

THESIS

This is to certify that the

dissertation entitled THE SYNTHESIS AND CHARACTERIZATION OF THE MOLYBDENUM-IRON-SULFUR CLUSTERS $(s_2 M o s_2 F e L_2)^{2-}$, $(s_2 M o s_2 F e s_2 F e L_2)^{3-}$, and $(s_2 M o s_2 F e s_2 F e s_2 M o s_2)^{4-}$ presented by

Robert Hugo Tieckelmann

has been accepted towards fulfillment of the requirements for

____degree in _____Chemistry PhD

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THE SYNTHESIS AND CHARACTERIZATION OF THE

MOLYBDENUM-IRON-SULFUR CLUSTERS

 $[s_2 Mos_2 Fel_2]^{2-}$, $[s_2 Mos_2 Fes_2 Fel_2]^{3-}$, and $[s_2 Mos_2 Fes_2 Fes_2 Mos_2]^{4-}$

Ву

Robert Hugo Tieckelmann

A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

ABSTRACT

THE SYNTHESIS AND CHARACTERIZATION OF THE MOLYBDENUM-IRON-SULFUR CLUSTERS [S₂MoS₂FeL₂]²⁻, [S₂MoS₂FeS₂FeL₂]³⁻, AND [S₂MoS₂FeS₂FeS₂MoS₂]⁴⁻

By

Robert Hugo Tieckelmann

The binuclear complexes, $[\text{FeMS}_4\text{Cl}_2]^{2-}$ (M = Mo,W), have been prepared by reaction of anhydrous ferrous chloride and tetrathiometallate. They can be converted to the $[\text{FeMS}_4(\text{SAr})_2]^{2-}$ ions by reaction with either triethylamine/ arylthiol or sodium thiolate. The thiolate complexes can be converted back to $[\text{FeMS}_4\text{Cl}_2]^{2-}$ by reaction with benzoyl chloride.

The trinuclear complexes, $[Fe_2MS_6(SAr)_2]^{3-}$ (M = Mo,W), have been prepared by reaction of either $[Fe_4S_4(SAr)_4]^{2-}$ or $[Fe_2S_2(SAr)_4]^{2-}$ with tetrathiometallates in 1:2 and 1:1 ratios, respectively. They do not exhibit ligand exchange chemistry similar to the binuclear complexes.

The tetranuclear complex, $[Fe_2Mo_2S_{10}]^{4-}$, has been prepared in low yield by reaction of $[Fe_4S_4(SAr)_4]^{2-}$ and

tetrathiometallate in a 1:4 ratio.

The X-ray crystal structures of the tetraethylammonium salts of $[FeMoS_{4}Cl_{2}]^{2-}$ and $[Fe_{2}MoS_{6}(S-p-Tol)_{2}]^{3-}$ have been determined. The binuclear complex contains the planar $\mathrm{FeS}_{2}\mathrm{Mo}$ subunit with terminal sulfides on molybdenum and chlorides on iron, resulting in essentially tetrahedral coordination about each metal atom. The trinuclear complex is a permutation of the dinuclear cluster with insertion of an FeS₂ moiety into the FeS₂Mo subunit to yield a linear FeS₂FeS₂Mo unit; terminal sulfides on the molybdenum and thiophenolates on the iron complete the structure. The tetranuclear complex is predicted to be an S₂MoS₂FeS₂FeS₂MoS₂ linear unit based on its method of synthesis, magnetic susceptibility, and reactivity.

Electronic spectral, magnetic susceptibility, and electrochemical data are reported for each complex. For the binuclear complexes, Mössbauer studies suggest an Fe(II)-Mo(VI) description with slight charge delocalization from iron to molybdenum via bridging sulfur atoms. For the trinuclear complexes, Mössbauer and ESR studies indicate an Fe(III)-Fe(II)-Mo(VI) description. The trinuclear and tetranuclear complexes may be viewed as reduced and super-reduced forms of the $[Fe_2S_2(SAr)_4]^{2-}$ ion, where each tetrathiometallate ligand stabilizes an adjacent Fe(II) site.

The major contributions to understanding the general

physical and chemical behavior of Mo(W)-Fe-S systems are the stability of the FeS₂Mo unit, the finding that the Fe₄S₄ core rearranges readily upon reaction with the tetrathiomolybdate(VI) anion, and the utility of these new complexes for calibrating the EXAFS spectra of the FeMo-cofactor. A variety of lines of evidence suggest that the FeS₂Mo unit will be an important structural fragment of the iron-molybdenum-cofactor of nitrogenase. То

George and Betty

for their <u>continuing</u> support, inspiration, and dedication to the education of their children;

and

to Stephanie

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time.

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LIST OF ABBREVIATIONS

<u>Solvents</u>:

DMA	=	N,N-dimethylacetamide
DMF	=	N,N-dimethylformamide
DMSO	=	dimethylsulfoxide
EtOH	=	ethanol
Et ₂ 0	=	diethylether
HMPA	=	hexamethylphosphoramide
MeCN	=	acetonitrile
МеОН	=	methanol
NMF	=	N-methylformamide

Reagents:

PhCOCl	=	benzoyl chloride
Et ₃ N	=	triethylamine
proton	sponge	= N,N,N',N'-tetramethyl-1,8-naphthalenediamine
crown	=	18-crown-6; 1,4,7,10,13,16-hexaoxacyclo-
		octadecane.

Miscellaneous:

Ar	=	aryl
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BM = Bohr magneton

Bz	= benzyl
Et	= ethyl
Et ₄ N	= tetraethylammonium
FeMoco	= iron-molybdenum-cofactor
IS	= isomer shift
Me	= methyl
Me ₄ N	= tetramethylammonium
Ph	= phenyl
Ph ₄ As	= tetraphenylarsonium
Ph ₄ P	= tetraphenylphosphonium
<u>p</u> -Tol	= <u>para</u> -tolyl
QS	<pre>= quadrupole splitting</pre>
SCE	= standard calomel electrode
Tol	= Toluene

I. INTRODUCTION

The 1977 report of the isolation¹ and characterization² of an iron-molybdenum cofactor (FeMoco) from the nitrogenase $enzyme^3$ marked the beginning of a new area of inorganic chemistry. The FeMo-cofactor was reported to contain eight iron atoms and six acid labile sulfur atoms per molybdenum atom in a low molecular weight inorganic subunit that was extremely sensitive to oxygen and moisture. It was also reported not to contain, in readily removable form, the classic $Fe_{11}S_{11}$ clusters that were known to exist in the nitrogenase enzyme.⁴ Extended X-ray Absorption Fine Structure (EXAFS) results⁵ indicated a molybdenum atom surrounded by four sulfur atoms at an average distance of 2.35 Å and by approximately three iron atoms at an average distance of about 2.71 Å. This limited amount of data was the basis used by synthetic chemists attempting to synthesize new Mo-Fe-S compounds. The rush to synthesize and characterize Mo-Fe-S systems that might mimic or resemble the chemical and physical properties of the FeMoco has grown steadily. Although as of this writing no synthetic Mo-Fe-S compounds closely approximate the reported stoichiometry and spectroscopic properties of the FeMoco, these contributions have significantly

increased our understanding of basic Mo-Fe-S chemistry and thereby provided a firmer foundation for eventual understanding of the FeMoco.

Two basic structural types of Mo-Fe-S compounds have been prepared. The first synthesized were the "cubane" Mo-Fe-S complexes^{6,7}, $[Fe_6Mo_2S_8(SR)_9]^{3-}$, $[Fe_6Mo_2S_9(SR)_8]^{3-}$ and $[Fe_7Mo_2S_8(SR)_{12}]^{3-,4-}$. These interesting systems have one specific structural component in common, the Fe_3MoS_4 cubic subunit. The second structural type is the "linear" Mo-Fe-S complexes, which includes binuclear complexes⁸⁻¹⁰, $[FeMoS_4R_2]^{2-}$ (R = SAr, OAr, Cl or $R_2 = S_5$); trinuclear complexes¹¹⁻¹³, $[Fe(MoS_4)_2]^{3-}$, $[Fe_2MoS_4Cl_4]^{2-}$, and $[Fe_2MoS_6(SAr)_2]^{3-}$; and a (presumed) tetranuclear system, $[Fe_2Mo_2S_{10}]^{4-}$. The structural component shared by all the linear systems is the planar FeS_2Mo subunit.

The research presented in this thesis describes the synthesis and characterization of the dinuclear compound, $[\text{FeMoS}_4\text{Cl}_2]^{2-}$; the trinuclear compounds, $[\text{Fe}_2\text{MoS}_6(\text{SAr})_2]^{3-}$; and the only tetranuclear compound known, $[\text{Fe}_2\text{Mo}_2\text{S}_{10}]^{4-}$. The synthesis and characterization of the tungsten analogues of the dinuclear and trinuclear compounds are also described.

II. EXPERIMENTAL

A. Materials and Methods

All operations were performed in an atmosphere of dinitrogen or argon purified by passage over hot BASF catalyst R 3-11 and supported P_2O_5 (Aquasorb). Solvents and reagents were degassed prior to use by repeated evacuation and flushing with purified dinitrogen or argon. -q0 tical spectra of all reagents having well characterized spectra were checked for purity with a UV-VIS spectrometer prior to each use. Acetonitrile was either Aldrich Chemical Company, Inc. Gold Label or distilled from CaH2. Propionitrile, toluene, tetrahydrofuran, and methanol were distilled from CaH₂, sodium/benzophenone, and magnesium methoxide, respectively. Dimethylsulfoxide, N,N-dimethylacetamide, and N,N-dimethylformamide were Aldrich Gold Label and used without further purification. Triethylamine and benzoylchloride were stored over 4 Å sieves and the latter was distilled to a trap submerged in liquid nitrogen prior to use. All mercaptans were obtained from Aldrich Chemical Company and used without further purification.

<u>o</u>-Xylyl- α , α '-dithiol¹⁴, sodium hydrosulfide¹⁵, 3,5dimethylpyridiniumhexafluorophosphate¹⁶, (Et₄N)₂MoS₉¹⁷, and anhydrous FeCl₂¹⁸ were prepared as described. Large single crystals of Na₂S·9H₂O were quickly rinsed in

distilled water and neat ethanol¹⁹ before weighing prior to use. Salts of tetrathiomolybdate and tetrathiotungstate anions were prepared by the methods described^{20a-20e}. Tetraethylammonium perchlorate was prepared via reaction of tetraethylammonium hydroxide and perchloric acid in water, followed by recrystallization from acetonitrile/ diethylether. Sodium <u>o</u>-xylyl- α , α '-dithiolate was prepared from the free dithiol and 2 equivalents of sodium methoxide in methanol; subsequent removal of solvent yielded a fine white powder. The sodium salt of thiocresol was provided by H. C. Silvis; it was prepared by reaction of the free thiol with one equivalent of sodium methoxide in methanol, evaporation to dryness, evaporation twice with acetonitrile and drying <u>in vacuo</u>. H. C. Silvis also provided (Et_uN)SPh²⁵, prepared as noted.

 $(Et_4N)_2[Fe_2S_2(S_2-0-xylyl)_2]^{14}$, $(Et_4N)_2[Fe_2S_2(SAr)_4]^{14}$, $(Et_4N)_2[Fe_4S_4Cl_4]^{21}$, $(Ph_4As)_2[Fe_4S_4Cl_4]^{21}$, $(Et_4N)_2[Fe_4S_4-(SR)_4]^{22-24}$, $(Ph_4As)_2[Fe_4S_4(SAr)_4]^{24}$, $(BzEt_3N)_2[Fe_4S_4-(SAr)_4]^{24}$, $(Et_4N)_2[FeMOS_4(SAr)_2]^8$ and $(Ph_4As)_2[FeMOS_4-(S-p-Tol)_2]^8$ were prepared by published methods.

Optical spectra were obtained by use of either a Cary 17 or a Cary 219 spectrophotometer. ¹H NMR spectra were obtained by use of a Varian T-60 spectrometer. Magnetic susceptibility measurements were performed at room temperature by use of an Alpha Faraday balance by using $Hg[Co(NCS)_4]$ as calibrant. Electrochemical measurements were made with a

PAR 174A polarographic analyzer employing either dc polarography (dropping mercury electrode) or cyclic voltammetry (platinum electrode). Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Melting points were obtained in sealed tubes <u>in vacuo</u> and are uncorrected. The Mössbauer experiments were performed by T. A. Kent and B. H. Huynh at the Gray Freshwater Biological Institute, University of Minnesota, Navarre, Minnesota. The Mossbauer spectrometer was of the constant acceleration type and has been described previously²⁶. Electron paramagnetic resonance spectra were obtained on a Bruker ER-200D instrument equipped with an Oxford liquid helium flow cryostat.

B. <u>Preparation of $(Et_4N)_2[FeMS_4Cl_2]</u></u>$

1. $(Et_4N)_2[FeMoS_4Cl_2]$

To a slurry of 0.29 g (2.28 mmol) of anhydrous FeCl₂ in 10 mL of acetonitrile, a solution of 1.0 g (2.06 mmol) of $(Et_4N)_2MoS_4$ in 100 mL of acetonitrile was added and vigorously stirred. After 10 hours the solution was filtered and the filtrate reduced <u>in vacuo</u> to ~40 mL. Cooling to -20°C gave the product as dark brown microcrystals; recrystallization from acetonitrile gave product as dark brown prisms (mp 217°C dec) in ~80% yield. Anal. Calcd for $C_{16}H_{40}Cl_2FeMoN_2S_4$: C, 31.43; H, 6.59; Fe, 9.13; Mo,

15.69; N, 4.58. Found: C, 31.63; H, 7.00; Fe, 9.16; Mo, 15.77; N, 4.76. The same compound was also obtained in low yield from an acetonitrile solution containing 1 equiv of $(Et_4N)_2MoS_4$ and 2 equiv of $(Et_4N)_2[Fe_4S_4Cl_4]$ after brief exposure to the atmosphere and subsequent anaerobic workup.

2. (Et₄N)₂[FeWS₄Cl₂]

To a slurry of 1.0 g (6.5 mmol) of anhydrous FeCl_2 in 50 mL of MeCN, a solution of 3.75 g (6.5 mmol) of $(\text{Et}_4\text{N})_2\text{WS}_4$ in 250 mL of MeCN was added and vigorously stirred. After 10 hours the solution was filtered, and the volume of the filtrate was reduced <u>in vacuo</u> at 45°C until microcrystals appeared (150 mL final volume). Cooling to -20°C gave the product as red-brown crystals. One recrystallization from warm MeCN (50°C) followed by cooling to -20°C yielded the product as red-brown prisms (mp 214-216°C dec) in 65% yield. Anal. Calcd for $C_{16}H_{40}Cl_2FeWN_2S_4$: C, 27.48; H, 5.77; N, 4.01; S, 18.34. Found: C, 27.93; H, 5.91; N, 4.32; S, 18.09.

C. <u>Preparation of $(Et_4N)_3[Fe_2MS_6(SAr)_2]</u></u>$

1. (Et₄N)₃[Fe₂MoS₆(SPh)₂]. Method A

To a solution of 1.50 g (3.09 mmol) of $(Et_4N)_2MoS_4$ in 100 mL of MeCN was added a solution of 2.70 g (3.09 mmol)

of (Et₄N)₂[Fe₂S₂(SPh)₄] in 400 mL of MeCN. Prolonged reaction (3-4 weeks) at room temperature resulted in the disappearance of the optical spectrum characteristic of MoS_{4}^{2-} and formation of product optical spectrum. The reaction mixture was filtered, and the solvent volume reduced at 50°C to ca. 200 mL. Cooling the solvent to -20°C afforded purple-black microcrystals which were collected while cold. Recrystallization was effected by dissolution in a minimum amount of MeCN at 50°C, filtration, and slow cooling to -20°C. Product yield is typically 40%; subsequent solvent reductions of the mother liquor followed by recrystallization increase the yield to 80%, mp 190-191°C (dec). Anal. Calcd for C₃₆H₇₀Fe₂MoN₃S₈: C, 42.85; H, 7.00; Fe, 11.07; Mo, 9.51; N, 4.16; S, 25.42. Found: C, 42.97; H, 7.24; Fe, 11.23; Mo, 8.97; N, 4.21; S, 25.45.

2. (Et₄N)₃[Fe₂MoS₆(SPh)₂]. Method B

To a solution of 1.85 g (3.82 mmol) of $(\text{Et}_4\text{N})_2\text{MoS}_4$ in 125 mL of MeCN at 45°C was added a solution of 2.0 g (1.91 mmol) of $(\text{Et}_4\text{N})_2[\text{Fe}_4\text{S}_4(\text{SPh})_4]$ in 75 mL of MeCN also at 45°C. Prolonged reaction (5-7 days) at room temperature resulted in the appearance of microcrystals; cooling to -20°C produced more crystals. The crystals were collected while cold and afforded the product in 60% yield (recrystallization as above). Further treatment of the

mother liquor through solvent reduction at 50°C increased yields to 90%.

3. <u>(Et₄N)₃[Fe₂MoS₆(S-p-Tol)₂]</u>

This compound was prepared by substituting $(Et_4N)_2$ -[Fe₄S₄(S-<u>p</u>-Tol)₄] for the tetramer in Method B above and obtained as purple-black microcrystals (mp 189-190°C dec.). Anal. Calcd for $C_{38}H_{74}Fe_2MoN_3S_8$: C, 44.01; H, 7.19; N, 4.05. Found: C, 44.01; H, 7.09; N, 4.23.

4. $(Et_4N)_3[Fe_2WS_6(SPh)_2]$

This compound was prepared by substituting $(Et_4N)_2WS_4$ for $(Et_4N)_2MoS_4$ in Methods A and B above. Reaction time for both methods was greater than those observed for the Mo analogues. For Method A reaction time was about three months, and reaction time for Method B was about 2-3 weeks. Product was recrystallized once from MeCN and obtained as red-black microcrystals (mp 181-182°C dec). Anal. Calcd for $C_{36}H_{70}Fe_2N_3S_8W$: C, 39.42; H, 6.43; N, 3.83. Found: C, 39.85; H, 6.57; N, 4.33.

5. <u>(Et₄N)₃[Fe₂WS₆(S-p-Tol)₂]</u>

This compound was prepared by substituting $(Et_4N)_2WS_4$ for $(Et_4N)_2MoS_4$ in Method B above and obtained as red-black microcrystals in 40% yield following recrystallization from MeCN (mp 178-180°C dec). Anal. Calcd for C₃₈H₇₄Fe₂-N₃S₈W; C, 40.57; H, 6.63; Fe, 9.93; N, 3.73; S, 22.80; W, 16.34. Found: C, 40.85; H, 6.71; Fe, 9.32; N, 3.79; S, 22.82; W, 15.92.

D. $(Et_4N)_4(Fe_2Mo_2S_{10})$

To a solution of 3.88 g (8.0 mmol) of $(Et_4N)_2MoS_4$ in 250 mL of MeCN was added a solution of 2.2 g (2.0 mmol) of $(Et_{\parallel}N)_{2}[Fe_{\parallel}S_{\parallel}(SPh)_{\parallel}]$ in 50 mL of MeCN. Prolonged reaction time (5-7 days) at room temperature resulted in the appearance of microcrystals; cooling to -20°C overnight produced more crystals. The crystals were collected; and spectroscopic characterization indicated that they consisted of (Et₄N)₃[Fe₂MoS₆(SPh)₂]. The mother liquor was reduced in volume until microcrystals formed, slowly cooled to -20°C, and stored at -20°C for 48 hours. The collection of crystals afforded a mixture of $({\rm Et}_4 {\rm N})_4 (Fe_2Mo_2S_{10})$ and $(Et_4N)_3[Fe_2MoS_6(SPh)_2]$. Subsequent treatment (solvent reduction, cooling, filtration) of the mother liquor yielded more of the crystalline mixture. The desired product was isolated in pure form following three recrystallizations from a minimum of MeCN at 35°C and cooling to -20°C. The product was obtained as blue-black microcrystals in low (< 15%) yield (mp > 250°C dec). Anal. Calcd for C₃₂H₈₀Fe₂Mo₂N₄S₁₀: C, 33.56; H, 7.04; Fe, 9.75; Mo, 16.76; N, 4.89; S, 28.00. Found: C, 33.80; H, 7.06; Fe, 9.88; Mo, 15.44; N, 4.97; S, 27.67.

E. Interconversion Reactions

1. $(Et_{4}N)_{2}[FeMoS_{4}Cl_{2}] \rightarrow (Et_{4}N)_{2}[FeMoS_{4}(SPh)_{2}]$

Treatment of a solution of 6.6 mg (ll µmol) of $(Et_4N)_2$ -[FeMoS₄Cl₂] in 6.75 mL of acetonitrile with 3.3 µL (24 µmol) of triethylamine and 2.4 µL (24 µmol) of thiophenol resulted in an immediate color change from orange-brown to red-orange. The optical spectrum of the solution showed that [FeMoS₄(SPh)₂]²⁻ was formed quantitatively.

2. $(Et_{\parallel}N)_{2}[FeMoS_{\parallel}(SPh)_{2}] \rightarrow (Et_{\parallel}N)_{2}[FeMoS_{\parallel}Cl_{2}]$

Treatment of a solution of 25 mg (0.33 µmol) of $(Et_4N)_2[FeMoS_4(SPh)_2]$ in 25 mL of acetonitrile with 9.0 µL (0.73 µmol) of benzoyl chloride resulted in an immediate color change from red-orange to orange-brown. The optical spectrum of the solution was consistent with quantitative formation of $[FeMoS_4Cl_2]^{2-}$.

F. <u>Reactions of (Et₁N)₂[FeMoS₄Cl₂] with Thiols</u>

1. EtSH, t-BuSH, or BzSH and Et_3N

A stock solution of 0.190 g (0.31 mmol) of $(\text{Et}_4\text{N})_2$ -[FeMoS₄Cl₂] in 20 mL of MeCN was prepared and checked for purity with an optical spectrum. To a 10 mL vial stoppered with a serum cap was added 7.5 mL of MeCN, 22 µL (0.23 mmol) of Et₃N, 0.23 mmol of thiol [either 17 µL EtSH, 26 μ L <u>t</u>-BuSH, 27 μ L BzSH, or 24 μ L PhSH (as a control)] and 2.5 mL (3.87 x 10⁻⁵ mol) of the stock solution. Each mixture was stirred 5-10 minutes; a color change was noted in each case. Optical spectra of each solution displayed a shift of absorbance features to lower energy (compared to features of starting material). These shifts are indicative of ligand substitution in the interconversion reactions mentioned above.

2. <u>BzSH and Et₃N, Preparative Scale</u>

A solution containing 0.330 mL (3.55 mmol) of $\text{Et}_{3}N$, 0.400 mL (3.41 mmol) of BzSH, and 20 mL of MeCN was prepared. Addition of the above solution to 0.973 g (1.59 mmol) of $(\text{Et}_{4}N)_{2}[\text{FeMoS}_{4}Cl_{2}]$ dissolved in 100 mL of MeCN resulted in a color change from brown to red-brown. Stirring the reaction mixture 2 hours, introduction of a 3-fold volume excess of THF, and overnight cooling to 0°C afforded a precipitate. The solid was collected, dried in vacuo, and recrystallized once from 45°C MeCN. Following overnight storage at -20°C, microcrystals were collected and redissolved in MeCN; their optical spectrum was that of the 583, 510, and 409 nm absorption features of the [Fe- $(MoS_{4})_{2}]^{3-}$ ion¹¹.

3. Attempted Preparation of $[FeMoS_4(S_2-o-xylyl)]^2$

To a stirred solution of 1.89 g (3.09 mmol) of $(\text{Et}_4\text{N})_2$ -[FeMoS₄Cl₂] in 100 mL of MeCN was added a solution of 0.54 g (3.17 mmol) of <u>o</u>-xylyl- α, α '-dithiol in 25 mL of MeCN. Addition of 0.70 mL (6.8 mmol) of Et₃N in 25 mL of MeCN resulted in a change in solution coloration from brown to red-brown. Overnight stirring yielded a copious precipitate and a clear supernatant liquid. Upon filtration and dissolution in fresh MeCN an optical spectrum of the precipitate displayed only a continually rising absorbance spectrum with decreasing wavelength.

4. Disodium \underline{o} -Xylyl- α , α '-dithiolate

To a slurry of 0.44 g (2.06 mmol) of the dithiol salt in 10 mL of MeCN, 1.26 g (2.06 mmol) of $(\text{Et}_4\text{N})_2[\text{FeMoS}_4\text{Cl}_2]$ dissolved in 60 mL of MeCN was added and vigorously stirred. The color of the solution changed quickly from brown to red-brown. Filtration removed sodium chloride, which was washed once with MeCN. The mother liquor was stored overnight at -20°C; subsequent inspection revealed a non-crystalline precipitate. After filtration, the mother liquor was reduced \sim 50 mL and 130 mL of THF introduced. This mixture was stored at -20°C overnight followed by collection of the precipitated solid. One recrystallization from a minimum of MeCN and cooling to -20°C afforded microcrystals with an optical spectrum identical to that of the $[Fe(MoS_4)_2]^{3-}$ ion¹¹.

G. Preparation of Sulfides

1. Crown Complex of Na₂S

A solution of 0.210 g (0.870 mmol) of $Na_2S \cdot 9H_2O$ in 10 mL of MeOH was added to a solution of 0.462 g (1.75 mmol) of 18-crown-6 in 10 mL of MeOH. The resulting clear solution was evaporated to dryness overnight leaving a fine white powder.

2. $(Et_{\parallel}N)HS$

Dissolution of 20 g (83.3 mmol) of $Na_2S \cdot 9H_2O$ in 350 mL of EtOH was followed by overnight stirring. The solution was then filtered, and evaporated to dryness. The white powder that remained was redissolved in a minimum of EtOH (200 mL), and to this solution was added a solution of 27.6 g (166.5 mmol) of Et_4NCl in 125 mL of EtOH. The precipitate that formed (NaCl) was separated by filtration, the solvent removed, and the resulting white powder dried in vacuo overnight. The powder was dissolved in a minimum of MeCN and the remaining NaCl removed via filtration. The MeCN was evaporated to dryness. Dissolution of this white solid in a minimum of 50°C MeCN and cooling to -20°C afforded large water-white crystals. Concentration of the

mother liquor and cooling to -20°C yielded additional crystalline solid. Recrystallization of the combined materials from a minimum of warm (50°C) MeCN and subsequent cooling to -20°C afforded water-white crystals in low ($\sim 20\%$) yield (mp > 250°C dec). Anal. Calcd for $C_8H_{21}NS$: C, 58.83; H, 12.96; N, 8.58; S, 19.63. Found: C, 58.47; H, 12.93; N, 8.70; S, 19.02. To distinguish ($Et_{4}N$)HS from $(Et_4N)_2S_2$ (Calcd for $C_{16}H_{40}N_2S_2$: C, 59.20; H, 12.42; N, 8.63; S, 19.75.), an iodimetric titration was performed. Solutions were prepared and standardized according to Skoog and West²⁷. A starch indicator was not employed; NaHS and $Na_2S \cdot 9H_2O$ were controls. Dissolution was effected in either EtOH or MeOH to avoid loss of sulfide as $H_{2}S$, and performed anaerobically to limit formation of sulfite. The solutions of the "unknown" and the controls exhibited a yellow color (confirmed as S_2^{2-}) immediately upon introduction of the standardized iodine solution to the sulfide solution. The hydrosulfide titrations ("unknown" and NaHS) had a distinct color change, at onehalf the equivalence point, from the previously mentioned yellow solution to a clear solution. Addition of the iodine titrant continued until a pale yellow color (confirmed as I_3^-) persisted for at least 30 s. These results established the "unknown" as best formulated as $(Et_{\mu}N)HS$. Confirmation of S_2^{2-} and I_3^{-} was established by comparison of samples from the titration runs with optical spectra of standard solutions of the two ions²⁸.
H. <u>Reactions of (Et₄N)₂[FeMoS₄Cl₂] with Sulfides</u>

1. Crown Complex of Na₂S

To a solution of 0.532 g (0.870 mmol) of $(\text{Et}_4\text{N})_2$ -[FeMoS₄Cl₂] in 50 mL of MeCN was added a slurry of 0.528 g (0.870 mmol) of the sulfide-crown complex in 30 mL of MeCN. An optical spectrum indicated a distinct red shift of absorbance features to lower energy. Storage at -20°C overnight was followed by an optical spectrum that displayed absorbance features corresponding to the [Fe₂Mo₂S₁₀]⁴⁻ anion.

2. $(Et_{\mu}N)HS$

A solution of 0.73 g (4.47 mmol) of $(Et_4N)HS$ in 100 mL of MeCN was slowly added to a solution of 1.55 g (2.5 mmol) of $(Et_4N)_2[FeMoS_4Cl_2]$ in 100 mL of MeCN. A change in color from brown to red-brown occurred immediately; an optical spectrum of the reaction mixture indicated formation of $[Fe(MoS_4)_2]^{3-}$. A 50 mL aliquot of the reaction mixture was removed and to it was added 0.10 g (0.60 mmol) of $(Et_4N)HS$. An optical spectrum indicated formation of $[Fe_2Mo_2S_{10}]^{4-}$. After 72 hours the 50 mL aliquot was filtered and the mother liquor reduced in solvent volume (to approximately 30 mL). This was followed by storage at -20°C for 5 months, at which time a microcrystalline solid was apparent. Collection of the crystals, drying in vacuo, and subsequent dissolution in MeCN yielded an optical spectrum whose absorbance features were indicative of $[Fe_2Mo_2S_{10}]^{4-}$ in good purity.

3. (Et₄N)HS and Proton Sponge

Three stock solutions were prepared: 1) $(\text{Et}_{4}\text{N})_{2}$ -[FeMoS₄Cl₂], 0.37 g (0.60 mmol) in 20 mL of MeCN; 2) (Et₄N)HS, 0.20 g (1.2 mmol) in 10 mL of MeCN; 3) proton sponge, 0.13 g (0.60 mmol) in 10 mL of MeCN. Samples each reagent [1.0 mL (0.03 mmol) of FeMoS₄Cl₂²⁻, 0.25 mL (0.03 mmol) of (Et₄N)HS, 0.50 mL (0.03 mmol) of proton sponge, 0.25 mL of MeCN] were mixed in a 5.0 mL gas tight syringe according to the following ratios: [FeMoS₄Cl₂]²⁻, (Et₄N)HS, proton sponge, MeCN; 1,0,0,4; 1,1,0,3; 1,1,1,1; 1,4,4,0. The order of introduction for each experiment (sulfide, proton sponge, FeMoS₄Cl₂²⁻) was followed by two optical spectra at approximately 5-10 minutes and 20-25 minutes. Experiment 4 was also checked with an optical spectrum after 18 hours. Experiments 2, 3, and 4 had absorbance features that indicated formation of [Fe(MoS₄)₂]³⁻.

I. <u>Reactions of (Q)₂[FeMoS₄(SAr)₂] with Sulfides</u>

1. NaHS

To a stirred slurry of ll mg (0.196 mmol) of NaHS in 5 mL of MeCN was added a solution of 100 mg (0.132 mmol)

of $(\text{Et}_4\text{N})_2[\text{FeMoS}_4(\text{SPh})_2]$ in 10 mL of MeCN. After stirring for 20 minutes the solution darkened considerably. Optical spectra of the reaction indicated complete formation of $[\text{Fe}(\text{MoS}_4)_2]^{3-}$ after 24 hours.

2. $(Et_{\parallel}N)HS$

A solution of 0.065 g (0.398 mmol) of $(Et_4N)HS$ in 2.5 mL of MeCN was dripped into a solution of 0.20 g (0.158 mmol) of $(Ph_4As)_2[FeMoS_4(SPh)_2]$ in 20 mL of MeCN. Optical spectra of the reaction mixture were obtained at 20 minutes, 40 minutes, 24 hours, and 48 hours. Absorbance features indicative of $[Fe(MoS_4)_2]^{3-}$ were present in all spectra.

3. (Et₄N)HS and Proton Sponge

Three stock solutions were prepared: 1) $(Ph_4As)_2$ -[FeMoS₄(S-p-Tol)₂], 0.78 g (0.60 mmol) in 20 mL of MeCN; 2) (Et₄N)HS, 0.37 g (1.2 mmol) in 10 mL of MeCN; 3) proton sponge, 0.13 g (0.60 mmol) in 10 mL of MeCN. Samples of each reagent [1.0 mL (0.03 mmol) of FeMoS₄(S-p-Tol)₂²⁻, 0.25 mL (0.03 mmol) of (Et₄N)HS, 0.50 mL (0.03 mmol) of proton sponge, 0.25 mL of MeCN] were mixed in a 5.0 mL gas tight syringe according to the following ratios: [FeMoS₄-(S-p-Tol)₂]², (Et₄N)HS, proton sponge, MeCN; 1,0,0,4; 1,1,0,3; 1,1,1,1; 1,2,2,0; 1,4,4,0. Each experiment (order of mixing the solutions was sulfide, proton sponge, $[FeMoS_4(S-p-Tol)_2]^{2-})$ was monitored by two optical spectra at approximately 5-10 minutes and 20-25 minutes. Spectra of the last four experiments had absorbance features that indicated formation of $[Fe(MoS_4)_2]^{3-}$.

J. <u>Reactions of (Et₄N)₃[Fe₂MoS₆(SAr)₂]</u>

1. Benzoyl Chloride

Dropwise introduction of a solution of 0.482 mL (4.15 mmol) of benzoyl chloride in 50 mL MeCN to a stirred slurry of 1.68 g (1.66 mmol) of $(\text{Et}_4\text{N})_3[\text{Fe}_2\text{MoS}_6(\text{SPh})_2]$ in 50 mL MeCN resulted in the dissolution of solid and a change in the solution color from purple to brown. Following overnight storage at -20°C, 450 mL of anhydrous Et_20 was added to the reaction mixture. After cooling to -20°C, the precipitated material was collected, dried in vacuo, recrystallized from a minimum of MeCN and cooled to -20°C. Subsequent attempts at crystallization through reduction of the solvent volume failed because the solution deposited films and slowly decomposed on standing.

2. Mos_{11}^{2-}

Dissolution of 0.11 g (0.11 mmol) of $(Et_4N)_3[Fe_2MoS_6-(S-p-Tol)_2]$ and 0.32 g (0.66 mmol) of $(Et_4N)_2MoS_4$ in 50 mL of MeCN followed by maintenance at 55°C for approximately 24 hours resulted in the appearance of optical features

attributable to $[Fe_2Mo_2S_{10}]^{4-}$. Continued heating (4 days) and monitoring of the reaction mixture revealed decomposition of all species except MoS_4^{2-} .

3. Sulfide and MoS_4^{2-}

Three stock solutions were prepared: 1) $(Et_4N)_3$ -[Fe₂MoS₆(SPh)₂], 0.469 g (0.465 mmol) in 50 mL of MeCN; 2) $(Et_4N)_2MoS_4$, 0.725 g (1.50 mmol) in 50 mL of MeCN; 3) (Et₄N)HS, 0.60 g (3.67 mmol) in 20 mL of MeCN. Into a 13 x 100 mm test tube equipped with a serum cap were introduced via syringe samples (0.50 mL MoS_{μ}^{2-} , 1.60 mL $Fe_{2}MoS_{6}(SPh)_{2}^{3-}$, 0.150 mL sulfide) of the above stock solutions according to the following ratios: $[Fe_2MoS_6(SPh)_2]^{3-}$, MoS²⁻, (Et₄N)HS; 1,0,0; 0,1,0; 2,2,1; 1,1,1; 1,2,1; 1,1,2; 1,0,1; 1,0,2. Each experiment (order of mixing was trimer, thiomolybdate, sulfide) was followed by 10 minutes of stirring and an optical spectrum was obtained. The mixture was then heated for 20 minutes at 60°C and another optical spectrum was obtained. Finally, the reaction mixtures were stored at room temperature for 7 hours culminating in another optical spectrum. All solutions containing sulfide were colored green and yielded optical spectra that had absorption features similar to the $[Fe_2Mo_2S_{10}]^{4-}$ ion (which is normally blue in solution). Generation of the green solutions is independent of the presence of MoS_4^{2-} .

K. <u>Reactions of $(Et_{\parallel}N)_{\parallel}[Fe_{2}Mo_{2}S_{10}]$ </u>

1. PhSH

Treatment of a stirred solution of 5.1 mg (4.45 µmol) of $(Et_4N)_4[Fe_2Mo_2S_{10}]$ in 1.0 mL MeCN with 4.5 µL (44.5 µmol) of PhSH in 0.5 mL MeCN afforded an instantaneous color change from blue to red-orange. An optical spectrum indicated 90% conversion to $(Et_4N)_2[FeMoS_4(SPh)_2]$.

2. Dilute Acid

A 5 to 10 mg (4.5 to 9.0 µmol) sample of $(Et_4N)_4$ -[Fe₂Mo₂S₁₀] was dissolved in 2.0 mL MeCN. To this sample 0.5 mL of 2N HCl was added. Evolution of a gas resulted, and qualitative testing indicated the absence of odors characteristic of PhSH and <u>p</u>-TolSH. A strong odor of H₂S was noted.

L. <u>Reactions of $Fe_{4}S_{4}$ Tetramers with $(Et_{4}N)_{2}MoS_{4}$ </u>

1. $(Et_{\mu}N)_{2}[Fe_{\mu}S_{\mu}(SEt)_{\mu}]$

A solution of 1.13 g (2.33 mmol) of $(Et_4N)_2MoS_4$ in 60 mL of MeCN was added to a stirred solution of 0.50 g (0.584 mmol) of $(Et_4N)_2[Fe_4S_4(SEt)_4]$ in 30 mL of MeCN. After 21 days storage at room temperature, reduction of the solvent volume (50%) at 45°C followed by storage at -15°C for 7 days yielded a microcrystalline precipitate. The crystals were collected and dried in vacuo; dissolution in MeCN gave a green solution whose optical spectrum indicated the presence of $(Et_{\parallel}N)_2MoS_{\parallel}$ and $(Et_{\parallel}N)_{\parallel}[Fe_2Mo_2S_{10}]$.

2. $(Et_4N)_2[Fe_4S_4(S-t-Bu)_4]$

A solution of 1.33 g (1.37 mmol) of $(\text{Et}_4\text{N})_2[\text{Fe}_4\text{S}_4-(\text{S}_{-t}-\text{Bu})_4]$ in 125 mL of MeCN, and a solution of 2.68 g (5.49 mmol) of $(\text{Et}_4\text{N})_2\text{MoS}_4$ in 200 mL of MeCN were warmed to 50°C and combined. The resulting solution was monitored via optical spectra for 21 days. There were no appreciable changes in optical features during this time period that indicated a reaction had occurred, however, reaction for another 21 days resulted in minute changes in the optical spectrum that indicated formation of $[\text{Fe}_2\text{Mo}_2\text{S}_{10}]^{4-}$ in very low yield.

3. $(Et_4N)_2[Fe_4S_4(S-p-Tol)_4]$

Introduction of a solution of 0.882 g (1.81 mmol) of $(Et_4N)_2MoS_4$ in 40 mL of MeCN to a solution of 0.250 g (0.226 mmol) of $(Et_4N)_2[Fe_4S_4(S-p-Tol)_4]$ in 25 mL of MeCN was followed by maintenance of the final solution temperature at 40°C for 30 hours. An optical spectrum of the cooled solution indicated that a reaction had occurred, whereupon the solvent was evaporated to dryness. Introduction of a minimum of MeCN, cooling to -20°C, and collection of the

resulting crystalline material afforded a solid whose optical spectrum had features representative of both $(Et_4N)_3[Fe_2MoS_6(S-p-Tol)_2]$ and $(Et_4N)_4[Fe_2Mo_2S_{10}]$. The crystals were redissolved in the mother liquor with the aid of additional MeCN and the solution was maintained at 50°C for 1 week. Reduction of the solvent volume at 50°C until crystals formed, cooling to -20°C overnight, and subsequent collection of the crystals revealed MoS_4^{2-} as the major product. Further workup of the mother liquor yielded crystalline material whose optical spectrum was dominated by the thiomolybdate anion.

M. Growth of (Et₄N)₃[Fe₂MoS₆(S-p-Tol)₂] Crystals

This experiment was performed according to $(\text{Et}_4\text{N})_3^-$ [Fe₂MoS₆(SAr)₂] preparative method B above. To a solution of 0.491 g (0.444 mmol) of $(\text{Et}_4\text{N})_2$ [Fe₄S₄(S-p-Tol)₄] in 32.5 mL of MeCN was added 0.430 g (0.887 mmol) of $(\text{Et}_4\text{N})_2^-$ MoS₄ in 34.5 mL of MeCN. Both solutions were at room temperature. The flask containing the final reaction mixture was free of internal imperfections (scratches). The reaction mixture was submerged in a dewar containing room temperature H₂O and stored in a closet free of light and drafts to insure thermal isolation. After 3 weeks reaction time inspection revealed many large crystals. The crystals were collected at room temperature, dried <u>in vacuo</u>, and not recrystallized. Optical spectra indicated that both the mother liquor and the crystals were of good purity.

III. RESULTS AND DISCUSSIONS

A. $(Et_{\parallel}N)_{2}[FeMS_{\parallel}Cl_{2}]$ (M = Mo, W)

1. Synthesis and Reactivity

The reaction of equimolar amounts of either tetrathiomolybdate (VI) or tetrathiotungstate(VI) with anhydrous ferrous chloride in MeCN results in formation of the $[S_2MS_2FeCl_2]^{2-}$ ions (M = Mo,W), isolated in high yield as tetraethylammonium salts. Reaction of the corresponding aryl thiolate derivatives, $[S_2MS_2Fe(SAr)_2]^{2-}$ (M = Mo,W), with 2 equivalents of benzoyl chloride in MeCN also affords the $[FeMS_4Cl_2]^{2-}$ ions:

$$[\text{FeMS}_4(\text{SAr})_2]^2 + 2\text{PhCOC1} \xrightarrow{\text{MeCN}} [\text{FeMS}_4\text{Cl}_2]^2 + 2\text{PhCOSAr}$$

(where formation of the thioester is presumed by analogy to Holm's results²¹). The reverse reactions (chloro derivative+ aryl thiolate derivative) can be accomplished by addition of either 2-3 equivalents of Et_3N and ArSH or 2 equivalents of NaSAr (Ar = Ph, p-Tol) in MeCN. The shift of the equilibrium to the desired product is aided in the chloro + thiolate conversions by excess $Et_3N/ArSH$ and by the formation of NaCl, respectively. Excess benzoyl chloride

in the thiolate + chloro conversion causes decomposition and formation of an insoluble black solid (presumably through acylation of terminal sulfide ligands). All conversions occur rapidly and essentially quantitatively and can be followed spectrophotometrically by appearance and disappearance of key absorption features (see Figures 3 and 4). While analogous behavior is observed for Fe_2S_2 and $Fe_{\parallel}S_{\parallel}$ clusters 21,29 , the FeMoS₄ cluster does not form the stable alkyl- and benzylthiolate compounds common to the dimeric and tetrameric iron salts. Early indications from spectroscopic scale experiments led to large preparative scale reactions, but subsequent workup of these reaction mixtures yielded insoluble solids or the $[Fe(MoS_4)_2]^{3-}$ ion as products. The Fe_2S_2 cluster was originally isolated¹⁴ as $[Fe_2S_2(S_2-o-xylyl)_2]^2$; attempts to utilize the chelate effect and isolate the FeMoS_4 analogue starting from $[FeMoS_{ll}Cl_{2}]^{2-}$ were also unsuccessful. Two methods, identical to these employed for aryl derivatives (o-xylyl dithiol plus 2 Et_3N or the sodium dithiolate) resulted in decomposition and the formation of $[Fe(MoS_4)_2]^{3-}$, respectively. Garner has reported³⁰ the structural characterization of the $[FeMoS_4(S_2-o-xylyl)]^2$ ion, which was synthesized from MoS_4^{2-} and $[Fe(S_2-\underline{0}-xylyl)_2]^{2-}$. Attempts employing the dithiolate and $[FeMoS_4Cl_2]^{2-}$ presumably result in reduction of the S2MoS2Fe core and subsequent decomposition in a reaction that is faster than simple displacement of halide by the dithiolate. Garner's method



Figure 1. Synthesis and Reactivity of $[FeMS_4Cl_2]^2$ -(M = Mo,W) in MeCN.

effectively avoids this problem by initial coordination of the dithiolate to the iron. The reactions discussed are summarized in Figure 1.

2. Structure

The structure of the $[FeMoS_4Cl_2]^{2-}$ ion is depicted in Figure 2, and selected interatomic distances and bond angles are listed in Tables I and II. The crystal structure consists of discrete cations and anions in a 4:2 ratio per unit cell with but one independent cation and one-half of the dianion per symmetric unit. Due to the location of the dianion at the crystallographic inversion center $(\bar{1})$, there is a twofold disorder of the FeCl_2 and MoS_2 portions of [Cl₂FeS₂MoS₂]²⁻. This structure was successfully refined as equivalent mixtures of Fe and Mo and Cl and S, yielding a crystallographically independent metal atom, M (M = (Fe + Mo)/2), and two independent terminal atoms, X_2 and X_3 (X = (S + C1)/2). The structure is best described as two tetrahedral units joined at a common edge. The six bond angles around the metal atom M range from 104.00° to 111.69°; the average (109.47°) is close to the ideal tetrahedral value of 109.49°. The Mo-Fe distance is 2.786(1) Å and, although the metal-metal distance may imply existence of a direct metal-metal interaction, detailed discussion of the electronic structure of the binuclear unit will be deferred to the Mössbauer discussion. The bridging metal-sulfur



Figure 2. Stereochemistry of the $[S_2MoS_2FeCl_2]^{2-}$ dianion. The crystallographic $C_1-\overline{1}$ site symmetry causes a two-fold disorder of the metal atoms (M = (Mo + Fe)/2) and the terminal ligands (X = (S + Cl)/2).

Bondeo	1 Distances	Nonbonded	Distances
M-M '	2.786(1)	S1S1'	3.566(3)
M-Sl	2.268(2)	S1X2	3.696(3)
M-Sl'	2.258(2)	S1X3	3.665(2)
M-X2	2.199(2)	S1'X2	3.674(2)
M-X3	2.200(2)	S1'X3	3.669(2)
		x2x3	3.583(3)

Table I. Interatomic Distances (Å) with Esd's for $(Et_4N)_2$ -[FeMoS₄Cl₂].

Table II. Bond Angles (deg) with Esd's for $(Et_4N)_2$ [FeMoS₄Cl₂].

	The Dia	nion	
M-Sl-M'	76.00(5)	S1'-M-X2	111.04(7)
SI-M-SI'	104.00(5)	Sl'-M-X3	110.77(7)
SI-M-X2	111.69(7)	X2-M-X3	109.06(8)
SI-M-X3	110.24(7)		

distances are longer (0.06 Å) than the terminal metal ligand distances. This trend is consistent with data from the $[(PhS)_2FeS_2^*MoS_2]^{2-}$ ion⁸ (the asterisk denotes bridgeing sulfurs) where bridging bonds (Mo-S* av 2.255(2) Å, Fe-S* av 2.264(2) Å) are substantially longer than the terminal bonds (Mo-S av 2.153(2) Å). Averaging both sets of data from the thiolate analogue (M-S* av 2.26 Å and M-X av 2.33 Å (Fe-S(Ph) av 2.307(2) Å)) yields values that are close to the values crystallographically averaged for the $[FeMoS_{\mu}Cl_2]^{2-}$ ion.

Comparison of $[FeMoS_4Cl_2]^{2-}$ (<u>I</u>) with other metal sulfide-chloride systems 31, 12, $[Cl_2FeS_2FeCl_2]^{2-}$ (II) and $[Cl_2FeS_2MoS_2FeCl_2]^{2-}$ (III), reveals interesting stereochemical similarities and differences (cf. Table III). First, the Mo-Fe distances in I and III are similar (2.786 (1) and 2.775(6) Å, respectively), while the Fe-Fe distance in \underline{II} is significantly shorter (2.716(1) Å). The trend may be correlated to the larger covalent radius of molybdenum (1.30 Å for Mo vs 1.17 Å for Fe)⁸. Second, the average metal bridging sulfur (M-S*) distances vary only slightly for the Mo-containing species (M-S*: I, 2.263(2) Å) compared to the much smaller value for II, 2.201(1) Å. Again this trend may be attributed to the larger covalent radius of molybdenum. Third, the metal-terminal ligand bonds (M-X: I, X = S, Cl; II and III, X = Cl) exhibit wide variations. The crystallographically averaged value

Table III. Selected Structural Parameters in the $[S_2MoS_2^*FeCl_2]^{2-}$ (<u>1</u>), $[Cl_2FeS_2^*FeCl_2]^{2-}$ (<u>11</u>), and $[Cl_2FeS_2^*MoS_2^*FeCl_2]^{2-}$ (<u>11</u>) Complexes.

Parameter ^a	<u>I</u>	<u>II</u> ³¹	<u>III</u> ¹²
M-Fe ^b	2.786(1)	2.716(1)	2.775(6)
Mo−S*			2.204(5)
Fe-S*	2.203(2)	2.201(1)	2.295(5)
Mo-S			
Fe-Cl	2.200(2)	2.252(1)	2.225(10)
S*S*	3.566(3)	3.463(1)	с
M-S*-Fe ^b	76.00(5)	76.21(3)	76.05(1)
S*-Mo-S*			109.5(1,9)
S*-Fe-S*	1 04.00(5)	103.79(3)	100.9(2)
S-Mo-S			
Cl-Fe-Cl	(109.00(0)	105.37(4)	110.2(9)

^aDistances in angstroms (Å) and angles in degrees (°).

 ^{b}M = Mo for <u>I</u> and <u>III</u>, Fe for <u>II</u>.

^cNot reported.

* Bridging sulfur atom.

for M-X of 2.200(2) Å in I is smallest, followed by an average value of 2.225(10) Å in III, and the largest average value of 2.252(1) Å determined for II. Since the thiolate analogue of I, $[(PhS)_2FeS_2^*MoS_2]^{2-}$, has an Mo-S bond average of 2.15 Å and II has an average of 2.25 Å for the Fe-Cl bonds, one would predict an average M-X bond of 2.20 Å for I, based on the twofold disorder of the dianion. This is in accord with the observed value. Last, the average bridging metal-sulfur-metal angle in all four complexes (including the thiolate analogue of I) is acute and constant at approximately 76°.

The tetraethylammonium cations of \underline{I} are crystallographically ordered with normal bond lengths and angles, and will not be discussed further.

Subsequent to the work on $(\text{Et}_4\text{N})_2[\text{FeMoS}_4\text{Cl}_2]^8$, Müller reported^{32,33} the structure of $[\text{Ph}_4\text{P}][\text{BzMe}_3\text{N}][\text{FeMoS}_4\text{Cl}_2]$. Detailing only the space group (P1), the cell parameters, and a few bond distances (Mo-Fe, 2.775 Å; Mo-S*, 2.27 Å; Mo-S, 2.18 Å), his work, in essence, agrees with the data reported above.

A single crystal x-ray structure of $(\text{Et}_4\text{N})_2[\text{FeWS}_4\text{Cl}_2]$ was not obtained. However, both Müller³⁴ and Coucouvanis³⁵ report work on this dianion, and indicate that the Wanalogue is isostructural with the Mo-analogue. Unfortunately, Müller reports only the space group and cell parameters for $[\text{Ph}_4\text{P}][\text{BzMe}_3\text{N}][\text{FeWS}_4\text{Cl}_2]$. Coucouvanis³⁵ reports slightly more information: Fe-W, 2.821(2) Å; M-S*, 2.203(8) Å; M-S, 2.276(8) Å; and M-S*-M, 76.4°(2). These data are not entirely consistent with the same parameters obtained for $[FeMoS_4Cl_2]^{2-}$. While the M-M bond and the M-S*-M angle are not significantly larger than expected, the values of the metal ligand bonds (terminal and bridging) seem to be reversed.

3. Electronic Spectra

The electronic absorption spectra of the $[FeMS_{II}Cl_{2}]^{2-1}$ ions (M = Mo,W) are shown in Figure 3; peak positions and molar absorptivities are presented in Table IV. The spectra of the chloro complexes are dominated by a pair of intense absorptions between 350 and 475 nm. They are thus similar to the spectra of the bis(tetrathiometallate) complexes of the first row transition metals 3^{36} , 3^7 . The latter display an essentially symmetrical splitting of the lowest energy $S \rightarrow Mo$ and $S \rightarrow W$ charge transfer transitions of the original tetrathiometallates (MoS_{μ}^{2-} , WS_{μ}^{2-}). This splitting is also observed in the $[FeMS_4Cl_2]^{2-}$ (M = Mo,W) electronic spectra, and Müller 34 and Coucouvanis 35 agree the effect is due to the lowering of the symmetry of the tetrathiometallate upon coordination of the ferrous chloride. Many other absorbance features are present in addition to those attributable to the tetrathiometallate transitions. Since low energy sulfide or chloride to iron charge transfer



Figure 3. Electronic spectra of $(Et_4N)_2[Cl_2FeS_2MoS_2]$ and $(Et_4N)_2[Cl_2FeS_2WS_2]$ in acetonitrile solution at 23°.

	[FeMoS ₄ C1 ₂] ²⁻	[FeWS4C12] ²⁻
Electronic spectral	1080(1.2),594(sh),	1030(1.0),522(0.51),
features, λ _{max} (ε) ^a	528(sh),469(64),	460(sh),415(6.1),
	432(48),314(124),	374(6.9),284(15.2),
	290(110).	242(14.1),254(sh).
Magnetic moment ^b	5.1 BM	5.1 BM
a		

Electronic Spectral Features and Magnetic Moments of $(Et_4N)_2[FeMS_4Cl_2]$

Complexes, M = Mo,W.

Table IV.

^aIn MeCN solution, except for low intensity features at $\lambda > 800 \text{ nm}$, which were measured in concentrated DMSO solution; 23°C. $\lambda_{\max}(\varepsilon)$ in nm (M⁻¹cm⁻¹ x 10⁻²).

 $^{\mathrm{b}}$ In the solid state at 23°C, corrected for diamagnetic contributions.

transitions will also appear in this general region, specific assignments would be speculative. A discussion of general trends is, however, appropriate. Comparison of the optical spectrum of the $[FeMoS_{\mu}Cl_{2}]^{2-}$ ion to that of the $[FeWS_{\mu}Cl_{2}]^{2}$ ion reveals a blue shift of the W \rightarrow S electronic features relative to the Mo \rightarrow S electronic This observation is consistent because the diffeatures. ference in orbital energies will be greater for W + S transitions than for Mo + S transitions. These expectations also hold for the WS_{\perp}^{2-} and MoS_{\perp}^{2-} optical spectra (Figure 4). Each dinuclear complex also displays a low intensity band in the near-IR (NIR) region. Although features in this general region are usually ascribed to ${}^{5}E + {}^{5}T_{2}$ transitions (see Holm³⁸ and Coucouvanis³⁹), the energies of the two bands are not sufficiently low to warrant such an assignment in this case. Coucouvanis 35 and Silvis²⁵ have suggested that the two bands are due to Fe \rightarrow Mo(W) transitions. More specifically, Coucouvanis proposes a schematic energy level diagram where the Fe d orbitals are located between predominantly sulfur molecular orbitals and the empty Mo(VI) and W(VI) d orbitals, enabling facile low energy electronic transitions from filled predominantly iron d orbitals to empty predominantly Mo, W d orbitals. Although identical, Silvis' assignment is based on the large half-widths and small extinction coefficients of the absorptions. Regardless of present



Figure 4. Electronic spectra of $(Et_4N)_2MoS_4$ and $(Et_4N)_2 - WS_4$ in acetonitrile solution at 23°C.

proposals, more detailed assignments must await more careful study of a significantly larger sample of bimetallic sulfur-containing systems.

4. Magnetic susceptibility

The Faraday method was used to obtain room temperature magnetic susceptibilities of solid samples of $(Et_{\downarrow N})_2$ -[FeMoS₄Cl₂], M = Mo,W. Both complexes yielded a value of 5.1 BM per formula unit, which is corrected for the diamagnetic contributions of the ligands and cations through use of Pascal's constants. Each case corresponds to a system containing four unpaired electrons (S = 2). While the simplest explanation would be a monomeric high-spin Fe (II) complex⁴⁰ (range 4.9-5.5 BM), the data might accommodate a strong intermolecular antiferromagnetic interaction between high-spin d^5 Fe(III) and d^1 Mo(V). The temperature dependence of the magnetic susceptibility was measured for the thiolate derivative⁸, $(Et_{\mu}N)_{2}$ [FeMoS₄- $(SPh)_4]$, to resolve this question, and to ascertain the possibility of intermolecular interactions. The results of the low temperature measurements on the solid and a magnetically dilute frozen DMF solution suggested that intermolecular interactions exist in the crystal due to long-range magnetic ordering. However, if an antiferromagnetically coupled Fe(III)-Mo(V) formulation is assumed, the energy necessary to populate spin states greater than

S = 2 would be much greater than the thermal energy at 370 K (|2J| >> kT). The latter consideration is not consistent with the Mössbauer data.

5. Mössbauer Spectroscopy

Application of Mössbauer spectroscopy to a chemical system that contains iron affords data that aid in understanding the immediate environment of the iron nucleus. Mössbauer spectroscopy was employed to assess the formal oxidation states of the metal centers in the $[FeMoS_4Cl_2]^{2-}$ ions, M = Mo,W. Two parameters, the isomer shift (IS) and the quadrupole splitting (QS), have been used to establish a data base that allows comparisons between well characterized iron systems and "new" iron systems. A detailed theoretical discussion will not be presented here, because, the Mössbauer effect is well known and sources that provide insight into its applications are numerous.⁴² The main focus in this and subsequent discussions will be the isomer shift. Correct interpretation of the $[FeMoS_{\mu}Cl_{2}]^{2-}$ Mössbauer results depends upon direct comparisons to established Fe-S systems, since Mo-Fe-S systems lack the abundance of physical data necessary to allow internal comparisons. In Figure 5, monomeric, dimeric, and tetrameric Fe-S systems are represented in a graph of IS vs formal oxidation state for iron in tetrahedral sulfur sites.^{6a} A distinct trend is evident and



Figure 5. Correlation diagram relating isomer shift to formal oxidation state for various iron-sulfur clusters

proves useful in determining the formal oxidation states of "new" iron environments. The $[FeMoS_{L}Cl_{2}]^{2-}$ ion exhibits IS (QS) values of 0.60 mm/s (2.12 mm/s) in a zero applied field (see Figure 6 and Table V). The values correspond well with analogous data for monomeric Fe(II) in a tetrahedral sulfur environment (IS (QS), 0.6 mm/s (3.3 mm/s)). As a check, the $[FeMoS_4Cl_2]^{2-}$ data was obtained in both solid form (diluted with boron nitride) and frozen solution (DMF) in order to avoid magnetic interactions in the solid state. The differences between IS (QS) values in both solid and solution form were negligible. Mossbauer data for other dinuclear Fe-M-S systems, including work on $[FeMoS_4Cl_2]^{2-}$ published^{34,35} subsequent to our studies, is also presented in Table V. Despite slight differences in the environment of each iron nucleus and the temperature of each study, it is clear that the dinuclear MoS_2Fe core is best characterized as an Fe(II)-Mo(VI) system that has slight delocalization of electron density from iron to molybdenum through the sulfur bridges. A similar effect is evident for the tungsten analogues, but the delocalization through the sulfur bridges seems somewhat diminished. This last observation is consistent with the electrochemical results of the $[FeWS_{\parallel}Cl_{2}]^{2-}$ ion.



Figure 6. Mössbauer spectrum of frozen DMF solution of $(Et_4N)_2[FeMoS_4Cl_2]$ recorded at 4.2 K and with zero applied field. Vertical bar indicates 1% absorption.

	[FeMoS ₄ C1 ₂] ²⁻ IS(QS) ^a	[FeWS ₄ C1 ₂] ²⁻ IS(QS)	[FeMoS ₄ (SPh) ₂] ²⁻ IS(QS)	[FeWS ₄ (SPh) ₂] ²⁻ IS(QS)
Tieckelmann, et al. ^{8,b}	0.60(2.12)	ы	0.47(1.63)	ы
Müller, et al. ³⁴ ,c	0.48(2.10)	0.52(2.27)	ک ۵	ත
Conconvanis, et al. ^{35,d,e}	0.48(2.06)	0.54(2.28)	0.33(1.94)	0.39(2.20)
Conconvanis, et al.35,d,f	0.59(2.14)	0.65(2.34)	0.44(1.96)	0.47(2.24)
^a IS, isomer sh ^b (Et ₄ N) ⁺ salts ^c [(Ph ₄ P)(BzMe ₃ ^d (Ph ₄ P) ⁺ salts ^e At room tempe ^f At liquid N ₂ ^g Not determine	<pre>ift in units of r , T = 4.2 K. N)]²⁺ salts, T = temperature</pre>	mm/s. QS, quad 295 K.	irupole splitting in	units of mm/s.

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6. Electrochemistry

The $[FeMS_{\mu}Cl_{2}]^{2-}$ ions (M = Mo,W) were studied by dc polarographic methods in approx. 1 mM solutions in Gold Label MeCN with 50 mM $(Et_{\mu}N)ClO_{\mu}$ as supporting electrolyte. Electrochemical scans over the range +1.0 to -2.0 V, versus the standard calomel electrode, revealed only one electrochemically irreversible reduction for each complex. The dropping mercury electrode (0.5 s/drop) was selected after initial experimental attempts with cyclic voltammetric methods employing platinum (flag), mercury (hanging drop), and carbon (glassy) electrodes. Absorption of the sulfurrich compounds on the last three electrodes enabled observation of only the cathodic wave in the cyclic voltammetric scan, since the anodic wave was often missing entirely (current flow severely restricted). This electrochemical behavior seems to be common for the general family of iron-molybdenum-sulfur complexes containing coordinated MoS_{ll}^{2-} .

The reductions for the molybdenum and tungsten analogues occurred at -1.23 and -1.35 V, respectively. The data are consistent with that of Müller³⁴. The slopes of the log $[i/i_d-i]$ vs. potential plot were 43 mV (Mo) and 100 mV (W); both values are far from the theoretically ideal value of 59 mV for a one electron reversible reduction. The low potential slope value for the molybdenum analogue suggests a chemical reaction occurring faster

than the rate of diffusion of the reduced species from the electrode surface. Silvis noted²⁵ that reduction of $(Et_{4}N)_{2}[FeMoS_{4}(SPh)_{2}]$ results in formation of $[Fe(MoS_{4})_{2}]^{3-}$. However, the value of the potential slope for the tungsten analogue indicates that this complex accepts less than one electron as the decomposition reaction occurs. The general difference in behavior was apparent during the actual electrochemical experiment; while the molybdenum system could be run without repeatedly cleaning the platinum counter electrode, the collection of reproducible data on the tungsten system required cleaning of the same counter electrode after each scan. Two other electrochemical studies on analogous systems qualitatively support the data presented here. Holm²¹ found that dimeric complexes of the type $[Fe_2S_2X_4]^{2-}$ (X = Cl, Br, I) exhibit irreversible reductions from -1.0 to -0.7 V without resolvable anodic processes, while Callahan and Piliero⁴¹ cite a difference in reduction potential for the series [Ni- $(MS_{\mu})_{2}]^{2-}$, $[Pd(MS_{\mu})_{2}]^{2-}$, and $[Pt(MS_{\mu})_{2}]^{2-}$ (M = Mo,W), where the tungsten compounds are reduced at more negative potentials than the molybdenum compounds.

7. Summary

Preparation of the $[\text{FeMS}_4\text{Cl}_2]^{2-}$ ions (M = Mo,W) from anhydrous FeCl₂ and MS₄²⁻ is a facile one step operation. The thiolate and chloro derivatives can be interconverted

by using simple, readily available reagents. The two complexes are essentially isostructural and are best represented as two tetrahedra joined at an edge. The optical spectra themselves are dominated by a splitting of features present in the electronic spectra of the parent thiometallate anions. Magnetic susceptibility, electrochemical, and Mössbauer results are consistent with a Fe(II)-M(VI) system with slight electron delocalization from Fe + M through the bridging sulfur atoms, but no direct metal-metal interaction. There is slightly less electron delocalization in the tungsten analogue.

B. $(Et_4N)_3[Fe_2MS_6(SAr)_2]$ (M = Mo,W; Ar = Ph, p-Tol).

1. Synthesis and Reactivity

The $[Fe_2MS_6(SAr)_2]^{3-}$ ions are formed in high yield as tetraethylammonium salts by two distinct reaction pathways. First, reaction of equimolar amounts of either tetrathiomolybdate(VI) or tetrathiotungstate(VI) and the $[Fe_2S_2(SPh)_4]^{2-}$ ion in MeCN for approx. 3 weeks (MoS_4^{2-}) or 4 months (WS_4^{2-}) yields the trianion in good purity. Second, reaction of 1 equivalent of the $[Fe_4S_4(SAr)_4]^{2-}$ ions (Ar = Ph, p-Tol) with 2 equivalents of either tetrathiomolybdate(VI) or tetrathiotungstate(VI) in MeCN for approx. 5 days (MoS_4^{2-}) or 3 weeks (WS_4^{2-}) yields the trianion in good purity. The second pathway is more desirable for the following reasons: 1) the reaction does not require spectral monitoring because completion is signified by the less soluble product crystallizing from solution, 2) the reaction time is decreased by a factor of 4. The latter may be due (in part) to the first reaction pathway requiring an oxidation-reduction step. The second reaction pathway only requires a cleavage of the $[Fe_4S_4(SAr)_4]^{2-}$ core into the desired product,

$$[Fe_4S_4(SAr)_4]^{2-} + 2MoS_4^{2-} \xrightarrow{MeCN} 2[Fe_2MoS_6(SAr)_2]^{3-}$$

In each case formation of the tungsten analogue requires prolonged reaction time (v^4 times longer), which is presumed to result from differences in the π -acceptor properties of the WS²⁻₄ and MoS²⁻₄ ions. In the first reaction pathway the better π -acceptor properties of the MoS²⁻₄ ion apparently facilitate the oxidation-reduction step through stabilization of an intermediate similar to that found during the conversion of the [Fe₂S₂]²⁺ core to the [Fe₄S₄]²⁺ core¹⁴. In the second reaction pathway the better π -acceptor properties of the MoS²⁻₄ ion facilitate the simpler cleavage via stabilization of an intermediate required by the migration of an ArS⁻ ion. The mechanism of the first reaction pathway also presumes the formation of disulfide as the oxidation half reaction.

 $2MoS_4^{2-}+2[Fe_2S_2(SAr)_4]^{2-} \xrightarrow{MeCN} 2[Fe_2MoS_6(SAr)_2]^{3-}+ArSSAr+2ArS^{-}$

Attempts at synthesizing the $[Fe_2MoS_6(SR)_2]^{3-}$ ions (R = Et, t-Bu) from alkyl-substituted Fe-S tetramers proved unsuccessful. This result is probably due to the instability of the alkylthiolate cluster intermediates compared to the arylthiolate analogues. A stable intermediate is necessary to facilitate ligand migration during the tetramer cleavage. Since alkylthiolates are more readily oxidized than arylthiolates, the observation that alkyl substituted Fe-S tetramers (where ligand is either ethanethiolate or t-butylthiolate) yield small amounts of the $[Fe_2Mo_2S_{10}]^{4-}$ ion and do not yield the $[Fe_2MoS_6(SR)_2]^{3-}$ ion supports this hypothesis.

After direct synthesis of an alkyl substituted trinuclear core was not successful, several attempts were made to synthesize the chloro derivative, $[Fe_2MoS_6Cl_2]^{3^-}$. The synthetic potential of this particular complex is obvious when compared to its counterparts²¹, $[Fe_2S_2Cl_4]^{2^-}$ and $[Fe_4S_4Cl_4]^{2^-}$. Two methods were employed: 1) use of 2 equivalents of benzoyl chloride with 1 equivalent of $[Fe_2MoS_6(SAr)_2]^{3^-}$ produced oils and films that decomposed on standing; and 2) combination of the $[Fe_4S_4Cl_4]^{2^-}$ ion with tetrathiomolybdate(VI) afforded the $[Fe(MoS_4)_2]^{3^-}$ ion in high yield²⁵.

The thermal stability in the range $45-65^{\circ}$ C of the $[Fe_2MoS_6(SAr)_2]^{3-}$ ions was studied in MeCN; the trinuclear anion readily decomposes when maintained at temperatures



Figure 7. Synthesis and Reactivity of $[Fe_2MS_6(SR)_2]^{3-}$ (M = Mo,W; R = Ph, p-Tol) in MeCN.

greater than 55°C for periods longer than 2 hours. In addition, reaction of one mole of the $[Fe_2MoS_6(S-p-Tol)_2]^{3-}$ ion with six moles of tetrathiomolybdate(VI) at a temperature of 55° for time periods longer than 2 hours affords minute amounts of the $[Fe_2Mo_2S_{10}]^{4-}$ anion, but the reaction mixture decomposes after 3-4 hours. These reactions are summarized in Figure 7.

2. Structure

The structure of the $[Fe_2MoS_6(S-p-Tol)_2]^{3-}$ ion is depicted in Figure 8, and selected interatomic distances and bond angles are listed in Tables VI and VII. The crystal structure consists of discrete cations and anions in a 6:2 ratio per unit cell. The structure is best described as containing three tetrahedral units: MoS_4 , FeS_4 , and S_2 - $Fe(SAr)_2$ joined at two common edges in a linear arrangement. The six bond angles around each metal atom [range: $102.53^{\circ}-116.89^{\circ}$ ($S_2Fe(SAr)_2$), 103.08-114.44 (FeS_4), and 105.25-111.14 (MoS_4)] nearly average (109.50°) to the ideal tetrahedral value of 109.54° . The MoFe distance is 2.778 Å, while the FeFe distance is 2.691 Å.

Several Mo-Fe-S compounds have well documented crystal structures and selected data, pertinent to the $[Fe_2MoS_6-(S-p-Tol)_2]^{3-}$ ion, are listed in Table VIII. The $[FeMoS_4-(SPh)_2]^{2-}$ ion (V) is similar to the $[Fe_2MoS_6(S-p-Tol)_2]^{3-}$



Figure 8. Stereochemistry of the $[S_2MoS_2FeS_2Fe(S-p-Tol)_2]^{3-}$ trianion. Hydrogen atoms are omitted for clarity.
		Bonded D	istances	·	
Mo-S8	2.153	Fe2-S4	2.188	Fel-S4	2.228
Mo-S7	2.172	Fe2-S3	2.193	Fel-S3	2.235
Mo-S6	2.240	Fe2-S1	2.315	Fel-S5	2.275
Mo-S5	2.248	Fe2-S2	2.326	Fel-S6	2.280
		Non-bonde	d Distance:	S	
Mo-Fel	2.778	S1-S2	3.783	S5-S6	3.566
Fe2-Fel	2.691	S3-S4	3.506	S7-S8	3.568

Table VI. Selected Interatomic Distances (Å) for $(Et_4N)_3$ -[Fe₂MoS₆(S-<u>p</u>-Tol)₂].

Table VII. Selected Bond Angles (deg) for $(Et_4N)_3[Fe_2Mo-S_6(S-p-Tol)_2]$.

S8-Mo-S7	111.14	S4-Fe2-S3	106.31	S4-Fel-S3	103.58
S8-Mo-S6	109.56	S4-Fe2-Sl	115.61	S4-Fel-S5	112.75
S8-Mo-S5	110.29	S4-Fe2-S2	106.62	S4-Fel-S6	111.69
S7-Mo-S6	110.25	S4-Fe2-Sl	102.53	S3-Fel-S5	111.62
S7-Mo-S5	110.18	S3-Fe2-S2	116.89	S3-Fel-S6	114.44
S6-Mo-S5	105.25	Sl-Fe2-S2	109.21	S5-Fel-S6	103.08
Fe2-Fel-M	o 176.29				
Fe2-S4-Fe	1 75.11	Mo-S5-Fe	1 75.77		
Fe2-S3-Fe	1 74.86	Мо-Ѕб-Ге	1 75.83		

ion (IV) in that both have Mo-S terminal bond distances that are smaller than the average Mo-S distance 36 in MoS_4^{2-} of 2.17 Å. The $[Fe(MoS_4)_2]^{3-}$ ion (VI) contains Mo-S terminal bonds distances that are similar, at 2.172 Å, to the MoS_{μ}^{2-} ion average. The bridging sulfur distances in IV vary somewhat (the three sets are averaged in pairs in Figure 9) and the results indicate a trend that is unusual within the class of "linear" Mo-Fe-S compounds. As further discussion will attest, IV is presumed to contain iron atoms in two distinct formal oxidation states 13 and is unique among Mo-Fe-S complexes in this respect. The distances within the FeS₂Fe(SAr)₂ subunit of <u>IV</u> are on first approximation similar to those in the parent compound, $(Et_4N)_2[Fe_2S_2(S-p-Tol)_2]$ (VII). The Fe-Fe distances are identical in <u>VII</u> and <u>IV</u> at 2.691 Å, and the average Fe-S bridging and Fe-S(Ar) terminal bond distances differ only slightly (~ 0.01 Å) between VII and IV. This observation is indicative of only a minor disturbance in the FeS₂Fe core of VII on displacement of thiolate upon coordination of MoS_4^{2-} . However, a closer look shows that the Fe_2S_2 framework is distorted at two locations when IV and VII are compared (Figures 8 and 9). The Fel-S* distances (nearest the Mo) are slightly decreased (0.043 Å) while the other Fel-S* distances are increased a similar amount (0.030 Å). This difference in bridging sulfur distances is clearly due to the coordinated MoS_2 moiety. Although

c1^{2.225}Fe^{2.295}S^{*} 2.20⁴Mo 2.20⁴S^{*} 2.295_Fe 2.225_{C12} $s_2^{2.163}Mo^{2.274}s_2^* 2.278Fel^{2.231}s_2^* 2.191Fe2^{2.321}s_2$ $s_2^{2.321}Fe \frac{2.201}{22}s_2^* \frac{2.201}{22}s_2^{2.321}Fe \frac{2.321}{22}s_2$ s₂2.172_{Mo}2.256_S*2.257_Fe 2.257_S* 2.256_{Mo} 2.172_S s₂ 2.200_{Mo}2.253_S 2.253_{Fe} 2.200_{C12} ^{S2.153}Mo^{2.255}S* 2.265_Fe 2.308_{S2} <u>VII</u>¹⁴, [Fe₂S₂(S-<u>P</u>-Tol)₄]²⁻ IV. [Fe2MoS6(S-P-Tol)2]³⁻ *Denotes bridging sulfur. <u>III</u>¹², $[MoS_4(FeCl_2)_2]^{2-}$ \underline{v}^{8} , [Femos₄(SPh)₂]²⁻ $\underline{\text{vl}}^{11}$, [Fe(Mos₄)₂]³⁻ I⁸, [FeMoS4C12]²⁻

Schematic Detailing of Averaged Pairs of Terminal and Bridging Sulfurs in "Linear" Mo-Fe-S Systems. Figure 9.

the effect is not as pronounced, the trend is visible in \underline{V} and the iron nearest the Mo in \underline{IV} will be tentatively designated as "ferrous" based on this similarity. Comparison of the Fe-Mo distance of 2.778 Å in \underline{IV} to the other systems in Table VIII yields some surprising results. Both \underline{III} and \underline{I} have Fe-Mo distances similar to \underline{IV} and \underline{V} and \underline{VI} have distinctly different Fe-Mo distances. This first pair have the longer Fe-Mo distances (Table VIII) and are designated Fe(II)-Mo(VI) systems⁸,12</sup> while the second pair have the shorter distances and their oxidation state assignments are split, \underline{V} is considered an Fe(II)-Mo(VI) complex⁸, but the assignment in \underline{VI} is mixed and tentatively assumed to be Mo(VI)-Fe(II)-Mo(V)¹¹. Obviously, no correlation between formal charges and the Mo-Fe distance exists.

The average bridging metal-sulfur-metal angle in <u>IV</u> is 75.39° and compares favorably to average values in other Mo-Fe-Ssystems of 75.18 for <u>V</u>, 74.77° for <u>VI</u>, and 76.1° for <u>III</u>. Compounds <u>IV</u>, <u>VI</u>, and <u>III</u> are the only known "linear" trimeric Mo-Fe-S systems, yet all three complexes deviate from being truly linear. The angle described by the metal centers has its smallest deviation in <u>III</u> with a value of 179.28°, <u>IV</u> and <u>VI</u> have larger deviations with values of 176.29° and 172.64°, respectively. Coucouvanis reasons that this apparent anomaly (in <u>VI</u>) is due to packing forces and the close proximity of several cation hydrogen atoms to two terminal sulfurs; a similar explantion might

	MoS ₂ FeC					
	IV	VII ¹⁴	<u>VI</u> 11	<u>111</u> 12	18	<mark>ر</mark> 8 2
Fe- Fe	2.691	2.691(1)		5.551(2)		
Fe-S*	2.211	2.201(1)				
Fe-S 🌒	2.278		2.257	2.295	2.263(5)	2.264(2)
Fe-S	2.321	2.312(1)				2.307(2)
Fe-Mo	2.778		2.740(1)	2.775(6)	2.786(1)	2.756(1)
Mo-S ^b	2.274		2.255(5)	2.204(5)	2.263(5)	2.255(2)
Mo-St	2.163		2.172(5)		2.200(2)	2.153(2)
Fe-Cl				2.225(10)	2.200(2)	
4 M-M-M	176.29		172.64(5)	179.38(7)		
4M-S-M	75.39		74.77(13)	76.1(1)	76.00(5)	75.18(6)

ESD's not available.

* Bridging sulfur atom (between iron atoms). * Bridging sulfur atom (between iron atom and molybdenum atom).

suffice for <u>IV</u>. In <u>IV</u> only two cations in the unit cell have been crystallographically resolved, while the four remaining cations remain disordered; meaningful discussion of the cations and their relationship to the angle of the metal centers is thus not possible.

A single crystal x-ray diffraction study of the $(Et_4N)_3[Fe_2WS_6(S-p-Tol)_2]$ complex is in progress.

3. Electronic Spectra

The electronic absorption spectra of the $(Et_4N)_3$ - $[Fe_2MS_6(S-p-Tol)_2]$ complexes (M = Mo,W) are shown in Figure 10; peak positions and molar absorptivities are presented in Table IX. The electronic spectra are similar to those of the $(Et_4N)_2[FeMS_4(S-p-Tol)_2]$ complexes^{8,25}, in that the visible region (400-600 nm) is dominated by intense absorptions, at least two of which clearly result from a splitting of the lowest energy sulfur \rightarrow metal charge transfer transitions of the parent tetrathiometalates (MoS_{4}^{2-} , WS_{4}^{2-}). The specific $S \rightarrow M$ assignments for the $[Fe_2MoS_6(S-\underline{p}-Tol)_2]^{3-1}$ ion (Mo-complex) and the $[Fe_2WS_6(S-p-Tol)_2]^{3-}$ ion (Wcomplex) are no clearer than the assignments were for the $[FeMoS_{\mu}(S-p-Tol)_{2}]^{2}$ and $[FeMoS_{\mu}Cl_{2}]^{2}$ ions. In the Mocomplex there is a triad of relatively sharp peaks in the 400-600 nm region and the assignment may be described as a splitting of the 467 nm absorption peak of the $\text{MoS}_{\text{L}}^{2-}$ ion into two absorption peaks at 442 nm and 510 nm. The



Figure 10. Electronic spectra of $(Et_4N)_3[(\underline{p}-TolS)_2FeS_2-FeS_2MoS_2]$ and $(Et_4N)_3[(\underline{p}-TolS)_2FeS_2FeS_2WS_2]$ in acetonitrile solution at 23°C.

Electronic 578(11.9),510(13.5),442(12.5) 572(sh),500(14.0),430(sh), spectral 344(24.0),300(sh),273 (30.5) 298(sh),360(sh),324(sh), features 2.3 BM 2.3 BM 2.4 BM		[Fe ₂ MoS ₆ (S-P-Tol) ₂] ³⁻	[Fe ₂ WS ₆ (S- <u>P</u> -Tol) ₂] ³⁻
Magnetic 2.4 BM momentsb 2.4 BM an work control on the second of the	Electronic spectral features ^a	578(11.9),510(13.5),442(12.5) 344(24.0),300(sh),273 (30.5)	572(sh),500(14.0),430(sh), 398(sh),360(sh),324(sh), 296(sh),275(39.0)
	Magnetic moments ^b	2.3 BM	2.4 BM
	a.	···· · · · · · · · · · · · · · · · · ·	

Electronic Spectral Features and Magnetic Moments of $(Et_4N)_3[Fe_2MS_6-$

Table IX.

"In the solid state at 23°C, corrected for diamagnetic contributions.

W-complex, exhibiting an electronic spectrum similar to $[FeWS_4(S-p-Tol)_2]^2$, only has one broad peak and a host of poorly resolved features in the 400-600 nm region. Specific assignments for the electronic spectrum of the W-complex and the remainder of the electronic spectrum of the Mo-complex would be speculative, and only detailed theoretical calculations will allow definitive assignments. A discussion of general trends would, however, be appropriate. The Mo and W complexes exhibit the same blue shift of absorption features (relative to one another) that is characteristic of both the parent tetrathiometalates and their simplest Mo(W)-Fe-S derivatives, the $[\text{FeMS}_{\mu}(R)_{2}]^{2-}$ ions (M = Mo,W; R = Cl, S-Aryl)²⁵. However neither complex (Mo or W) displays the low energy, low intensity bands in the near-IR (NIR) region that are characteristic^{35,25} of the $[FeMS_{\mu}R_{2}]^{2-}$ ions mentioned above and the $[MoS_4(FeCl_2)_2]^{2-}$ ion. A similar absorption does not exist for the $[Fe(MoS_4)_2]^{3-}$ ion¹¹. The only other electronic feature that $[Fe(MoS_{\mu})_2]^{3-}$ and $[FeMoS_{6-}]^{3-}$ $(S-\underline{p}-Tol)_2]^{3-}$ share is their "reduced" (trianionic) form as their most stable conformation. The electronic spectrum of the $[Fe(MoS_{\mu})_{2}]^{3-}$ ion¹¹ has essentially the same triad of absorption peaks present in the electronic spectrum of the Fe₂Mo-complex, differing in the positions and the relative magnitudes of the molar absorptivity values. The electronic spectrum of $[Fe_2MoS_6(S-p-Tol)_2]^{3-}$ is unique and similarities

to the spectra of both the $[FeMoS_4(S-p-Tol)_2]^{2-}$ and the $[Fe(MoS_4)_2]^{3-}$ ions indicate that qualitative electronic assignments may not require detailed theoretical calculations on all three Mo-Fe-S systems.

4. Magnetic Susceptibility

Room temperature magnetic susceptibility data were obtained via the Faraday method on solid samples of $(Et_4N)_3[Fe_2MS_6(SAr)_2]$ (M = Mo,W; Ar = Ph, p-Tol). The four trinuclear complexes yielded values of 2.2-2.4 BM per formula unit (Table X); each value was corrected for the diamagnetic contributions of the ligands and cations by use of Pascal's constants. Each case corresponds to an Fe(II) (S = 5/2) system antiferromagnetically coupled to an Fe(III) (S = 2) system resulting in an S = 1/2 adduct. The distinction between an Fe(III)-Fe(II)-Mo(VI) formulation and an Fe(III)-Fe(III)-Mo(V) formulation cannot be based solely on the magnetic susceptibility results. The following Mössbauer results lend more support to the Fe(III)-Fe(II)-Mo(VI) assignment.

5. Mössbauer Spectroscopy

Figure 11 depicts the Mossbauer spectrum of $(Et_4N)_3$ -[Fe₂MoS₆(SPh)₂] at 4.2 K in a small (<1kG) applied magnetic field. The solid sample was diluted with boron nitride.

Complex	Magnetic Moment ^a
(Et ₄ N) ₃ [S ₂ MS ₂ FeS ₂ Fe(SAr) ₂] ^b	
M=Mo, Ar=Ph	2.27
M=Mo, Ar= <u>p</u> -Tol	2.22
M=W, Ar=Ph	2.36
M=W, Ar= <u>p</u> -Tol	2.42
$(Et_4N)_2[S_2MS_2Fe(SAr)_2]^{25,c}$	
M=Mo, Ar=Ph	4.89
M=W, Ar=Ph	4.90
[(PPh ₃) ₂ N)] ₂ (Et ₄ N)[S ₂ MoS ₂ FeS ₂ MoS ₂] ^{11,d}	3.85
(Ph ₄ P) ₂ [Cl ₂ FeS ₂ MoS ₂ FeCl ₂] ^{12,e}	6.64
^a All values corrected for diamagnetic co ^{BM.} ^b At 295 K.	ntributions,units c
^C At 296 K.	
^d At 303 K.	
^e At 300 K.	

Table X.	Magnetic Susceptibility Data for the $(Et_4N)_3$ -
	$[Fe_2MS_6(SAr)_2]$ Complexes (M = Mo,W and Ar =
	Ph, <u>p</u> -Tol) and Selected $Mo(W)$ -Fe-S Complexes.



Figure 11. Mössbauer spectrum of $(Et_4N)_3[S_2MoS_2FeS_2Fe(SPh)_2]$ recorded at 4.2 K and with 600 G applied field.

The trinuclear complex exhibits two quadrupole doublets of essentially equal intensity, rather than a magnetic spec-This result is indicative of rapid electronic trum. relaxation in the complex. For doublet A the parameters are an IS of 0.42 mm/s and a QS of 1.41 mm/s, while for doublet B the IS is 0.30 mm/s with a QS of 0.68 The doublet A parameters are very similar to mm/s. those obtained for $(Et_{\parallel}N)_{2}[FeMoS_{\parallel}(SPh)_{2}]$ (Table V), and suggest that the iron atom nearest the molybdenum be designated ferrous. The doublet B parameters resemble those obtained for high-spin Fe(III) in tetrahedral sulfur environments (eq. oxidized rubredoxin⁴⁴: IS, 0.32 mm/ s; QS, 0.50 mm/s); therefore the iron ligated by thiolate will be designated ferric. Comparison to Figure 5 yields formal oxidation states of 2.35 for the iron of doublet A and 2.65 for the iron of doublet B. These results are consistent with the magnetic data discussed previously. Since the $(Et_4N)_3[Fe_2MoS_6(SPh)_2]$ system cannot be directly compared to any other linear Mo-Fe-S system because no other Mo-Fe-S system contains two distinct iron sites, comparison of individual iron sites to particular complexes must suffice. It is clear, however, that the $[Fe_2MoS_6(SAr)_2]^{3-}$ ion is best described as an Fe(II)-Fe(III) system.

Recently, a derivative, $[Fe_2MoS_{11}]^{3-}$, of the above trinuclear system was prepared by Silvis²⁵; subsequent

characterization by Mossbauer spectroscopy also yielded two quadrupole doublets (doublet A: IS, 0.44 mm/s; QS, 1.41 mm/s and doublet B: IS, 0.32 mm/s; QS 0.92 mm/s). The data are consistent with the formulation mentioned above.

6. Electrochemistry

The $[Fe_2MS_6(SAr)_2]^{3-}$ ions (M = Mo,W; Ar = Ph, <u>p</u>-Tol) were studied by dc polarographic methods in approximately 1 mM solutions in Gold Label MeCN with 50 mM (Et $_4$ N)- ClO_4 as supporting electrolyte. Electrochemical scans were run over the range +1.0 to -2.0 V (versus the standard calomel electrode), and the results are listed in Table XI. Each trinuclear molybdenum complex exhibited reversible electrochemical reductions at about -1.2 V and -1.9 V and an irreversible electrochemical oxidation at about +0.1 to +0.2 V. Each trinuclear tungsten complex exhibited only one electrochemically reversible reduction at approximately -1.3 V and no resolvable oxidation waves. These complexes displayed the same behavior with cyclic voltammetric methods mentioned earlier for the $[FeMoS_{\parallel}Cl_{2}]^{2-}$ ions (M = Mo,W), requiring use of polarography at the dropping mercury electrode (0.5 s/drop). The slopes of the log $[i/i_d-i]$ vs potential plot were all in the range 58-80 mV for the reductions and ∿160 mV for the oxidations (see Table XI). The slope values

Table XI. Electrochemical Data for the $(Et_4N)_3[Fe_2MS_6-(SAr)_2]$ Series M=Mo,W and Ar=Ph, <u>p</u>-Tol.

Ma	Ar	Red _l (Slope) ^b	Red ₂ (slope) ^b	Ox (Slope) ^C
Мо	Ph	-1.25(73)	-1.87(58)	+0.2(154)
Мо	p-Tol	-1.27(80)	-1.92(58)	+0.1(163)
W	Ph	-1.31(63)		
W	<u>p</u> -Tol	-1.35(63)		

^al mM solution of [Fe₂MS₆(SAr)₂]³⁻, 50 mM (Et₄N)ClO₄, Gold Label MeCN, 23°C,

^bReduction (slope of log (i/i_d-i) vs. E plot) in units of V (mV).

^cOxidation (slope of log (i/i_d-i) vs. E plot) in units of V (mV).

 f_{or} the reduction waves approximate the theoretically ideal value of 59 mV for a one electron reversible reduction.

Direct comparison of the electrochemical behavior of these trinuclear Mo(W)-Fe-S complexes to other Mo(W)-Fe-S complexes is important since similarities to the $(Et_4N)_2$ - $[FeMS_4(SAr)_2]$ series²⁵ (M = Mo,W; Ar = Ph, <u>p</u>-Tol) are significant enough to warrant discussion. Results from the trinuclear and dinuclear series indicate that the W-analogues are harder to reduce, an effect already attributed to the diminished π -acceptor properties of WS_{μ}^{2-} compared to MoS_{μ}^{2-} and projected into the Mo(W)-Fe-S systems. In addition, results from both series show that the first reductions occur at essentially the same potentials, differing in that the dinuclear complexes yield irreversible reductions and the trinuclear complexes yield essentially reversible reductions. This is not unusual considering the presence of an Fe(III) center in the trinuclear complexes, a feature that is absent in the dinuclear complexes. The Mo-trinuclear complexes have a second electrochemically reversible reduction potential which implies either an exceptional ability to stabilize charge throughout the anionic Mo-Fe-S core that is absent in the W-analogues or the formation of Mo(V). Electrochemical data for the $[MoS_4(FeCl_2)_2]^{2-}$ ion are not available, but the $[Fe(MoS_4)_2]^{3-}$ ion exhibits a "quasi-reversible" reduction at -1.8 V and

an irreversible oxidation at -0.10 V (both values vs. S.C.E.)¹¹.

7. Electron Spin Resonance Spectroscopy

Further support for the Fe(III)-Fe(II) core structure of the $[Fe_2MS_6(SAr)_2]^{3-}$ ions (M = Mo,W and Ar = Ph, <u>p</u>-Tol) was achieved through a study of the EPR spectra of $(Et_4N)_3$ - $[Fe_2MoS_6(S-p-Tol)_2]$ and $(Et_4N)_3[Fe_2WS_6(S-p-Tol)_2]$. The room-temperature magnetic susceptibility study indicated an antiferromagnetically coupled Fe(III)-Fe(II) system that resulted in an S = 1/2 ground state. Frozen solutions of the two trinuclear complexes in MeCN were examined by using an applied microwave frequency of 9.45 GHz (X-band) and a power of 2 mW at 4.2 K. An intense, isotropic signal was observed at g = 1.957 for the Mo-analogue and at g = 1.870for the W-analogue (Figure 12). Larger deviations from the ideal g = 2 value are expected for the W-analogue because of larger contributions of spin-orbit coupling. The ESR signals were double integrated according to the method of Ayscough⁴³ (using $CuSO_{\mu}$ as a standard), indicating that the trinuclear systems contain 1.3 and 1.2 unpaired electrons per formula unit for the Mo and W analogues, respectively. This experiment included a power study to insure that the signals were not saturated. The isotropic nature of the signals is presumably due to the extent of the delocalization of the unpaired spin density

Figure 12. ESR spectra of (Et₄N)₃[S₂MoS₂FeS₂Fe(SPh)₂] in frozen acetonitrile solution. Conditions of ESR spectroscopy. Top spectrum: modulation amplitude, 5 G; magnetic field sweep rate, 120 s; time constant, 0.3 s. Bottom spectrum: modulation amplitude, 1 G; magnetic field sweep rate, 200 s; time constant, 0.2 s; instrument gain, 500.





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over the metal centers, effectively decreasing the contributions of the spin-orbit coupling constant. However, the lack of hyperfine interactions from either ^{95}Mo or ^{97}Mo (I = 5/2, abundance 15.72% and 9.46%, respectively) indicates negligible delocalization of the unpaired electron onto the Mo atom.

8. Summary

The $[Fe_2MoS_6(SAr)_2]^{3-}$ ions (M = Mo,W and Ar = Ph, p-Tol) can be prepared by two methods: (1) reaction of equivalent amounts of $(Et_4N)_2]Fe_2S_2(SAr)_4]$ and $(Et_4N)_2-$ MS₄, or (2) reaction of $(Et_4N)_2[Fe_4S_4(SAr)_4]$ and $(Et_4N)_2-$ MS₄ in a 1:2 ratio. The structure of the $(Et_4N)_3[Fe_2-$ MoS₆(S-p-Tol)₂] complex is best described as a nearly linear arrangement of three tetrahedral moieties (MoS₄, FeS₄, and FeS₂(SAr)₂) joined at two common edges. The trinuclear complexes exhibit complex electronic spectra distinct from other Mo(W)-Fe-S systems. Magnetic susceptibility, electrochemical, ESR, and Mössbauer results support an Fe(III)-Fe(II)-M(VI) system and an S = 1/2 ground state.

C. $(Et_4N)_2[Fe_2Mo_2S_{10}]$

1. Synthesis and Reactivity

Reaction of $(Et_{\parallel}N)_{2}MoS_{\parallel}$ and $(Et_{\parallel}N)_{2}[Fe_{\parallel}S_{\parallel}(SAr)_{\parallel}]$ (Ar = Ph, p-Tol) in a 4:1 ratio in MeCN results in initial precipitation of crystalline $(Et_4N)_3[Fe_2MoS_6(SAr)_2]$ after approximately five days. The trinuclear product is then If the mother liquor is isolated for another collected. five day period and the resulting crystalline material is collected, spectroscopic characterization suggests that it is predominantly impure $(Et_4N)_3[Fe_2MoS_6(SAr)_2]$. Repeated recrystallization affords in low yield a new Mo-Fe-S cluster, which analyzes as $(Et_4N)_4[Fe_2Mo_2S_{10}]$. The low yield may be due to the necessity of an oxidation-reduction reaction to produce this "super-reduced" Fe^{II}S₂ core, stabilized through coordination of two tetrathiomolybdate (VI) moieties. The analogous reaction with $(Et_4N)_2WS_4$ and $(Et_4N)_2[Fe_4S_4(SAr)_4]$ does <u>not</u> yield $[Fe_2 W_2S_{10}$ ⁴⁻. The $[Fe_2Mo_2S_{10}]^{4-}$ ion is presumed to have an Mo(VI)-Fe(II)-Fe(II)-Mo(VI) metal configuration, as shown schematically in Figure 13. Due to the proximity of the two Fe(II) nuclei, the $[Fe_2Mo_2S_{10}]^{4-}$ ion should be particularly sensitive to attack by aryl thiols and acids. Reaction of excess ArSH (Ar = Ph, \underline{p} -Tol) with the [Fe₂- $Mo_2S_{10}]^{4-}$ ion affords the $[FeMoS_4(SAr)_2]^{2-}$ ions in quantitative yield (as determined spectrophotometrically).

Also, decomposition of the $[Fe_2Mo_2S_{10}]^{4-}$ ion with excess 6N HCl gives gaseous products among which the distinctive odor of ArSH is definitely absent. These observations and the method of synthesis lend indirect yet substantial evidence for the proposed structure of the $[Fe_2Mo_2S_{10}]^{4-}$ ion. Potential for an alternative synthesis therefore exists, namely combination of the dinuclear complexes, $[FeMoS_4R_2]^{2-}$ where R = SPh, S-p-Tol, or Cl, and sulfide to yield the $[Fe_2Mo_2S_{10}]^{4-}$ ion.

$$2[FeMos_4R_2]^2 + 2s^2 - \frac{MeCN}{m} [Fe_2Mo_2S_{10}]^4 + 4R^2$$

A number of sulfide sources were employed in attempts to carry out the above reaction: (1) a crown complex of Na₂S, (2) NaHS, (3) (Et₄N)HS, and (4) (Et₄N)HS and proton sponge. Reagents (2) and (4) produced the very stable $[Fe(MoS_4)_2]^{3-}$ ion¹¹ on reaction with equivalent amounts of one of the $[FeMoS_4R_2]^{2-}$ ions. Reaction of reagent (1) with the $[FeMoS_4Cl_2]^{2-}$ ion in a 1:1 ratio resulted in a solution that gave an electronic spectrum similar to that of the $[Fe_2Mo_2S_{10}]^{4-}$ ion; unfortunately, similarities between the solubility of the crown complex of NaCl (as product) and the desired product prevented isolation of pure $[Fe_2Mo_2 S_{10}]^{4-}$. Finally, reaction of reagent (3) with the [FeMo- $S_4Cl_2]^{2-}$ ion in a 1:1 ratio also produced the $[Fe(MoS_4)_2]^{3-}$ ion¹¹, but addition of excess (Et₄N)HS followed by filtration

of a presumed decomposition product and storage of the mother liquor at -20°C for approximately five months afforded the $[Fe_2Mo_2S_{10}]^{4-}$ ion in extremely low yield. As a result, the only even moderately practical synthesis of the $(Et_4N)_4[Fe_2Mo_2S_{10}]$ complex is via the tetrathiomolybate (VI) and $[Fe_{4}S_{4}(SAr)_{4}]^{2-}$ route. Attempts to improve the yield of the tetrathiomolybdate(VI) route took three forms: first, addition of a large excess of tetrathiomolybdate (VI); second, reaction at elevated temperature; and third, use of alkylthiolate Fe-S tetramers. The first method compounded the difficulty of isolating pure product due to contamination by the MoS_{ll}^{2-} salt, while the second method induced rapid decomposition of the entire reaction mixture after heating at 55°C for time periods that exceeded 2 hours. The third method produced the $[Fe_{2}Mo_{2}S_{10}]^{4}$ ion in low, almost minute, quantities when the $[Fe_{\mu}S_{\mu}(SEt)_{2}]^{2-}$ and $[Fe_{\mu}S_{\mu}(S-t-Bu)_{\mu}]^{2-}$ tetramers were used. These complexes were thought more suitable because after shorter reaction times (i.e., weeks) they did not yield alkyltrimers (i.e., $[Fe_2MoS_6(SR)_2]^{3-}$ where R = alkyl), but instead gave solutions whose spectra exhibited lower energy absorption features possibly attributable to the $[Fe_2Mo_2S_{10}]^4$ complex.

Despite severe limitations encountered in the aforementioned sulfide attempts, the potential of this synthetic route cannot be entirely disregarded. The sulfide sources

used were not satisfactory from a synthetic viewpoint. Synthesis of a Q_2S salt (where Q^+ = tetraalkylammonium cation or lithium) could provide the necessary means to generate the $[Fe_2Mo_2S_{10}]^{4-}$ ion from smaller fragments. Also, should this synthetic method prove viable for the $[FeMoS_4L_2]^{2-}$ ions (L = SAr, Cl), successful synthesis of the $[Fe_2W_2S_{10}]^{4-}$ complex might prove possible. The synthesis and reactivity are summarized in Figure 13.

2. Electronic Spectrum

The electronic absorption spectrum of $(Et_4N)_4[Fe_2 Mo_2S_{10}$] is shown in Figure 14; peak positions and molar absorptivities are compiled in Table XII. Deep blue solutions of the complex in MeCN exhibit an electronic spectrum characteristic of the general class of Mo-Fe-S compounds. Most notable are two peaks (518 and 608 nm) that are the longest wavelength features observed in any Mo-Fe-S complex to date. Qualitatively, this is in accord with the length of the metal-sulfur network; the longer the metal-sulfur network, the lower the energy of the first visible absorption band. The absorption pair, 518 and 608 nm, are two members of an absorption triad common to $[Fe_2Mos_6(SAr)_2]^{3-1}$ and $[Fe(MoS_{\mu})_{2}]^{3-}$ ions¹¹, occurring at 578, 510, and 442 nm and 583, 510, and 409 nm, respectively. The last member of the $[Fe_2Mo_2S_{10}]^{4-}$ triad is found at 398 nm and represents the largest high energy shift within this group. It is



Figure 13. Synthesis and Reactivity of $[Fe_2Mo_2S_{10}]^4$ in MeCN.



Figure 14. Electronic spectrum of $(Et_4N)_4[Fe_2Mo_2S_{10}]$ in acetonitrile solution at 23°C.

Table XII. Selected Physical Data for the $(Et_4N)_4[Fe_2-Mo_2S_{10}]$ Complex.

Electronic	604(16.3), 518(15.0), 450(sh)
spectral	398(23.8), 347(32.4), 320(sh),
features ^a	296(sh), 224(55.7)
Magnetic	
$susceptibility^b$	1.35 BM
Electrochemical data ^C	Reduction: -1.54 V (irrev)

^aIn MeCN solution at 23°C, $\lambda_{max}(\epsilon)$ in nm (M⁻¹cm⁻¹ x 10⁻³).

^bIn solid state at 23°C, corrected for diamagnetic contributions.

^cat 22°C, 50 mM (Et₄N)ClO₄, MeCN, dme.

clear from the electronic absorption spectra of $[Fe_2Mo_2-S_{10}]^{4-}$, $[Fe_2Mo_5(SAr)_2]^{3-}$, and $[Fe(MoS_4)_2]^{3-}$ that the complexes are rather similar in electronic structure.

3. Magnetic Susceptibility

The room temperature magnetic susceptibility of solid $(Et_4N)_4[Fe_2Mo_2S_{10}]$ was determined according to the Faraday method. The complex yielded a value of 1.35 BM per formula unit at 295 K (the value is corrected for the diamagnetic contributions of the ligands and cations). This value is smaller than the ideal S = 1/2 value of 1.73 BM and supports the proposed formulation, in which two Fe(II) nuclei are linked through sulfur bridges. The proposed structure provides for antiferromagnetic coupling of the two Fe(II) S = 2) systems, yielding a reduced value of the effective magnetic moment. This corrected magnetic moment correlates well with the corrected magnetic moment of the parent iron-sulfur dimer³, $[Fe_2S_2(S-p-Tol)_{\mu}]^{2-}$, which has a magnetic moment of 1.98 BM per mole. The slightly larger magnetic moment of the 2Fe dimer is attributed to the two Fe(III), S = 5/2, centers. Since the $[Fe_2Mo_2S_{10}]^4$ complex is essentially a doubly reduced Fe_2S_2 core stabilized by two tetrathiomolybdate ligands, the comparison between the binuclear 2Fe system and the tetranuclear 2Fe-2Mo system is particularly useful. Other considerations are the possibility that intermolecular interactions may be

present in addition to the intramolecular effects. Solid and solution Mossbauer and variable temperature susceptibility studies will be necessary for a more complete understanding of the magnetic properties of this new Mo-Fe-S system.

4. Electrochemistry

The $(Et_4N)_4[Fe_2Mo_2S_{10}]$ complex was studied by dc polarographic methods in approximately 1 mM solutions in Gold Label MeCN containing ca. 50 mM (Et₄N)ClO₄; a dropping mercury electrode (0.5 s/drop) was the working electrode. Electrochemical scans over the range +1.0 to -2.0 V (versus the standard calomel electrode) exhibited a single reduction at -1.54 V and no discernible oxidation wave. The slope of the log $[i/i_d-i]$ vs. potential plot was 70 mV for the 2Fe-2Mo complex, indicating quasi-reversible electrochemical behavior. The absence of a welldefined oxidation was entirely consistent with similar observations for the other Mo-Fe-S systems discussed above. The reduction occurs at relatively negative potential, but is consistent with the value of the reduction for the $[Fe(MoS_{\mu})_{2}]^{3-}$ ion at -1.8 V¹¹ and the understanding that the tetranuclear complex is already a highly reduced system.

5. Summary

Preparation of the $(Et_4N)[Fe_2Mo_2S_{10}]$ complex can be accomplished by several means, but only the reaction of 4 equivalents of tetrathiomolybdate (VI) with 1 equivalent of $[Fe_{\mu}S_{\mu}(SAr)_{\mu}]^{2-}$ (Ar = Ph, <u>p</u>-Tol) provides the complex in approximately 15% yield in a reasonable length of time. The 2Fe-2Mo complex is best formulated as a linear arrangement of four metal atoms (Mo-Fe-Fe-Mo) with six bridging sulfur atoms and four terminal sulfur atoms. All metal atoms are predicted to be approximately tetrahedrally coordinated by sulfur atoms. The 2Fe-2Mo complex exhibits an electronic spectrum similar to the two trimeric complexes, $[Fe_2MoS_6(S-p-Tol)_2]^{3-}$ and $[Fe(MoS_4)_2]^{3-}$; all three complexes are considered to be highly "reduced" Mo-Fe-S systems. Reactivity studies and electrochemical and magnetic susceptibility data support the proposed structure, and suggest formal assignment of oxidation states as Mo(VI)-Fe(II)-Fe(II)-Mo(VI).

IV. CONCLUSIONS

The $[FeMS_4Cl_2]^{2-}$ complexes (M = Mo,W) are the simplest Mo(W)-Fe-S structural units known and can be prepared through combination of equivalent amounts of MS_{4}^{2-} and FeCl₂ in MeCN. X-ray diffraction studies have shown that the anions exhibit essentially tetrahedral coordination about each metal atom. The dinuclear complexes can be converted to a number of products including the thiolate derivatives, $[FeMS_{4}(SAr)_{2}]^{2-}$ (M = Mo,W and Ar = Ph, <u>p</u>-Tol), and the $[Fe_2Mo_2S_{10}]^{4-}$ ion by appropriate methods. These reactions are performed with retention of the FeS2Mo core and suggest that this core is a relatively stable inorganic unit. Magnetic susceptibility and Mössbauer spectroscopy studies indicate that the FeS₂Mo core is best described as containing a high spin Fe(II)-Mo(VI) interaction. Electronic absorption and dc polarographic studies have also been performed. Differences between the molybdenum and tungsten derivatives are small but predictable.

The $[Fe_2MS_6(SAr)_2]^{3-}$ complexes (M = Mo,W and Ar = Ph, p-Tol) represent the next Mo(W)-Fe-S structural type of the three member series presented in this text. The trinuclear complexes may be prepared through combination of tetrathiomolybdate (VI) with $[Fe_4S_4(SAr)_4]^{2-}$ or

 $[Fe_2S_2(SAr)_4]^{2-}$ in MeCN solution. The structure of the $[Fe_2MoS_6(S-p-Tol)_2]^{3-}$ ion indicates that the metal atoms are arranged linearly and tetrahedrally coordinated with sulfur and thiolate. Replacement of the terminal thiolate ligands by halide, as observed for $[FeMS_4(SAr)_2]^{2-}$ ions, is not possible. Magnetic susceptibility, and ESR and Mössbauer spectra suggest an antiferromagnetically coupled high spin Fe(III)-Fe(II)-Mo(VI) configuration. Electronic absorption and dc polarographic studies have also been performed. The $[Fe_2MS_6(SAr)_2]^{3-}$ ions are more sensitive to oxygen and moisture and attack by electrophilic reagents than their $[FeMS_4(SAr)_2]^{2-}$ counterparts.

The $[Fe_2Mo_2S_{10}]^{4-}$ complex, the last member of the series, may be prepared in low yield by a number of means, but the most useful is a permutation of the tetrathiomolybdate (VI) and aryl tetramer method used for the $[Fe_2MoS_6(SAr)_2]^{3-}$ ions. The structure of the tetranuclear anion has not yet been determined. However, the reactivity, electronic absorption spectrum, and the magnetic susceptibility studies on the $[Fe_2Mo_2S_{10}]^{4-}$ complex indicate that it probably contains a linear array of metal atoms with each metal atom tetrahedrally coordinated by sulfur atoms. A dc polarographic study was also performed.

The $[Fe_2MS_6(SAr)_2]^{3-}$ and $[Fe_2Mo_2S_{10}]^{4-}$ complexes may be viewed as containing singly and doubly reduced forms of the $[Fe_2S_2]^{2+}$ core found in the $[Fe_2S_2(SAr)_2]^{2-}$ ion,

where in each case the ferrous iron state is stabilized through coordination of a tetrathiomolybdate (VI) ligand.

The synthesis and characterization of this series of di-, tri-, and tetranuclear complexes provide some insight regarding the nature of the iron-molybdenum-cofactor of nitrogenase. Structural and stoichiometric arguments preclude consideration of these complexes as detailed models for the FeMo-cofactor. The major contributions to understanding the general physical and chemical behavior of Mo-Fe-S and W-Fe-S systems are the evident stability of the FeS₂Mo unit, the finding that the Fe₄S₄ core rearranges readily upon reaction with the tetrathiomolybdate (VI) anion, and the utility of these new complexes for calibrating the EXAFS spectra of the FeMo-cofactor. A variety of lines of evidence suggest that the FeS₂Mo unit will be an important structural fragment of the ironmolybdenum-cofactor of nitrogenase.

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(d) $(Et_4N)_2MoS_4$, $(BzEt_3N)_2MoS_4$, $(Ph_4As)_2MoS_4$, $(Et_4N)_2-WS_4$: via a metathesis reaction with either $(NH_4)_2MS_4$ or K_2MS_4 (M = Mo,W) and the appropriate quaternary ammonium or arsonium salt, see also 6(a). Т
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