂S₈(I) and K₂Hg₃Ge₂S₈(II) with Standard Deviations in Parentheses

Selected Bond Distances (Å)					
	(I)	(II)		(I)	(II)
Hg(1)-S(2)	2.331(6)	2.361(8)	mean(M-S)	2.39(3)	2.22(3)
Hg(2)-S(1)	2.787(7)	2.778(9)	K-S(1)	3.217(8)	3.23(1)
Hg(2)-S(1)	2.818(6)	2.85(1)	K-S(2)	3.37(1)	3.32(2)
Hg(2)-S(3)	2.419(5)	2.436(9)	K-S(2)	3.215(8)	3.20(1)
Hg(2)-S(4)	2.432(5)	2.436(9)	K-S(3)	3.304(9)	3.34(1)
M-S(1)	2.356(6)	2.18(1)	K-S(3)	3.452(9)	3.38(1)
M-S(2)	2.426(6)	2.25(1)	K-S(4)	3.163(9)	3.16(1)
M-S(3)	2.390(7)	2.22(1)	K-S(4)	3.545(9)	3.46(1)
M-S(4)	2.377(6)	2.23(1)	mean(K-S)	3.32(14)	3.30(11)

Selected Bond Angles (deg)					
	(I)	(II)		(I)	(II)
S(3)-M-S(4)	113.6(2)	113.0(4)	S(1)-M-S(4)	109.2(2)	110.1(4)
S(2)-Hg(1)-S(2)	177.0(4)	177.8(7)	S(2)-M-S(3)	107.1(2)	107.3(4)
S(1)-Hg(2)-S(1)	124.7(3)	119.9(5)	S(2)-M-S(4)	104.9(2)	102.4(4)
S(1)-Hg(2)-S(3)	98.6(2)	100.8(3)	Hg(1)-S(2)-M	97.9(2)	99.1(4)
S(1)-Hg(2)-S(4)	88.8(2)	89.3(3)	Hg(2)-S(3)-M	99.8(2)	101.0(4)
S(1)-Hg(2)-S(3)	91.5(2)	91.5(3)	Hg(2)-S(4)-M	102.0(2)	102.5(3)
S(1)-Hg(2)-S(4)	93.3(2)	94.3(3)	Hg(2)-S(1)-Hg(2)	122.8(3)	117.6(5)
S(3)-Hg(2)-S(4)	166.8(2)	163.8(3)	Hg(2)-S(1)-M	108.9(2)	110.8(4)
S(1)-M-S(2)	111.5(2)	112.0(4)	Hg(2)-S(1)-M	113.6(2)	115.2(3)
S(1)-M-S(3)	110.5(2)	111.7(4)			

*M= Sn (I) or Ge (II)

The K^+ cations of (III) and (IV) are both surrounded by seven sulfur atoms with the average $K^+ \cdots S$ distances at 3.32(14) Å and 3.30(11) Å respectively.

Structure of $K_6Zn_4Sn_5S_{17}$ (V)

Compound (V) has a complicated three-dimensional structure which is made up by linking tetrahedrally coordinated Sn^{4+} ions and $[Zn_4Sn_4S_{17}]^{10-}$ clusters via sulfur atoms in a vertex-sharing fashion, as shown in Figure 7-7. The $[Zn_4Sn_4S_{17}]^{10-}$ cluster, shown in Figure 7-8, is actually a fragment of the ZnS wurtzite type structure which features boat-form six-membered rings. It contains a sulfur atom at its center tetrahedrally bonded to four Zn atoms. The four triangular faces of the $[SZn_4]^{6+}$ tetrahedron are then capped with four $[SnS_4]^{4-}$ tetrahedra in a face-sharing fashion. The resulting $[Zn_4Sn_4S_{17}]^{10-}$ clusters possess pseudo-tetrahedral site symmetry and are practically functioning as huge tetrahedral $[MS_4]^{10-}$ ($M=[Zn_4Sn_4S_{13}]$) building blocks. The linkage of Sn^{4+} and $[Zn_4Sn_4S_{17}]^{10-}$ generates three different types of tunnels in which charge balancing potassium cations are located: type (a) is formed by connecting Sn^{4+} and $[MS_4]^{10-}$ tetrahedra in a helix way along a 2_1 screw axis in the $\langle 001 \rangle$ crystallographic direction (see Figure 7-7); type (b) is wide and flat and is enclosed by four $[M/SnS_4]$ chains running along the $\langle 010 \rangle$ or $\langle 100 \rangle$ direction (see Figure 7-9); type (c) is formed by connecting Sn^{4+} and $[MS_4]^{10-}$ tetrahedra in a helix way along a pseudo- 3_1 screw axis in the $\langle 1\bar{1}0 \rangle$ or $\langle 110 \rangle$ direction (see Figure 7-10). (V) crystallizes in a noncentrosymmetric tetragonal space group. Four fold improper rotation axes pass through the Sn(1) atom of the $[SnS_4]^{4-}$ units

and S(1) atoms at the center of $[\text{Zn}_4\text{Sn}_4\text{S}_{17}]^{10-}$ clusters. The absence of a center of symmetry is clearly visible in Figure 7-9.

Selected bond distances and angles are given in Table 7-24. The average Sn-S and Zn-S distances are 2.40(3)Å and 2.339(9)Å respectively. The S-M-S angles do not deviate very much from those of a perfect tetrahedron. Only slight deviations occur at Sn(1) and S(1) and reduce the site symmetry from T_d to S_4 .

There are three crystallographically distinct potassium cations. K(1) is sandwiched by two $[\text{Zn}_4\text{Sn}_4\text{S}_{17}]^{10-}$ clusters, each providing four S(3) atoms for coordination. K(2) is located at the intersection of two sets of tunnels running along the crystallographic $\langle 001 \rangle$ axis and $\langle 1\bar{1}0 \rangle$ (or $\langle 110 \rangle$) axis. K(3) is located between two K(2)'s in the same tunnels running along the $\langle 1\bar{1}0 \rangle$ or $\langle 110 \rangle$ axis, as shown in Figure 7-10. All potassium cations are eight-coordinated. The average K-S distance for K(1) and K(2) is normal at 3.37(12)Å. K(3) is located in a wider cavity inside the tunnels, surrounded by four S(2) atoms from four $[\text{Zn}_4\text{Sn}_4\text{S}_{17}]^{10-}$ clusters and four S(4) atoms from two $[\text{SnS}_4]^{4-}$ tetrahedra. The size of the cavity is however too large for a K^+ cation (the center is 3.784Å to S(2) and 3.944Å to S(4)). The crystallographic data suggest that K(3) is not localized at a certain position but is "rattling" around the center of the cavity.

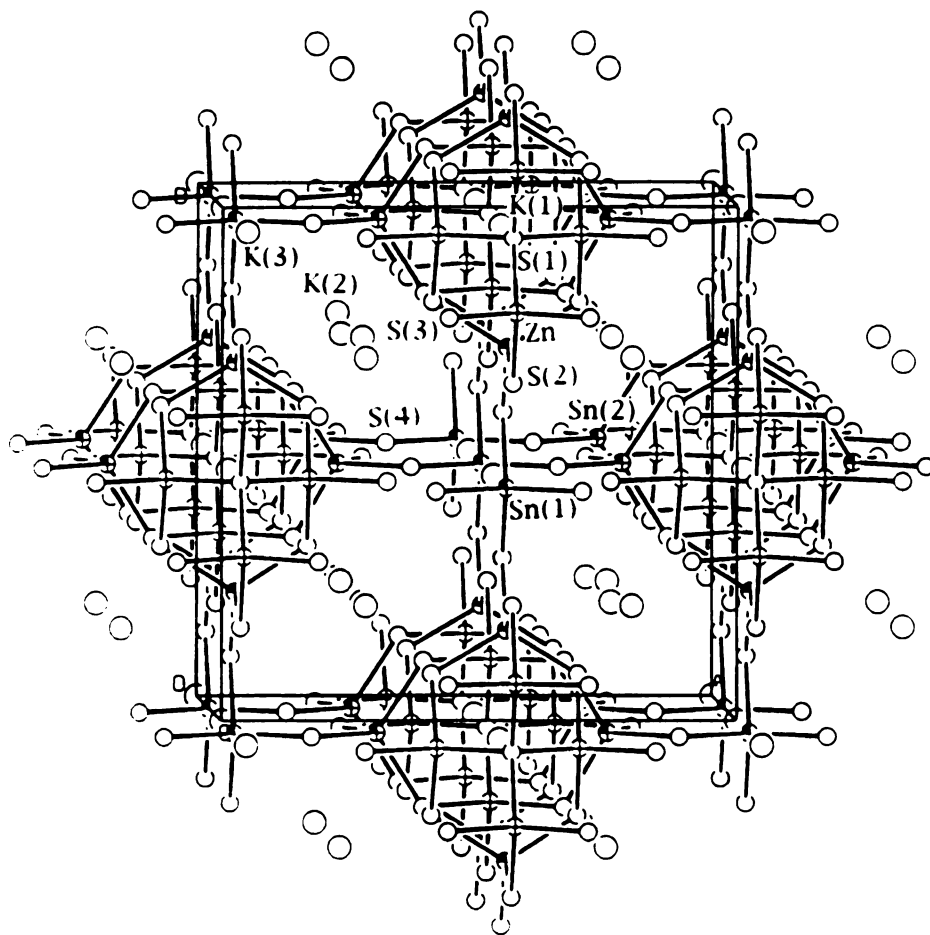


Figure 7-7: ORTEP representation and labeling scheme of $K_6Zn_4Sn_5S_{17}$. View down the c-axis.

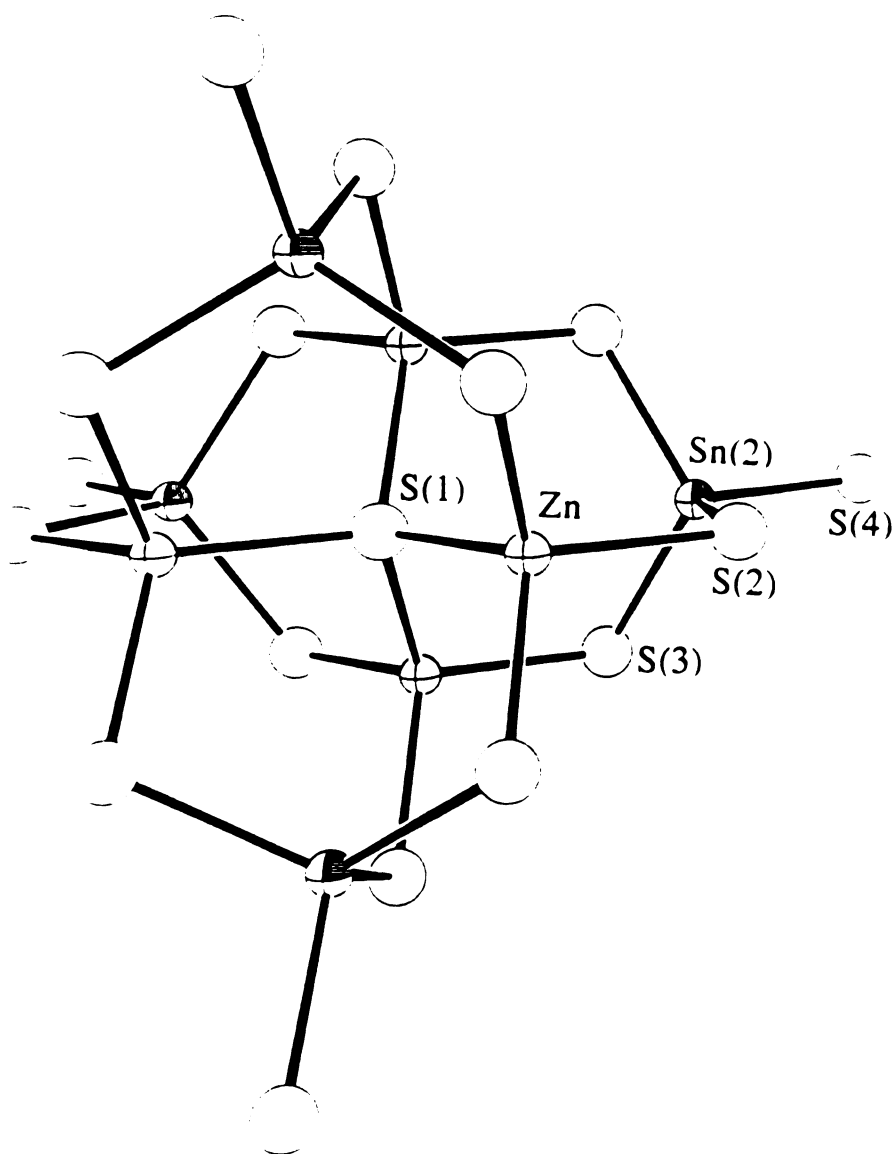


Figure 7-8: $[\text{Zn}_4\text{Sn}_4\text{S}_{17}]^{10-}$ cluster, the building block of $\text{K}_6\text{Zn}_4\text{Sn}_5\text{S}_{17}$, is a fragment of Wurtzite type structure.

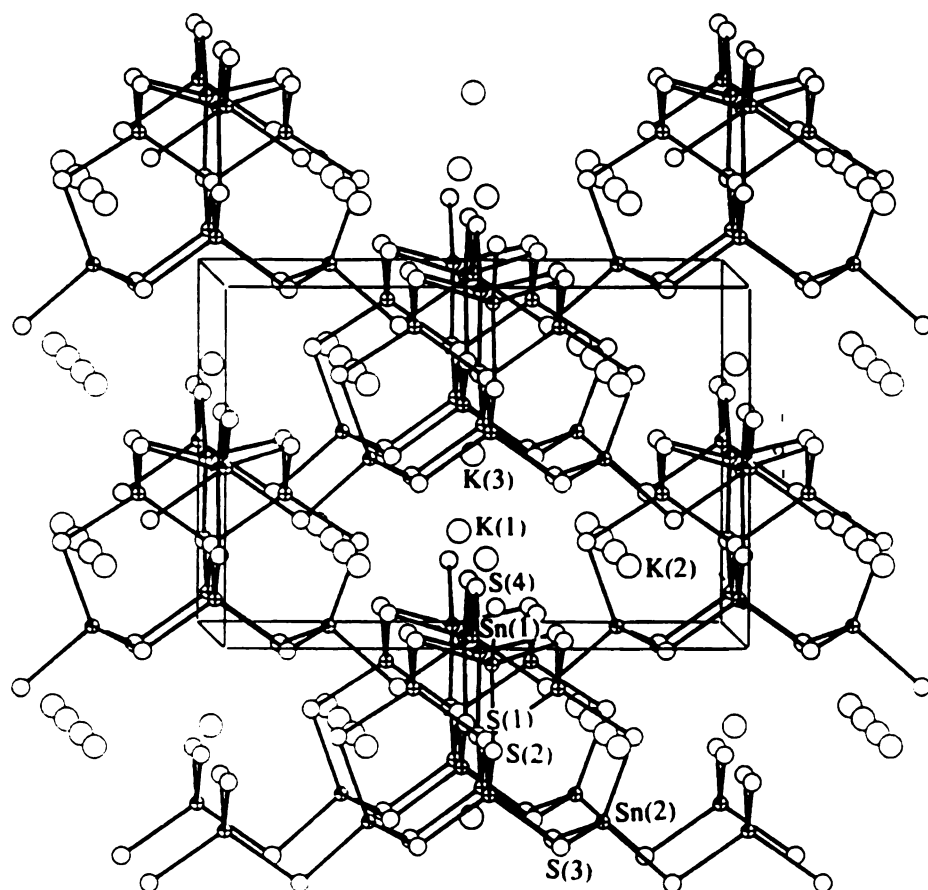


Figure 7-9: ORTEP representation and labeling scheme of $K_6Zn_4Sn_5S_{17}$. View down the a- or b-axis. This view shows the polar character of the structure. K(1) cations are located inside the wide and narrow tunnels parallel to the a- or b-axis.

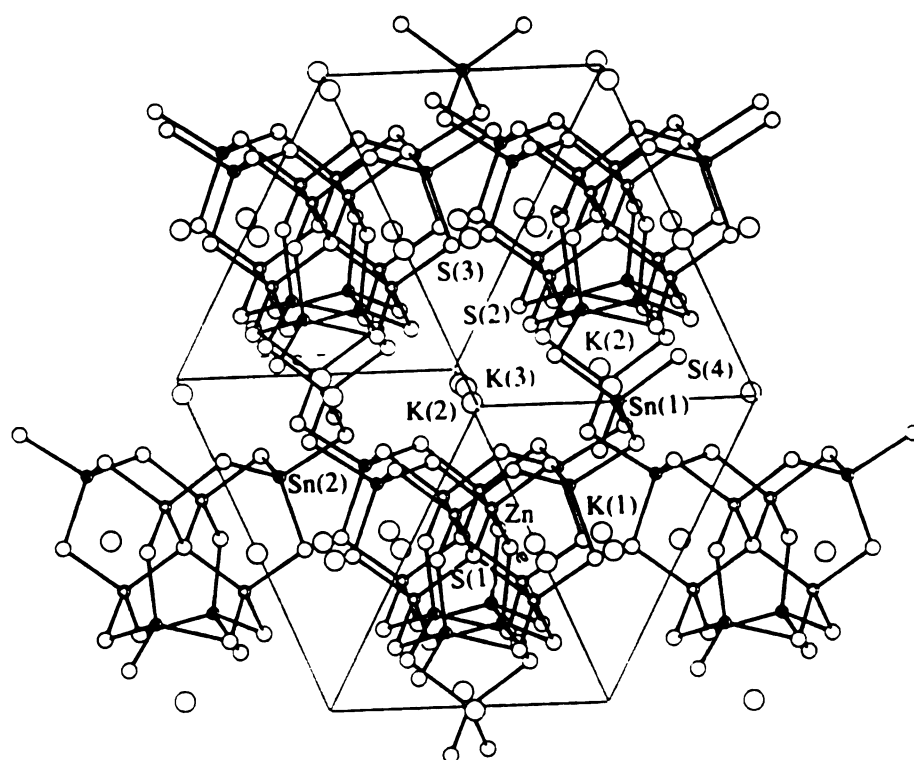


Figure 7-10: ORTEP representation and labeling scheme of $K_6Zn_4Sn_5S_{17}$. View down the a or $\langle 110 \rangle$ or $\langle 1\bar{1}0 \rangle$ direction. K(2) and K(3) are located inside the tunnels.

Table 7-24. Selected Bond Distances (Å) and Angles (deg) for K₆Zn₄Sn₅S₁₇ with Standard Deviations in Parentheses

Selected Bond Distances (Å)

Sn(1)-S(4)	2.402(6)x4	K(1)-S(3)	3.431(4)x8
Sn(2)-S(2)	2.372(6)	K(2)-S(2)	3.381(1)x2
Sn(2)-S(3)	2.369(4)x2	K(2)-S(3)	3.358(4)x2
Sn(2)-S(4)	2.448(6)	K(2)-S(3)	3.116(5)x2
mean(Sn-S)	2.40(3)	mean(K(1,2)-S)	3.37(12)
Zn-S(1)	2.342(2)	K(3)-S(2)	3.784(6)x4
Zn-S(2)	2.350(6)	K(3)-S(4)	3.944(5)x4
Zn-S(3)	2.332(4)x2	mean(K(3)-S)	3.86(11)
mean(Zn-S)	2.339(9)		

Selected Bond Angles (deg)

S(4)-Sn(1)-S(4)	109.1(1)x4	S(1)-Zn-S(3)	110.6(1)x2
S(4)-Sn(1)-S(4)	110.2(3)x2	S(2)-Zn-S(3)	107.2(1)x2
S(2)-Sn(2)-S(3)	113.3(1)x2	S(3)-Zn-S(3)	108.5(2)
S(2)-Sn(2)-S(4)	111.7(2)	Zn-S(1)-Zn	109.30(5)x4
S(3)-Sn(2)-S(3)	111.8(2)	Zn-S(1)-Zn	109.8(1)x2
S(3)-Sn(2)-S(4)	102.9(1)x2	Sn(2)-S(2)-Zn	102.6(2)
S(3)-Sn(2)-S(4)	102.9(1)	Sn(2)-S(3)-Zn	104.9(1)
S(1)-Zn-S(2)	112.5(2)	Sn(1)-S(4)-Sn(2)	103.6(2)

Rb₂ZnSn₂S₆ (VI) and Cs₂MnSn₂S₆ (VII)

Compounds (VI) and (VII) are isostructural, forming a new three-dimensional structure type with corner-sharing tetrathiometalates as building blocks, as shown in Figure 7-11. In order to have a better view of the structure, it can be divided into layers perpendicular to the b-axis, as shown in Figure 7-12. Each layer is related to its adjacent layer by a two-fold improper rotation symmetry parallel to the b-axis, thus resulting in a noncentrosymmetric space group ($P2_1$, #4). One such discrete layer consists of slightly twisted boat-shaped $[(M\text{Sn}_2\text{S}_3)\text{S}_6]^{4-}$ ($M=\text{Mn}$ or Zn) six-membered rings connected by sharing four of their six terminal sulfur atoms. The remaining two axial sulfur atoms, S(6), link the adjacent layers above and below, extending to three-dimensional frameworks and forming parallel tunnels running along $\langle 100 \rangle$ and $\langle 001 \rangle$ axes. These tunnels are narrow ($\sim 3.2\text{\AA}$), so free movement of Cs^+ or Rb^+ cations along the tunnels is not expected. The charge balancing cations are located at the cavities near the boundary of the tunnels.

Selected bond distances and angles for (V) and (VI) are given in Table 7-25 and 7-26 respectively. The average Sn-S distances for (V) and (VI) are similar at $2.38(4)\text{\AA}$ and $2.39(4)\text{\AA}$ respectively and are comparable to those of other $[\text{SnS}_4]^{4-}$ containing compounds. The average Mn-S distance ($2.44(3)\text{\AA}$) is significantly larger than that of Zn-S ($2.356(3)\text{\AA}$). This explains why the lattice of (V) is stabilized by larger Cs^+ cations while (V) is stabilized by Rb^+ cations. The coordination environments for Cs^+ and Rb^+ ions in (V) and (VI) respectively are similar with an average $\text{Cs}^+\cdots\text{S}$ distance of $3.70(16)\text{\AA}$ and an average $\text{Rb}^+\cdots\text{S}$ distance of $3.61(22)\text{\AA}$. The corresponding S-Sn-S and S-M-S ($M=\text{Mn}$ or Zn) angles in

(V) and (VI) are comparable and deviate from those of a perfect tetrahedra.

Even though it is possible that Sn and Mn or Zn are disordered at metal sites due to their similarity of ionic radii, their reasonable temperature factors based on the structure refinements of crystallographic data indicate an ordered model. The perfect paramagnetic behavior of (V) also suggests the current ordered model in which Mn atoms are separated by a Sn and two S atoms, resulting in negligible magnetic dipole-dipole coupling due to long Mn...Mn distances (7.098(1)Å, 7.434(1)Å and 7.842(1)Å). (VI) is diamagnetic because both Sn^{4+} and Zn^{2+} do not contain unpaired electrons.

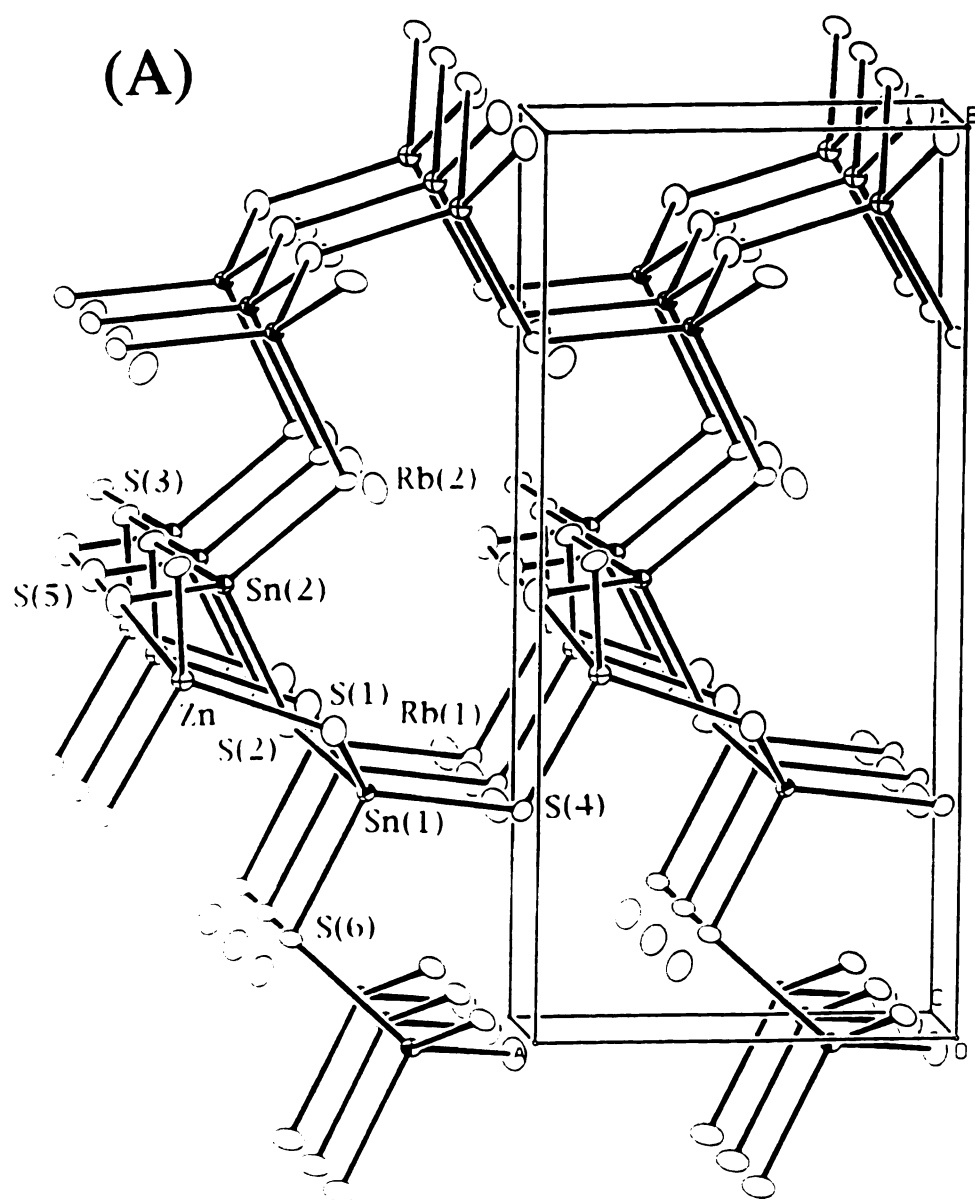
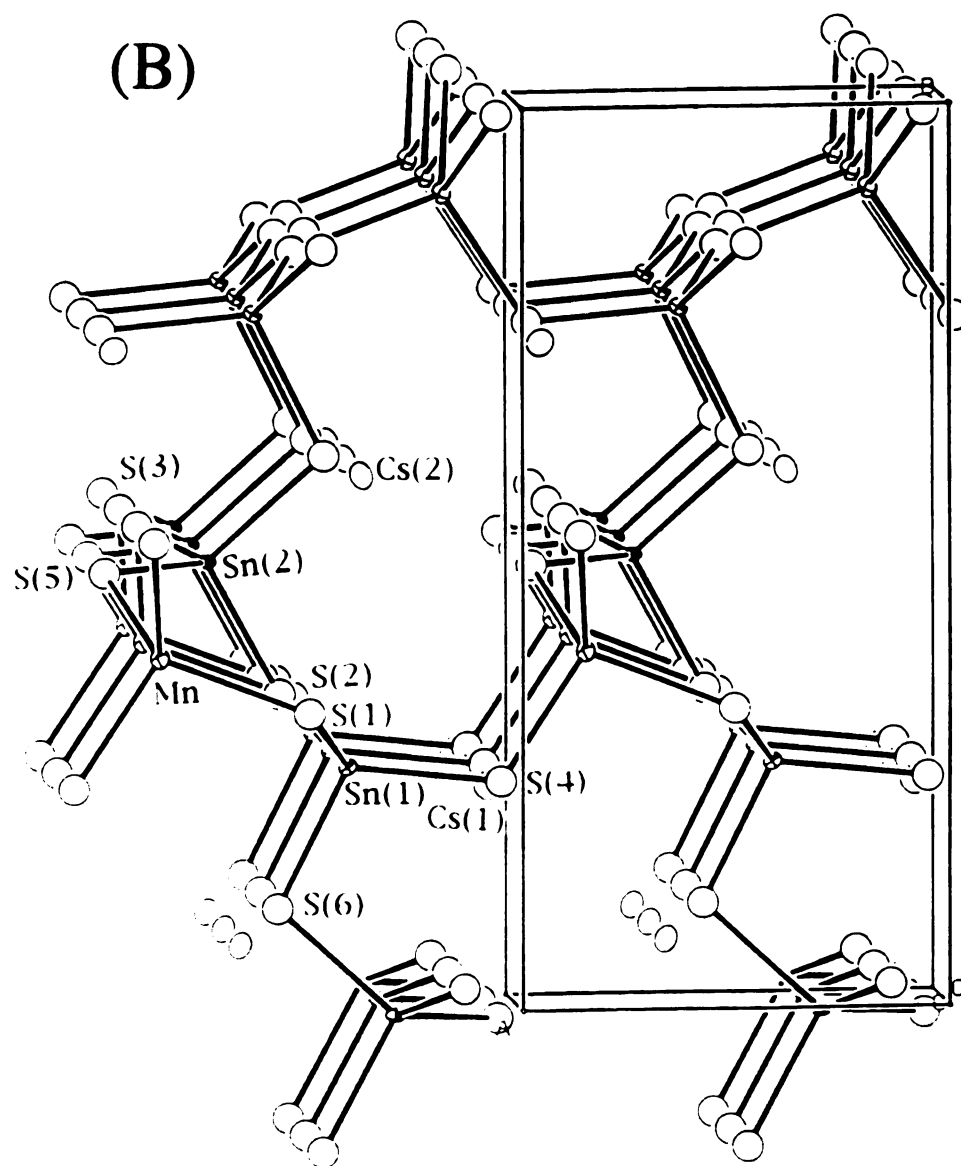


Figure 7-11: ORTEP representation and labeling scheme of (A) $\text{Rb}_2\text{ZnSn}_2\text{S}_6$ and (B) $\text{Cs}_2\text{MnSn}_2\text{S}_6$.



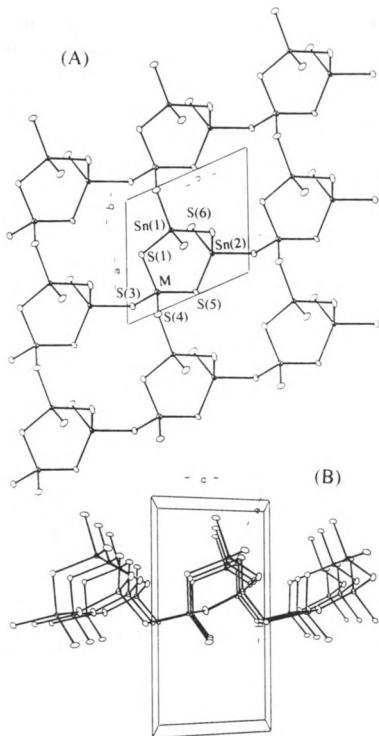


Figure 7-12: A single layer of the $[\text{MSn}_2\text{S}_6]^{2-}$ ($M=\text{Zn}$ or Mn) framework. Its adjacent layers above and below are related according to $P2_1$ symmetry. View down (A) b-axis and (B) a-axis.

Table 7-25. Selected Bond Distances(Å) and Angles (deg) for Rb₂ZnSn₂S₆ with Standard Deviations in Parentheses

Selected Bond Distances (Å)			
Sn(1)-S(1)	2.346(4)	Rb(1)-S(2)	3.704(4)
Sn(1)-S(2)	2.413(4)	Rb(1)-S(2)	3.602(4)
Sn(1)-S(4)	2.352(4)	Rb(1)-S(3)	3.235(4)
Sn(1)-S(6)	2.451(4)	Rb(1)-S(4)	3.437(4)
Sn(2)-S(2)	2.409(4)	Rb(1)-S(5)	3.376(5)
Sn(2)-S(3)	2.373(4)	Rb(1)-S(6)	3.686(4)
Sn(2)-S(5)	2.349(4)	Rb(2)-S(1)	3.419(4)
Sn(2)-S(6)	2.408(4)	Rb(2)-S(3)	3.585(4)
mean (Sn-S)	2.39(4)	Rb(2)-S(3)	3.481(4)
Zn-S(1)	2.359(4)	Rb(2)-S(4)	3.298(4)
Zn-S(3)	2.357(4)	Rb(2)-S(5)	3.469(4)
Zn-S(4)	2.352(4)	Rb(2)-S(6)	3.690(5)
Zn-S(5)	2.355(4)	Rb(2)-S(6)	3.724(5)
mean(Zn-S)	2.356(3)	mean(Rb-S)	3.51(16)
Rb(1)-S(1)	3.466(4)		

Selected Bond Angles (deg)			
S(1)-Sn(1)-S(2)	117.4(1)	S(1)-Zn-S(3)	108.7(1)
S(1)-Sn(1)-S(4)	110.8(1)	S(1)-Zn-S(4)	101.6(1)
S(1)-Sn(1)-S(6)	112.2(1)	S(1)-Zn-S(5)	117.9(1)
S(2)-Sn(1)-S(4)	113.5(1)	S(3)-Zn-S(4)	117.7(1)
S(2)-Sn(1)-S(6)	92.2(1)	S(3)-Zn-S(5)	100.2(2)
S(4)-Sn(1)-S(6)	109.3(1)	S(4)-Zn-S(5)	111.6(1)
S(2)-Sn(2)-S(3)	101.3(1)	Sn(1)-S(1)-Zn	113.3(1)
S(2)-Sn(2)-S(5)	112.6(1)	Sn(1)-S(2)-Sn(2)	109.5(1)
S(2)-Sn(2)-S(6)	106.5(1)	Sn(2)-S(3)-Zn	113.1(2)
S(3)-Sn(2)-S(5)	112.3(1)	Sn(1)-S(4)-Zn	114.2(2)
S(3)-Sn(2)-S(6)	108.6(1)	Sn(2)-S(5)-Zn	111.7(1)
S(5)-Sn(2)-S(6)	114.5(1)	Sn(1)-S(6)-Sn(2)	103.6(1)

Table 7-26. Selected Bond Distances (Å) and Angles (deg) of Cs₂MnSn₂S₆ with Standard Deviations in Parentheses

Selected Bond Distances (Å)			
Sn(1)-S(1)	2.349(9)	Cs(1)-S(2)	3.80(1)
Sn(1)-S(2)	2.424(8)	Cs(1)-S(3)	3.373(8)
Sn(1)-S(4)	2.342(8)	Cs(1)-S(4)	3.558(9)
Sn(1)-S(6)	2.439(8)	Cs(1)-S(4)	3.888(9)
Sn(2)-S(2)	2.396(8)	Cs(1)-S(5)	3.66(1)
Sn(2)-S(3)	2.361(8)	Cs(1)-S(5)	3.97(1)
Sn(2)-S(5)	2.343(8)	Cs(1)-S(6)	3.746(8)
Sn(2)-S(6)	2.423(8)	Cs(2)-S(1)	3.815(9)
mean(Sn-S)	2.38(4)	Cs(2)-S(1)	3.604(9)
Mn-S(1)	2.43(1)	Cs(2)-S(3)	3.686(9)
Mn-S(3)	2.457(9)	Cs(2)-S(3)	3.570(9)
Mn-S(4)	2.401(9)	Cs(2)-S(4)	3.498(8)
Mn-S(5)	2.459(9)	Cs(2)-S(5)	3.598(8)
mean(Mn-S)	2.44(3)	Cs(2)-S(6)	3.795(9)
Cs(1)-S(1)	3.581(9)	Cs(2)-S(6)	3.816(9)
Cs(1)-S(2)	3.904(9)	mean(Cs-S)	3.70(16)
Selected Bond Angles (deg)			
S(1)-Sn(1)-S(2)	117.0(3)	S(1)-Mn-S(3)	110.5(3)
S(1)-Sn(1)-S(4)	110.7(3)	S(1)-Mn-S(4)	103.0(3)
S(1)-Sn(1)-S(6)	112.1(3)	S(1)-Mn-S(5)	115.5(3)
S(2)-Sn(1)-S(4)	113.1(3)	S(3)-Mn-S(4)	117.8(3)
S(2)-Sn(1)-S(6)	93.6(3)	S(3)-Mn-S(5)	98.4(3)
S(4)-Sn(1)-S(6)	109.0(3)	S(4)-Mn-S(5)	112.3(3)
S(2)-Sn(2)-S(3)	100.3(3)	Sn(1)-S(1)-Mn	115.7(3)
S(2)-Sn(2)-S(5)	115.6(3)	Sn(1)-S(2)-Sn(2)	112.7(3)
S(2)-Sn(2)-S(6)	105.5(3)	Sn(2)-S(3)-Mn	115.3(3)
S(3)-Sn(2)-S(5)	112.2(3)	Sn(1)-S(4)-Mn	118.2(3)
S(3)-Sn(2)-S(6)	109.4(3)	Sn(2)-S(5)-Mn	113.4(3)
S(5)-Sn(2)-S(6)	113.0(3)	Sn(1)-S(6)-Sn(2)	104.3(3)

Structure of K_2MnSnS_4 (VIII)

Compound (VIII) has a two-dimensional structure which is crystallographically isomorphous to the KInS_2 structure with Sn and Mn disordered at In sites. (VIII) consists of corner-sharing MS_4 tetrahedra ($\text{M}=\text{Mn}$ or Sn) which forms $[\text{M}_4\text{S}_{10}]^{8-}$ tetrameric clusters. The $[\text{M}_4\text{S}_{10}]^{8-}$ tetramers, having the same geometry of discrete P_4O_{10} molecules, are constructed with fused chair-formed six-membered rings. They are then linked by sharing their terminal sulfur atoms to form a two-dimensional framework as shown in Figure 7-13. The layered structure of (VIII) is related to that of $\text{Rb}_2\text{Cu}_2\text{Sn}_2\text{S}_6$ and can also be viewed as a derivative of the ZnS zinc blende adamantine structure type (see Chapter 6.). K_2MnSnS_4 has a single layer of adamantine framework, while $\text{Rb}_2\text{Cu}_2\text{Sn}_2\text{S}_6$ contains two fused layers. Potassium cations are located between the layers to balance the charge, as shown in Figure 7-14. Each of the two crystallographically distinct K^+ cations is surrounded by six sulfur atoms. The coordination environment of the K^+ cations is similar to that of Rb^+ cations in $\text{Rb}_2\text{Cu}_2\text{Sn}_2\text{S}_6$. The average $\text{K}^+\cdots\text{S}$ distance is $3.29(11)\text{\AA}$, as shown in Table 7-27.

Since the $[\text{M}_4\text{S}_{10}]^{8-}$ anion has pseudo-tetrahedral site symmetry, the chemical environment at the metal sites is similar. During the structure refinement of X-ray diffraction data, Mn and Sn could not be distinguished and are found to be statistically disordered at the metal sites in a 1:1 ratio.

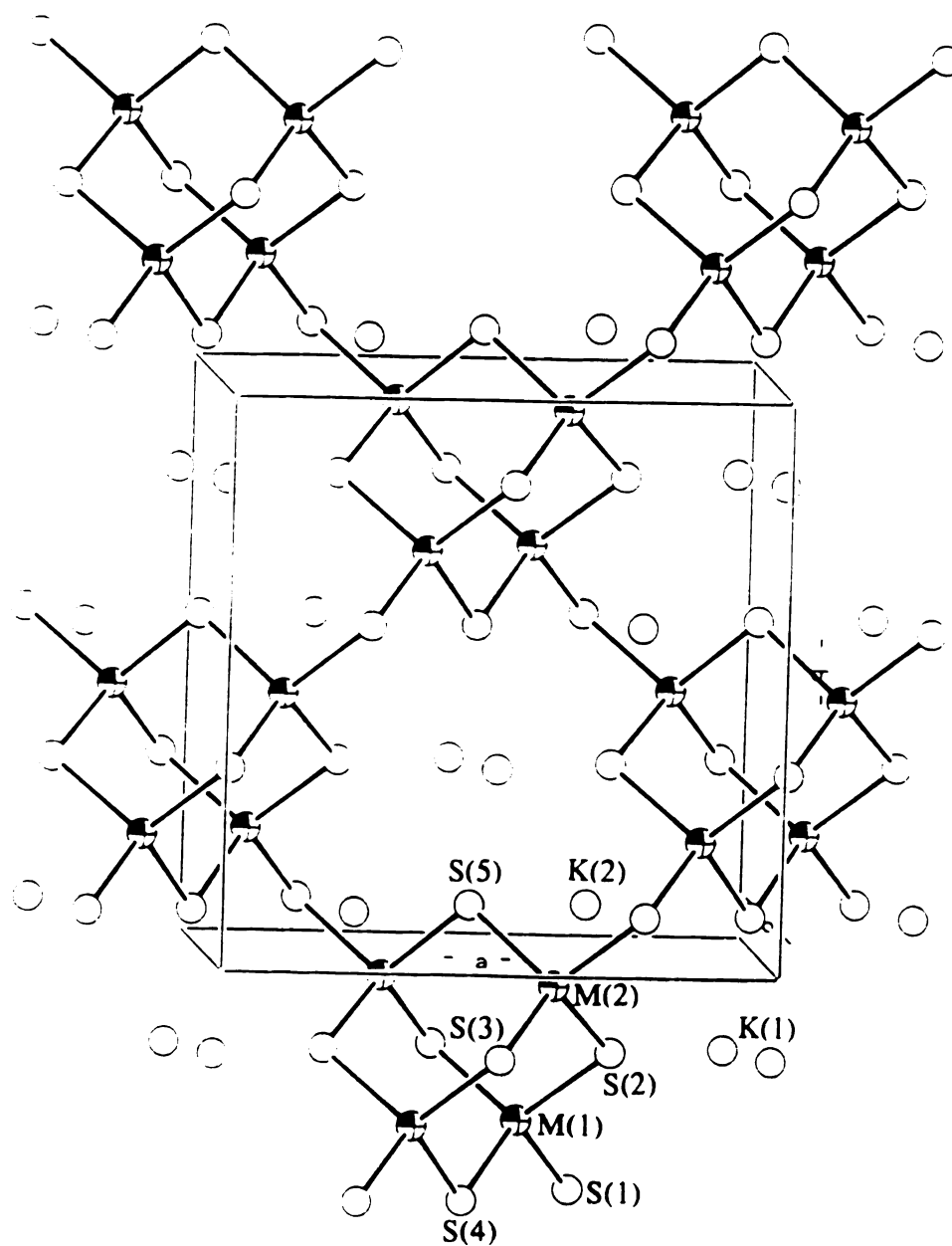


Figure 7-13: ORTEP representation and labeling scheme of K_2MnSnS_4 . View down the c -axis. Mn^{2+} and Sn^{4+} ions are statistically disordered among the M sites.

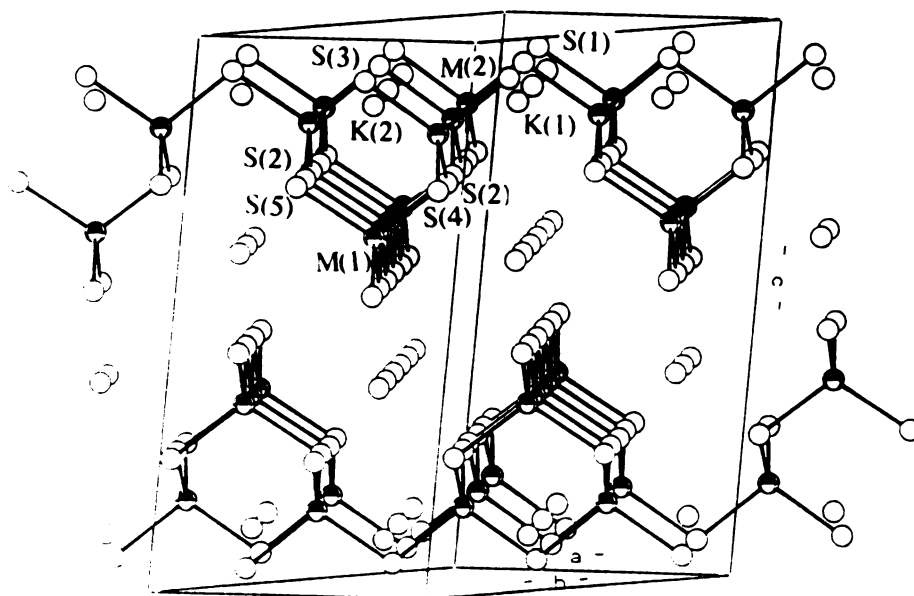


Figure 7-14: ORTEP representation and labeling scheme of K_2MnSnS_4 . View parallel to the layers. Double layers of potassium cations are located between the $[MnSnS_4]^{2-}$ slabs.

Table 7-27. Selected Bond Distances (Å) and Angles (deg) for K₂MnSnS₄ with Standard Deviations in Parentheses

Selected Bond Distances (Å)

M(1)-S(1)	2.33(1)	K(1)-S(1)	3.30(1)
M(1)-S(2)	2.446(8)	K(1)-S(2)	3.298(9)
M(1)-S(3)	2.417(8)	K(1)-S(2)	3.28(1)
M(1)-S(4)	2.460(6)	K(1)-S(3)	3.15(1)
M(2)-S(1)	2.347(9)	K(1)-S(4)	3.22(1)
M(2)-S(2)	2.371(8)	K(1)-S(5)	3.36(1)
M(2)-S(3)	2.446(9)	K(2)-S(1)	3.24(1)
M(2)-S5	2.358(7)	K(2)-S(2)	3.46(1)
mean(M-S)	2.40(5)	K(2)-S(2)	3.33(1)
M(1)-M(1)	3.885(3)	K(2)-S(3)	3.09(1)
M(2)-M(2)	3.875(3)	K(2)-S(4)	3.395(7)
M(1)-M(2)	3.801(3)	K(2)-S(5)	3.397(8)
M(1)-M(2)	3.854(3)	mean(K-S)	3.29(11)
M(1)-M(2)	3.881(3)		
mean(M-M)	3.86(3)		

Selected Bond Angles (deg)

S(1)-M(1)-S(2)	108.6(3)	S(1)-M(2)-S(5)	109.4(3)
S(1)-M(1)-S(3)	106.7(3)	S(2)-M(2)-S(3)	113.7(3)
S(1)-M(1)-S(4)	106.7(3)	S(2)-M(2)-S(5)	107.1(2)
S(2)-M(1)-S(3)	111.1(3)	S(3)-M(2)-S(5)	111.9(2)
S(2)-M(1)-S(4)	110.5(2)	M(1)-S(1)-M(2)	111.1(4)
S(3)-M(1)-S(4)	113.0(2)	M(1)-S(2)-M(2)	107.4(2)
S(1)-M(2)-S(2)	107.4(3)	M(2)-S(5)-M(2)	110.6(5)
S(1)-M(2)-S(3)	107.2(3)		

It should be noted that in $\text{Cs}_2\text{MnSn}_2\text{S}_6$ (VII), the Mn and Sn are readily distinguished during the structure refinement. In (VII), the average Mn-S bond distance is slightly longer than that of Sn-S (2.44(3)Å and 2.38(4)Å respectively), while in (VIII) the average M-S distance is 2.40(5)Å (see Table 7-27) which falls in the range of common Sn-S and Mn-S distances. The magnetic susceptibility measurement (see Section 3.4) as a function of temperature also reveals the disordered model with a smooth transition from a paramagnetic to antiferromagnetic state, suggesting different ways of Mn-Mn magnetic dipole coupling due to the shorter Mn-Mn distances based on a disordered model.

$\text{Cs}_2\text{In}_2\text{Ge}_2\text{S}_8$ (IX)

$\text{Cs}_2\text{In}_2\text{Ge}_2\text{S}_8$ has a two-dimensional structure and is isostructural to $\text{Tl}_2\text{In}_2\text{Si}_2\text{S}_8$.¹⁹ In (IX), In and Ge atoms are disordered among the three crystallographically distinct metal sites. Similar disorder among In and Si sites is also observed in $\text{Tl}_2\text{In}_2\text{Si}_2\text{S}_8$. The structure of (IX) is shown in Figure 7-15. It consists of similar parallel $[\text{MS}_3]_n$ chains as found in (I) and (II), cross-linked by $\text{M}'_2\text{S}_6$ edge-sharing bitetrahedra symmetrically at both sides of every two M atoms in a vertex-sharing fashion. The same connectivity is also found in $\text{K}_2\text{Ga}_2\text{Sn}_2\text{S}_8$ ^{3d} which crystallizes in a triclinic space group ($P\bar{1}$, #2), while (IX) crystallizes in an orthorhombic space group (Pnma, #62)). $\text{K}_2\text{In}_2\text{Ge}_2\text{S}_8$ and $\text{K}_2\text{Ga}_2\text{Ge}_2\text{S}_4$ ^{3d} are structurally similar but differ in the arrangements of the $\text{M}'_2\text{S}_6$ bitetrahedra. They adopt an unsymmetrical zigzag connectivity pattern along the $[\text{MS}_3]_n$ chains in the same fashion as found in (I) and (II), in which $\text{M}'\text{S}_4$ tetrahedra instead of $\text{M}'_2\text{S}_6$ bitetrahedra are used to link the $[\text{MS}_3]_n$ chains. Metal

atoms are also found to be disordered in the above three structurally related compounds.

Selected bond distances and angles are given in Table 7-28. In the edge-sharing bitetrahedron, the average M(1)-S distance (2.35(2)Å) is longer than the M(2)-S distance (2.27(2)Å). The difference is consistent with the higher In population at M(1) sites than at M(2) sites. M(1) sites are occupied by 50% In, while M(2) sites are occupied by 30% In. The average M-S distance of M(3) sites is slightly longer at 2.36(2)Å which also reflects the slightly higher In population of 60% at these sites. These M-S distances are between typical Ge-S and In-S distances as given in previous sections. The dependence of M-S distances on occupancy at metal sites is also observed in $\text{Tl}_2\text{Si}_2\text{In}_2\text{S}_8$, in which the corresponding M(1)~M(3) sites are occupied by 42%, 9% and 67% of In respectively. The degree of disorder at metal sites in $\text{Tl}_2\text{Si}_2\text{In}_2\text{S}_8$ is less than that of (IX) because the atomic size difference between Si and In is larger.

Two, crystallographically distinct, Cs^+ cations located between the layers, as shown in Figure 7-16, are both surrounded by 9 sulfur atoms respectively. The average $\text{Cs}^+\cdots\text{S}$ distance is 3.74(13)Å. .

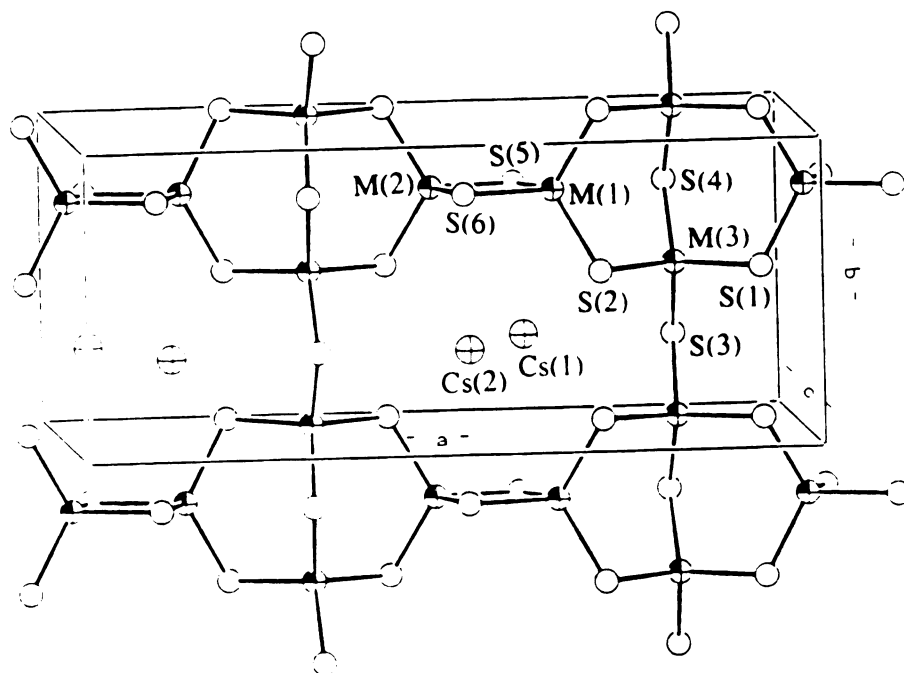


Figure 7-15: ORTEP representation and labeling scheme of the layered structure of $\text{Cs}_2\text{In}_2\text{Ge}_2\text{S}_8$. View down the c -axis. In and Ge are disordered among the M sites.

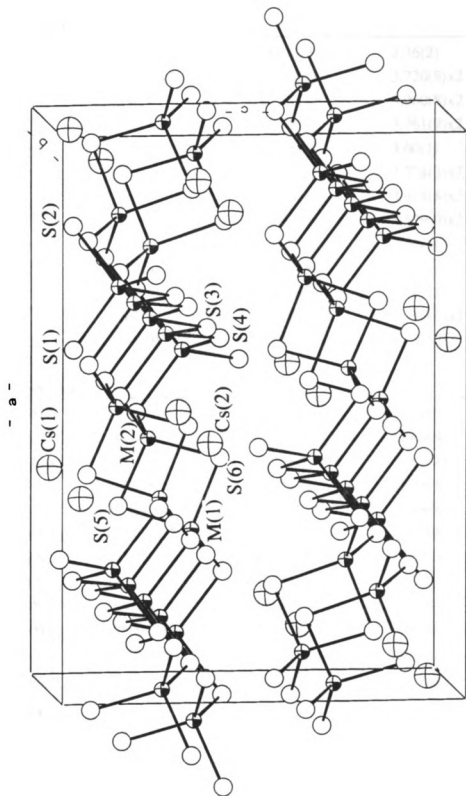


Figure 7-16: ORTEP representation and labeling scheme of the layered structure of $\text{Cs}_2\text{In}_2\text{Ge}_2\text{S}_8$. View parallel to the layers.

Table 7-28. Selected Bond Distances (Å) and Angles (deg) of Cs₂In₂Ge₂S₈ with Standard Deviations in Parentheses

Selected Bond Distances (Å)			
M(1)-M(2)	3.135(5)	mean(M(3)-S)	2.36(2)
M(1)-S(2)	2.313(9)x2	Cs(1)-S(1)	3.720(8)x2
M(1)-S(5)	2.38(1)	Cs(1)-S(1)	3.960(8)x2
M(1)-S(6)	2.38(1)	Cs(1)-S(2)	3.761(9)x2
mean(M(1)-S)	2.35(4)	Cs(1)-S(3)	3.60(1)
M(2)-S(1)	2.255(8)x2	Cs(1)-S(5)	3.774(3)x2
M(2)-S(5)	2.26(1)	Cs(2)-S(1)	3.914(8)x2
M(2)-S(6)	2.29(1)	Cs(2)-S(2)	3.679(9)x2
mean(M(2)-S)	2.27(2)	Cs(2)-S(3)	3.60(1)
M(3)-S(1)	2.382(8)	Cs(2)-S(4)	3.53(1)
M(3)-S(2)	2.368(9)	Cs(2)-S(6)	3.59(1)
M(3)-S(3)	2.367(8)	Cs(2)-S(6)	3.710(1)x2
M(3)-S(4)	2.340(9)	mean(Cs-S)	3.74(13)
Selected Bond Angles (deg)			
S(2)-M(1)-S(2)	113.6(4)	S(1)-M(3)-S(2)	107.0(3)
S(2)-M(1)-S(5)	115.7(3)x2	S(1)-M(3)-S(3)	109.9(4)
S(2)-M(1)-S(6)	108.3(3)	S(1)-M(3)-S(4)	113.2(4)
S(2)-M(1)-S(5)	115.7(3)	S(2)-M(3)-S(3)	112.4(4)
S(5)-M(1)-S(6)	92.7(4)	S(2)-M(3)-S(4)	110.4(4)
M(1)-M(2)-S(1)	122.8(2)x2	S(3)-M(3)-S(4)	104.0(4)
M(1)-M(2)-S(5)	49.0(3)	M(2)-S(1)-M(3)	102.3(3)
M(1)-M(2)-S(6)	49.1(3)	M(1)-S(2)-M(3)	99.2(3)
S(1)-M(2)-S(1)	114.2(4)	M(3)-S(3)-M(3)	101.6(5)
S(1)-M(2)-S(5)	108.8(3)x2	M(3)-S(4)-M(3)	106.2(5)
S(1)-M(2)-S(6)	112.8(3)x2	M(1)-S(5)-M(2)	85.0(4)
S(5)-M(2)-S(6)	98.1(4)	M(1)-S(6)-M(2)	84.2(4)

*M=In or Ge

Cs₂MnSn₃Se₈ (X) and its Comparison to Cs₂In₂Ge₂S₈

As shown in Figure 7-17, the structure of (X) is almost identical to that of Cs₂In₂Ge₂S₈ (see Figure 7-15) except that it crystallizes in a different space group (P2₁2₁2₁, #19) and all the metal sites in (X) are ordered and distinguishable by X-ray diffraction techniques. The structure of (X) is made up by [MnSnSe₆]_n⁶ⁿ⁻ chains, corresponding to [MS₃]_n chains in (IX), cross-linked by [Sn₂Se₆]⁴⁻ bitetrahedra in the same fashion as described in the previous section. A mirror plane passing through M(1), M(2), S(4), S(5) and S(6) in (IX) (see Figure 7-15) is destroyed by substituting M(3) sites in (IX) with Sn(3) and Mn atoms alternately along the chain. This also removes the centers of inversion which are located between two layers since three perpendicular mirrors are required for an orthorhombic structure to be centrosymmetric. Figure 7-18 shows a view parallel to the anionic layers. The two distinct Cs⁺ cations are located at the similar positions relative to the anionic layers as in (IX). The average Cs⁺...Se distance is 3.92(17)Å.

Selected bond distances and angles are given in Table 7-29. The average Mn-Se distance is almost the same as that of Sn-Se distances. It is surprising that no disorder among the metal sites is observed in (X) despite the similar size of the metals. The [Sn₂Se₆]⁴⁻ bitetrahedral fragment in (X) is comparable to Cs₄Sn₂Se₆²⁰ and Na₄Sn₂Se₆·13H₂O.²¹ In the two discrete [Sn₂Se₆]⁴⁻ anions, the average Sn-Se(terminal) distance (2.460Å) is shorter than the average Sn-Se(bridging) distance (2.587Å). In (X) the same distances are 2.50(3)Å and 2.569(9)Å respectively.

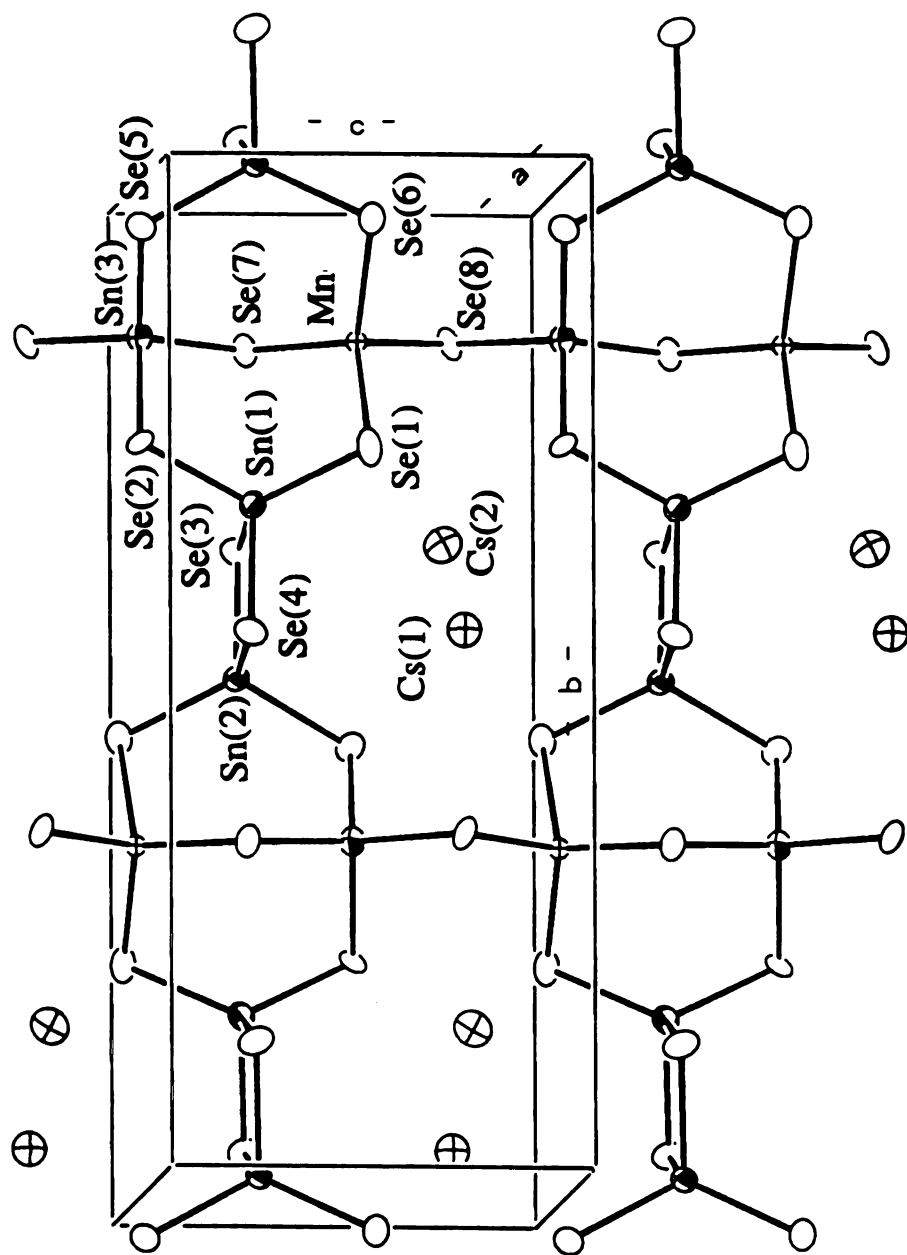


Figure 7-17: ORTEP representation and labeling scheme of the layered structure of $\text{Cs}_2\text{MnSn}_3\text{Se}_8$. View down the a -axis. Note that there is no disorder among Mn and Sn.

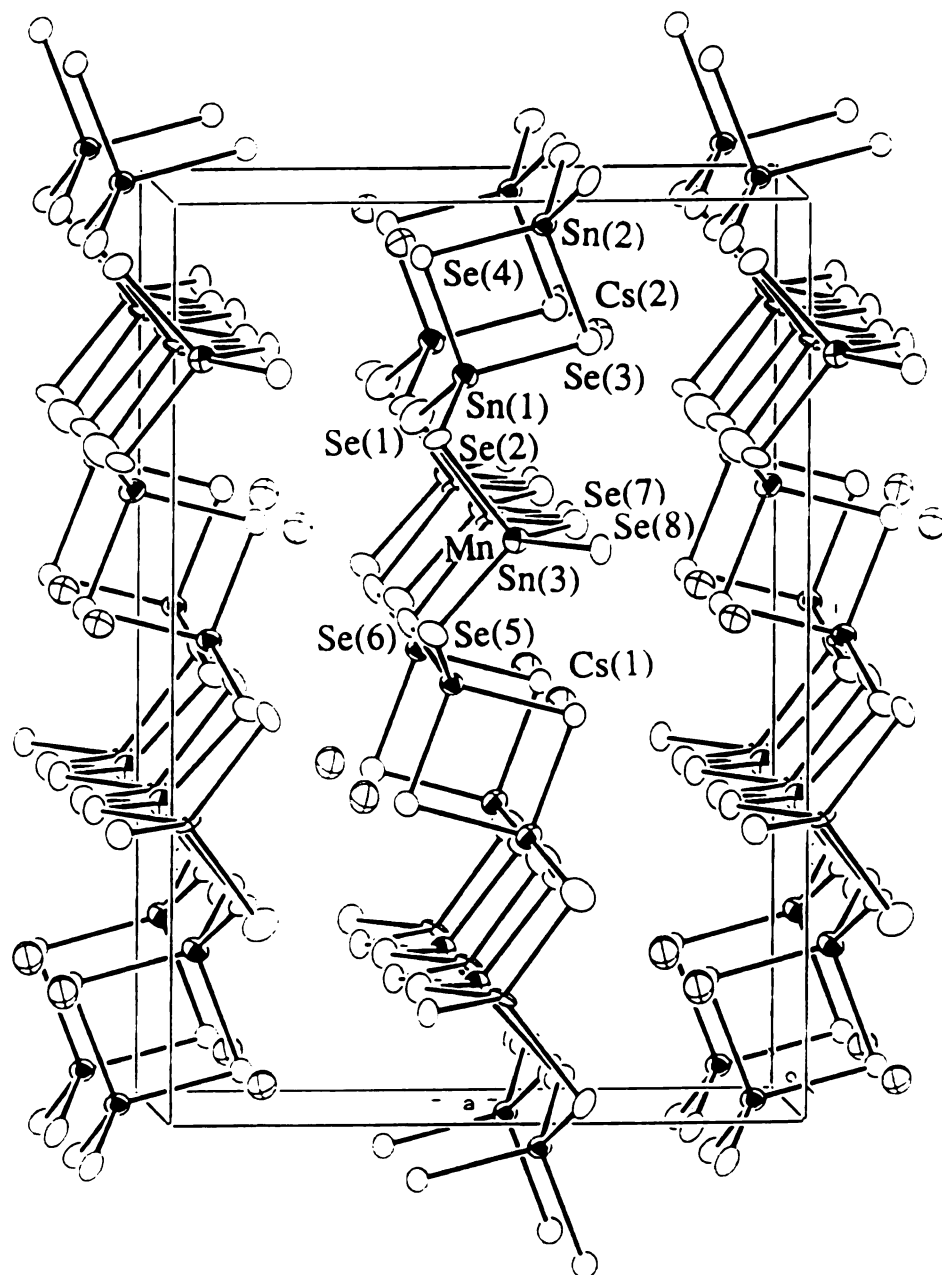


Figure 7-18: ORTEP representation and labeling scheme of the layered structure of $\text{Cs}_2\text{MnSn}_3\text{Se}_8$. View parallel to the layers.

Table 7-29. Selected Bond Distances (Å) and Angles (deg) for Cs₂MnSn₃Se₈ with Standard Deviations in Parentheses

Selected Bond Distances (Å)

Sn(1)-Se(1)	2.472(9)	Cs(1)-Se(1)	3.781(8)
Sn(1)-Se(2)	2.525(9)	Cs(1)-Se(2)	3.910(7)
Sn(1)-Se(3)	2.565(5)	Cs(1)-Se(4)	3.99(1)
Sn(1)-Se(4)	2.575(4)	Cs(1)-Se(4)	3.91(1)
Sn(2)-Se(3)	2.562(4)	Cs(1)-Se(4)	3.685(4)
Sn(2)-Se(4)	2.553(5)	Cs(1)-Se(5)	4.109(8)
Sn(2)-Se(5)	2.550(8)	Cs(1)-Se(6)	4.065(8)
Sn(2)-Se(6)	2.465(8)	Cs(1)-Se(7)	3.699(5)
Sn(3)-Se(2)	2.618(7)	Cs(1)-Se(8)	3.731(5)
Sn(3)-Se(5)	2.517(7)	Cs(2)-Se(1)	3.925(9)
Sn(3)-Se(7)	2.483(7)	Cs(2)-Se(2)	3.929(8)
Sn(3)-Se(8)	2.487(7)	Cs(2)-Se(3)	3.92(1)
mean(Sn-Se)	2.53(5)	Cs(2)-Se(3)	4.05(1)
Mn-Se(1)	2.53(1)	Cs(2)-Se(5)	3.861(8)
Mn-Se(6)	2.66(1)	Cs(2)-Se(5)	4.294(7)
Mn-Se(7)	2.49(1)	Cs(2)-Se(6)	3.899(8)
Mn-Se(8)	2.542(9)	Cs(2)-Se(6)	4.116(8)
mean(Mn-Se)	2.56(7)	Cs(2)-Se(8)	3.677(5)
		mean(Cs-Se)	3.92(17)

Selected Bond Angles (deg)

Se(1)-Sn(1)-Se(2)	117.9(2)	Se(5)-Sn(3)-Se(8)	111.1(3)
Se(1)-Sn(1)-Se(3)	115.8(3)	Se(7)-Sn(3)-Se(8)	109.2(2)
Se(1)-Sn(1)-Se(4)	107.8(3)	Sn(1)-Se(1)-Mn	95.9(3)
Se(2)-Sn(1)-Se(3)	112.0(3)	Sn(1)-Se(2)-Sn(3)	96.1(3)
Se(2)-Sn(1)-Se(4)	104.4(3)	Sn(1)-Se(3)-Sn(2)	84.1(1)
Se(3)-Sn(1)-Se(4)	95.6(1)	Sn(1)-Se(4)-Sn(2)	84.1(1)
Se(3)-Sn(2)-Se(4)	96.2(1)	Sn(2)-Se(5)-Sn(3)	99.1(3)
Se(3)-Sn(2)-Se(5)	108.3(3)	Sn(2)-Se(6)-Mn	96.5(3)
Se(3)-Sn(2)-Se(6)	109.6(3)	Sn(3)-Se(7)-Mn	108.5(2)

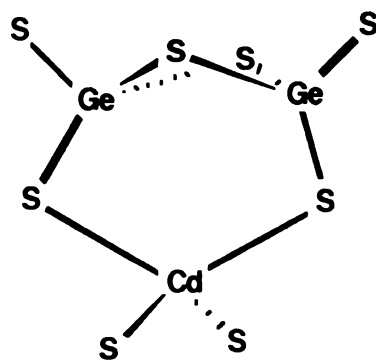
Table 7-29. (cont'd)

Se(4)-Sn(2)-Se(5)	108.6(3)	Sn(3)-Se(8)-Mn	100.6(2)
Se(4)-Sn(2)-Se(6)	113.5(3)	Se(1)-Mn-Se(6)	106.6(3)
Se(5)-Sn(2)-Se(6)	118.3(2)	Se(1)-Mn-Se(7)	112.4(4)
Se(2)-Sn(3)-Se(5)	100.0(2)	Se(1)-Mn-Se(8)	113.3(4)
Se(2)-Sn(3)-Se(7)	110.0(2)	Se(6)-Mn-Se(7)	115.7(3)
Se(2)-Sn(3)-Se(8)	110.0(2)	Se(6)-Mn-Se(8)	108.8(3)
Se(5)-Sn(3)-Se(7)	116.1(3)	Se(7)-Mn-Se(8)	100.0(3)

In the $[\text{Sn}_2\text{Se}_6]^{4-}$ fragment, the average Se-Sn-Se angle ($95.9(4)^\circ$) in the Sn_2Se_2 rhombus is slightly larger than 90° while the average Sn-Se-Sn angle ($84.1(1)^\circ$) is smaller. The Se-Sn-Se angles opposite to those in the Sn_2Se_2 rhombus are wider and close to 120° , averaging $118.1(3)^\circ$. These angles are close to those observed in the isolated $[\text{Sn}_2\text{Se}_6]^{4-}$ anions. The $[\text{SnSe}_4]^{4-}$ fragment in (X) is also comparable to the isolated anions of $\text{Na}_4\text{SnSe}_4 \cdot 16\text{H}_2\text{O}^{22}$ in which the average Sn-Se distance is $2.52(1)\text{\AA}$ vs. $2.53(6)\text{\AA}$ in (X). The average Mn-Se distance in (X) is $2.56(7)\text{\AA}$, which is close to $2.57(4)\text{\AA}$ found in Ba_2MnSe_3 .²³

Rb₂CdGe₂S₆ (XI)

Compound (XI) has a two-dimensional structure which contains CdS_4 and GeS_4 tetrahedra as building blocks as shown in Figure 7-19. The repeating unit, shown in Scheme II, can be readily recognized in the structure as



Scheme II

two fused six-membered rings and is constructed by two edge-sharing GeS_4 tetrahedra and one CdS_4 tetrahedron. This repeating unit adopts a C_2 symmetry with a two fold rotation axis passing through the Cd atom and the center of the Ge_2S_2 four-membered ring. The anionic layer is formed

by linking the four terminal sulfur atoms. A single anionic layer of (XI) is noncentrosymmetric. Nevertheless, it forms centrosymmetric lattice with centers of inversion located between the layers as illustrated by Figure 7-20. Charge balancing Rb^+ cations are located between two layers and surrounded by seven sulfur atoms with the average $\text{Rb}^+\cdots\text{S}$ distance of $3.64(18)\text{\AA}$.

The torsion angle of Ge-S(1)-S(1)-Ge is 145.8° in the butterfly-like Ge_2S_2 four-membered ring. As shown in Table 7-30, the S(1)-Ge-S(1) angle in the Ge_2S_2 four-membered ring is much less than that of an ideal tetrahedron and are close to 90 degrees. This results in slightly longer Ge-S(1) distances due to stronger electronic repulsion between the Ge-S(1) bonds. The average Ge-S distance is normal at $2.22(6)\text{\AA}$. In the absence of similar strain around Cd atoms, the S-Cd-S angles and Cd-S distances do not exhibit such variations. The average Cd-S distance at $2.53(2)\text{\AA}$ is normal for Cd-S bonds and considerably longer than that of Ge-S distances. For comparison, in another mixed Cd/Ge sulfide, $\text{Cu}_2\text{CdGeS}_4$,²⁴ the average Cd-S and Ge-S distances are $2.55\text{\AA}$ and $2.22\text{\AA}$ respectively. As a matter of fact, Figure 7-19 and 7-20 illustrate that the size of the CdS_4 tetrahedron is comparable to that of the edge-sharing Ge_2S_6 dimer. It is interesting to note that $\text{K}_2\text{HgSn}_2\text{S}_6$ (I), $\text{K}_2\text{GeIn}_2\text{S}_6$ (II), $\text{Rb}_2\text{ZnSn}_2\text{S}_6$ (VI) and $\text{Cs}_2\text{MnSn}_2\text{S}_6$ (VII) have the same stoichiometry as (XI). However, they form different structure types due to different arrangements of tetrahedral building blocks. The relative sizes of the metal centers in these quaternary compounds seem to be important to determine the structures.

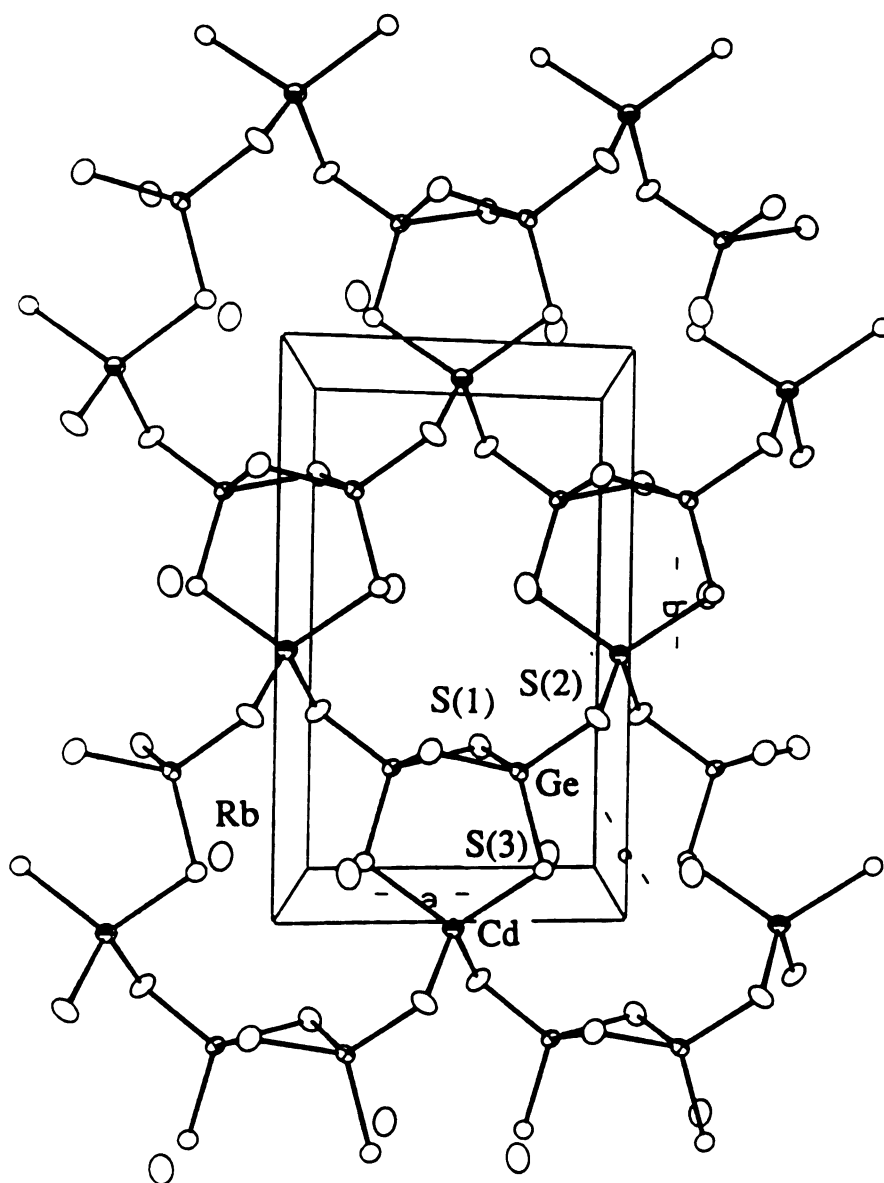
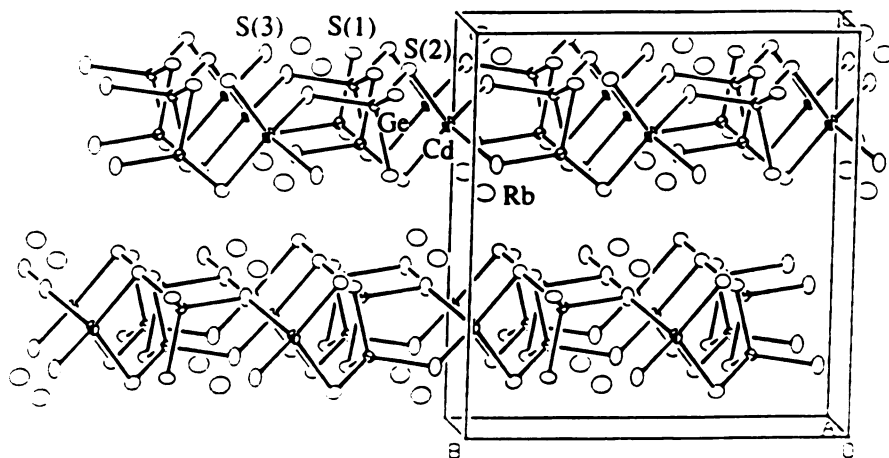


Figure 7-19: ORTEP representation and labeling scheme of the layered structure of $\text{Rb}_2\text{CdGe}_2\text{S}_6$. View down the c-axis.

(A)



(B)

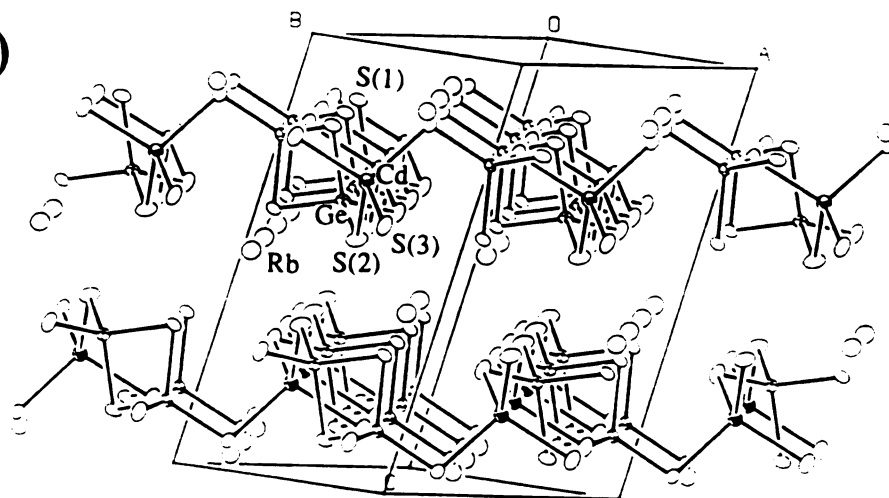


Figure 7-20: ORTEP representation and labeling scheme of the layered structure of $\text{Rb}_2\text{CdGe}_2\text{S}_6$. View down the (A) a -axis and (B) $\langle 110 \rangle$ direction.

Table 7-30. Selected Bond Distances (Å) and Angles (deg) for Rb₂CdGe₂S₆ with Standard Deviations in Parentheses

Selected Bond Distances (Å)			
Cd-S(2)	2.544(2)x2	Rb-S(1)	3.380(2)
Cd-S(3)	2.512(2)x2	Rb-S(1)	3.679(2)
mean(Cd-S)	2.53(2)	Rb-S(2)	3.384(2)
Ge-S(1)	2.274(2)	Rb-S(2)	3.406(2)
Ge-S(1)	2.272(2)	Rb-S(3)	3.725(2)
Ge-S(2)	2.167(2)	Rb-S(3)	3.241(2)
Ge-S(3)	2.182(2)	Rb-S(3)	3.578(2)
mean(Ge-S)	2.22(6)	mean(Rb-S)	3.64(18)
Selected Bond Angles (deg)			
S(2)-Cd-S(2)	114.3(1)	S(1)-Ge-S(1)	92.19(8)
S(2)-Cd-S(3)	105.83(6)x2	S(1)-Ge-S(3)	111.03(8)
S(2)-Cd-S(3)	108.75(7)x2	S(1)-Ge-S(3)	113.25(8)
S(3)-Cd-S(3)	113.60(9)	Ge-S(1)-Ge	83.03(7)
S(2)-Ge-S(3)	108.25(8)	Cd-S(2)-Ge	104.92(8)
S(1)-Ge-S(2)	116.04(8)	Cd-S(3)-Ge	107.34(7)
S(1)-Ge-S(2)	115.51(8)		

3.3. Spectroscopy

3.4. Magnetic Susceptibility Measurements

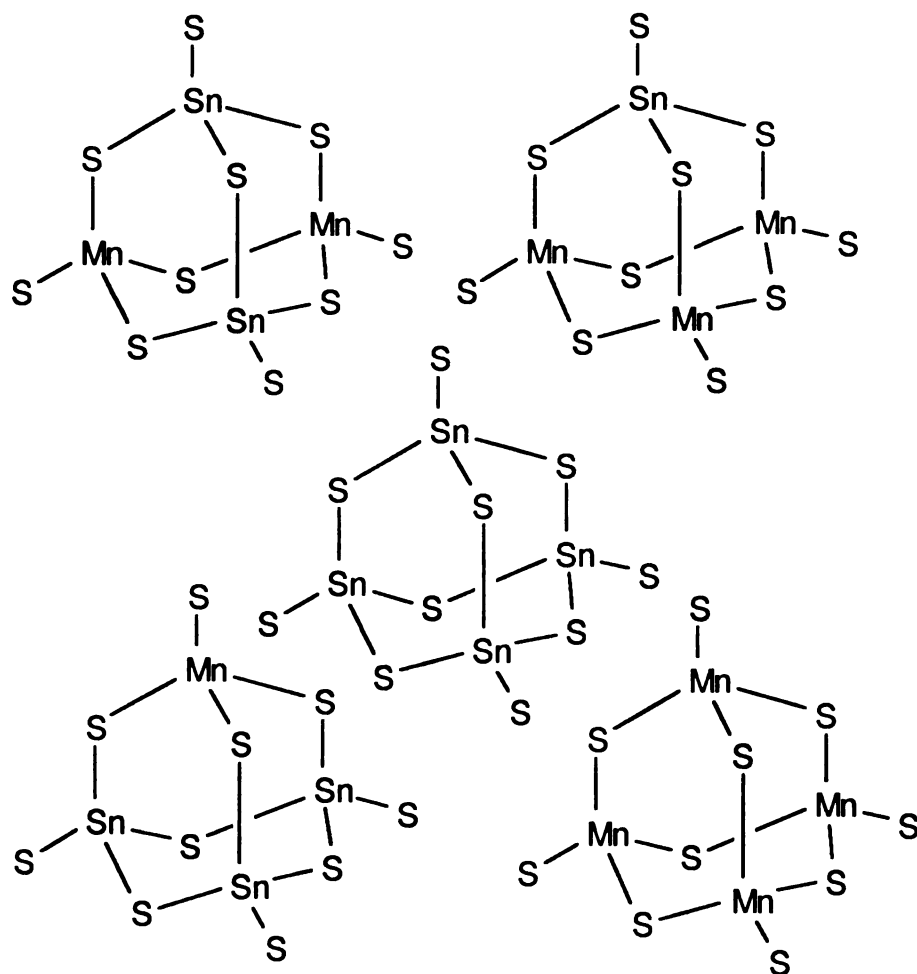
Cs₂MnSn₂S₆

Measurements of magnetization versus applied magnetic field were performed at 5 K and 300 K. At both temperatures, the magnetic susceptibilities of the sample were magnetic field independent up to 5000 Gauss, as shown in Figure 7-21. Variable temperature magnetic susceptibility data were collected at a magnetic field of 5000 Gauss with an ascending temperature ramp from 5 K to 300 K. Figure 7-22 shows the relationship between the reciprocal of molar magnetic susceptibilities and temperatures. It exhibits Curie-Weiss behavior ($\chi = C/(T + \theta)$, where χ is magnetic susceptibility, C is Curie constant, T is the experimental temperature and θ is Weiss temperature) above the Néel temperature of 9 K at which antiferromagnetic transition occurs. The slope of the straight line in the Curie-Weiss region gives the value of C at 4.21 (K·emu·mol⁻¹). The interception at the temperature axis from the extrapolated straight line give a θ value of -22.7 K. The effective magnetic moment, μ_{eff} , related to the number of unpaired electrons, is 5.78 BM, which is calculated by using the equation: $\chi = (N\beta^2\mu^2)/(3k(T + \theta))$ or $\mu = 2.828(\chi(T + \theta))^{1/2}$ when N , β and k are substituted. (N : Avogadro's number; β : Bohr magneton; k =Boltzmann's constant). The theoretical magnetic moment, μ_s , based on electron spin only, is given by $\mu_s = g[S(S + 1)]^{1/2}$, where g =gyromagnetic ratio, ~ 2.00 , S =the sum of the spin quantum numbers for unpaired

electrons. The calculated μ_s value, 5.92 BM, based on high spin Mn^{2+} ions with $S=5/2$, is consistent to the observed result.

K_2MnSnS_4

Figure 7-23 shows that for K_2MnSnS_4 the magnetization is magnetic field independence at both 5 K and 300 K. At 5 K, a small hysteresis loop occurs around zero field. Variable temperature magnetic susceptibility measurements under the applied field of 1000 Gauss and 5000 Gauss were shown in Figure 7-24. At both fields, K_2MnSnS_4 exhibits a smooth antiferromagnetic transition resulting from the coupling of disordered $\text{Mn}^{2+}(S=5/2)$ spins. The possible distributions of Mn^{2+} centers are shown in Scheme III. The increase of magnetic susceptibility below 10 K is due to the paramagnetic contribution of a small amount of MnS impurity, which dominates at low temperatures.



Scheme III

The metal-metal distances in the $[M_4S_{10}]$ cluster of K_2MnSnS_4 are shorter ($3.885(3)\text{\AA}$, $3.875(3)\text{\AA}$, $3.801(3)\text{\AA}$, $3.854(3)\text{\AA}$ and $3.881(3)\text{\AA}$) than those in $Cs_2MnSn_2S_6$ ($7.098(1)\text{\AA}$, $7.434(1)\text{\AA}$ and $7.842(1)\text{\AA}$). The interactions between the magnetic dipoles of Mn^{2+} is stronger so that its magnetic behavior deviates from paramagnetism in the temperature range between 5 K and 300 K.

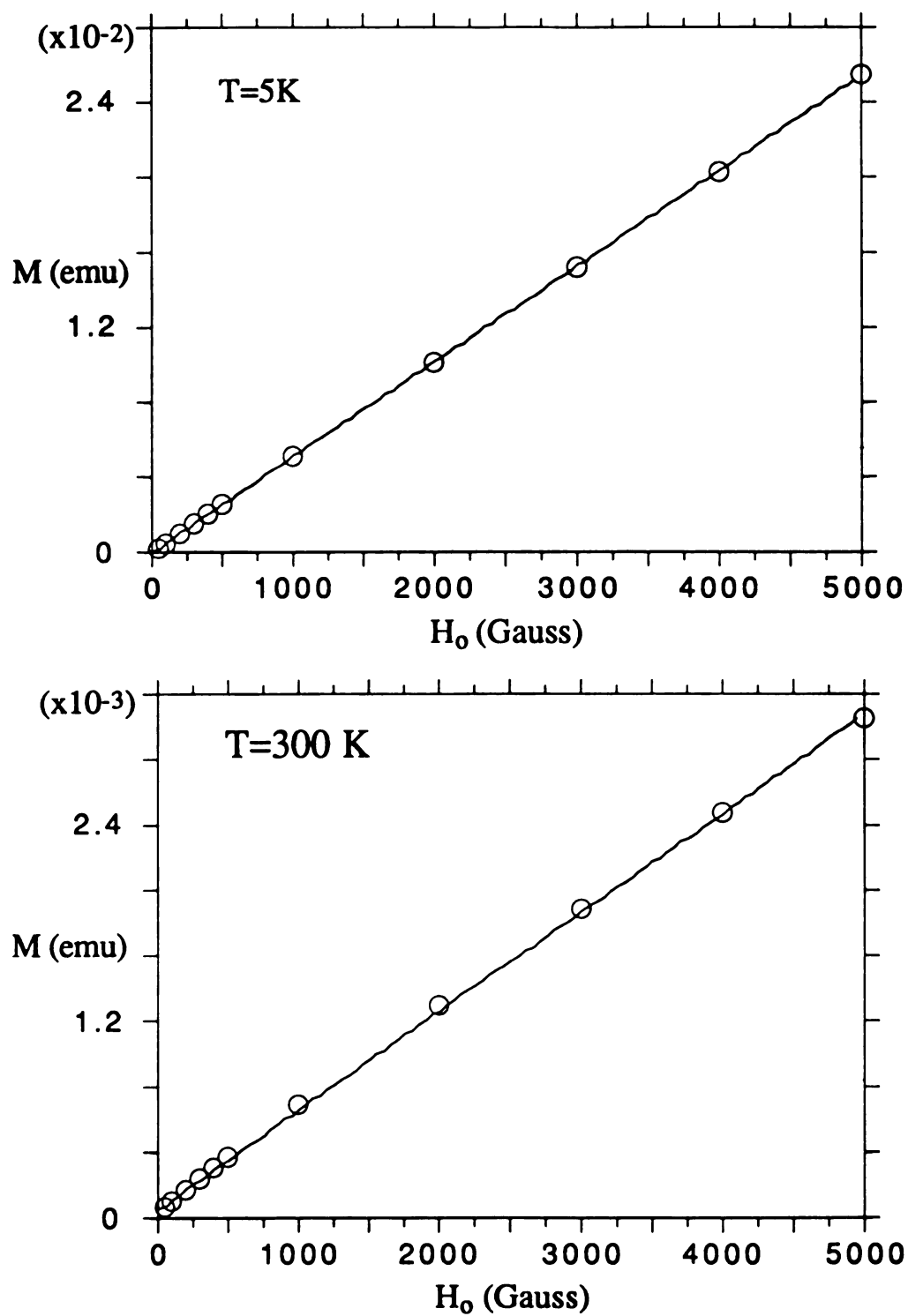


Figure 7-21: The relationships of magnetization vs. applied magnetic field for $\text{Cs}_2\text{MnSn}_2\text{S}_6$ at 5 K and 300 K.

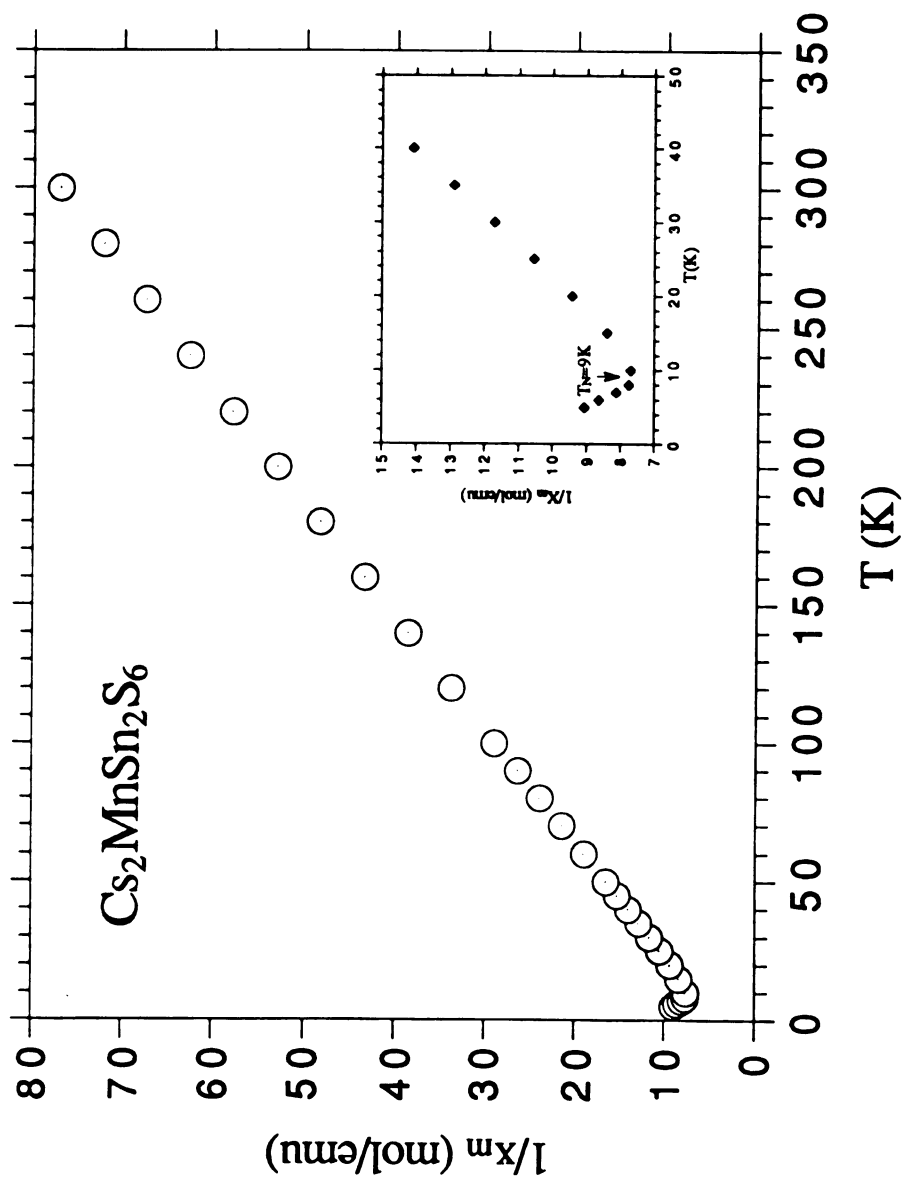


Figure 7-22: The relationship of $1/\chi_m$ vs. T shows paramagnetism of $\text{Cs}_2\text{MnSn}_2\text{S}_6$ above $T_N=9$ K.

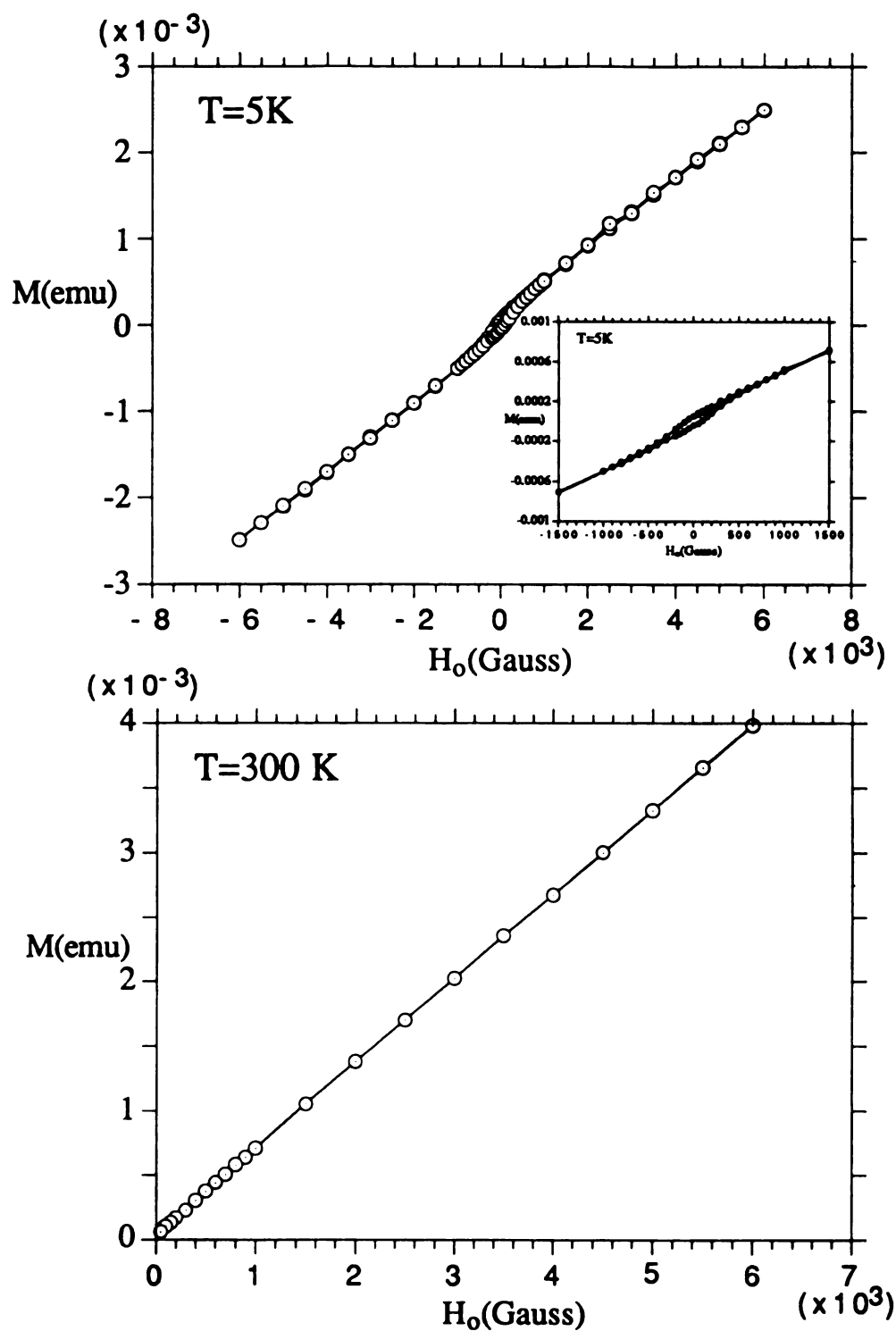


Figure 7-23: The relationship of sample magnetization vs. applied magnetic field for K_2MnSnS_4 at 5 K and 300 K.

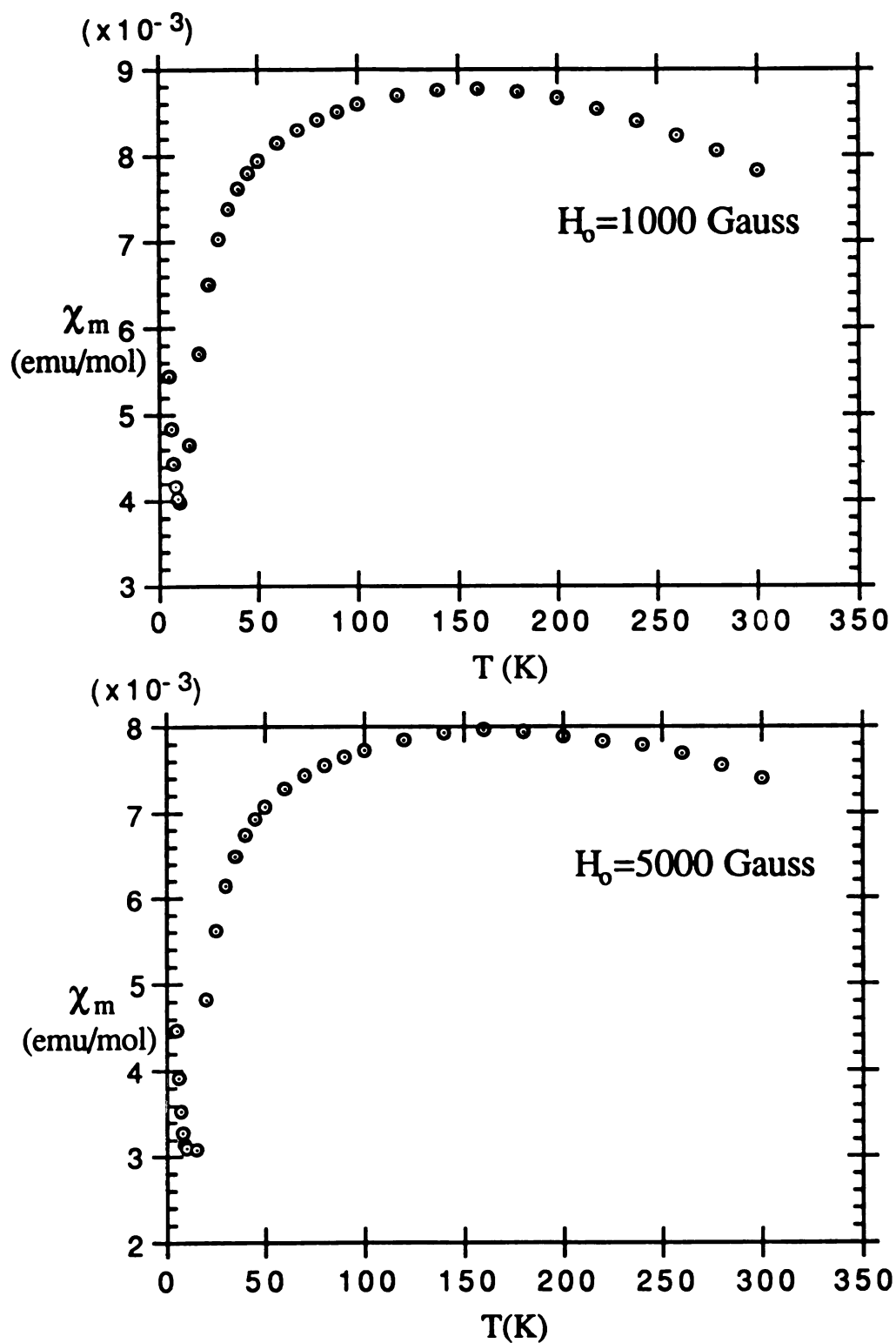


Figure 7-24: The χ_m vs. T plots for K_2MnSnS_4 at both 1000 and 5000 Gauss exhibit a smooth very broad antiferromagnetic transition.

Solid State Optical Spectroscopy

The UV-Vis-Near IR solid state spectra of (III)~(IX) and (XI) exhibit steep absorption edges from which optical band gaps can be derived. The optical spectra of compounds (I), (II) and (X) were not taken because not enough pure materials could be obtained. The spectra are shown in Figure 7-25. The summary of their optical band gaps are given in Table 7-31. The band gaps are all consistent with the colors. These results suggest all these compounds are semiconductors in nature.

Vibrational Spectroscopy

The vibrational spectra and absorption frequencies for (III)~(XI) are given in Figure 7-26 and Table 7-32 respectively. These quaternary compounds exhibits more complicated spectra due to more possible vibrational modes. All the absorption frequencies fall in the range between 130 cm^{-1} and 450 cm^{-1} . This make it difficult for assignment. $\text{K}_2\text{Hg}_3\text{Sn}_2\text{S}_8$ and $\text{K}_2\text{Hg}_3\text{Ge}_2\text{S}_8$ are isostructural and therefore their vibrational spectra have similar patterns except that all the absorption bands shift, understandably, to higher frequencies in the spectrum of $\text{K}_2\text{Hg}_3\text{Ge}_2\text{S}_8$. Another pair of isostructural compounds, $\text{Rb}_2\text{ZnSn}_2\text{S}_6$ and $\text{Cs}_2\text{MnSn}_2\text{S}_6$, also exhibit similar vibrational spectra with little shift of absorption frequencies.

Table 7-31. Summary of the Optical Band Gaps (eV) for K₂Hg₃Sn₂S₈ (III) K₂Hg₃Ge₂S₈ (IV) K₆Zn₄Sn₅S₁₇ (V) Rb₂ZnSn₂S₆ (VI) Cs₂MnSn₂S₆ (VII) K₂MnSnS₄ (VIII) Cs₂In₂Ge₂S₈ (IX) Rb₂CdGe₂S₆ (XI).

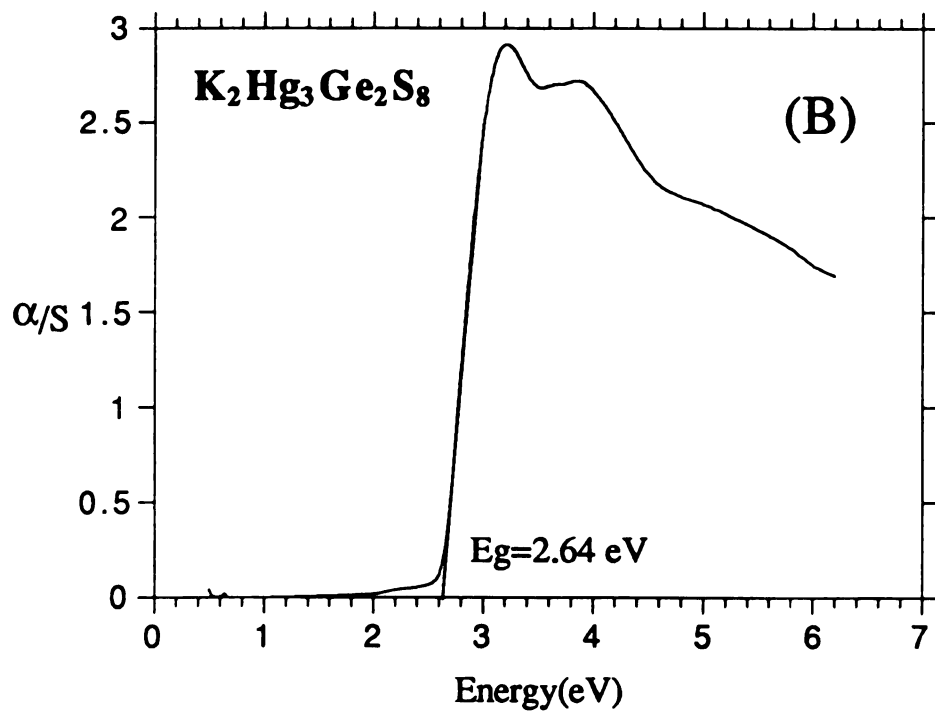
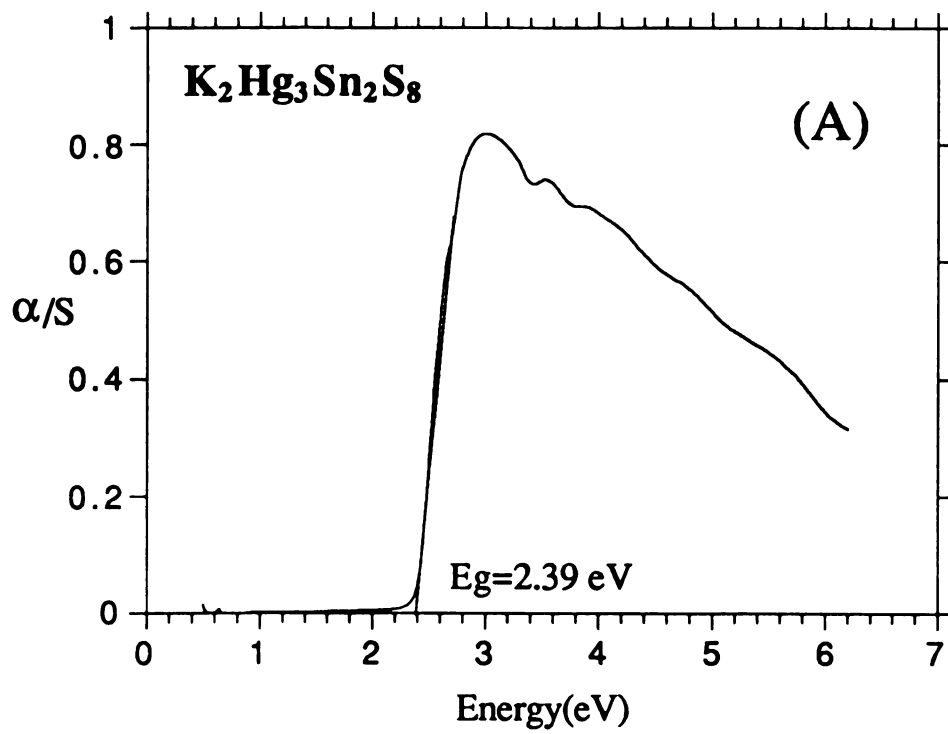
compound	E _g (eV)	color	compound	E _g (eV)	color
K ₂ Hg ₃ Sn ₂ S ₈	2.39	bright yellow	Cs ₂ MnSn ₂ S	2.58	light brown
K ₂ Hg ₃ Ge ₂ S ₈	2.64	light yellow	6	2.08, 2.39	orange
K ₆ Zn ₄ Sn ₅ S ₁	2.94	white	K ₂ MnSnS ₄	3.06	white
7	3.00	white	Cs ₂ In ₂ Ge ₂ S	3.31	white
Rb ₂ ZnSn ₂ S ₆			8		
			Rb ₂ CdGe ₂ S		
			6		

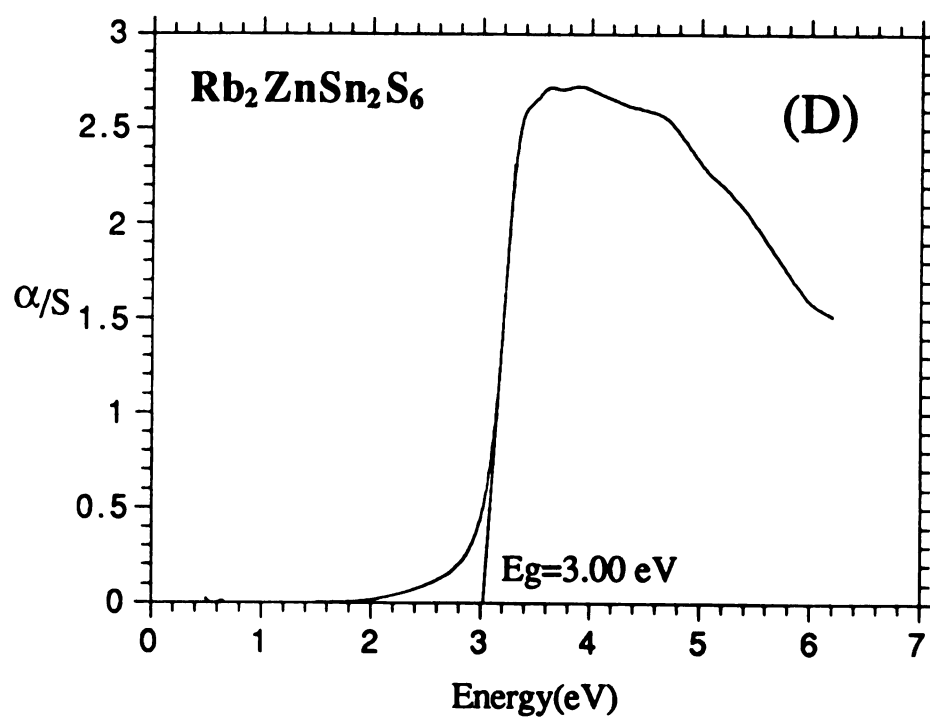
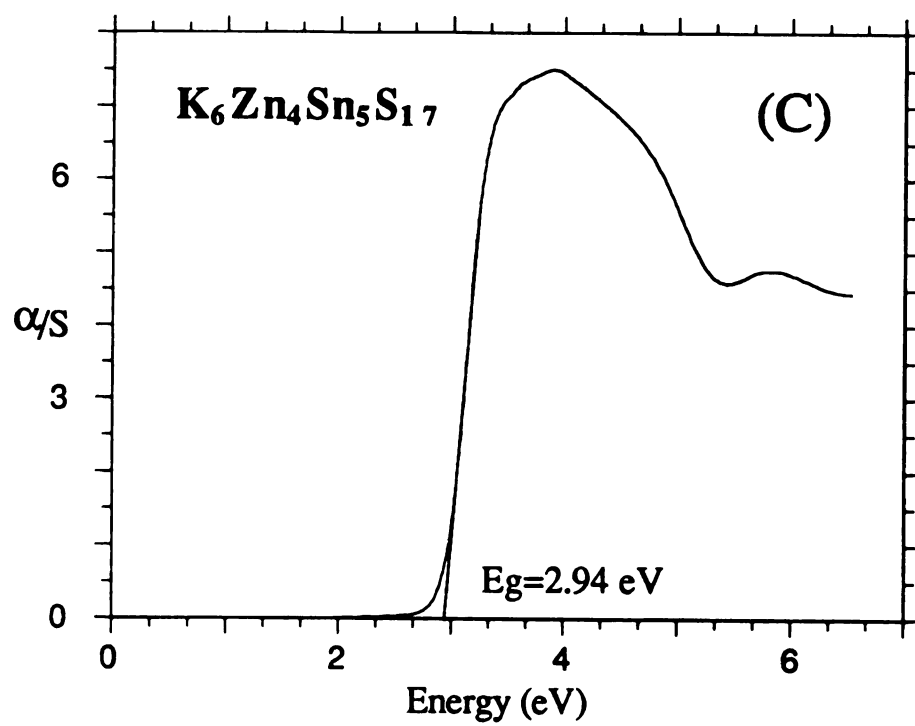
Table 7-32. Summary of Absorption Frequencies (cm⁻¹) of Vibrational Spectra for (III)~(XI)^a

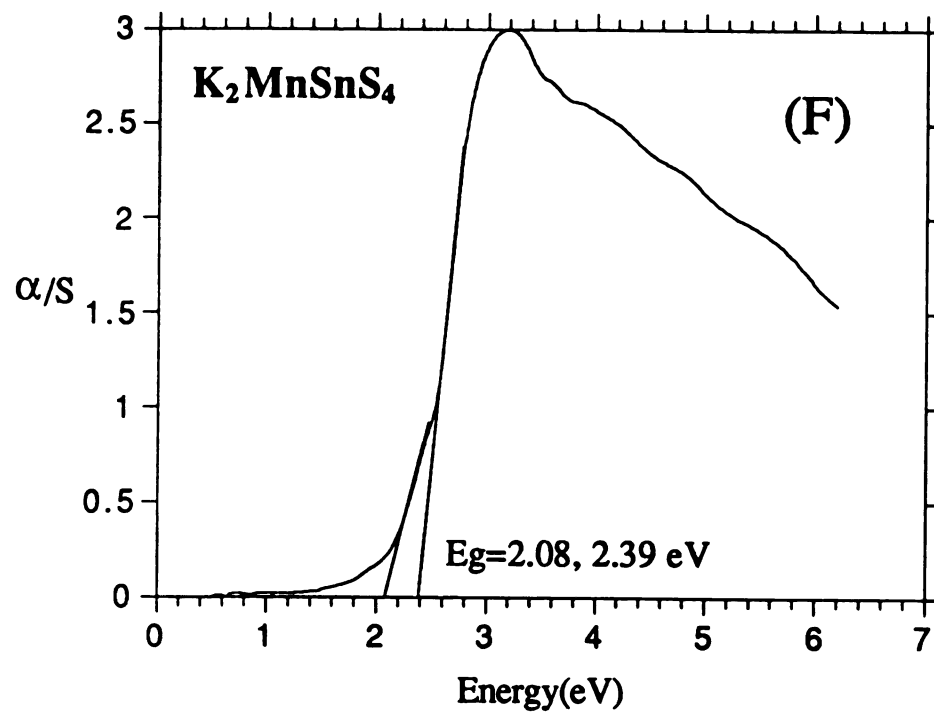
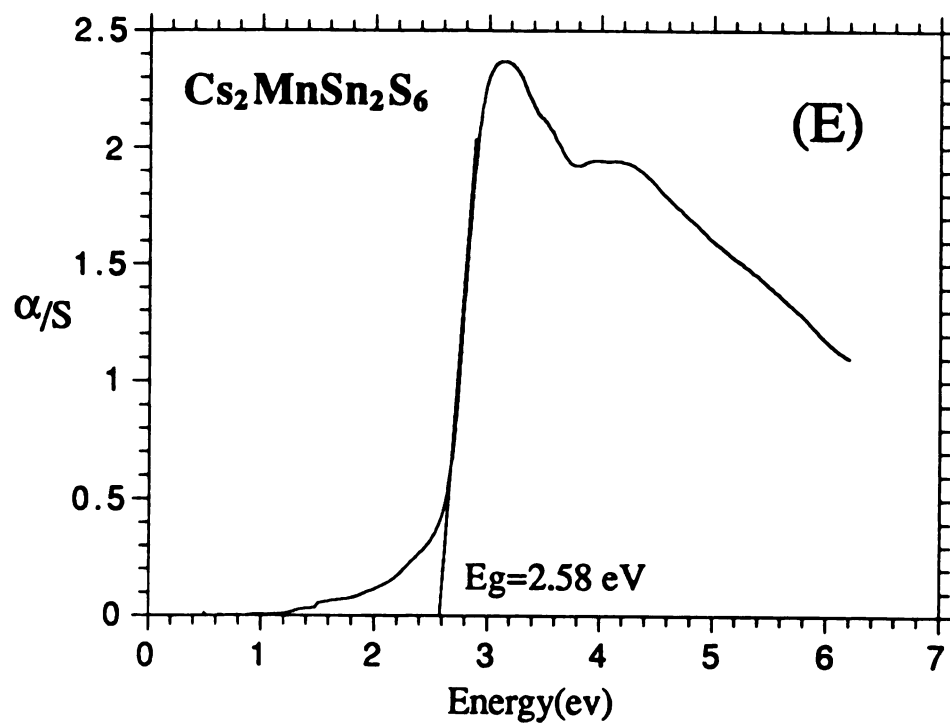
compound	frequency (cm ⁻¹)
K ₂ Hg ₃ Sn ₂ S ₈	383(s), 356(sh), 345(s), 316(w), 296(m), 169(m)
K ₂ Hg ₂ Ge ₂ S ₈	421(s), 393(m), 377(s), 371(sh), 353(m), 312(m), 297(sh), 211(sh), 198 (s), 148(w), 134(w)
K ₆ Zn ₄ Sn ₅ S ₁₇	387(s), 361(m), 342(s), 307(w), 278(s), 262(sh), 153(m)
Rb ₂ ZnSn ₂ S ₆	390(m), 380(m), 369(s), 351(m), 332(s), 321(w), 304(s), 275(m), 256(s), 142(s)
Cs ₂ MnSn ₂ S ₆	381(s), 371(sh), 366(m), 328(s), 318(w), 299(s), 278(m), 257(s), 139(m)
K ₂ MnSnS ₄	376(sh), 369(s), 360(s), 327(s), 311(m), 303(sh), 265(s), 246(sh), 180(w), 164(w), 148(w)
Cs ₂ In ₂ Ge ₂ S ₈	416(sh), 399(sh), 375(sh), 364(sh), 328(s), 315(sh), 294(sh), 280(sh), 181(s), 152(m)
Cs ₂ MnSn ₃ Se ₈	275(sh), 266(m), 256(m), 238(w), 227(m), 207(s), 199(sh), 181(m), 168(w)
Rb ₂ CdGe ₂ S ₆	413(s), 403(sh), 389(s), 331(s), 294(w), 282(m), 244(s), 226(w), 209(m), 202(sh), 190(w), 169(m), 156(w), 146(m)

^a (s): strong; (m): medium; (w): weak; (sh): shoulder

Figure 7-25: Optical absorption spectra of (A) $\text{K}_2\text{Hg}_3\text{Sn}_2\text{S}_8$, (B) $\text{K}_2\text{Hg}_3\text{Ge}_2\text{S}_8$, (C) $\text{K}_6\text{Zn}_4\text{Sn}_5\text{S}_{17}$, (D) $\text{Rb}_2\text{ZnSn}_2\text{S}_6$, (E) $\text{Cs}_2\text{MnSn}_2\text{S}_6$, (F) K_2MnSnS_4 , (G) $\text{Cs}_2\text{In}_2\text{Ge}_2\text{S}_8$ and (H) $\text{Rb}_2\text{CdGe}_2\text{S}_6$.







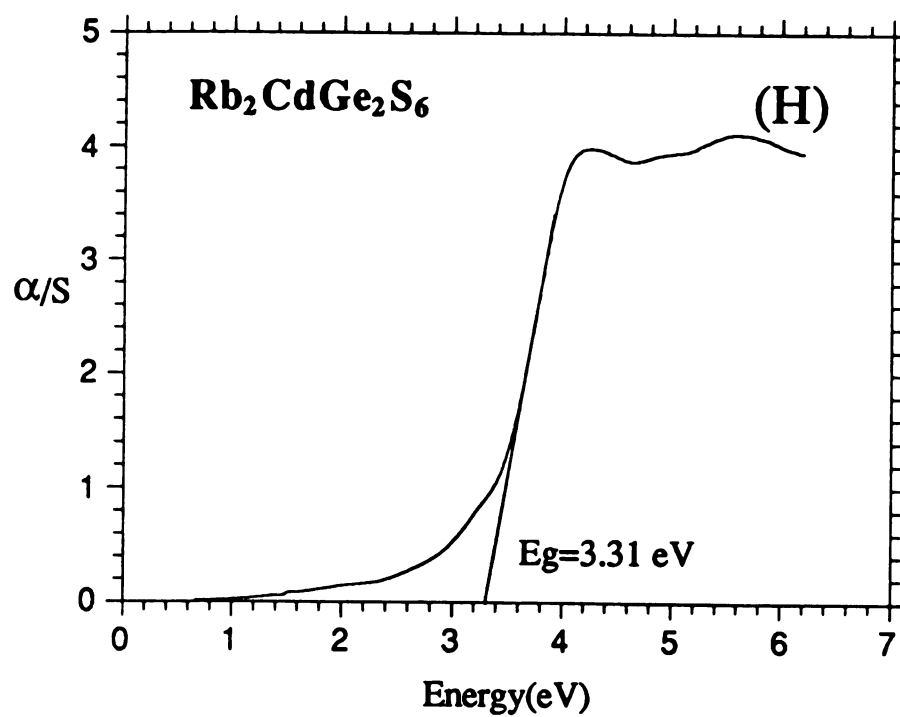
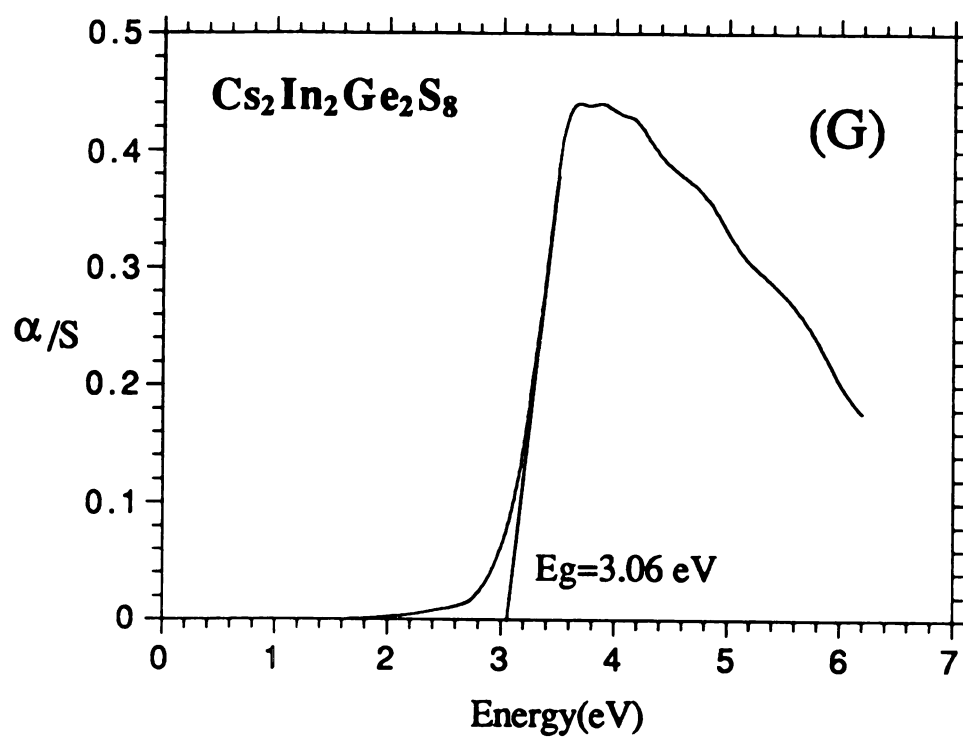
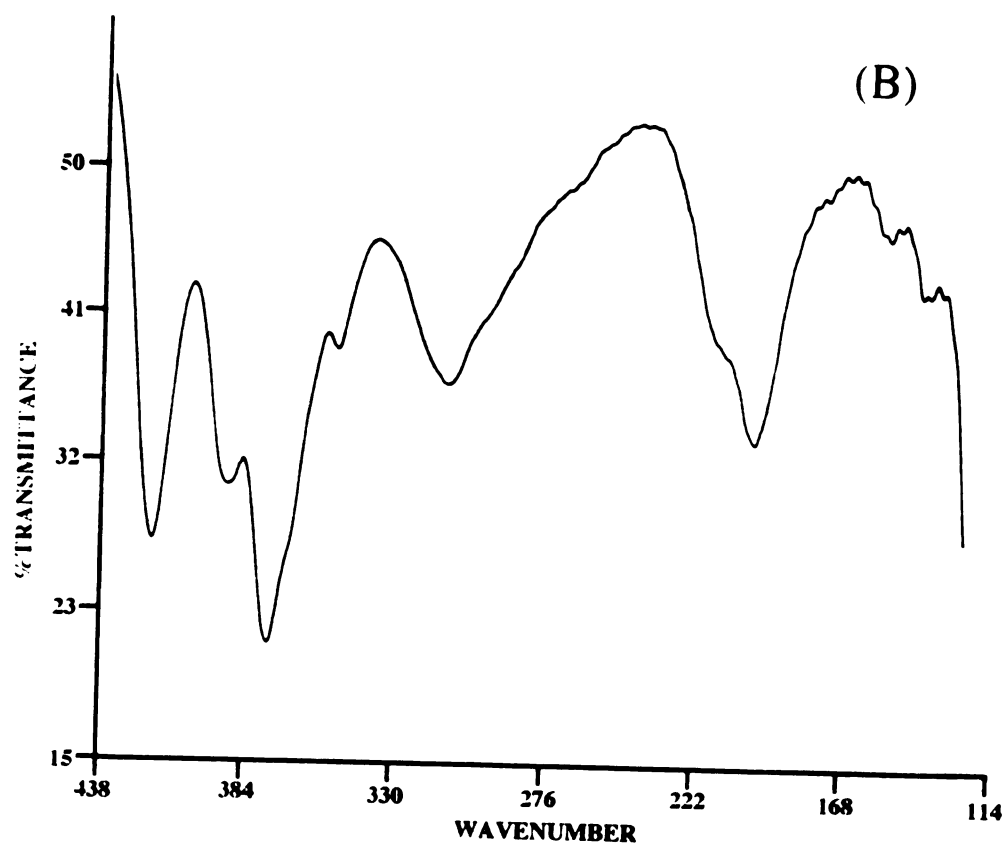
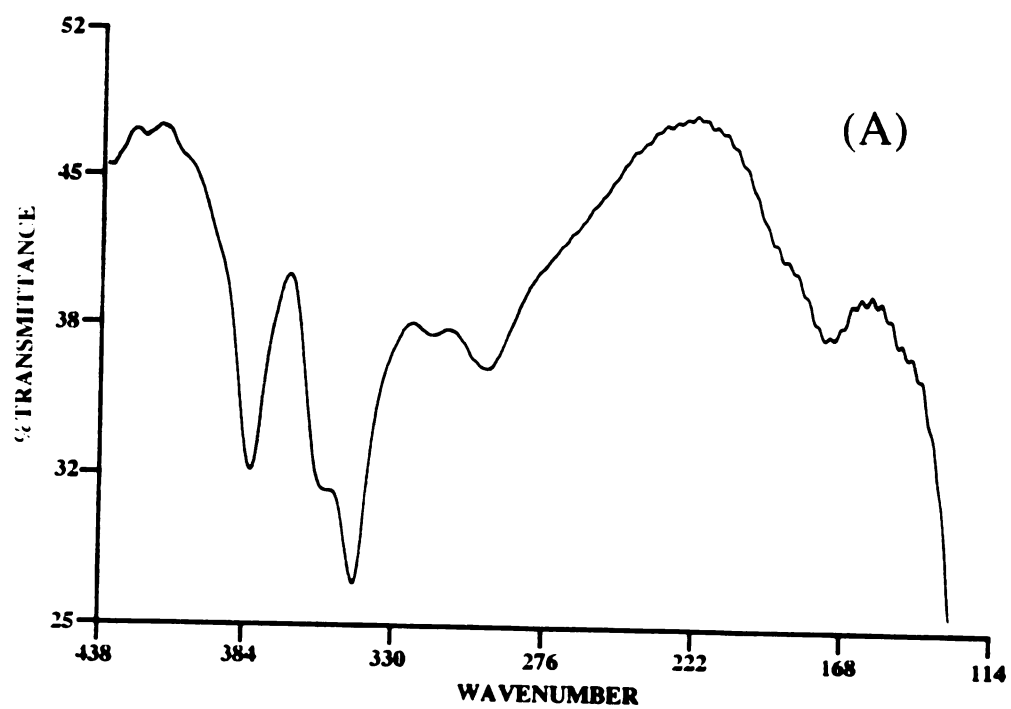
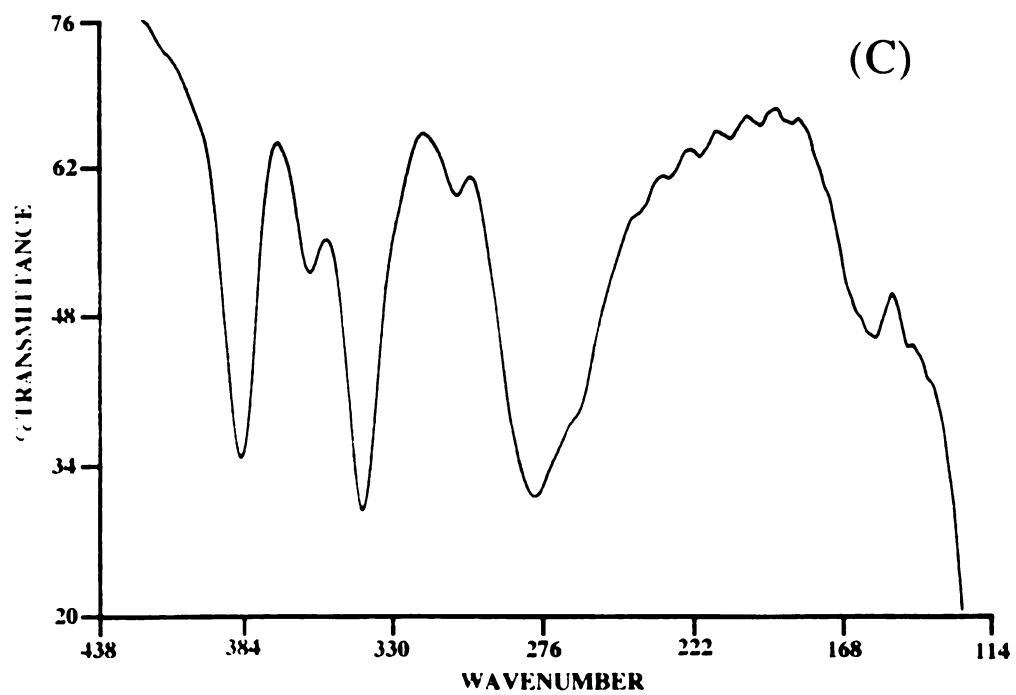
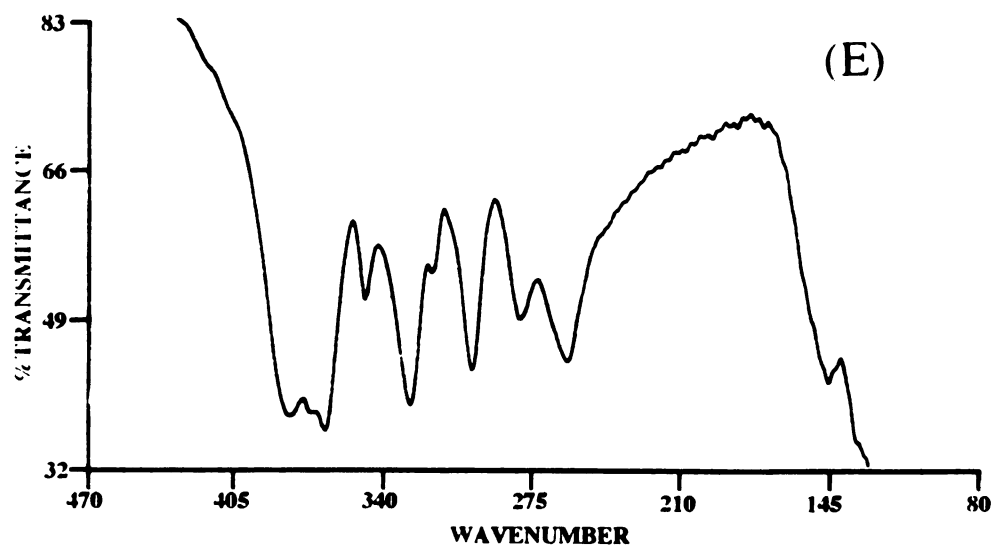
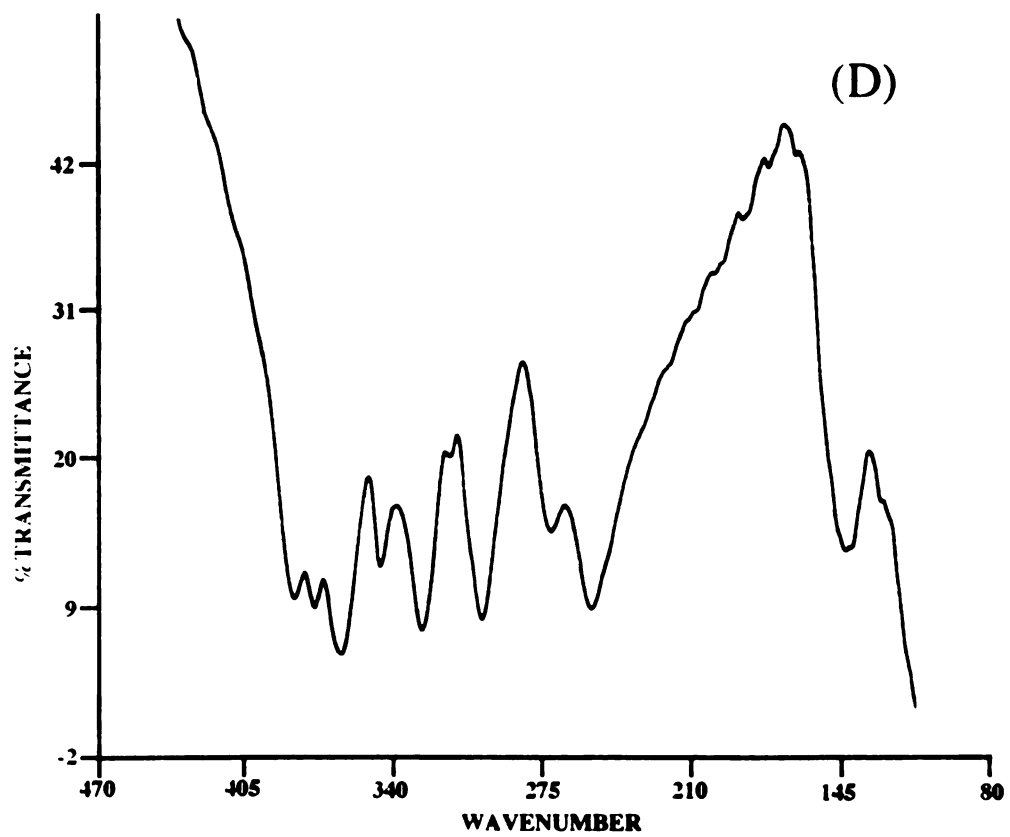
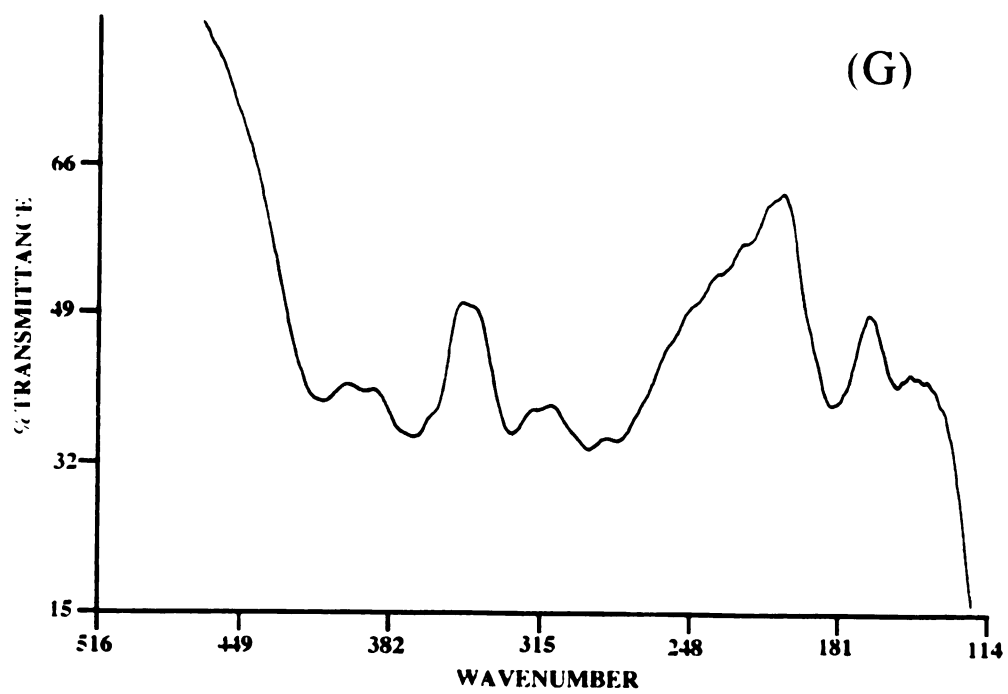
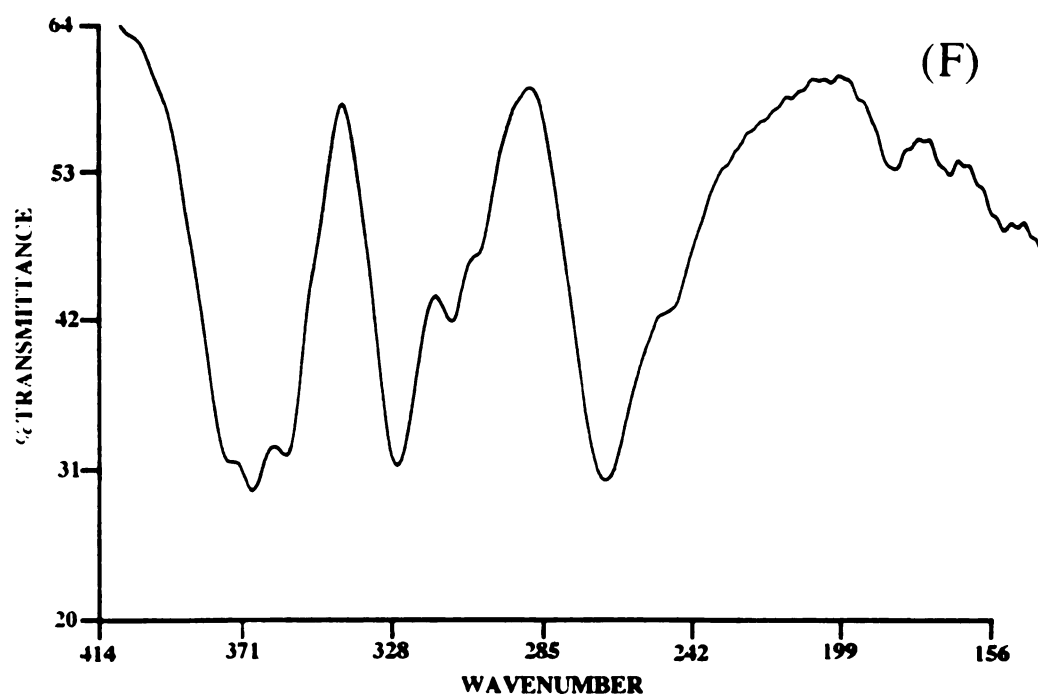


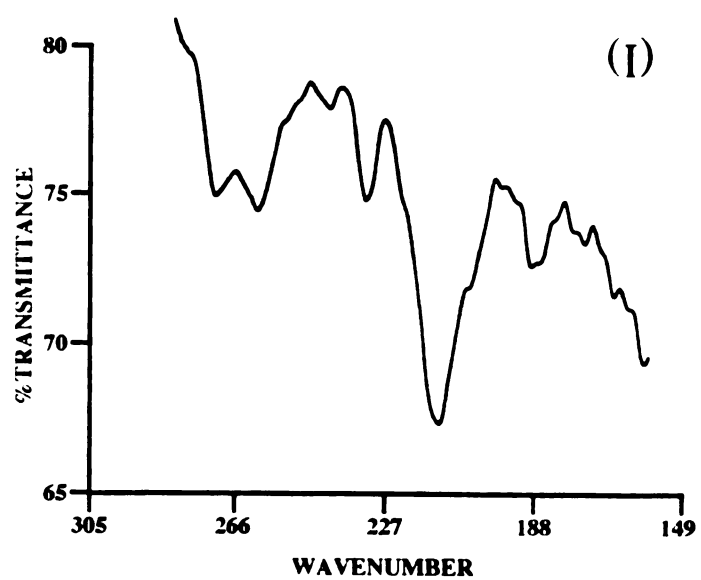
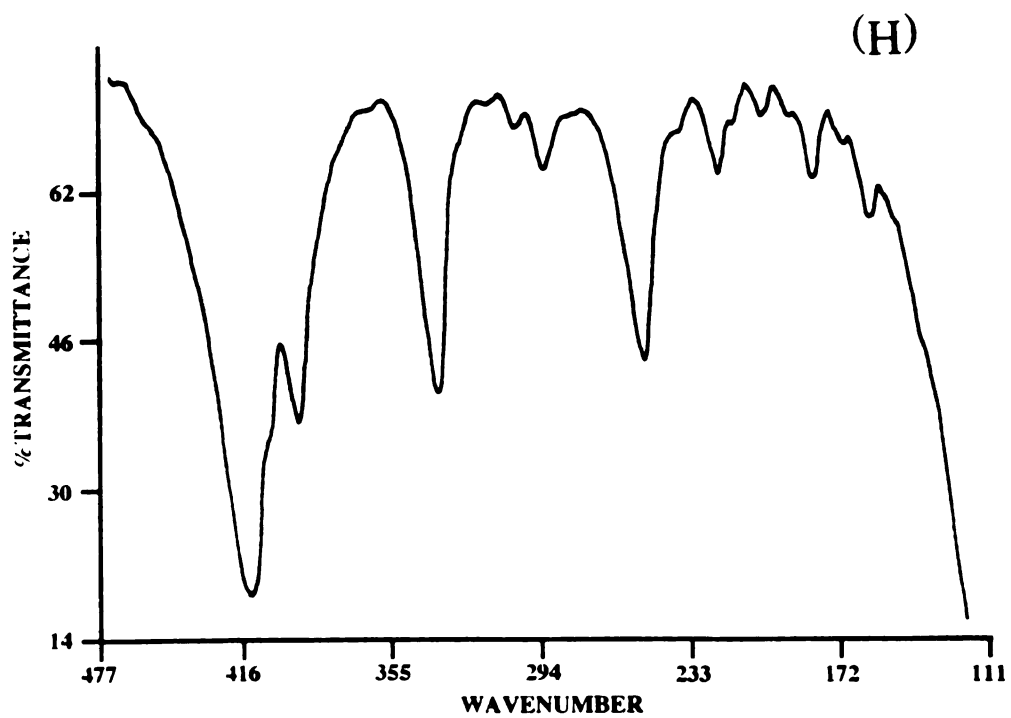
Figure 7-26: Infrared spectra of (A) $\text{K}_2\text{Hg}_3\text{Sn}_2\text{S}_8$, (B) $\text{K}_2\text{Hg}_3\text{Ge}_2\text{S}_8$, (C) $\text{K}_6\text{Zn}_4\text{Sn}_5\text{S}_{17}$, (D) $\text{Rb}_2\text{ZnSn}_2\text{S}_6$, (E) $\text{Cs}_2\text{MnSn}_2\text{S}_6$, (F) K_2MnSnS_4 , (G) $\text{Cs}_2\text{In}_2\text{Ge}_2\text{S}_8$ (H) $\text{Cs}_2\text{MnSn}_3\text{Se}_8$ and (I) $\text{Rb}_2\text{CdGe}_2\text{S}_6$.











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