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THE SYNTHESIS, CHARACTERIZATION, AND REACTIVITY OF MOLYBDENUM AND TUNGSTEN - IRON - SULFUR COMPLEXES

Ву

Harry Craig Silvis

A DISSERTATION

Submitted to

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ABSTRACT

THE SYNTHESIS, CHARACTERIZATION, AND REACTIVITY OF MOLYBDENUM AND TUNGSTEN - IRON - SULFUR COMPLEXES

Bу

Harry Craig Silvis

The binuclear complexes $[FeMS_{4}X_{2}]^{2-}$ (M = Mo, W; X = SAr, OAr) have been prepared by ligand exchange reactions with $[FeMS_4Cl_2]^{2-}$ and either triethylamine/aryl thiol or sodium thiolate or phenolate. The thiolate and phenolate complexes react with benzoyl chloride to form $[FeMS_4Cl_2]^{2-}$. The X-ray crystal structures of the tetraethylammonium salts of $[FeMoS_4(SPh)_2]^2$, $[FeWS_4(SPh)_2]^2$, and $[FeMoS_4-$ (OPh)₂]²⁻•MeCN have been determined. All structures contain a bimetallic unit bridged by two sulfides, with terminal sulfides on molybdenum or tungsten and thiolate or phenolate ligands on iron. The optical and infrared spectra of these complexes have been obtained. Electrochemical measurements demonstrate a single irreversible reduction between -1.0 and -2.0 volts. Mössbauer spectra have been recorded at 4.2 K in zero applied magnetic field and show simple quadrupole doublets. Magnetic susceptibility measurements

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at room temperature on all binuclear complexes yield $\mu_{eff}^{corr} = 4.9 - 5.1$ BM, consistent with an S = 2 ground state. Temperature-dependent magnetic susceptibility results and magnetic Mössbauer data on $[\text{FeMoS}_4(\text{SPh})_2]^{2-}$ suggest an Fe(II) - Mo(VI) description of these complexes. Proton NMR spectra of these complexes show isotropically shifted resonances for the aromatic ring protons which increase with decreasing temperature. The pattern of these shifts indicate that they arise from dominant contact interactions. Evidence suggests that $[\text{FeMoS}_4(\text{SPh})_2]^{2-}$ and $[\text{FeMoS}_4\text{Cl}_2]^{2-}$ are converted to $[\text{Fe}(\text{MoS}_4)_2]^{3-}$ under reducing conditions. The reactivity of the FeS₂Mo core towards a variety of other reagents has been examined.

The trinuclear complex $[Fe_2MoS_{11}]^{3-}$ has been synthesized. Its optical, infrared, and Mössbauer spectra suggest that it possesses a core structure analogous to that of $[Fe_2MoS_6-(S-p-Tol)_2]^{3-}$.

Reactions of $[Fe_4S_4X_4]^{2-}$ (X = SPh, S-<u>t</u>-Bu, and Cl) with MoS_4^{2-} have been examined. When X = S-<u>t</u>-Bu or Cl, the primary product is $[Fe(MoS_4)_2]^{3-}$. When X = SPh, the product is $[Fe_2MoS_6(SPh)_2]^{3-}$.

The reactions of the complexes $[MoS_9]^{2-}$, $[Mo_2(SPh)_9]^{3-}$, $[MoO(SPh)_4]^-$, and $[MoCl_6]^{3-}$ with a variety of iron species have been investigated in an attempt to synthesize new cluster complexes.

To Cindy, Harry, Louise, and Grace.

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Thank you.

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LIST OF ABBREVIATIONS

<u>Solvents</u>:

MeCN =	acetonitrile
MeOH =	methanol
EtOH =	ethanol
Et ₂ 0 =	diethyl ether
THF =	tetrahydrofuran
NMF =	N-methylformamide
DMF =	N,N-dimethylformamide
DMA =	N,N-dimethylacetamide
DMSO =	dimethylsulfoxide
HMPA =	hexamethylphosphoramide

<u>Reagents</u>:

PhCOCl	= benzoyl chloride
MeI	= methyl iodide
MeMgCl	= methylmagnesium chloride
Et ₃ N	= triethylamine
Me ₃ py·HCl	= trimethylpyridine hydrochloride
ACN	= acenaphthalene

Miscellaneous:

Et ₄ N	=	tetraethylammonium
Me ₄ N	=	tetramethylammonium
Ph ₄ As	=	tetraphenylarsonium
Ph	=	phenyl
<u>p</u> -tol	=	<u>para-tolyl</u>
Bz	=	benzyl
Me	=	methyl
Et	=	ethyl
BM	=	Bohr magneton
SCE	=	standard calomel electrode

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I. INTRODUCTION

In recent years, there has been an increased interest in the structure and function of inorganic metal complexes within biological systems. Actual modeling of these metal centers outside their native protein environments has met with mixed success. The most notable example of this to date has been the synthesis of one, two, and four ironsulfur complexes, which mimic those found in the ferredoxin and rubredoxin electron-transfer proteins.¹

Lately, much attention has been focused on the enzyme, nitrogenase, which is responsible for the catalytic reduction of dinitrogen to ammonia in aerobic and anaerobic micro-organisms. The enzyme itself consists of two components. The first is an iron protein (MW \sim 60,000), containing four iron atoms and four acid-labile sulfur atoms (<u>i.e.</u>, sulfide) per molecule. Spectroscopic and cluster displacement evidence indicate that the iron and sulfur are arranged in a normal Fe₄S₄ cluster complex.² The second component is a molybdenum-iron protein (MW \sim 220,000), which contains ca. 32 iron atoms, 32 sulfides, and 2 molybdenum atoms per molecule.² Roughly half of the iron and sulfide are arranged in Fe₄S₄ centers, where one of the iron atoms in each cluster is distinguishable from

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the other three by Mössbauer spectroscopy.³ The Mössbauer parameters of the unique iron atom resemble those of highspin iron (II) in a tetrahedral sulfur environment.⁴ The remaining iron, sulfur, and molybdenum are contained within a low molecular weight cofactor,⁵ which can be separated from the rest of the iron-molybdenum protein. This cofactor contains six to eight iron atoms and ca. six sulfides per molybdenum atom in a unique cluster arrangement. Relevant spectroscopic methods employed to characterize the cofactor include electron paramagnetic resonance (EPR). Mössbauer, and extended X-ray absorption fine structure (EXAFS) spectroscopy. The low-temperature (6-20 K) EPR spectrum of the cofactor displays an axial signal⁶ with slight rhombic distortion (g-values 2.0, 3.8, and 4.3). This spectrum corresponds to one of the Kramers doublets of an S = 3/2 system.⁶,⁷ Cofactor from organisms grown on 95 Mo (I = 5/2) shows no detectable hyperfine broadening in the EPR spectrum, in contrast to results from organisms grown on 57 Fe (I = 1/2).⁸ Molybdenum K-edge EXAFS results indicate two⁹ or three¹⁰ iron atoms at ca. 2.71 Å and four or five sulfur atoms at ca. 2.35 Å as nearest neighbors to the molybdenum.

The actual reaction sequence which results in dinitrogen reduction involves reductive dephosphorylation. For every two electrons transferred to substrate, at least four ATP molecules are hydrolyzed to ADP.¹¹ Studies

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indicate that electrons are transferred from external reductant (reduced ferredoxin) to the iron protein, then to the molybdenum-iron protein, and ultimately to substrate.² Furthermore, recent results suggest that oxygen ligands may be coordinated to the iron atoms within the cofactor.¹²⁻¹⁴

Due to the extreme oxygen sensitivity and other difficulties in purification of the cofactor, resolution of the structure by crystallographic techniques in the near future seems unlikely. Therefore, in order to ascertain the structure and functioning of this unprecedented arrangement of iron, molybdenum, and sulfur, it seemed worthwhile to synthesize polynuclear metal complexes containing these elements, characterize them, and investigate their reactivity.

Intensive synthetic efforts by several groups have resulted in two basic categories of Fe-Mo-S compounds. The first includes the so-called "cubane" complexes such as $[Fe_6Mo_2S_8(SR)_9]^{3-}$, $[Fe_6Mo_2S_9(SR)_8]^{3-}$, $[Fe_7Mo_2S_8(SR)_{12}]^{3-,4-}$, and $[Fe_4MoS_4(SR)_3(C_6H_4O_2)_3]^{3-}$, synthesized by Holm¹⁵ and Garner.¹⁶ They result from "self-assembly" reactions involving simple reagents analogous to the strategy used to prepare the ferredoxin analogs. The common feature of all these complexes is the Fe_3MoS_4 core unit. However, the stoichiometry and EXAFS results for these complexes indicate that they are not true synthetic models for the

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cofactor.15a

The second class of Fe-Mo-S complexes are those possessing the FeS₂Mo core unit. They include heteronuclear dimers of the type $[FeMoS_4X_2]^{2-}$ (X = SAr, OAr, Cl or X₂ = S_5)¹⁷⁻¹⁹ and various linear trimers^{20,21} such as $[Fe_2MoS_6X_2]^{3-}$ (X = SAr; X₂ = S_5), $[Fe(MoS_4)_2]^{3-}$, and $[Fe_2MoS_4Cl_2]^{2-}$. A linear tetramer of formula $[Fe_2Mo_2S_{10}]^{4-}$ has also been prepared.²²

The research described herein deals primarily with the synthesis, characterization, and selected reactivity of the heteronuclear dimer complexes, $[\text{FeMS}_4X_2]^{2-}$ (X = SAr, OAr) and the trimeric complex, $[\text{Fe}_2\text{MoS}_{11}]^{3-}$. In addition, tungsten analogs of the dimeric complexes have been prepared, and their properties compared to their molybdenum counter parts.

II. EXPERIMENTAL

A. Materials and Methods

All operations were performed in an atmosphere of dinitrogen prepurified by sequential passage over hot BASF R3-11 catalyst to remove oxygen and through supported phosphorus pentoxide (Aquasorb) to remove water. Solutions and solvents were degassed prior to use by repeated evacuation and flushing with purified dinitrogen. MeCN, MeOH, and THF were distilled from calcium hydride, magnesium methoxide, and sodium/benzophenone or lithium aluminum hydride, respectively. NMF and HMPA were vacuum distilled from barium oxide. PhCOCl and MeI were distilled from barium oxide and 4 Å molecular sieves, respectively, at room temperature by using a liquid nitrogen trap. Spectrograde DMA (Aldrich Chemical Co., Gold Label), along with Et₃N, were stored over 4 Å molecular sieves. PhOH and \underline{p} -TolOH were vacuum sublimed and distilled, respectively, by Walter Cleland. ACN was recrystallized from MeOH. Thiols and all other reagents were of commercial reagent grade and used without further purification. Ammonium 23 and tetraalkylammonium^{15a} salts of tetrathiomolybdate and tetrathiotungstate, $(Et_4N)_2[FeMoS_4Cl_2]$,¹⁷ $(Et_4N)_2[Fe_4S_4 (SPh)_{\mu}],^{24} (Me_{\mu}N)_{2}[Fe_{\mu}S_{\mu}(S-\underline{t}-Bu)_{\mu}],^{24} (Et_{\mu}N)_{3}[Mo_{2}(SPh)_{9}],^{25}$

 $(Et_4N)[MoO(SPh)_4]$,²⁵ and $(Et_4N)_2[MoS_9]^{26}$ were prepared by published procedures. Ferrous chloride,²⁷ $(Et_4N)_2$ - $[Fe_2S_2(SPh)_42]^{28}$ and $(Et_4N)_2[Fe_4S_4Cl_4]^{29}$ were prepared by Robert Tieckelmann as described.

 $(Et_4N)_3[MoCl_6]$ was prepared by electrolyzing a solution of molybdenum trioxide dissolved in 6N hydrochloric acid for four hours at -2.2 volts. Three equivalents of Et_4NCl were added and the solution was saturated with hydrogen chloride gas. Addition of EtOH and subsequent cooling to -20°C yielded the product, $(Et_4N)_3[MoCl_6]$, as red plate-like crystals in 16% yield.

Tetraethylammonium thiophenoxide was prepared by adding PhSH to a solution containing one equivalent of NaOMe in MeOH, and then adding this solution to one containing one equivalent of Et_4 NCl in isopropanol. Sodium chloride precipitated immediately and was filtered off. Volume reduction of the filtrate caused separation of the product as white crystals in 80% yield. These were filtered, washed with hexane, and dried in vacuo. An NMR spectrum indicated the absence of water and other solvents.

Sodium salts of thiophenols and phenols were prepared by reaction with one equivalent of NaOMe in MeOH, evaporation to dryness, evaporation twice with MeCN and drying in vacuo. Stock solutions of sodium or lithium acenaphthalenide were generated by reaction of the metal with ACN in DMA. The concentration of ACN radical anion was determined by titration with a standard solution of iodine in DMA. Methylmagnesium chloride was purchased from Aldrich Chemical Co. as a THF solution and was assayed according to the method of Gilman.³⁰

Optical spectra were recorded by means of a Cary Model 17 or Cary 219 spectrophotometer. Infrared spectra were obtained with a Perkin-Elmer Model 457 grating spectrophotometer by using Nujol mulls between polyethylene plates. Proton NMR spectra were taken by means of a Bruker Model WH-180 or WM-250 Fourier transform spectrometer. Roomtemperature magnetic susceptibility measurements were performed with an Alpha Faraday balance by using $Hg[Co(SCN)_{\mu}]$ as a calibrant. Variable temperature data were obtained at Bell Laboratories by J. V. Waszczak using a Faraday-type apparatus already described.³¹ Electrochemical measurements were made with a PAR Model 174A polarographic analyzer employing either dc polarography (dropping mercury electrode) or cyclic voltammetry (platinum electrode). EPR spectra were recorded by means of a Varian E-4 spectrometer operating at 9.1 GHz and equipped with an Oxford cryostat for operation from 4 to 300° K. The Mossbauer spectra were obtained by T. A. Kent and B. H. Huynh at the Gray Freshwater Biology Laboratory, University of Minnesota, Navarre, Minnesota. The Mössbauer spectrometer was of the constant acceleration type and has been described elsewhere.³² The velocity scale of the instrument was calibrated with iron foil at room temperature. Melting

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B. <u>Preparation of $(Et_4N)_2[FeMS_4(SR)_2]$ (M = Mo, W; R =</u> Ph, <u>p</u>-Tol)

1. [FeMoS₄(SPh)₂]²⁻. Method A.

To 2.45 g of the compound formulated as $(\text{Et}_4\text{N})_3^ [\text{Fe}(\text{MoS}_4)_2]^{20a}$ was added a solution of 37 mL of PhSH and 50 mL of Et₃N (\sim 300 eq. of (Et₃NH)(SPh)) in 40 mL of MeCN. The solution changed from red-violet to red-orange upon stirring for 1-2 h. The product precipitated as brick red microcrystals upon the addition of 100 mL of THF. It was filtered, washed with THF, and then redissolved in an MeCN/THF mixture (\sim 3:1) at room temperature, filtered, and cooled to -20°C. The product crystallized as 1-2 mm redblack prisms in \geq 50% yield (mp 126-128°C dec). Anal. Calcd for C₂₈H₅₀N₂S₆FeMo: C, 44.32; H, 6.64; N, 3.69; S, 25.35; Fe, 7.36; Mo, 12.64. Found: C, 44.20; H, 6.42; N, 3.86; S, 25.50; Fe, 7.55; Mo, 13.02.

2. <u>Method B</u>.

To 0.20 g (0.33 mmol) of $(Et_4N)_2[FeMoS_4Cl_2]$ was added a solution containing 0.13 mL of PhSH and 0.18 mL of Et_3N (1.3 mmol of $(Et_3NH)(SPh)$) in 15 mL of MeCN. The reaction was instantaneous as indicated by an immediate color change from yellow-brown to red-orange. The crude product was precipitated as microcrystals by the slow addition of 40 mL of THF, filtered, washed with THF, and recrystallized as above (yield \sim 45%).

3. $[FeMoS_4(S-p-Tol)_2]^{2-}$. Method A.

This compound was prepared by Method A above and obtained as red-black prisms (mp 131-134°C dec) after recrystallization from MeCN/THF. Anal. Calcd for $C_{30}H_{54}N_2$ - S_6 FeMo: C, 45.78; H, 6.92; N, 3.56. Found: C, 45.77; H, 6.80; N, 3.58. Method B also afforded this compound if a large excess (~100 eq.) of PhSH/Et₃N was used.

4. Method C

To 0.86 g (1.41 mmol) of $(\text{Et}_4\text{N})_2[\text{FeMoS}_4\text{Cl}_2]$ was added 0.44 g (3.01 mmol) of NaS-p-Tol. The solids were slurried in 40 mL of MeCN and allowed to stir overnight, whereupon the color of the solution changed from yellow-brown to redorange with precipitation of NaCl. The solution was reduced in volume by $\sim 25\%$ in vacuo and then filtered. Upon the slow addition of THF, red microcrystals precipitated. These were filtered, washed with THF, and recrystallized as described above (yield $\sim 80\%$).

5. $[FeWS_4(SPh)_2]^{2-}$. Method B.

This compound was prepared by Method B above and afforded dark red prisms (mp 129-131°C dec) after recrystallization from MeCN/THF. Anal. Calcd for $C_{28}H_{50}N_2S_6FeW$: C, 39.71; H, 5.95; N, 3.31; S, 22.72; Fe, 6.60; W, 21.71. Found: C, 39.59; H, 6.10; N, 3.34; S, 22.88; Fe, 6.66; W, 21.47.

6. $[FeWS_4(S-p-Tol)_2]^{2-}$. Method B.

This compound was likewise prepared by Method B and obtained as dark red prisms (mp 169-172°C dec) after recrystallization from MeCN/THF. Anal. Calcd for $C_{30}H_{54}-N_2S_6FeW$: C, 41.18; H, 6.22; N, 3.20. Found: C, 41.54; H, 6.22; N, 3.30.

- C. Preparation of $(Et_4 N)_2 [FeMS_4 (OR)_2]$ (M = Mo, W; R = Ph, p-Tol).
 - 1. $[FeMoS_4(OPh)_2]^2$

A mixture of 5.74 g (9.39 mmol) of $(\text{Et}_4\text{N})_2[\text{FeMoS}_4\text{Cl}_2]$ and 2.45 g (21.1 mmol) of anhydrous NaOPh were taken up in 250 mL of MeCN. Upon being stirred overnight, the color of the solution changed from yellow-brown to red-orange accompanied by precipitation of finely divided NaCl. The volume was reduced to ~150 mL in vacuo and the mixture
was filtered. With the addition of 200 mL of anhydrous Et_2O , the product precipitated as small, brick red plates, which were filtered, washed with Et_2O , and vacuum dried. The product was dissolved in a minimum of MeCN/Et₂O (~2:1), filtered, and cooled to -20°C, whereupon the product crystal-lized as 1-2 mm dark red plates in 65% yield (mp 87-90°C dec). Anal. Calcd for $C_{28}H_{50}N_2O_2S_4FeMo$: C, 46.27; H, 6.94; N, 3.86; S, 17.65. Found: C, 46.84; H, 6.70; N, 3.56; S, 16.98. When saturated solutions of this compound were allowed to cool very slowly, the material crystallized as an MeCN solvate (1:1). These crystals were 3-4 mm blades which were more suitable for X-ray analysis than the unsolvated material.

2. $[FeMoS_4(0-p-Tol)_2]^{2-}$.

This compound was prepared in the same manner as the -OPh analog described above. After recrystallization from MeCN/Et₂O, the product was obtained as ca. 1 mm dark red plates in 60% yield (mp 112-115°C dec). Anal. Calcd for $C_{30}H_{54}N_2O_2S_4FeMo$: C, 47.73; H, 7.21; N, 3.71. Found: C, 48.40; H, 7.48; N, 3.50.

3. [FeWS4(OPh)2]²⁻

This compound was likewise prepared as described above, using $(Et_4N)_2[FeWS_4Cl_2]^{33}$ and NaOPh. Upon recrystallization

from MeCN/THF (\sim 2:1), the product was obtained as wellformed 3-4 mm golden blades (mp 126-130°C dec). Elemental analysis results indicated the product to be a 1:1 MeCN solvate. This was confirmed by NMR methods as well. Anal. Calcd for $C_{30}H_{53}N_{3}O_{2}S_{4}FeW$: C, 42.11; H, 6.24; N, 4.91; S, 14.99. Found: C, 42.49; H, 6.36; N, 4.77; S, 14.63.

4. [FeWS4(0-p-Tol)2]2-

This compound was synthesized by the same method used to prepare the -OPh analog. Recrystallization from MeCN/ THF afforded the product as 1-2 mm gold-brown plates in 45% yield (mp 138-140°C dec). Anal. Calcd for $C_{30}H_{54}N_2$ - O_2S_4FeW : C, 42.76; H, 6.46; N, 3.32. Found: C, 43.43; H, 6.66; N, 3.29.

D. <u>Preparation of (Et₄N)₃[Fe₂MoS₁₁]</u>

1. $(Et_4N)_2[Fe_2S_{12}]$

A solution of 3.1 g (18.5 mmol) of anhydrous FeCl₃ in 15 mL of MeCN was quickly filtered and added to one containing 17.7 g (74.0 mmol) of $(Et_4N)(SPh)$ in 150 mL of MeCN. The resultant purple-brown mixture was added to 4.8 g (148.0 mmol) of elemental sulfur. Upon being stirred overnight, the mixture turned deep red-brown and much of the product precipitated as black microcrystals. Upon addition of 75 mL of THF, the remainder of the product separated. After filtration, the solid was dissolved in a minimum of warm MeCN/DMSO (\sim 9:1, v/v), filtered, and allowed to cool to -20°C. The product crystallized as small black prisms; the optical spectrum in MeCN corresponded exactly to that described by Coucouvanis and coworkers, who report an alternate synthesis.³⁴

2. <u>(Et₄N)₃[Fe₂MoS₁₁]</u>

A solution of 1.7 g (2.3 mmol) of $(\text{Et}_4\text{N})_2[\text{Fe}_2\text{S}_{12}]$ and 1.1 g (2.3 mmol) of $(\text{Et}_4)_2\text{MoS}_4$ in 150 mL of MeCN was allowed to stir until the optical spectrum of the reaction solution became constant (\sim 4 days). The product was precipitated in microcrystalline form by the slow addition of Et₂0, filtered, washed with Et₂0, and dried in vacuo. It was then dissolved in a minimum of MeCN/Et₂0 (\sim 2:1) at room temperature, filtered, and allowed to cool slowly to -20°C, whereupon the product precipitated in microcrystalline form. It was filtered, washed with Et₂0, and vacuum dried. The yield was ca. 50% (mp 205-207°C dec). Anal. Calcd for C₂₄H₆₀N₃S₁₁Fe₂Mo: C, 30.31; H, 6.36; N, 4.42; S, 37.09. Found: C, 30.07; H, 6.06; N, 4.22; S, 38.02. Efforts to prepare the tungsten compound by an analogous route failed.

E. Interconversion Chemistry

1. $[FeMoS_4(SPh)_2]^2 \rightarrow [FeMoS_4Cl_2]^2$

To 8.0 mL of a 11.0 mM solution of $(\text{Et}_4\text{N})_2[\text{FeMoS}_4-(\text{SPh})_2]$ in MeCN was added 210 µL of a 0.86 M solution of PhCOCl in MeCN. The color of the reaction solution changed from red-orange to yellow-brown within five minutes. An optical spectrum of the solution confirmed quantitative formation of $[\text{FeMoS}_4\text{Cl}_2]^{2-}$.

2. $[FeMoS_4(SPh)_2]^2 \rightarrow [FeMoS_9]^2$

Reaction of 0.30 g (0.28 mmol) of $(Ph_4As)_2[FeMoS_4 (SPh)_2]$ with 0.04 g (1.25 mmol) of elemental sulfur in 40 mL of MeCN for two days resulted in a gradual color change from red-orange to red-brown. The optical spectrum of the reaction solution corresponded exactly to that of $[FeMoS_9]^{2-}$ prepared by a different procedure.^{19a}

3. $\frac{[\text{FeMoS}_{4}(\text{OPh})_{2}]^{2-} \rightarrow [\text{FeMoS}_{4}\text{Cl}_{2}]^{2-}}{\text{FeMoS}_{4}\text{Cl}_{2}}$

To 5.0 mL of an 8.6 mM solution of $(\text{Et}_4\text{N})_2[\text{FeMoS}_4-(\text{OPh})_2]$ in MeCN was added 100 $_{\mu}\text{L}$ of an 0.86 M solution of PhCOC1 in MeCN. The color of the solution quickly changed from red-orange to yellow-brown and the optical spectrum indicated quantitative formation of $[\text{FeMoS}_4\text{Cl}_2]^{2-}$.

4.
$$[FeMoS_4(OPh)_2]^2 \rightarrow [FeMoS_4(SPh)_2]^2$$

To ca. 3 mL of an 8.6 mM solution of $(Et_4N)_2[FeMoS_4-(OPh)_2]$ in MeCN was added ca. 1 mL of MeCN containing 50 µL (\sim 20 eq.) of PhSH. The solution color immediately changed from red to red-orange. The optical spectrum of the solution showed that $[FeMoS_4(SPh)_2]^{2-}$ had been formed quantitatively.

5. <u>Tungsten Analog Interconversions</u>

The analogous interconversions outlined in parts 1-4 were observed for the tungsten analogs, $[FeWS_4(SPh)_2]^{2-}$ and $[FeWS_4(OPh)_2]^{2-}$.

F. Reaction of $[FeMoS_4(SPh)_2]^2$ with Acenaphthalene Radical Anion

To a solution containing 3.54 mmol of $(Ph_4As)_2[FeMoS_4-(SPh)_2]$ in 40 mL of DMA was added 3.24 mL (1.1 eq.) of a 1.2 M solution of Na⁺ACN⁺ in THF. The color of the solution changed from red-orange to brown. A black, amorphous solid precipitated upon the slow addition of Et_2O . This solid was filtered, washed with Et_2O , and dried in vacuo. Extraction of the solid with THF gave a brown solution whose optical spectrum was simply a rising absorbance. All attempts to crystallize the brown material met with failure as it slowly decomposed in solution. The remaining solid was soluble in DMSO and only sparingly soluble in DMA or MeCN. Optical spectra of the solid in DMSO/MeCN or DMA resembled those spectra^{20a} obtained for $[Fe(MoS_4)_2]^{3-}$, with peak absorbances near 590, 510, 340, and 290 nm. Also, upon reaction with excess $Et_3N/PhSH$, the compound formed $[FeMoS_4(SPh)_2]^{2-}$, as does $[Fe(MoS_4)_2]^{3-}$. All attempts to recrystallize the material from various solvent systems were unsuccessful.

G. Reaction of $[FeMoS_{4}(SPh)_{2}]^{2}$ with Ferric Chloride and Thiophenoxide

To a filtered solution of 0.80 g (4.9 mmol) of anhydrous FeCl₃ in 30 mL of MeCN was added a solution containing 1.9 mL (18.8 mmol) of PhSH and 2.7 mL (19.5 mmol) of Et_3N in 10 mL of MeCN. A dark green slurry was formed, which became an intense brown solution upon the addition of $1.2 \, \mathrm{g}$ (1.6 mmol) of $(Et_4N)_2$ [FeMoS₄(SPh)₂] in 60 mL of MeCN. The solution was stirred overnight, reduced in volume by ca. 30%, and then filtered. The slow addition of 50 mL of THF to the filtrate precipitated black microcrystals which were filtered off, washed with THF, and dried in vacuo. They were then redissolved in a minimum of MeCN/THF ($\sqrt{4:1}$), filtered, and allowed to cool slowly to -20°C, whereupon small black plates crystallized. These were filtered, washed with THF, and vacuum dried. The optical spectrum of the product in MeCN contained shoulders at ca. 350 and

450 nm on a rising absorbance. The product was recrystallized once more for elemental analysis. Calcd for $(Et_4N)_3$ - $[Fe_6Mo_2S_8(SPh)_9]$, $C_{78}H_{105}N_3S_{17}Fe_6Mo_2$: C, 43.44; H, 4.91; N, 1.95; S, 25.27; Fe, 15.54; Mo, 8.90. Found: C, 44.06; H, 5.22; N, 2.06; S, 23.45; Fe, 15.10; Mo, 8.54. An NMR spectrum of the compound in d₆-DMSO demonstrated broad peaks at -13.0, -5.5, and +3.5 ppm relative to tetramethylsilane for the protons of the phenyl rings. The NMR and analytical data identified the compound as $(Et_4N)_3[Fe_6Mo_2S_8(SPh)_9]$, which had been previously synthesized by Garner and Coworkers.¹⁶

H. <u>Reactions of (Et₄N)₂[FeMoS₄Cl₂]</u>

1. Methyl Iodide

A solution containing 2.33 g (9.60 mmol) of Et_{3}MeNI and 0.30 g (0.96 mmol) of $(\text{Et}_{4}\text{N})_{2}[\text{FeMoS}_{4}\text{Cl}_{2}]$ in 20 mL of MeCN was prepared. The optical spectrum of the solution was monitored for ca. 4 h to verify that iodide was not substituting for chloride in the complex ion. To this solution was added one containing 0.12 mL (1.92 mmol) of MeI in ca. 5 mL of MeCN. A brown solid precipitated immediately and was filtered, washed with MeCN and dried in vacuo. The solid displayed no solubility in common solvents but did dissolve in 6N nitric acid. The optical spectrum of the filtrate was identical to that reported^{20b} for $[Cl_2FeS_2MoS_2FeCl_2]^{2-}$. Addition of 0.20 g (0.41 mmol) of $(Et_4N)_2MoS_4$ in DMF resulted in quantitative conversion to $[FeMoS_4Cl_2]^{2-}$.

2. Benzoyl Chloride

A solution of 90 μ L (0.78 mmol) of PhCOCl in ca. 2 mL of MeCN was slowly added to 22 mL of a 17.7 mM solution (0.39 mmol) of $(Et_4N)_2$ [FeMoS₄Cl₂] in MeCN. A brown solid precipitated during the addition, leaving a nearly colorless filtrate. The filtered solid was insoluble in MeCN, DMSO, and toluene.

3. Methyl Magnesium Chloride

 $({\rm Et}_4{\rm N})_2$ [FeMoS₄Cl₂], 0.11 g (0.18 mmol), was dissolved in 25 mL of HMPA by prolonged stirring. To this solution was added 150 µL (0.53 mmol) of a 3.6 M solution of MeMgCl in THF in dropwise fashion. The color of the solution gradually turned from yellow-brown to red-brown upon stirring, and some solid material precipitated. This was filtered, washed with THF, and vacuum dried. The product was a mixture of light and dark solids. The light material gave a positive chloride test and was most likely magnesium chloride. The dark solid dissolved in MeCN and gave an optical spectrum consistent with $[Fe(MoS_4)_2]^{3-}$. The optical spectrum of the pale filtrate showed only a rising absorbance at short wavelengths.

4. Sodium Diethyldithiocarbamate

 $(Et_4N)_2[FeMoS_4Cl_2]$, 0.12 g (0.20 mmol), and 0.05 g (0.22 mmol) of NaEt₂NCS₂ were slurried in 30 mL of MeCN. Within fifteen minutes, the color of the solution changed from yellow-brown to deep red-violet. An optical spectrum of the reaction mixture revealed formation of $[Fe(MoS_4)_2]^{3-}$.

5. Sodium Benzylthiolate

To 1.0 g (2.0 mmol) of $(Me_4N)_2[FeMoS_4Cl_2]$ was added 0.61 g (4.17 mmol) of NaSCH₂Ph. Both solids were taken up in 50 mL of MeCN and stirred overnight. A significant amount of amorphous solid precipitated and was filtered, washed with MeCN, and vacuum dried. The solid dissolved only in DMSO and water and demonstrated a spectrum corresponding to MoS_4^{2-} . The filtrate was reduced in volume by ca. 50%, filtered, and combined with an equal volume of THF. A small amount (\sim 20 mg) of black solid precipitated; its optical spectrum in MeCN corresponded to mixture of $[Fe(MoS_4)_2]^{3-}$ and MoS_4^{2-} .

I. Reactions of $[Fe_4S_4X_4]^2$ (X = S-t-Bu, SPh, and Cl

1. X = S-t-Butyl

A solution containing 0.10 g (0.12 mmol) of $(Me_4N)_2$ -[Fe₄S₄(S-<u>t</u>-Bu)₄] and 0.23 g (0.48 mmol) of $(Et_4N)_2MoS_4$ in 50 mL of MeCN was prepared. Optical spectra of the reaction solution taken at intervals up to four days indicated no reaction had taken place.

2. $X = S-t-Butyl with Me_3 py \cdot HCl$

To a flask containing 0.68 g (0.79 mmol) of solid $(Me_4N)_2[Fe_4S_4(S-t-Bu)_4]$ was added a solution of 1.18 g (3.18 mmol) of $(Me_4N)_2MoS_4$ dissolved in 40 mL of MeCN and 30 mL of NMF. To this deep orange-brown solution was added a solution containing 0.50 g (3.18 mmol) of Me_3py ·HCl in 50 mL of MeCN. Upon addition of this latter solution, the reaction mixture turned an intense red-violet. After stirring overnight, no evidence of decomposition was noted. THF (~100 mL) was then added to the solution and a violet-black, amorphous solid precipitated; it was filtered, washed with THF, and dried in vacuo. Stirring of the amorphous solid in MeCN overnight resulted in conversion to microcrystals which were filtered, washed with MeCN, and vacuum dried. Anal. Calcd for $C_{48}H_{120}N_6S_{20}Fe_4Mo_4$: C, 17.02; H, 4.30; N, 4.96; S, 37.87; Fe, 13.19; Mo, 22.66

Found: C, 16.94; H, 4.46; N, 4.81; S, 37.65; Fe, 12.90; Mo, 22.32.

3. X = SPhenyl

A solution of 1.54 g (3.17 mmol) of $(\text{Et}_4\text{N})_2\text{MoS}_4$ in 100 mL of warm (~30°C) MeCN. This solution was added to a flask containing 0.83 g (0.79 mmol) of solid $(\text{Et}_4\text{N})_2[\text{Fe}_4\text{S}_4-(\text{SPh})_4]$, which dissolved upon stirring overnight. After several days of stirring, a red-black of microcrystalline material precipitated, which was filtered, washed with THF, and dried in vacuo. The optical spectrum corresponded exactly²¹ to that of $[\text{Fe}_2\text{MoS}_6(\text{SPh})_2]^{3-}$.

4. X = Chloride

To a flask containing 0.40 g (0.53 mmol) of $(\text{Et}_4\text{N})_2$ -[Fe₄S₄Cl₄] solid was added a solution of 1.03 g (2.12 mmol) of $(\text{Et}_4\text{N})_2\text{MoS}_4$ in 70 mL of MeCN. After being stirred overnight, the optical spectrum of the reaction mixture revealed formation of [Fe(MoS₄)₂]³⁻ in high yield.

J. Reactions of $[MoS_9]^{2-}$

1. Triethylammonium Thiophenoxide

A solution of 0.30 mL (3.00 mmol) of PhSH and 0.42 mL (3.00 mmol) of Et_3N in 15 mL of MeCN was added to 0.16 g

(0.25 mmol) of solid $(Et_4N)_2[MoS_9]$. The solid dissolved slowly upon being stirred overnight, and the optical spectrum of the reaction mixture indicated quantitative formation of MoS_4^{2-} .

2. Ferrous Chloride

To a flask containing 0.04 g (0.32 mmol) of anhydrous ferrous chloride and 0.20 g (0.32 mmol) of $(\text{Et}_4\text{N})_2[\text{MoS}_9]$ was added 20 mL of MeCN and 2 mL of DMSO. The solution was stirred for ca. two days, at which point a small amount of solid precipitated. The optical spectrum of the supernate was that of $[\text{FeMoS}_4\text{Cl}_2]^{2-}$.

3. Sodium Ethylthiolate and Ferrous Chloride

To a slurry of 0.55 g (4.35 mmol) of ferrous chloride in 50 mL of MeCN was added a solution of 1.46 g (17.4 mmol) of NaSEt in 30 mL of MeOH. The mixture became intensely red within ca. 5 minutes. The color gradually changed to green-brown upon the addition of a slurry of 0.94 g (1.45 mmol) of $(Et_4N)_2[MoS_9]$ in MeCN. The optical spectrum of the reaction solution after being stirred for 48h contained maxima at 594, 509, 396, and 321 nm, and roughly corresponded to the spectrum reported²² for the $[Fe_2Mo_2S_{10}]^{4-}$ ion. The filtrate was reduced in volume in vacuo, and ca. 150 mL of Et_2O was then slowly introduced. This resulted in precipitation of an oily black material that slowly solidified upon prolonged stirring. The solid was filtered, washed with Et_20 , and vacuum dried. The optical spectrum of the solid in MeCN was the same as that of the reaction mixture; indicative of $[\text{Fe}_2\text{Mo}_2\text{S}_{10}]^{4-}$ formation. The spectrum of the filtrate more closely resembled that of $[\text{Fe}_- (\text{MoS}_4)_2]^{3-}$. An attempt was made to recrystallize the solid from MeCN, but it slowly decomposed upon standing in solution.

4. Ferric Chloride and Sodium Thiophenolate

To a solution containing 0.40 g (17.4 mmol) of sodium metal in 15 mL of MeOH was added 1.8 mL (17.6 mmol) of To this was added a filtered solution of 0.71 g PhSH. (4.35 mmol) of anhydrous ferric chloride in 20 mL of MeCN, resulting in a deep purple-brown slurry. Addition of 0.93 g (1.45 mmol) of $(Et_4N)_2[MoS_9]$ and 0.75 g (4.53 mmol) of $Et_{4}NC1$ in 30 mL of MeCN caused an immediate color change to an intense red-brown. After being stirred overnight, a white solid (NaCl) had precipitated from the reaction mixture. The volume of the solution was reduced in vacuo by ca. 50%, and the sodium chloride was filtered off. Slow addition of Et_00 to the filtrate resulted in precipitation of a black oil that partially solidified upon stirring. The supernatant liquid was separated by filtration, and the product was extracted with ca. 60 mL of MeCN and filtered.

The optical spectrum of the filtered solution showed essentially a rising absorbance with features at 580, 510, 440, and 350 nm. Slow cooling of the solution to -20°C resulted in precipitation of an amorphous solid that would not redissolve upon warming. This slow decomposition of the material prevented further purification.

5. $(Et_{\parallel}N)_{2}[Fe_{\parallel}S_{\parallel}(SPh)_{\parallel}]$

A mixture of 0.30 g (0.29 mmol) of $(\text{Et}_4\text{N})_2[\text{Fe}_4\text{S}_4(\text{SPh})_4]$ and 0.37 g (0.58 mmol) of $(\text{Et}_4\text{N})_2[\text{MoS}_9]$ was dissolved in 40 mL of MeCN and allowed to stir for four days. Slow addition of Et_20 resulted in separation of a dark oil that quickly solidified. The material was filtered, washed with Et_20 , and vacuum dried. The optical spectrum of the solid in MeCN corresponded exactly to that of $[\text{Fe}_2\text{MoS}_{11}]^3$.

6. <u>Na₂[Fe(CO)₄]·1-1.5 Dioxane</u>

A solution of 0.50 g (1.46 mmol) of $Na_2[Fe(CO)_4]$. 1-1.5 dioxane in 30 mL of DMA was added to a solution of 0.47 g (0.73 mmol) of $(Et_4N)_2[MoS_9]$ in 100 mL of DMA. Upon stirring overnight, the color of the solution changed from brown to red and a gray solid precipitated; which, after filtration, was found to be soluble only in 6N hydrochloric acid with evolution of hydrogen sulfide gas. The optical spectrum of the filtrate was analogous to that of MoS_4^{2-} in DMA.

K. <u>Reactions of [MoCl₆]³⁻</u>

1. (Et₄N)₂[Fe₂S₂(SPh)₄]

A solution containing 0.027 g (0.038 mmol) of $(\text{Et}_4\text{N})_3$ -[MoCl₆] in 10 mL of MeCN was added to a slurry of 0.10 g (0.12 mmol) of $(\text{Et}_4\text{N})_2[\text{Fe}_2\text{S}_2(\text{SPh})_4]$ in MeCN. The mixture was allowed to stir for several days and periodic observation of the optical spectrum showed only slow conversion of $[\text{Fe}_2\text{S}_2(\text{SPh})_4]^{2-}$ to $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$.

2. Ferric Chloride and Thiophenolate

A solution containing 2.6 mL (25.7 mmol) of PhSH and 3.6 mL (25.7 mmol) of Et_3N in 10 mL of MeCN was added to a solution containing 1.0 g (1.43 mmol) of $(Et_4N)_3[MoCl_6]$ dissolved in 50 mL of MeCN. This solution was then added to a filtered solution of 0.70 g (4.28 mmol) of anhydrous ferric chloride in 20 mL of MeCN. After being stirred for 24 h, 1.0 g (31.2 mmol) of solid sulfur was added and upon stirring overnight, the solution became an intense redbrown color. At this point, the solution was reduced in volume by ca. 50% in vacuo, and then filtered. Addition of ca. 100 mL of THF resulted in precipitation of a light red solid whose optical spectrum in MeCN, after filtration, matched that of $[MoCl_6]^{3-}$. As a control, the analogous reaction was performed with the omission of $(Et_4N)_3[MoCl_6]$ and identical results were obtained. The product remaining in solution was subsequently identified³⁴ as $[Fe_2S_{12}]^{2-}$

3. Thiophenolate

A solution containing 0.15 g (0.21 mmol) of $(\text{Et}_{4}\text{N})_{3}^{-}$ [MoCl₆], 0.36 mL (2.60 mmol) of Et₃N, and 0.26 mL (2.55 mmol) of PhSH in 25 mL of MeCN was allowed to reflux overnight. The color of the solution changed from pink to deep red-violet and the optical spectrum of the reaction mixture contained a maximum at 550 nm. Brief exposure of an aliquot of the reaction solution to air produced an intense blue solution whose optical spectrum contained a maximum at 590 nm. These observations identified²⁵ the initial product as $[\text{Mo}_{2}(\text{SPh})_{9}]^{3-}$, which reacts with oxygen³⁵ to form $[\text{MoO}(\text{SPh})_{4}]^{-}$.

L. <u>Reactions of [Mo₂(SPh)₉]³⁻</u>

1. $(Et_4N)_2[Fe_2S_2(SPh)_4]$

To a flask containing 0.42 g (0.48 mmol) of $(\text{Et}_4\text{N})_2$ -[Fe₂S₂(SPh)₄] slurried in 100 mL of MeCN, was added 9.4 mL (0.48 mmol) of a 0.05 M solution of $(\text{Et}_4\text{N})_3[\text{Mo}_2(\text{SPh})_9]$. After stirring overnight, there was no apparent color change in the solution and most of the iron dimer remained undissolved. The optical spectrum of the supernatant liquid was simply that of $[\text{Mo}_2(\text{SPh})_9]^3$. Heating of the reaction mixture for ca. 40 h at 45-50°C resulted in dissolution of the solid and a change in the optical spectrum to a rising absorbance. Subsequent slow cooling of the solution to -20°C resulted in precipitation of an oily black solid that would not redissolve upon warming.

2. $(Et_4N)_2[Fe_2S_{12}]$

To a solution containing 5.9 mL (0.42 mmol) of 0.07 M $(Et_4N)_3[Mo_2(SPh)_9]$ in 20 mL of MeCN was added a solution containing 0.63 g (0.83 mmol) of $(Et_4N)_2[Fe_2S_{12}]$ dissolved in 100 mL of MeCN. After being stirred overnight, THF was slowly added to the reaction mixture and a black oil immediately separated out. The supernatant liquid was decanted, and the oil was taken into a minimum of MeCN/THF, filtered, and slowly cooled to -20°C. This precipitated an amorphous black solid that would not redissolve upon warming. This insoluble material was filtered off, and the filtrate was recooled to -20°C, yielding more insoluble residue.

3. <u>(Et₄N)₂[Fe₄S₄Cl₄]</u>

A solution containing 0.23 g (0.31 mmol) of $(Et_4N)_2$ -[Fe₄S₄Cl₄] dissolved in 50 mL of MeCN was prepared. To this was added 11.9 mL (0.61 mmol) of a 0.05 M stock solution of $(Et_4N)_3[Mo_2(SPh)_9]$ in MeCN. The reaction mixture was allowed to stir until the optical spectrum remained constant, at which point THF was slowly introduced. A dark oil was deposited on the walls of the flask and did not solidify upon prolonged stirring. The supernatant liquid was decanted, and the oil was dried in vacuo. The optical spectrum of the oil in MeCN was a rising absorbance with a slight maximum at 450 nm, possibly corresponding to $[Fe_4S_4(SPh)_4]^{2-}$. The filtrate decomposed upon standing.

M. Reaction of Ferrous Chloride with [MoO(SPh)4]

Addition of a solution of 0.70 g (0.103 mmol) of (Et_4N) -[MoO(SPh)₄] dissolved in 70 mL of MeCN to a slurry of 0.13 g (0.103 mmol) of anhydrous ferrous chloride in MeCN resulted in a gradual (~3h) color change of the reaction solution from deep blue to deep orange-brown. Addition of nonpolar solvents such as THF, Et_2O , and toluene to small aliquots of the reaction mixture all resulted in separation of a red oil, but addition of the reaction solution to an excess of isopropanol precipitated the product as an orange, amorphous powder. These results are exactly analogous to those obtained by Dance, Wedd, and coworkers, who examined³⁶ the reaction between [MoO(SPh)₄]⁻ and FeCl₃ in MeCN. They formulated the product as $(Et_4N)[Mo_2O_2(SPh)_6C1]$.

III. RESULTS AND DISCUSSION

A.
$$[FeMS_4(SR)_2]^2$$
 (M = Mo, W; R = Ph, p-Tol)

1. Synthesis and Interconversions

The aryl thiol complexes, $(Et_4N)_2[FeMS_4(SR)_2]$, can be prepared in high yield by a variety of pathways: (i) by reaction of $(Et_4N)_2$ [FeMS₄Cl₂] with 2-4 equivalents of RS⁻; (ii) by treatment of $(Et_4N)_3[Fe(MS_4)_2]$ with a large excess of RSH/Et₃N; (iii) by reaction^{19b} of MS_4^{2-} with $[Fe(SR)_4]^{2-}$. Route (i) can be viewed as a simple ligand exchange of thiolate for chloride and can be accomplished with either RSH/Et₃N or NaSR. Use of the latter reagent results in a 20-30% higher yield of the thiolate complex, probably due to precipitation of sodium chloride, which drives the reaction to completion. Pathway (ii) demonstrates the degradation of a trinuclear species to a dinuclear one under extreme conditions, i.e., reaction with ca. 300-400 equivalents of RSH/Et₃N. This reaction is also accompanied by oxidation of the metal centers. Method (iii) represents substitution of two thiolate ligands by the tetrathiometallate, which acts as a bidentate ligand.

Once formed, the species $[FeMS_4(SR)_2]^{2-}$ can be converted into other dimeric complex ions by reactions with

simple reagents. Treatment of the thiolate complex with two equivalents of PhCOCl in MeCN gives rise to the chloro complex, [FeMS₄Cl₂]²⁻, in quantitative yield. The reaction presumably proceeds via thioester formation:

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

This reactivity is identical with that $observed^{29}$ for the Fe_4S_4 and Fe_2S_2 thiolate complexes towards PhCOC1. Use of excess reagent results in immediate decomposition, which may result from acylation of terminal sulfide ligands.

Similarly, reaction of $[\text{FeMS}_4(\text{SR})_2]^{2-}$ with excess sulfur in MeCN results in gradual formation of $[\text{FeMS}_9]^{2-}$, which contains the S_5^{2-} ion as a bidentate ligand on the iron atom. Presumably, this occurs by partial reduction of elemental sulfur with concomitant oxidation of thiolate. The complex ion, $[\text{FeMS}_9]^{2-}$, was first synthesized by Coucouvanis and coworkers^{19a} by reaction of $[\text{FeMS}_4(\text{SR})_2]^{2-}$ with five equivalents of benzyl trisulfide. The S_5^{2-} ligand, although not common, has been reported before in³⁷ $[\text{Pt}(\text{S}_5)_3]^{2-}$, $[\text{Ti}(\text{Cp})_2(\text{S}_5)]$,³⁸ and the dimeric complex,³⁴ $[\text{Fe}_2\text{S}_{12}]^{2-}$. The reaction scheme given in Figure 1 summarizes the synthesis and reactivity of the $[\text{FeMS}_4(\text{SR})_2]^{2-}$ complexes. Figure 1. Syntheses and reactivity of $[FeMS_4(SPh)_2]^{2-}$ -(M = Mo, W).



Figure 1

It is evident that reactions of the $[\text{FeMS}_4(\text{SR})_2]^{2-}$ ion proceed with retention of the FeS_2M core structure, analogous to the reactions observed for the FeS_2Fe unit.²⁹ Also, no differences in reactivity are noted when molybdenum is replaced by tungsten.

2. <u>Structure</u>

The crystal structure of $(Et_4N)_2[FeMoS_4(SPh)_2]$ is shown in Figure 2, and significant bond distances and angles are listed in Tables I and II. The structure consists of discrete cations and anions in an 8:4 ratio per unit cell with one independent dianion and two independent cations per asymmetric unit. The tetraethylammonium cations are crystallographically ordered, possess normal bond lengths and angles, and will not be discussed further.

The structure of the anion reveals nearly tetrahedral coordination by sulfur atoms around each metal center. The sulfur-metal-sulfur bond angles range from 104° to 117°, with the average being very close to the ideal tetrahedral angle of 109.5°. Although the Fe-Mo distance is 2.756 (1) Å, which is within the range of a metal-metal bond, magnetic susceptibility measurements and Mossbauer results, to be discussed later, suggest that no direct metal-metal interaction exists.

Within the anion structure, the terminal Mo-S distances (2.153 (2) Å) are significantly shorter (0.10 Å) than the

Figure 2. X-ray crystal structure of $(Et_4N)_2[FeMoS_4(SPh)_2]$. Ellipsoids represent fifty percent probability.



Distance	(Et ₄ N) ₂ [FeMoS ₄ (SPh) ₂]	(Et ₄ N) ₂ [FeWS ₄ (SPh) ₂]
M-Fe	2.756(1)	2.772(1)
M-Sl	2.253(2)	2.239(2)
M- S2	2.256(2)	2.250(2)
M-S3	2.149(2)	2.156(2)
M-54	2.157(2)	2.162(2)
Fe-Sl	2.262(2)	2.286(2)
Fe-S2	2.267(2)	2.289(2)
Fe-S5	2.299(2)	2.296(2)
Fe-S6	2.315(2)	2.315(2)
S5-C1	1.772(6)	1.763(5)
S6-C7	1.776(6)	1.761(4)
	Nonbonded Distanc	es
SlS2	3.576(2)	3.581(2)
S1S3	3.600(3)	3.595(3)
SlS4	3.603(3)	3.599(2)
S2S3	3.619(3)	3.615(3)
S2S4	3.627(3)	3.627(3)
S3S4	3.556(3)	3.550(3)
S1S5	3.840(2)	3.863(3)
S1S6	3.553(2)	3.572(3)
s2s5	3.809(3)	3.830(3)
S2S6	3.911(3)	3.928(3)
\$5S6	3.672(3)	3.690(3)

Table I. Selected Interatomic Distances (Å) with Esd's for $(Et_4N)_2[FeMS_4(SPh)_2]$ (M = Mo, W).

	(Et ₄ N) ₂ [FeMoS ₄ (SPh) ₂]	$(Et_{4}N)_{2}[FeWS_{4}(SPh)_{2}]$
M-Sl-Fe	75.26(6)	75.55(4)
M-S2-Fe	75.10(6)	75.26(4)
S1-M-S2	104.97(6)	105.87(6)
S1-M-S3	109.72(8)	109.76(7)
SI-M-S4	109.60(8)	109.74(8)
S2-M-S3	110.45(8)	110.23(8)
S2-M-S4	110.56(8)	110.57(8)
S3-M-S4	111.34(8)	110.58(9)
Sl-Fe-S2	104.33(7)	103.03(6)
Sl-Fe-S5	114.70(7)	114.97(8)
Sl-Fe-S6	101.85(7)	101.96(7)
S2-Fe-S5	113.09(7)	113.28(7)
S2-Fe-S6	117.21(8)	117.09(8)
S5-Fe-S6	105.44(7)	106.35(8)
Fe-S5-C1	112.36(22)	112.93(16)
Fe-S6-C7	111.56(22)	111.08(16)

Table II. Selected Bond Angles (deg) with Esd's for $(Et_4N)_2[FeMS_4(SPh)_2]$ (M = Mo, W).

bridging Mo-S distances. However, these distances still represent the longest terminal Mo-S distances reported to date with the exception of the average Mo-S distance³⁹ in free MoS_4^{2-} of 2.17 Å. One explanation may be that upon coordination, the molybdenum atom loses electron density from the sulfur atoms that become bridging ligands to iron. This effect may be offset to some extent by contracting the terminal Mo-S distances, thereby increasing the electron density at molybdenum. The average bridging Fe-S distance (2.264 (2) Å) is similar to the bridging Mo-S distance (2.255 (2) Å), but is shorter than the average terminal Fe-S(Ph) distance of 2.307 (2) Å.

Comparison of the $[FeMos_4(SPh)_2]^{2-}$ anion structure with that²⁸ of $[Fe_2S_2(S-p-To1)_4]^{2-}$ reveals distinct similarities. The Fe-Fe distance in the latter complex is 2.691 (1) Å, ca. 0.07 Å shorter than the Fe-Mo distance in the former. This can be related to the larger radius of molybdenum. The average bridging Fe-S distance in $[Fe_2S_2(S-p-To1)_4]^{2-}$ is 2.201 (1) Å and is substantially shorter, ca. 0.06 Å, than both the bridging Fe-S and Mo-S distances in $[FeMoS_2-(SPh)_4]^{2-}$. The terminal Fe-S (p-To1) distance in the FeS_2Fe dimer is nearly identical with that of the FeS_2Mo dimer, even though the former is formally iron(III) and the latter is iron(II). This is in contrast to the observed Fe-S distances⁴⁰ in the $[Fe(S_2-p-Xy1)_2]^{2-,3-}$ complexes, which demonstrate a lengthening of the Fe-S distance of 0.088 Å in going from iron(III) to iron(II). Figure 3. X-ray crystal structure of $(Et_4N)_2[FeWS_4-(SPh)_2]$. Ellipsoids represent fifty percent probability.



The structure of $(Et_4N)_2[FeWS_4(SPh)_2]$ is presented in Figure 3. Pertinent bond distances and angles are given in Tables I and II. The compound is isostructural with the molybdenum analog. In the $[FeWS_4(SPh)_2]^{2-}$ anion structure, the Fe-W distance is 2.772 (1) Å, which is only slightly longer (0.016 \AA) than the Fe-Mo distance in the molybdenum counterpart. This similarity is expected inasmuch as the covalent radii of molybdenum and tungsten are essentially the same, ca. 1.30 Å. Likewise, the terminal Fe-S(Ph) and W-S distances are almost identical with those of the molybdenum compound. The only minor discrepency between the structures of the two anions arises in the bridging metal-sulfur bond lengths. In $[FeWS_4(SPh)_2]^{2-}$, the bridging W-S distance is shorter (0.010 Å), and the bridging Fe-S distance is longer (0.024 Å) than the corresponding distances in the molybdenum analog. This difference may reflect a higher affinity for sulfur by tungsten, relative to molybdenum. However, the terminal W-S distance is similar to that observed for $[Zn(WS_{\mu})_{2}]^{2-}$ (2.159 (2) <u>vs</u> 2.156 (6) Å).

3. Optical and Infrared Spectra

The optical spectra of $[\text{FeMoS}_4(\text{SPh})_2]^{2-}$ and $[\text{FeWS}_4-(\text{SPh})_2]^{2-}$ are shown in Figure 4, while pertinent data are presented in Table III. The spectra of both complexes contain intense absorptions between 300 and 500 nm. These results are similar to those obtained for bis(tetrathio-metallate) complexes of first-row transition metals.^{39,42}

Figure 4. Electronic spectra of $(Et_4N)_2[FeMS_4-$ (SPh)₂] (M = Mo, W) in acetonitrile solution at 23°C.



Table III.	Electronic and Infrared Spectral Ligand Protons of $(Et_{4N})_{2}$ [FeMS $_{4}X_{2}$ [Fe2MoS ₁₁].	Features, and Isotro] (M = Mo, W; X = S/	ppic Shifts of Ar, OAr) and (Et ₄ N) ₃ -
	Electronic Spectral Features ^a	Infrared Features ^b	Isotropic Shifts ^c
M = Mo; X = SPh	930(0.11), 610(sh), 545(sh), 488(9.5), 420(8.6), 335(16.2), 300(17.3),266(25.8)	503, 488, 446	39(<u>о</u> -Н), -31.2(<u>m</u> -Н), 46.6(<u>р</u> -Н)
M = Mo; X = S- <u>p</u> -Tol	550(sh), 488(9.7), 421(8.4), 332(15.9), 301(17.6), 267(26.8)	ŋ	40(o-H), -31.7(<u>m</u> -H), -48.7(<u>p</u> -CH ₃)
X = Mo; X = OPh	<pre>1010(sh), 750(0.17), 530(sh), 471(9.8), 391(7.5), 314(14.7), 232(19.7)</pre>	515, 481, 441	45(<u>о</u> -Н), -43.5(<u>m</u> -Н), 47.б(<u>р</u> -Н)
M = Mo; X = O- <u>p</u> -Tol	530(sh), 473(9.9), 400(7.7), 320(sh), 304(16.6)	טי	43(<u>ο</u> -H) ^f , -40.6(<u>m</u> -H) ^f , -46.0(<u>p</u> -CH ₃) ^f
[Fe2MoS ₁₁] ^{3.}	<pre>- 580(8.1), 550(sh), 509(9.6), 440(11.3), 405(sh), 348(18.0), 296(18.6)</pre>	497, 480, 442	
M = W; X = SPh	1150(sh), 920(0.11), 540(sh), 460(sh), 434(8.8), 364(11.4), 296(sh), 270(29.4)	486, 423, 357	37(<u>o</u> -H), -30.1(<u>m</u> -H), 44.3(<u>p</u> -H)
M = W; X = S- <u>P</u> -Tol	540(sh), 460(8.5), 435(8.5), 366(11.6), 296(sh), 270(29.4)	q	$38(\underline{o}-H), -30.3(\underline{m}-H), -46.1(\underline{p}-CH_3)$

.

	Electronic Spectral Features ^a	Infrared Features ^b	Isotropic Shifts ^c
M = W; X = OPh	1070(sh), 780(0.14), 450(sh), 415(9.3), 369(9.4), 287(21.2), 240(27.6)	482, 437, 355	42(<u>0</u> -H), -42.7(<u>m</u> -H), 43.5(<u>p</u> -H)
M = W; X = O- <u>p</u> -Tol	455(sh), 416(9.2), 370(8.8), 289(19.3), 246(25.9)	ט	44(o-H), -43.4(m-H), -48.5(p-CH ₃)
^a In MeCN solu λmax (ε) in bIn Nujol mul cIn CD ₃ CN sol -2.28; PhOH: dNot determin f50°C. f50°C.	ttion for features at <700 nm; DM nm (M ⁻¹ cm ⁻¹ x 10^{-3}). ls between polyethylene plates a ution; shifts vs diamagnetic ref -7.02; p-TolOH: -6.85, -2.21; 2 led.	SO solution for thomage of the solution for the standard for the second shifts downfie to the shifts downfie t	se >700 nm; 23°C;); p-TolSH: -7.10, 1d of TMS are negative.

Continued.

Table III.

They reflect splitting of the degenerate S+Mo or S+W charge-transfer transitions in the free tetrathiometallate into components at both higher and lower energy due to lowering of symmetry upon coordination to iron. The spectra also exhibit other features, and since this region will undoubtedly contain thiolate- and sulfide-to-iron chargetransfer bands as well, 28,29,45 exact assignments of optical transitions between 300-500 nm would only be speculation. Each feature in the spectrum of $[FeWS_4(SPh)_2]^{2-}$ is shifted to higher energy by ca. 30 nm with respect to that of $[FeMoS_4(SPh)_2]^2$, much as the absorptions of WS_4^2 are blue-shifted relative to those of $\text{MoS}_{4}^{2-}.$ In view of the expected higher orbital energy difference between sulfur and tungsten vs sulfur and molybdenum, this behavior seems reasonable, at least for those charge-transfer transitions within the tetrathiometallate unit. Substitution of chloride for thiolate on iron causes a slight shift ($\sim 10-20$ nm) to higher energy in this region. Qualitatively, one might expect such behavior due to the slightly greater orbital energy difference between chlorine and iron vs sulfur and iron. Below 290 nm, very intense absorption bands are observed. These undoubtedly contain internal ligand $(\pi \rightarrow \pi^*)$ excitation bands when the terminal ligand is thiolate.

Other transitions due to charge-transfer between metal centers or to d-d transitions localized on one metal center are possible. High spin iron(II) in
tetrahedral symmetry is expected to have a characteristic ${}^{5}E \rightarrow {}^{5}T_{2}$ transition, with the energy of this absorption equal to the tetrahedral crystal field splitting, Δ_{+} . This band has been noted 44 for the complex $[Fe(SPh)_{4}]^{2-}$ and occurs at 1700 nm ($\epsilon \sim 100 \text{ M}^{-1} \text{ cm}^{-1}$). For the complexes $[N(R_2PS)_2]$ Fe and $[HC(R_2PS)_2]$ Fe, this band is observed⁴⁵ near 2700 nm ($\varepsilon \sim 100 \text{ M}^{-1} \text{ cm}^{-1}$). Similarly, Holm and coworkers report 40 a broad band for this transition at 1800 nm ($\epsilon \sim 120 \text{ M}^{-1} \text{ cm}^{-1}$) for $[Fe(S_2 - \underline{o} - Xy1)_2]^2$. The asymmetry of this latter band is attributed to a small splitting of the t2 orbitals due to deviations from ideal tetrahedral symmetry. No such absorptions are observed for $[FeMoS_4(SPh)_2]^2$ and $[FeWS_4(SPh)_2]^2$ at such low energies, at least out to ca. 2200 nm. Instead, broad, asymmetrical absorptions between 900 and 1100 nm ($_{\rm E}$ $_{\rm 100}$ $\rm M^{-1} cm^{-1})$ are observed. These are illustrated in Figure 5. If these are indeed $E \rightarrow T_2$ transitions, they reflect a nearly <u>two-</u> <u>fold</u> increase in the magnitude of Δ_t relative to $[Fe(SPh)_{\mu}]^{2-1}$ and $[Fe(S_2-\underline{o}-Xy1)_2]^2$ ($\sim 10,000 \text{ cm}^{-1} \underline{vs}$ 5700 cm⁻¹); this seems unlikely. Also, the calculated value of Δ_t , based on the energy of the ${}^{4}A_{2} \rightarrow {}^{4}T_{1}(P)$ transition, 42 for $[Co(WS_{4})_{2}]^{2-}$ is <u>smaller</u> than that reported ⁴⁰ for [Co- $(SPh)_{\mu}]^{2-}$ ($\sqrt{2400 \text{ cm}^{-1}} \text{ vs} \sqrt{4000 \text{ cm}^{-1}}$), implying that tetrathiometallates are not strong crystal field splitting ligands relative to aryl thiolates. Noting these trends, it seems unlikely that a simple ${}^{5}E \rightarrow {}^{5}T_{2}$ d-d transition

Figure 5. Near-infrared spectra of $(Et_4N)_2[FeMoS_4-(SPh)_2]$ (A), $(Et_4N)_2[FeMoS_4(OPh)_2]$ (B), and $(Et_4N)_2[FeMoS_4Cl_2]$ (C) in dimethylsulfoxide solution at 23°C.



is responsible for the observed near-IR absorptions.

An alternative assignment would be an intervalence charge-transfer between the metal centers, i.e., Fe(II)- $M_O(VI) \xrightarrow{h_V} Fe(III)-M_O(V)$. Most intervalence bands have large half-widths 46 ($\sim 2000-6000 \text{ cm}^{-1}$) and extinction coefficients ranging from 500-5000 $M^{-1} cm^{-1}$. Also, they typically obey (±10%) the relation, $\Delta = (v_{\tau \tau} \cdot 2310)^{1/2}$ at 300 K, 47 where v_{TTT} is the frequency of the absorption maximum in cm^{-1} and Δ is the half-width of the absorption. The approximate half-widths of the near-IR bands of $[FeMoS_{\mu} (SPh)_{2}^{2-}$ and $[FeWS_{\mu}(SPh)_{2}]^{2-}$ are ca. 5800 and 5200 cm⁻¹, respectively, and are within 15% of the calculated values. The asymmetric nature of these bands, i.e., a peak with a shoulder, suggests that they really consist of two components which makes the determination of v_{TT} and Δ difficult. It is possible that they represent an intervalence chargetransfer and a thiolate-to-molybdenum or tungsten chargetransfer which are very close in energy. In support of this, the analogous band observed for $[FeMoS_4Cl_2]^{2-}$ is nearly symmetrical.

Although these absorptions resemble intervalence bands in position and half-width, their extinction coefficients are very low, ca. 110 M^{-1} cm⁻¹. Therefore, actual assessment of the nature of these near-IR absorptions will have to await measurements on a variety of other binuclear systems containing tetrathiometallate centers.

The infrared spectra of the molybdenum and tungsten thiolate dimers, in the region of 250-600 cm⁻¹, demonstrate the typical splitting pattern observed for tetrathiometallate anions coordinated to a metal atom.^{39,42} Terminal sulfur-metal stretches are shifted to higher energy and bridging sulfur-metal stretches to lower energy, relative to the degenerate vibrations of the free tetrathiometallate. These data appear in Table III.

4. Electrochemistry

The electrochemical behavior of the complexes, [FeMS] - $(SR)_{2}^{2-}$ (M = Mo, W and R = Ph, <u>p</u>-Tol), has been examined by using polarographic and cyclic voltammetric techniques. Significant data are presented in Table IV. All measurements were made in MeCN solutions containing 0.05 M $[Et_4N][ClO_4]$ as supporting electrolyte and recorded relative to a standard calomel reference electrode. Due to problems with adsorption of these sulfur-rich complexes onto conventional electrode surfaces such as platinum and glassy carbon, attempts to use cyclic voltammetry to study electrochemical behavior met with little success. The cathodic wave was of reasonable shape and magnitude, but the anodic wave was featureless and indicated a sharp decrease in current. In the case of platinum, the electrode surface was usually discolored after a single scan. Polarography, employing a dropping mercury electrode,

[Fe	$MS_{4}X_{2}$ (M = M	o, W; X = SAr	, OAr) and (Et	4N)3[Fe2MoS ₁₁].	
	ε ^{1/2} , v ^a	μΑ/mM Fe ^a , i _D /C	Slope, mV	ucorr, BM ^b	IS (QS), mm/s
M = Mo; X = SPh	-1.28	2.8	88	4.89	0.47(1.63) ^e
M = Mo; X = S- <u>p</u> -Tol	-1.30	2.8	72	ט	ט
M = Mo; X = OPh	-1.51	2.6	72	5.08	0.57(1.20) ^f
M = Mo; X = O- <u>p</u> -Tol	-1.56	2.7	77	q	д
[Fe ₂ MoS ₁₁] ³⁻	-1.25	2.7	48µ	2.50 (per Fe)	A: 0.44(1.41) ^f B: 0.32(0.92)
M = W; X = SPh	-1.41	2.9	113 ¹	4.90	0.51(1.92) ^g
M = W; X = S- <u>p</u> -Tol	-1.42	2.9	89	IJ	q
M = W; X = OPh	-1.66	2.5	76	5.07	ъ
M = W; X = 0- <u>p</u> -Tol	-1.74	2.7	76	q	q

Electrochemical Data, Magnetic Moments, and Mössbauer Parameters for $({\rm Et}_{\rm l}{}^{\rm N})_2$ -Table IV.

Table IV. Continued.

```
<sup>a</sup>In MeCN solution at 23°C <u>vs</u> SCE; all are average values of 2-3 scans; 5 mV/s, 2 drops/sec.
                                                                                                                                                                                                                                                                                                                                              <sup>1</sup>High concentration (5.2 mM).
                                               <sup>b</sup>In the solid state at 23°C.
                                                                                                                                                                                                                   fPolycrystalline sample.
                                                                                                                                                                                                                                                                                                        h<sub>Maxima</sub> distorted.
                                                                                                                                                                                                                                                              <sup>g</sup>In DMA solution.
                                                                                                                                                                             <sup>e</sup>In DMF solution.
                                                                                                                                d<sub>Not</sub> determined.
                                                                                          <sup>c</sup>At 4.2 K.
```

proved to be the most useful method for studying these complexes. This system permits continual generation of a fresh electrode surface two times a second. Well-formed polarographic waves were obtained that permitted a more quantitative analysis. Significant electrochemical data appear in Table IV.

Examination of the electrochemistry of these complexes over the potential range 0.0 to -2.0 V yielded only one electrochemical reduction between -1.0 and -2.0 V in each case. At potentials lower than -2.0 V, very high currents were observed, presumably corresponding to ligand reduction. Plots of log $[i/(i_D-i)] \underline{vs}$ voltage for each complex gave slopes much higher than the theoretical value (59 mV) for a single, one-electron reversible reduction. These results are similar to those²⁹ obtained for the dimeric species, $[Fe_2S_2X_4]^{2-}$ (X = halide), which also demonstrate irreversible reductions over the same potential range. However, they are contrary to those obtained²⁸ for $[Fe_2S_2-(SR)_4]^{2-}$, which undergoes two reversible one-electron reduction processes.

In order to further examine the irreversible nature of the reduction of the $[\text{FeMS}_4(\text{SR})_2]^{2-}$ complexes, attempts were made to generate a trianion with a chemical reductant, namely sodium acenaphthalenide (Na⁺ACN⁻). This radical anion has a reduction potential of -1.6 V <u>vs</u> SCE, and is well suited as a one-electron reductant. Addition of

successive, one equivalent aliquots of Na⁺ACN⁺ in THF to solutions of $[FeMoS_{\mu}(SPh)_{2}]^{2-}$ in DMA, followed by rapid freezing and investigation by EPR spectroscopy over a range of temperatures and microwave powers showed no evidence for the formation of a stable, half-integral spin species. Likewise, examination of a frozen DMA solution of $[{\rm FeMoS}_{\rm ll}-$ (SPh)₂]²⁻ containing one equivalent of ACN⁻ by Mössbauer spectroscopy at 4.2 K revealed a complex spectrum attributable to a mixture of products. Also, a large scale reaction of a DMA solution of $[FeMoS_{\mu}(SPh)_{2}]^{2-}$ with 1-3 equivalents of ACN yielded a product whose optical spectrum resembled that of $[Fe(MoS_4)_2]^{3-}$. This latter result is in accord with those obtained upon exposing $[FeMoS_4Cl_2]^{2-}$ to other potential reducing agents, as will be discussed in detail Therefore, spectroscopic and electrochemical, as later. well as chemical, evidence suggests that the reduced species, $[FeMoS_4(SPh)_2]^{3-}$, does not possess any reasonable stability.

The reduction potentials of $[FeMoS_4(SPh)_2]^{2-}$ and $[FeWS_4(SPh)_2]^{2-}$ are -1.28 V and -1.41 V, respectively; substitution of tungsten for molybdenum thus makes the complex harder to reduce. This behavior is analogous to results ⁴⁸ obtained for the bis(tetrathiometallate) anions, $[Ni(MS_4)_2]^{2-}$, $[Pd(MS_4)_2]^{2-}$, and $[Pt(MS_4)_2]^{2-}$ (M = Mo, W). These latter complexes also exhibit more negative reduction potentials when molybdenum is replaced by tungsten.

This effect may be due to the lower electron-withdrawing (π -acceptor) properties of WS²⁻₄ relative to MoS²⁻₄, as predicted by theoretical (SCC EH) calculations,⁴⁹ on the [FeMoS₄Cl₂]²⁻ and [FeWS₄Cl₂]²⁻ ions. This effect also manifests itself in the ⁵⁷Fe Mössbauer results on the two thiolate dimers. These results will be discussed in detail in a later section, but briefly they indicate greater "ferric" character for the iron atom in the molybdenum complex, which correlates well with the observed greater ease of reduction for the molybdenum dimer.

Substitution of <u>p</u>-TolS for PhS results in a slight (10-20 mV) decrease in the reduction potentials of both the molybdenum and tungsten dimers. This is in accord with results obtained for the Fe_4S_4 and Fe_2S_2 thiolate complexes, 28,43 and can be explained by simple inductive effects of the electron-releasing methyl groups on the phenyl rings.

5. Magnetic Susceptibility

The room temperature magnetic susceptibilities of the compounds, $(\text{Et}_4\text{N})_2[\text{FeMS}_4(\text{SPh})_2]$ (M = Mo, W), have been determined by the Faraday method. These data give rise to effective magnetic moments of 4.89 BM for M = Mo and 4.90 BM for M = W. These values have been corrected for diamagnetic contributions to the susceptibility from the

ligands and cations by use of Pascal's constants. These effective magnetic moments are consistent with the presence of four unpaired electrons in an S = 2 ground state in these molecules. This configuration could conceivably correspond to either a high-spin Fe(II)-Mo(VI) system or to a high-spin Fe(III)-Mo(V) system with appreciable antiferromagnetic coupling between iron (d^5) and molybdenum (d^1) ions at room temperature.

In order to examine this question further, the temperature-dependent susceptibility of a polycrystalline sample of $(Et_{4}N)_{2}[FeMoS_{4}(SPh)_{2}]$ was measured from 4.2 to 300 K. The sample was found to be free of ferromagnetic impurities by noting no change in the susceptibility as a function of applied field at 300 K. The temperature-dependent susceptibility datawere found to conform to the Curie-Weiss formula, $\chi = C/(T+\theta) + \chi_{o}$, over the temperature range 30-300 K. A least-squares analysis provided θ = 4.2 K, C = 3.187 emu·K/mol, and χ_0 = -5.96 x 10⁻⁴ emu/mol. The resulting plot of χ_M vs T is shown in Figure 6. Deviation from Curie-Weiss Law was noted below 30 K, with a maximum in the plot at egle 8 K followed by a rapid decrease in the susceptibility down to 4.2 K. The antiferromagnetic coupling noted could arise from two sources: (i) an intramolecular coupling between high spin Fe(III) and Mo(V); (ii) an intermolecular interaction between neighboring ions in the crystalline lattice. In order to distinguish

Figure 6. Magnetic susceptibility of $(Et_4N)_2[FeMoS_4-(SPh)_2]$ as a function of temperature in the solid state (•) and in N,N-dimethylformamide glass (•), obtained in 0.16-T applied field. The left vertical axis refers to the solid, and the right to the frozen solution.



between these two alternatives, the temperature-dependent susceptibility of a magnetically "dilute" frozen solution of the same compound in DMF was measured. In this case, no antiferromagnetic interaction was observed down to 4.2 K; this plot is also presented in Figure 6. These data suggest that the antiferromagnetic interaction is intermolecular in nature and is simply a function of the crystalline lattice. Also, if the coupled Fe(III)-Mo(V) description were correct, the energy difference between S = 2 and S > 2 would have to be <u>much</u> larger than thermal energy even at 300 K, and this seems unlikely.

6. Mössbauer spectra

The successful interpretation of 57 Fe Mössbauer spectra can provide useful insight towards assigning formal oxidation state(s) to iron atom(s) in complex molecules. Since magnetic susceptibility measurements cannot completely rule out the possibility of an Fe(III)-Mo(V) interaction, Mössbauer spectra of frozen DMF solutions of $(Et_4N)_2[FeMS_4 (SPh)_2]$ (M = Mo, W) were recorded both in the absence and presence of an applied magnetic field. Solution samples were free of intermolecular magnetic interactions, thus supplying more easily interpreted spectra compared to solid samples. However, spectra of polycrystalline samples diluted with boron nitride were also obtained.

The isomer shift measured for the solid samples was essentially the same as that obtained for the solution samples while the quadrupole splitting of the former was ca. 0.10 mm/s lower than the latter.

The rigorous theoretical treatment of zero-field or magnetic Mössbauer phenomenon is very complex and will not be presented here. Instead, semi-quantitative interpretations of the theory and data obtained will be presented.

In order to assess the formal oxidation state of an iron atom in a molecule based on the δ and ΔE_Q values, one must compare the observed values to those of complexes with similar coordination environments and known oxidation states. Unfortunately, the relative lack of well-characterized Mo/Fe/S and W/Fe/S systems, from a Mössbauer standpoint, prevents such a direct comparison. Instead, one must resort to the Mössbauer data reported for the monomeric, dimeric, and tetrameric, iron-sulfur centers which formally contain Fe²⁺, Fe³⁺, and Fe^{2.5+} or Fe^{2.25+}, respectively.¹⁵

The 4.2 K Mössbauer spectra of the molybdenum and tungsten thiolate dimers are presented in Figures 7 and 8, respectively, while relevant parameters are listed in Table IV. The plot relating isomer shift to formal oxidation state¹⁵ is given in Figure 9. The isomer shifts (quadrupole splitting) of the molybdenum and tungsten thiolate dimers are 0.47 mm/s (1.63 mm/s) and 0.51 mm/s (1.92 mm/s),

Figure 7. Mössbauer spectrum of $(Et_4N)_2[FeMoS_4(SPh)_2]$ in frozen N,N-dimethylformamide solution recorded at 4.2 K with zero applied field. Vertical bar indicates one percent absorption.



Figure 8. Mössbauer spectrum of $(Et_4N)_2[FeWS_4(SPh)_2]$ in frozen N,N-dimethylacetamide solution recorded at 4.2 K with zero applied field. Vertical bar indicates one percent absorption.



Figure 9. Correlation diagram relating isomer shift to formal oxidation state for various iron-sulfur centers.^{15a}



respectively. The analogous data for monomeric high-spin iron(II) and iron(III) in a tetrahedral sulfur environment are 0.6 mm/s (3.28 mm/s) and 0.13 mm/s (0.57 mm/s), respectively. Comparison of the isomer shifts observed for $[FeMoS_4(SPh)_2]^{2-}$ and $[FeWS_4(SPh)_2]^{2-}$ to those of the documented iron-sulfur predicts a formal oxidation state for iron of +2.6 in the molybdenum dimer and +2.5 in the tungsten dimer. Regardless of whether the absolute magnitudes of these calculated values are correct, their relative order correlates well with electrochemical results, i.e., greater "ferrous" character for iron in $[FeWS_4 (SPh)_2]^{2-}$. Likewise, it follows the generally observed trend that Mo(VI) complexes are easier to reduce than their W(VI) counterparts.

Because the dependence of the isomer shift on the formal oxidation state of iron in the iron-sulfur culsters may not be the same as for the molybdenum and tungsten thiolate dimers, the spectrum of $(Et_4N)_2[FeMoS_4(SPh)_2]$ in applied magnetic fields was examined. These spectra are complex, but can be simulated⁵⁰ very well by spectral calculations based on a tetrahedral, high-spin, ferrous model. Also, the hyperfine parameters obtained from the magnetic Mössbauer spectrum indicate anisotropy in at least one direction. Qualitatively, this result is expected for a high-spin ferrous system where a non-symmetrical electronic field gradient prevails.

Indeed, the magnetic Mössbauer spectrum of reduced (Fe(II)) rubredoxin,⁵¹ an iron-sulfur protein with an FeS₄ center,⁵² also demonstrates magnetic anisotropy in its hyperfine parameters, while the oxidized form of the protein (Fe(III)) shows very little hyperfine anisotropy.

In conclusion, Mössbauer results on the molybdenum and tungsten thiolate dimers suggest that they are best described as an Fe(II)-M(VI) system with slight delocalization of electron density through bridging sulfide ligands to either molybdenum or tungsten.

7. Proton Magnetic Resonance Spectra

The isotropic shifts for the protons of the aromatic thiolate ligands in the complexes, $(Et_4N)_2[FeMS_4(SR)_2]$ (M = Mo, W; R = Ph, p-Tol), have been measured as a function of temperature in deuterated MeCN or DMSO. Selected spectra of the molybdenum complexes are shown in Figure 10 and room temperature chemical shifts for all complexes are listed in Table III.

Before a discussion of the actual data is given, a brief investigation into the factors contributing to the observed shifts is in order. The observed isotropic shift is really the sum of two separate elements:⁵³ The contact shift and the dipolar shift. This can be expressed as follows: Figure 10. NMR spectra of $(Et_4N)_2[FeMoS_4(SPh)_2]$ in CD_3SOCD_3 at 69 (A) and 17°C (B), along with NMR spectra of $(Et_4N)_2[FeMoS_4(S-p-Tol)_2]$ in CD_3CN at -45 (E), 25 (D), and 75°C (C). Small amounts of impurity are denoted by X. Chemical shifts are in parts per million from Me₄Si.



$$\left(\frac{\Delta H}{H}\right)^{\text{isotropic}} = \left(\frac{\Delta H}{H}\right)^{\text{contact}} + \left(\frac{\Delta H}{H}\right)^{\text{dipolar}}$$

The contact term results from direct unpaired spin delocalization onto the magnetic nucleus being observed. The magnitude of this shift is given by the equation,⁵³

$$\left(\frac{\Delta H}{H}\right)^{\text{contact}} = - \frac{A \gamma_e}{\gamma_H} \frac{\text{gBS}(S+1)}{3 \text{kT}}$$
,

where A is the proton-electron coupling constant; $\gamma_{\rm H}$ and $\gamma_{\rm e}$ are the gyromagnetic ratios of the proton and electron respectively; g is the nuclear g factor and B is the Bohr magneton. The key point is that the contact term is directly proportional to the susceptibility of the system, inversely proportional to the temperature, and not a function of distance from the paramagnetic center. On the other hand, the dipolar term is given by the relation,⁵³

$$\left(\frac{\Delta H}{H}\right)^{\text{dipolar}} = -\left(\chi_{\parallel} - \chi_{\perp}\right) \left[\frac{3\cos^2\theta - 1}{r^3}\right] ,$$

where $\chi_{||}$ and $\chi_{||}$ are the axial components of the magnetic susceptibility; θ is the angle between the magnetic axis

and the nucleus in question; and r is the distance between the nucleus and the paramagnetic center. Without single crystal magnetic anisotropy measurements, the dipolar term cannot be assessed, but its effects, particularly the $1/r^3$ dependence, can be observed in the NMR spectrum. For ligands with aromatic ring systems, the easiest way to distinguish which of these terms is dominant is to substitute methyl groups for hydrogen atoms. The coupling constant for the interaction between unpaired spin density on carbon with the hydrogen nucleus is opposite in sign to that between two carbon atoms. 53 The net result is an isotropic shift in the opposite direction and of comparable magnitude for the protons of the methyl group relative to that of the replaced proton.

The usual convention for reporting chemical shifts in paramagnetic complexes designates those shifts which are downfield of the diamagnetic reference as negative and those upfield as positive. This convention will be adhered to in subsequent discussions. Resonances for the tetraethylammonium cations were broadened significantly, but were only slightly shifted and will not be discussed further.

At 297 K, isotropic shifts for the phenyl ring proton resonances for $[FeMoS_4(SPh)_2]^{2-}$ are observed at +46.6 ppm, ca. +39 ppm, and -31.2 ppm relative to free PhSH in CD_3CN . The resonance at ca. +39 ppm is very broad and is not

observable at low temperatures. Since dipolar linewidth broadening is expected to have a $1/r^6$ dependence,⁵³ this resonance has been assigned to the <u>ortho</u> protons. Upon substitution of the proton in the <u>para</u> position by a methyl group, the resonance at +46.6 ppm disappears and a resonance with three times the intensity appears at -48.7 ppm. This phenomenon signifies that the contact term in the isotropic shift expression is dominant.

The smaller isotropic shift for the <u>ortho</u> proton may reflect some contribution from the dipolar term in the opposite (downfield) direction. Since an asymmetrical system such as this would be expected to experience some degree of magnetic anisotropy, the dipolar term must be considered. And, inasmuch as this component is a function of $1/r^3$, the <u>ortho</u> position would certainly be affected the most. This trend is observed for other metal-sulfur centers as well and the relative ratios of isotropic shifts for a variety of complexes is presented in Table VI.

The analogous isotropic shifts for the $[\text{FeWS}_4(\text{SPh})_2]^{2-}$ complex occur at +44.3 ppm, ca. +37 ppm, and -30.1 ppm. The broad resonance at ca. +37 ppm is again attributable to the <u>ortho</u> protons. As with the molybdenum complex, replacement of the <u>para</u> proton with a methyl group results in the appearance of a new resonance at -46.2 ppm and the disappearance of the +44.3 ppm resonance, again suggesting that dominant contact interactions are operative.

In comparing the magnitudes of the shifts of $[FeMoS]_{\mu}$ - $(SR)_2^2$ to those of $[FeWS_4(SR)_2^2]$, one finds less than 1-2 ppm difference for any position on the phenyl ring at comparable temperatures. This suggests that the mechanism of spin delocalization responsible for the observed dominant contact shifts is relatively localized at iron and is virtually unaffected by substitution of tungsten for molvbdenum. This is in contrast to electrochemical and Mossbauer results already discussed, which demonstrate sensitivity to such an interchange. This observation is reasonable when one considers a qualitative approach⁵⁴ to the delocalization mechanism for contact shifts. The iron atom contains populated d orbitals, most of which are only half-filled. Antiparallel charge-transfer from sulfur to iron would leave unpaired spin on sulfur, which could be delocalized around the phenyl ring via π molecular orbitals:



Spin density of one sign would be placed at the <u>ortho</u> and <u>para</u> positions and by correlation effects, opposite spin would be imparted to the <u>meta</u> and <u>p</u>-methyl positions. In

effect, this mechanism would liken the thiolate ligand to a benzyl radical in its delocalization pattern.⁵⁴

The isotropically shifted ligand proton resonances are also quite temperature dependent. Plots of the isotropic shift as a function of temperature for the molybdenum and tungsten thiolate dimers are presented in Figures 11 and 12, respectively. The magnitudes of the shifts for all ring positions increases with decreasing temperature. This is in accord⁵³ with the simple Curie-Weiss behavior of the magnetic susceptibility (X) measured for the molybdenum complex and the direct proportionality between X and the magnitude of the contact term in the net isotropic shift expression. In particular, no evidence for deviations from Curie-Weiss behavior at high temperatures (v100°C) due to antiferromagnetic coupling, i.e., Fe(III)-Mo(V), are observed in the NMR spectra.

8. <u>Summary</u>

In conclusion, the $[\text{FeMS}_4(\text{SR})_2]^{2-}$ (M = Mo, W; R = Ph, p-Tol) complexes can be readily prepared and converted into chloro and S_5^{2-} analogs. From a structural standpoint, the tetraethylammonium salts are isomorphous and nearly isostructural. Their optical and infrared spectra reflect the expected differences based on those properties of the parent tetrathiometallate anions. Magnetic susceptibility measurements and proton NMR results for these

Figure 11. Temperature dependence of <u>m</u>-H, <u>p</u>-H, and <u>p</u>- CH_3 resonances of $(Et_4N)_2[FeMoS_4(SPh)_2]$ in CD_3SOCD_3 (•) and CD_3CN (•), and of $(Et_4N)_2[FeMoS_4(S-p-To1)_2]$ in CD_3CN (•) solution.



Figure 12. Temperature dependence of $\underline{m}-H$, $\underline{p}-H$, and $\underline{p}-CH_3$ resonances of $(Et_4N)_2[FeWS_4(SPh)_2]$ in CD_3CN (•) and of $(Et_4N)_2[FeWS_4(S-\underline{p}-Tol)_2]$ in CD_3CN (•).



complexes are nearly independent of metal substitution. Significant differences between M = Mo and W are observed in electrochemical measurements and Mössbauer spectra, and are consistent with greater "ferrous" character in the tungsten complexes due to less electron withdrawal by tungsten relative to molybdenum.

B. $[FeMS_4(OR)_2]^2$ (M = Mo, W; R = Ph, <u>p</u>-Tol)

1. Synthesis and Interconversions

The phenolate complexes, $(Et_4N)_2[FeMS_4(OR)_2]$, can be synthesized by reaction of $(Et_4N)_2[FeMS_4Cl_2]$ with the anhydrous sodium salt of the appropriate phenol. This represents a simple ligand exchange reaction where concomitant precipitation of sodium chloride from MeCN drives the reaction to completion in a short time. Attempts to prepare and isolate the molybdenum complex by addition of an excess of PhOH/Et₃N to an MeCN solution of $[FeMoS_4Cl_2]^2$ met with failure. Optical spectra of the reaction mixture indicated quantitative formation of the phenolate complex under these conditions, but when nonpolar solvent is introduced to precipitate the product, only unreacted $(Et_4N)_2$ - $[FeMoS_4Cl_2]$ separates out. This result is in contrast to the preparation of the aryl thiol complexes previously discussed, which can be isolated via this latter route. This is most likely related to the greater solubility of

the phenolate complex and does not necessarily suggest that thiolate is a much better ligand than phenolate for iron (II) in these dimeric complexes.

Unlike their thiolate analogs, the tetraethylammonium salts of $[\text{FeMS}_4(\text{OPh})_2]^{2-}$ are isolated as 1:1 MeCN solvates when saturated solutions are allowed to cool very slowly. The presence of solvent molecules has been established by elemental analysis, X-ray crystallography, and NMR techniques, and suggests that the phenolate complexes may not be isostructural with their thiolate analogs. The complexes can be obtained in unsolvated form by rapid precipitation from MeCN with THF or Et_2O .

Once prepared and isolated, the phenolate complexes are quite stable in the absence of oxygen and moisture. They demonstrate interconversion chemistry analogous to the thiolate complexes already discussed. For example, treatment with two equivalents of PhCOCl in MeCN results in a rapid conversion to the corresponding dimeric chloro complex. Presumably, this occurs via the same mechanism that has been documented for the Fe_4S_4 and Fe_2S_2 thiolate complexes,²⁹ i.e., benzoylation of the coordinated ligand.

Reaction of the phenolate complexes with a slight excess of PhSH in MeCN results in quantitative formation of the corresponding thiolate species. This can be viewed as simple protonation of the phenolate ligand by the stronger acid, PhSH. The overall reactivity of the
Figure 13. Synthesis and reactivity of $[FeMS_4(OPh)_2]^{2-}$ (M = Mo, W).



Figure 13

phenolate complexes is illustrated in Figure 13.

It is apparent that the phenolate dimers are analogous to their thiolate counterparts in that they possess reasonable stability and undergo reactivity with retention of the FeS₂M core.

2. Structure

The crystal structure (Et₄N)₂[FeMoS₄(OPh)₂]·MeCN has been solved and is illustrated in Figure 14. Important bond distances and angles are listed in Table V. The structure contains discrete cations, anions, and MeCN molecules in a 2:1:1 ratio. The structure is not disordered in any way, but due to near perfect alignment of the solvent molecules on a major crystal symmetry axis, the cations possess a pseudosymmetry that is different from that of the anions. This complication has resulted in a current refinement factor of 14%. Use of anisotropic thermal parameters for all atoms and non-standard refinement techniques are currently being employed to resolve this problem. Unfortunately, this difficulty prevents any meaningful comparisons with the thiolate analog structure, which has been more extensively refined. At present, nearly all core bond distances in the phenolate complex structure are ${\sim}0.03~{
m \AA}$ longer than corresponding ones in the thiolate species. In view of the fact that bond distances usually shorten as the level of refinement increases, this discrepancy

Figure 14. X-ray crystal structure of $(Et_4N)_2[FeMoS_4-$ (OPh)₂]·MeCN. Ellipsoids represent fifty percent probability.



Distances				
Mo-Fe	2.797	Fe-S2	2.308	
Mo-Sl	2.279	Fe-05 1.861		
Mo-S2	2.266	Fe-06	Fe-06 1.932	
Mo-S3	2.107	05-01	05-01 1.362	
Mo-S4	2.144	06-C7 1.206		
Fe-Sl	2.273			
Angles				
Mo-Sl-Fe	75.81	S1-Fe-S2	103.83	
Mo-S2-Fe	75.38	S1-Fe-05 113.23		
S1-Mo-S2	104.98	Sl-Fe-06 111.84		
S1-Mo-S3	108.53	S2-Fe-05 111.82		
SI-Mo-S4	109.64	S2-Fe-06 114.04		
S2-Mo-S3	110.71	05-Fe-06 102.43		
S2-Mo-S4	108.91	Fe-05-Cl 133.09		
S3-Mo-S4	113.70	Fe-06-C7 135.43		

Table V. Selected Interatomic Distances (Å) and Angles (deg) for $(Et_4N)_2[FeMoS_4(OPh)_2]$ ·MeCN.

may become negligible.

Certain gross structural differences that will not be altered significantly by further refinement can be mentioned. The most obvious of these are the relative orientations of the phenyl rings in either structure. Since both structures have been portrayed using nearly the same perspective, one can see that the phenyl rings are nearly coplanar in $[\text{FeMoS}_4(\text{OPh})_2]^{2-}$, but close to perpendicular in $[\text{FeMoS}_4(\text{SPh})_2]^{2-}$.

Analysis of the iron-oxygen distances is difficult due to the lack of structurally characterized tetrahedral iron(II)-oxygen complexes and the relatively low level of refinement in the structure. The current average Fe-O distance is 1.90 Å, which is ~ 0.1 Å shorter than the average terminal Fe-O distance⁵⁵ in $[Fe(C_5H_7O_2)_2]_2$. The corresponding average distance⁵⁶ in $[Fe(C_5H_7O_2)_3]$ is 1.95 Å. As the Fe-O distance in $[FeMOS_4(OPh)_2]^2$ will undoubtedly shorten slightly upon further refinement, it may indicate a rather strong interaction between iron and oxygen in these complexes. Further evidence of this is presented in the following sections.

3. Optical and Infrared Spectra

The optical spectra of the $[FeMS_4(OPh)_2]^{2-}$ (M = Mo, W) are shown in Figure 15, while significant data are presented in Table III. As with their thiolate analogs,

Figure 15. Electronic spectra of $(Et_4N)_2[FeMS_4(OPh)_2]$ (M = Mo, W) in acetonitrile solution at 23°C.



these complexes demonstrate intense absorptions between 300 and 500 nm. This result is again attributed to splitting of degenerate sulfur \rightarrow molybdenum or tungsten charge-transfer transitions upon coordination to iron. Also, the optical spectrum of $[\text{FeWS}_4(\text{OPh})_2]^{2-}$ is shifted to higher energy relative to $[\text{FeMoS}_4(\text{OPh})_2]^{2-}$, analogous to the trend observed for the thiolate complexes, and presumably occurs for reasons already discussed in Section III.A.3. Below 300 nm, both complexes demonstrate very intense absorptions that are undoubtedly due, in part, to ligand $\pi \rightarrow \pi^*$ transitions.

It was initially hoped that spectra of these complexes might aid in assigning the terminal ligand \rightarrow iron chargetransfer transition(s), since the only physical perturbation is substitution of oxygen for sulfur. The spectra exhibit a variety of differences with respect to those of the thiolate analogs, preventing such qualitative analysis. The most obvious of these is that the spectra are blueshifted relative to those of the corresponding thiolate complexes. These results are similar to those observed upon substitution of chloride for thiolate; they seem to correlate to the relative electronegativities of the ligand atoms. Unlike the thiolate complexes, inductive effects observed when p-Tolo⁻ is substituted for PhO⁻ cause significant perturbation (\sim 5-10 nm) of the absorption maxima.

Broad, asymmetrical absorptions are observed in the near-infrared region at ca. 750 nm ($\epsilon = 170 \text{ M}^{-1} \text{ cm}^{-1}$) and

780 ($\epsilon = 140 \text{ M}^{-1} \text{ cm}^{-1}$) for [FeMoS₄(OPh)₂]²⁻ and [FeWS₄-OPh)₂]²⁻, respectively. The spectrum of the molybdenum complex is shown in Figure 5. These near-infrared spectra are blue-shifted by more than 100 nm from the corresponding absorpances recorded for the thiolate analogs. For comparison, the ${}^{5}T_{2g} \rightarrow {}^{5}E_{g}$ d-d transition 57 for octahedral $[Fe(OH_2)_6]^{2+}$ occurs at ca. 1000 nm. Owing to the greater magnitude of octahedral vs tetrahedral crystal field splitting energies, it is doubtful that these higherenergy, near-IR absorptions of the phenolate complexes can be satisfactorally explained by simple ${}^{5}E \rightarrow {}^{5}T_{2}$ d-d transi-Intervalence charge-transfer between metal centers, tions. as discussed in Section III.A.3. could account for these absorptions, but such an assignment will have to await further characterization of known tetrathiometallate complexes.

The phenolate dimers represent the first synthetic examples of molybdenum-iron-sulfur compounds containing oxygen ligation on iron. Because of this, direct comparisons to other similar systems are not possible. Fortunately, preliminary results⁵⁸ indicate that oxygen analogs of the one, two, and four iron-sulfur centers possess reasonable stability and are synthetically accessible. In particular, spectral measurements on $[Fe(OPh)_4]^{2-}$ and $[Fe_2S_2(OPh)_4]^{2-}$ should prove useful in interpreting optical data for the molybdenum and tungsten phenolate dimers. Infrared spectra for both $[\text{FeMoS}_4(\text{OPh})_2]^{2-}$ and $[\text{FeWS}_4-(\text{OPh})_2]^{2-}$ between 250-600 cm⁻¹ show splitting of the single metal-sulfur stretch observed for the parent tetrathio metallate into components at slightly higher and lower energies upon coordination to iron, analogous to spectra obtained for the thiolate complexes.

4. Electrochemistry

Electrochemical measurements on the complexes, $(Et_4N)_2$ -[FeMS₄(OR)₂] (M = Mo, W; R = Ph, <u>p</u>-Tol), have been performed by using dc polarography and cyclic voltammetry. All pertinent information is given in Table IV, along with that obtained for the thiolate analogs obtained under identical conditions. As mentioned before, results obtained by using polarography with a dropping mercury electrode were superior to those acquired using cyclic voltammetry.

Electrochemical measurements on the phenolate complexes from 0.0 V to -2.0 V (\underline{vs} SCE) indicate only one electrochemically irreversible reduction. The irreversible nature of this single reduction is based on slopes (72-77 mV) derived from plots of log [i/(i_D-i)] <u>vs</u> voltage. These values are significantly greater than the theoretical value of 59 mV for a one-electron reversible reduction.

The reduction potentials of the molybdenum and tungsten phenolate dimers are -1.52 V and -1.68 V, respectively. As with the thiolate analogs, the tungsten complex is more difficult to reduce (by ~160 mV) than its molybdenum counterpart. This result agrees with the observed trend that tungsten complexes generally possess more negative reduction potentials than corresponding molybdenum complexes.

As mentioned, the reduction potentials of the phenolate dimers are significantly more negative (~ 250 mV) than those of the corresponding thiolate complexes. These results are in contrast to those obtained¹⁷ for the $[FeMoS_{\mu}Cl_{2}]^{2-}$ ion, which suggests that substitution of a more electronegative ligand atom, i.e., chlorine, results in a complex that is easier to reduce (10 mV). However, they are in agreement with those obtained ⁵⁹ for the $[Fe_{\mu}S_{\mu}(OPh)_{\mu}]^{2-}$ complex, which indicates that phenolate ligation to iron in these metal-sulfur systems results in a complex that is more difficult to reduce, relative to its thiolate analog. This trend implies that oxygen ligation tends to stabilize the oxidized form of these complexes to a greater extent than sulfur. Mössbauer and NMR results, to be discussed later, reinforce the observed trend in electrochemistry.

Furthermore, greater average negative shifts in reduction potential are observed when <u>p</u>-Tolo⁻ replaces PhO⁻, than when <u>p</u>-Tols⁻ is substituted for PhS⁻ (\sim 50 mV <u>vs</u> \sim 15 mV). The direction of the shift can be explained as before by a simple inductive effect of the electronreleasing p-methyl group.

5. Magnetic Susceptibility

The room temperature magnetic susceptibilities of the complexes, $(Et_4N)_2[FeMS_4(OPh)_2]$ ·MeCN (M = Mo, W), have been measured by using the Faraday method. Data obtained have been corrected for diamagnetic contributions due to ligands, cations, and solvent molecules using Pascal's constants. These data appear in Table IV, along with that for the thiolate complexes. The experimental values of the magnetic moments for the molybdenum and tungsten phenolate dimers are 5.08 BM and 5.07 BM, respectively, and are in accord with an S = 2 ground state, i.e., four unpaired electrons. They also compare well with the values obtained for the thiolate analogs, within experimental uncertainty. Again, the question of a high-spin Fe(III)-Mo(V) or a high-spin Fe(II)-Mo(VI) interaction arises. Mössbauer results, to be discussed next, suggest that the latter is a better description of the formal oxidation states.

6. Mössbauer Spectra

The zero-field Mössbauer spectrum of a polycrystalline sample of $(Et_4N)_2[FeMoS_4(OPh)_2]$ ·MeCN diluted with boron nitride has been recorded at 4.2 K. The spectrum is shown in Figure 16 and relevant parameters are listed in Table IV. The observed isomer shift is 0.57 mm/s and

Figure 16. Mössbauer spectrum of $(Et_4N)_2[FeMoS_4(OPh)_2]$. MeCN in the solid state diluted with boron nitride at 4.2 K with zero applied field. Vertical bar indicates one percent absorption.



the quadrupole splitting is 1.20 mm/s. The asymmetric nature of the quadrupole doublet is probably due to a slightly non-random distribution of crystal orientations in the sample. To date, no solution Mössbauer data on $[\text{FeMoS}_4(\text{OPh})_2]^{2-}$ have been obtained. Also, none are available for the tungsten analog, thus preventing comparisons to the molybdenum complex.

Fortunately, solid sample data for $[\text{FeMoS}_4(\text{SPh})_2]^{2-}$ have been obtained. The measured isomer shift is 0.47 mm/s and quadrupole splitting is 1.73 mm/s. The isomer shift for the phenolate complex, 0.57 mm/s, is significantly higher than that of the thiolate analog, and, together with the change in quadrupole splitting (0.53 mm/s), reflects a significant rearrangement of charge around the iron nucleus in the phenolate complex.

Comparing the observed isomer shift for the phenolate dimer with tabulated values for iron in various tetrahedral sulfur environments^{15a} yields a formal oxidation state on iron of +2.3 (see Figure 9). This represents a significant increase in ferrous character (0.10 mm/s) for the phenolate complex relative to its thiolate analog, and certainly would not be predicted by simple electronegativity arguments. These results parallel those obtained¹⁷ for the [FeMoS₄Cl₂]²⁻ ion, which yields an isomer shift of 0.60 mm/s. For comparison, substitution of phenolate for thiolate on the Fe₄S₄ core increases⁵⁹ the

isomer shift by ca. 0.1 mm/s.

The higher ferrous character of the iron in the phenolate dimer is in accord with observed electrochemical results already discussed. Together, they suggest a significant increase in the d electron density around the iron nucleus which has the net effect of screening the nucleus from existing s electron density, thereby increasing the isomer shift. One possible explanation for the above phenomenon would be a notable degree of covalency in the iron-oxygen interaction. Proton NMR results (vida infra) also support such an interpretation.

Based on results obtained when tungsten is substituted for molybdenum in the thiolate dimers, the isomer shift of the $[\text{FeWS}_4(\text{OPh})_2]^{2-}$ complex should be $\sim 0.6 \text{ mm/s}$. Verification of this prediction will have to await future measurements.

7. Nuclear Magnetic Resonance Spectra

Proton NMR spectra of the complexes, $(Et_4N)_2[FeMS_4-(OR)_2]$ ·MeCN (M = Mo, W; R = Ph, <u>p</u>-Tol), have been recorded as a function of temperature in CD₃CN; isotropic chemical shifts are observed for the ligand protons. Typical spectra for $[FeMoS_4(OR)_2]^{2-}$ complexes are presented in Figure 17 and the isotropic shifts at room temperature are listed in Table III. Plots of chemical shift <u>vs</u> temperature for both the molybdenum and tungsten phenolate dimers

Figure 17. NMR spectra of $(Et_4N)_2[FeMoS_4(OPh)_2]$ in CD_3CN at 50°C (A) and of $(Et_4N)_2[FeMoS_4-(O-p-Tol)_2]$ in CD_3CN at 50°C (B). Small amounts of impurity are denoted by X. Chemical shifts are in parts per million from Me_4Si .



Figure 17

appear in Figures 18 and 19, respectively. As before, those shifts downfield of tetramethylsilane are negative in sign; those upfield are positive. Likewise, all shifts are reported relative to their diamagnetic references.

At 297 K, the measured isotropic shifts for $[FeMoS_{\mu} (OPh)_{3}^{2-}$ are +47.6 ppm, ca. +45 ppm, and -43.5 ppm. The resonance at +45 ppm is very broad and has been assigned to the ortho hydrogens for reasons already discussed in Section III.A.7. Upon substitution of a methyl group in the para position, the resonance at +47.6 ppm disappears and a new resonance at three times the intensity appears downfield at -50.2 ppm (at 293 K). This effect is again indicative of a dominant contact term in the net isotropic shift expression, similar to results observed for the thiolate complexes. Magnitudes of isotropic shifts, relative to those of the meta protons, are listed in Table VI. The general trend of para > ortho > meta is obeyed, but the relative shifts for ortho and para are less than corresponding values for $[FeMoS_{\mu}(SPh)_{2}]^{2-}$. This effect is due to a greater increase in the meta shift (~12 ppm), relative to ortho and para (v6 and v1 ppm, respectively), and may represent an enhanced contribution by the dipolar term in the opposite direction, due to closer proximity to the paramagnetic center.

Similar results are noted for the $[FeWS_4(OPh)_2]^{2-}$ ion, whose isotropic shifts at 293 K are +45.3 ppm, ca. +42 ppm,

Figure 18. Temperature dependence of <u>m</u>-H, <u>p</u>-H, and <u>p</u>-CH₃ resonances of $(Et_4N)_2[FeMoS_4(OPh)_2]$ in CD₃CN (**O**) and of $(Et_4N)_2[FeMoS_4(O-p-To1)_2]$ in CD₃CN (**D**).



Figure 18

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Figure 19. Temperature dependence of <u>m</u>-H, <u>p</u>-H, and

<u>p</u>-CH<sub>3</sub> resonances of (Et_4N)_2[FeWS_4(OPh)_2]

in CD<sub>3</sub>CN (•) and of (Et_4N)_2[FeWS_4(O-p-Tol)_2]

in CD<sub>3</sub>CN (•).
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Complex	ortho	meta	para
[FeMoS4(SPh)2] ²⁻	1.25	1.00	1.49
$[FeMoS_4(OPh)_2]^2$	1.03	1.00	1.09
[Fe ₂ S ₂ (SPh) ₄] ^{2-b}	1.09	1.00	1.81
$[Fe_4S_4(SPh)_4]^{2-c}$	1.34	1.00	1.96
$[Fe_4S_4(OPh)_4]^{2-a}$	1.04	1.00	1.29
$[Fe_4S_4(SPh)_4]^{3-e}$	g	1.00	1.68
[Fe6Mo2S8(SPh)9] ^{3-f,h}	g	1.00	1.73

Table VI. Comparison of Relative Isotropic Shifts^a for Various Metal-Sulfur Centers in CD₃CN Solution.

^aRelative to <u>meta</u> shift; 22-25°C.

^bReference 67.

^cReference 69.

^dReference 59.

^eReference 68.

f_{Reference 70.}

g_{Obscured}.

^hIn CD_3SOCD_3 solution.

and -42.7 ppm for the <u>para</u>, <u>ortho</u>, and <u>meta</u> protons, respectively. The resonance for the <u>p</u>-methyl protons shifts downfield to -48.5 ppm, again demonstrating the typical pattern for a dominant contact interaction. Little change is noted in the magnitude of the isotropic shifts at all ring positions when tungsten is substituted for molybdenum, again suggesting that the spin delocalization mechanism is not sensitive to changes at the other end of the molecule.

Qualitatively, one might expect significant changes in the absolute magnitudes of corresponding chemical shifts when thiolate is replaced by phenolate. Experimentally, the shifts for the phenolate complexes are significantly larger than those of the thiolate complexes, particularly for the ortho and meta positions (45 vs 39 ppm and -43.5 vs -31.2 ppm, respectively, for the molybdenum complexes). This occurs for the para resonance as well, but to a lesser extent (47.6 vs 46.6 ppm). These data are similar to NMR results⁵⁹ obtained for $[Fe_{\mu}S_{\mu}(OPh)_{\mu}]^{2-}$ vs $[Fe_{\mu}S_{\mu}(SPh)_{\mu}]^{2-}$, and clearly indicates more delocalization of unpaired spin density when phenolate replaces thiolate as a ligand on The actual explanation for this effect may be due to iron. a combination of several factors: (i) the anomalously short iron-oxygen distance; (ii) some degree of covalency in the iron-oxygen interaction; (iii) the improved orbital energy match between oxygen and carbon vs sulfur and

carbon, which should enhance the delocalization of unpaired spin density into the remainder of the phenyl ring.

The temperature dependence of the observed isotropic shifts parallels that obtained for the thiolate analogs. The relative magnitudes of all shifts increases with decreasing temperature. These data are indicative of simple Curie-Weiss behavior of the magnetic susceptibility, similar to that observed for $(Et_4N)_2[FeMoS_4(SPh)_2]$. Quantitative treatment of this will have to await the results of magnetic susceptibility measurements as a function of temperature.

8. Summary

Both the molybdenum and tungsten phenolate dimers can be readily prepared and isolated in crystalline form as their tetraethylammonium salts. They can be readily converted into the thiolate and chloro analogs by treatment with PhSH and PhCOC1, respectively. Dissimilarities in optical and infrared spectra can be related to analogous differences in these properties for the free tetrathiometallates. Magnetic susceptibility and proton NMR results are essentially insensitive to replacement of molybdenum by tungsten. Electrochemical measurements show a more negative reduction potential for the tungsten dimer, in accord with the suggested reasons in Section III.B.4.

C. Comparisons Between Phenolate and Thiolate Ligation

Both classes of dinuclear complexes are most readily accessible by ligand exchange reactions via combination of the $[\text{FeMS}_4\text{Cl}_2]^{2-}$ (M = Mo, W) ion with the anhydrous sodium salt of the appropriate ligand. The $[\text{FeMS}_4(\text{OPh})_2]^{2-}$ (M = Mo, W) species can be isolated as a l:l MeCN solvate when allowed to crystallize slowly. Once obtained as their tetraethylammonium salts, all complexes react slowly with air and moisture in the solid form, but are much more sensitive to these reagents in solution. Both the thiolate and phenolate dimers react with two equivalents of PhCOCl in MeCN to yield the $[\text{FeMS}_4\text{Cl}_2]^{2-}$ complex in quantitative fashion.

Direct structural comparisons between the $[\text{FeMoS}_4-\text{SPh})_2]^{2-}$ and $[\text{FeMoS}_4(\text{OPh})_2]^{2-}$ ions are difficult due to the dissimilarity in their respective refinement factors. Average FeS_2MS_2 core bond distances for the phenolate complex are currently ca. 0.03 Å larger than corresponding distances in the thiolate complex. The only major difference between the two structures is the relative orientation of the phenyl rings.

The optical spectra of the phenolate complexes are blueshifted and bear little resemblance to those of the thiolate analogs, thus preventing direct assignment of the terminal ligand \rightarrow iron charge-transfer transition(s). All complexes demonstrate low intensity bands between 750 nm and

1200 nm, which are most likely ascribable to intervalence charge-transfer transitions.

Room temperature magnetic susceptibility measurements on all complexes are consistent with an S = 2 ground state. Proton NMR results indicate simple Curie-Weiss magnetic behavior down to 233 K for the phenolate and thiolate dimers.

The following trends are observed for Mossbauer parameters, electrochemical measurements, and proton NMR results, respectively:

- (i) The isomer shift is larger for the phenolate analog, indicating that the iron atom in that complex more closely resembles iron(II).
- (ii) The phenolate complexes are more difficult to reduce than their thiolate analogs.
- (iii) Isotropic shifts for the phenolate complexes are significantly larger than corresponding shifts for the thiolate species.

In conclusion, these latter comparisons demonstrate that a simple electrostatic model of these systems based on the relative electronegativities of sulfur and oxygen is not adequate and that the iron-oxygen interaction possesses notable covalent character.

D. $[Fe_2MoS_{11}]^{3-}$

1. Synthesis

The trinuclear species, $(Et_4N)_3[Fe_2MoS_{11}]$, can be prepared by reaction of $(Et_4N)_2MoS_4$ with $(Et_4N)_2[Fe_2S_{12}]$ in MeCN. Unlike the syntheses of the dimeric complexes already discussed, which involves ligand displacement, the reaction to form $[Fe_2MoS_{11}]^{3-}$ involves an oxidation-reduction process. In the course of the reaction, the FeS2Fe core is reduced by one electron, accompanied by presumed oxidation of the displaced S_5^{2-} ligand. This is analogous²¹ to the reaction sequence yielding the $[Fe_2Mos_6(SPh)_2]^{3-}$ complex ion from a mixture of MoS_4^{2-} and $[Fe_2S_2(SPh)_4]^{2-}$ in MeCN. The reaction to form $[Fe_2MoS_{11}]^{3-}$ proceeds at a substantially faster rate than the reaction that yields $[Fe_2MoS_6(SPh)_2]^{3-}$ (3-4 d vs 2 wk). In attempting to explain this difference in relative rates, one would certainly have to take into account the relative lability and ease of oxidation of bidentate S_5^{2-} vs two thiophenolate ligands. The fact that reduction of the Fe₂S₂ core does occur is in accord with the high affinity of MoS^{2-}_{4} for iron(II) rather than iron(III).

Once prepared, $(Et_4N)_3[Fe_2MoS_{11}]$ is much more sensitive to oxygen and protic solvents than the dimeric complexes. This behavior seems reasonable because the complex can be likened to reduced FeS₂Fe core

stabilized by MoS_4^{2-} . To date, the reduced dimeric species, $[Fe_2S_2(SR)_4]^{3-}$, has only been generated in solution⁶⁰ and is extremely susceptible to oxidation, analogous to the reduced tetrameric complex,⁶¹ $[Fe_4S_4(SPh)_4]^{3-}$.

Attempts to prepare the tungsten analog, $[Fe_2WS_{11}]^{3-}$, by an identical procedure failed. The optical spectrum of the reaction mixture after ca. two weeks at room temperature was that of the unreacted starting materials. This parallels the observation⁶² that $[Fe_2WS_6(SPh)_2]^{3-}$ cannot be prepared from $[Fe_2S_2(SPh)_4]^{2-}$ and WS_4^{2-} .

A comment should be made concerning the preparation of the starting material, $(Et_4N)_2[Fe_2S_{12}]$. The published procedure³⁴ involves reaction of $[Fe(SPh)_4]^{2-}$ with five equivalents of benzyl trisulfide. It was discovered that this complex can be easily prepared by reaction of less sophisticated reagents, namely ferric chloride, $(Et_4N)(SPh)$, and excess elemental sulfur. Indeed, any Fe-S or Fe-Mo-S synthesis reported to date involving benzyl trisulfide can also be carried out with an excess of sulfur.

2. Optical and Infrared Spectra

The optical spectrum of $(\text{Et}_4\text{N})_3[\text{Fe}_2\text{MoS}_{11}]$ in MeCN has been obtained and is shown in Figure 20. Intense absorptions between 700 and 300 nm are observed, which is consistent with results on the other tetrathiometallate systems already discussed, and again reflects splitting of the 475 nm band Figure 20. Electronic spectrum of $(Et_4N)_3[Fe_2MoS_{11}]$ in acetonitrile solution at 23°C.



of free MoS_4^{2-} into bands at higher and lower energy as the degeneracy of the sulfide ligands is broken by coordination to another metal center. Other features in addition to $S \rightarrow Mo$ charge-transfer absorptions are observed in the spectrum, and undoubtedly arise from $S \rightarrow Fe$ charge-transfer, as well as internal polysulfide ligand transitions.

Maxima in the spectrum of $[Fe_2MoS_1]^{3-}$ occur at nearly the same positions as those²¹ of the thiophenolate analog, $[Fe_2MoS_6(SPh)_2]^{3-}$. Indeed, the optical spectrum of the former complex resembles that of the latter set on a gradually rising absorbance. This phenomenon is exactly analogous to that observed 19a with [FeMoSg]²⁻ and $[FeMoS_{\mu}(SPh)_{2}]^{2-}$. From these two cases, it would appear that little perturbation of the electronic energy levels within the metal-sulfur core occurs when bidentate S_5^{2-} replaces two thiophenolate ligands. This is in contrast, however, to the observation that the optical spectrum 34 of $[Fe_2S_{12}]^{2-}$ differs markedly from that of its thiolate analog, 28 [Fe₂S₂(SPh)₄]²⁻. The spectrum of the former complex has absorption maxima at 370 and 445 nm, while the latter complex displays maxima at 270, 333, and 490 nm. The infrared spectrum of $(Et_4N)_3[Fe_2MoS_{11}]$ exhibits the splitting pattern typical of tetrathiomolybdate coordinated to a first-row transition metal. Absorbances assignable to molybdenum-sulfur stretches are observed at 497, 480, and 442 cm⁻¹, compared with the single band for free MoS_{μ}^{2-} at 472 cm⁻¹.

3. Electrochemistry

The electrochemical behavior of $(Et_4N)_3[Fe_2MoS_{11}]$ in MeCN solution has been examined between 0.0 and -2.0 V by using dc polarography with a dropping mercury electrode. Only one obvious reduction process occurs within this range, with a half-wave potential of -1.25 V vs SCE. The current associated with this process is 2.7 µA per mM iron and agrees well with the measured average value for the dimeric complexes already discussed (2.8 μ A per mM Fe). The polarographic wave is distorted at its maximum and beyond by what appears to be another ill-defined, multistep reduction process. This process could correspond to further reduction of the metal-sulfur core, but more likely to adsorption or reduction of the polysulfide ligand. This hypothesis depends on the observation 2^{8} that the $[Fe_2S_2(SR)_{\mu}]^{2-}$ complexes demonstrate two electrochemical reductions, while the $[Fe_2S_{12}]^2$ ion shows³⁴ no well-defined reduction characteristics, possibly for the same reason, i.e., polysulfide ligand reduction.

Plots of log $[i/(i_D-i)]$ <u>vs</u> voltage yield an average slope of 48 mV, which is substantially lower than the theoretical value of 59 mV for an electrochemically reversible one-electron process. It is unlikely, however, that the observed reduction process is actually reversible in nature, since the polarographic wave
is severely distorted near the maximum, which would certainly affect the calculated value of the slope. Also, the thiophenolate analog, $[Fe_2MoS_6(SPh)_2]^{3-}$, exhibits only one electrochemically <u>irreversible</u> reduction at -1.1 V <u>vs</u> SCE.

4. Magnetic Susceptibility

The room-temperature magnetic susceptibility of $(Et_4N)_3$ -[Fe2MoS11] has been determined by the Faraday method. After correcting for diamagnetism associated with the cations and sulfur atoms, the calculated magnetic moment is 2.50 BM per iron atom (3.54 BM per formula unit). This value is higher than the spin-only value of 1.73 BM which might be expected for a system containing high-spin iron(III) and high-spin iron(II) in a coupled arrangement to yield a net S = 1/2 state. This discrepancy could arise from three sources: (i) a significant amount of orbital contribution to the observed magnetic moment; (ii) some population of higher spin states at room temperature; (iii) a considerable amount of simple paramagnetic (hs Fe^{3+}) impurity. In view of the results obtained for the iron-sulfur centers, the second alternative seems most likely. The room-temperature magnetic moment for the antiferromagnetically coupled system, $[Fe_{\downarrow}S_{\downarrow}(SPh)_{\downarrow}]^{2-}$, is 1.08 BM per iron atom.⁶¹ Upon reduction by one electron, the same complex yields a magnetic moment of 2.18 BM per iron.

The coupled dimeric complex, $[Fe_2S_2(SPh)_4]^{2-}$, has a magnetic moment of 1.40 BM per iron (1.98 BM per mole) at 14°C,²⁸ demonstrating some population of a higher spin state at this temperature (J ~150 cm⁻¹). Since the complex, $[Fe_2MoS_{11}]^{3-}$, is essentially a reduced FeS_2Fe core stabilized by MoS_4^{2-} , one might expect its effective magnetic moment per iron to be higher than 1.40 BM (1.98 BM per mole).

In contrast, the effective magnetic moment of $(Et_4N)_3$ -[Fe2MoS6(SPh)2] is 1.6 BM per iron atom (2.2 BM per mole).⁶² This value is 0.9 BM per iron (1.3 BM per mole) lower than that obtained for $(Et_4N)_3[Fe_2MoS_{11}]$. This discrepancy could arise from intermolecular interactions at room temperature similar to the magnetic behavior of a solid sample of $(Et_4N)_2[FeMoS_4(SPh)_2]$ at low temperature. Also, the proton NMR spectra of $[Fe_2MoS_6(SPh)_2]^{3-}$ show isotropic shifts for the ligand protons that decrease with increasing temperature (25 -75°C), which is opposite in behavior to similar measurements²⁸ on $[Fe_2S_2(SPh)_4]^{2-}$. If the Fe_2Mo unit is an antiferromagnetically coupled system, the NMR data imply that its Neel temperature is lower than room temperature, unlike the FeS₂Fe unit, whose magnetic moment and isotropic shifts are still increasing at room temperature.

It is clear that in order to quantitatively assess the magnetic behavior of these trimeric complexes in relation

to observed results for the FeS2Fe dimer, both solid and solution temperature-dependent susceptibility data will have to be obtained, which should be straightforward once the recently-purchased SQUID susceptometer is operational.

5. Mössbauer Spectrum

The Mossbauer spectrum of a polycrystalline sample of $(Et_4N)_3[Fe_2MoS_{11}]$ diluted with boron nitride was obtained at 4.2 K in a weak applied magnetic field of 600 G. This spectrum is shown in Figure 21. Two slightly asymmetrical quadrupole doublets are observed instead of a magnetic spectrum, which implies that the complex experiences rapid electronic relaxation at 4.2 K. The outer quadrupole doublet, iron A, has an isomer shift of 0.44 mm/s and a quadrupole These parameters are similar to splitting of 1.41 mm/s. those for the iron site in $[FeMoS_{4}(SPh)_{2}]^{2-}$ (IS = 0.47; QS = 1.63 mm/s, and correspond to a formal oxidation state of +2.7 for iron A. In view of this, it seems logical that iron A is that coordinated to tetrathiomolybdate. These parameters also agree well with those²¹ of one iron site in $[Fe_2Mos_6(SPh)_2]^{3-}$ (IS = 0.42; QS = 1.41 mm/s).

The second site, iron B, possesses an isomer shift of 0.32 mm/s and a quadrupole splitting of 0.92 mm/s. This isomer shift corresponds to a formal oxidation state of +2.9 for iron B (see Figure 9), and again compares well with the second iron site in $[Fe_2MoS_6(SPh)_2]^{3-}$

Figure 21. Mössbauer spectrum of $(Et_4N)_3[Fe_2MoS_{11}]$ in the solid state diluted with boron nitride at 4.2 K in a 600 G applied field. Vertical bar indicates one percent absorption.



(IS = 0.30 mm/s). The quadrupole splitting observed for iron B is 0.24 mm/s greater than that measured for the corresponding iron site in the thiolate analog, and suggests a high degree of asymmetry in the electric field gradient experienced by the iron nucleus at site B in $[Fe_2MoS_{11}]^{3-}$. This effect is probably a consequence of the difference in terminal ligands on iron B, i.e., S_5^{2-} <u>vs</u> thiolate. Unfortunately, the Mössbauer parameters of $[Fe_2S_{12}]^{2-}$ have not been reported, thus preventing a direct comparison to its thiolate analog, $[Fe_2S_2(SPh)_4]^{2-}$ (IS = 0.17; QS = 0.32 mm/s). It has only been stated that they are "similar".³⁴

The key point is the resolution of two distinct iron sites for $[Fe_2MoS_{11}]^{3-}$ by Mössbauer spectroscopy, which offers further evidence for a core structure analogous to that ⁶² of $[Fe_2MoS_6(S-p-To1)_2]^{3-}$.

6. Electron Paramagnetic Resonance Spectra

A frozen solution of $(Et_4N)_3[Fe_2MoS_{11}]$ in DMA has been examined by ESR spectroscopy with an applied microwave frequency of 9.089 GHz and a power of 10 mW. At 10 K, an intense, isotropic signal is observed at g = 2.0043, and is analogous to the observed²¹ g value of 2.005 for the $[Fe_2MoS_6(SPh)_2]^{3-}$ complex.

Exact reasons for the isotropic nature of the signal at g = 2.0043 are unclear but may result from a high

degree of delocalization of the unpaired spin density over the metal centers, which would have the effect of decreasing the spin-orbit coupling constant. It can be said that the unpaired spin is not delocalized onto the molybdenum atom to any great extent, since no perturbations due to ${}^{95}\text{Mo}$ (I = 5/2) and ${}^{97}\text{Mo}$ (I = 5/2) nuclear hyperfine coupling are observed in the spectra.

7. Conclusions

The polysulfide complex $[Fe_2MoS_{11}]^{3-}$, can be prepared by direct reaction of $[Fe_2S_{12}]^{2-}$ and MoS_4^{2-} and isolated as the tetraethylammonium salt. The air-sensitive complex demonstrates optical and infrared properties in accord with bidentate tetrathiomolybdate coordination to iron. Mössbauer, ESR, and magnetic susceptibility results are qualitatively similar to those of the $[Fe_2MoS_6(SPh)_2]^{3-}$ complex, and in conjunction with elemental analysis data, support the proposed structure:



E. <u>Reactions of [FeMoS₄(SPh)₂]²⁻</u>

1. Acenaphthalene Radical Anion

Previous electrochemical results demonstrated the occurrence of an irreversible reduction process for the $[FeMoS_{\mu}(SPh)_{2}]^{2-}$ anion. In order to examine this phenomenon on a larger scale, several attempts were made to reduce $[FeMoS_{\mu}(SPh)_{2}]^{2-}$ in DMA with one to three equivalents of sodium or lithium acenaphthalenide in THF. In all cases, the product was a black, amorphous solid. All attempts at crystallization from a variety of solvent systems failed. The product was only soluble in high dielectric solvents such as DMSO, NMF, and to a slight extent, DMA. Complete dissolution of the product in these solvents was not possible indicating that some decomposition had taken place. Also, no distinguishable difference in solubility was noted when lithium instead of sodium acenaphthalenide was employed, suggesting that the product was not a salt of either of these metals. The optical spectrum of the solid in DMA/MeCN contained strong absorbances at 590, 510, 340, and 290 nm, strongly resembling the spectrum of the $[Fe(MoS_{\mu})_{2}]^{3-}$ ion,^{20a} and would represent not only reduction, since the $[Fe(MoS_{\mu})_{2}]^{3-}$ complex formally contains either molybdenum (V) or iron(I), but also substantial rearrangement of the starting material, $[FeMoS_4(SPh)_2]^{2-}$. Similar results have

been observed upon treatment of $[FeMoS_4Cl_2]^{2-}$ with other potential reductants, such as MeMgCl and NaEt₂NCS₂ (to be discussed later), as well as $(Et_4N)_2S.^{62}$ The product also reacts with an excess of PhSH/Et₃N to yield $[FeMoS_4(SPh)_2]^{2-}$, as does a genuine sample of $[Fe(MoS_4)_2]^{3-}$.

Examination of frozen solutions of $[\text{FeMoS}_4(\text{SPh})_2]^{2-}$ containing one to three equivalents of sodium acenaphthalenide by EPR spectroscopy did not show evidence for formation of any distinct half-integer spin systems. Therefore, chemical and spectroscopic evidence do not support the existence of $[\text{FeMoS}_4(\text{SPh})_2]^{3-}$ as a stable species.

2. Ferric Chloride and Thiophenolate

A reaction analogous to that¹⁶ leading to formation of $[Fe_6Mo_2S_8(SPh)_9]^{3-}$ was performed with an equimolar amount of $[FeMoS_4(SPh)_2]^{2-}$ in place of MoS_4^{2-} . It was hoped that the product might be a higher order cluster complex containing an even higher iron to molybdenum ratio than $[Fe_6Mo_2S_8(SPh)_9]^{3-}$, and thereby be a better approximation to the observed stoichiometry for the nitrogenase co-factor (\sim 6:1). The reaction product was readily purified by recrystallization. Unfortunately, elemental analysis and proton NMR results identified the product as simply $(Et_4N)_3[Fe_6Mo_2S_8(SPh)_9]$. This reaction is significant in that it demonstrates that the FeS₂Mo core of the thiolate dimer complex can be an intermediate in self-assembly

F. <u>Reactions of $[FeMoS_4C1_2]^{2-}$ </u>

1. Methyl Iodide

The reactivity of the terminal sulfur atoms on molybdenum in the $[FeMoS_4Cl_2]^{2-}$ complex has been explored. These sulfur atoms possess some net negative charge and might be expected to be susceptible to electrophilic attack by a reagent such as MeI. Reaction of $[FeMoS_{\mu}Cl_{2}]^{2-}$ with two equivalents of MeI in MeCN resulted in precipitation of an amorphous brown solid, which demonstrated no solubility in common solvents but which did dissolve in dilute nitric The solid is most likely a simple molybdenum sulfide acid. such as MoS₂ or MoS₂, judging from its solubility properties. The optical spectrum of the filtrate was identical with that reported for $[Fe_2MoS_4Cl_4]^2$. This latter complex dissociates in more polar solvents into $FeCl_{2} + [FeMoS_{4}Cl_{2}]^{2-}$, and this was observed in the optical spectrum upon addition of DMF to the solution. Quantitative conversion to [FeMo- $S_{\mu}Cl_{2}]^{2-}$ was accomplished upon addition of MoS_{μ}^{2-} .

Judging from these results, it appears that alkylation of a terminal sulfur atom does occur, but that the resulting product is unstable and immediately decomposes into an insoluble molybdenum sulfide and free FeCl₂, which can then coordinate to remaining $[\text{FeMoS}_4\text{Cl}_2]^{2-}$ to yield $[\text{Fe}_2\text{MoS}_4\text{Cl}_4]^{2-}$. This latter complex contains no terminal sulfur atoms and should not be as susceptible to attack

by MeI as the $[FeMoS_4Cl_2]^{2-}$ complex.

2. Benzoyl Chloride

In addition to the attempted alkylation described above, the reactivity of the terminal sulfur atoms towards acylation was examined. Reaction of $[\text{FeMoS}_4\text{Cl}_2]^{2-}$ with two equivalents of PhCOCl in MeCN resulted in immediate precipitation of a dark solid, leaving behind a colorless filtrate. The solid displayed no solubility in common solvents, but did dissolve in dilute nitric acid. The solid was most likely MoS₃ or MoS₂, indicating that decomposition had taken place. The reaction was not investigated further.

3. Methylmagnesium Chloride

In view of the successful ligand substitution reactions involving treatment of $[\text{FeMoS}_4\text{Cl}_2]^{2-}$ with sodium phenolate or thiolate, an attempt to form an organometallic analog was performed. The reaction of ca. three equivalents of MeMgCl in THF with one equivalent of $[\text{FeMoS}_4\text{Cl}_2]^{2-}$ in HMPA resulted in the formation of a purple-black amorphous solid mixed with magnesium chloride. The dark solid was slightly soluble in MeCN and gave an optical spectrum in that solvent identical with that reported^{20a} for $[\text{Fe(MoS}_4)_2]^{3-}$. This qualitatively suggests that reduction is preferred over simple carbon-iron sigma bond formation in this system. The reductive nature of this reaction is in accord with earlier results (Section III.E.1), which also suggest that $[Fe(MoS_4)_2]^{3-}$ is the preferred product when iron-molybdenum dimers are exposed to reducing conditions.

4. Sodium Benzylthiolate

In considering the fact that the Fe_4S_4 center coordinates benzyl, alkyl, and aryl thiols, the reaction between $[FeMoS_4Cl_2]^{2-}$ and the anhydrous sodium salt of benzyl thiol was attempted. Reaction conditions analogous to those used to prepare the aryl thiolate dimers were employed. Upon stirring a mixture of $(Et_4N)_2[FeMoS_4Cl_2]$ and two equivalents of $NaSCH_2Ph$ in MeCN, an amorphous redbrown solid precipitated; its optical spectrum corresponded to that of MoS_4^{2-} . Subsequent workup of the filtrate revealed formation of a small amount of $[Fe(MoS_4)_2]^{3-}$.

The above results suggest that benzyl thiolate, and probably alkyl thiolates as well, are too reducing in nature to stabilize the FeS_2MoS_2 core. This is evidenced by the formation of the reduced species, $[\text{Fe}(\text{MoS}_4)_2]^{3-}$, in small yield. However, attempts to prepare the $[\text{FeMoS}_4 \text{S},\text{S}-\underline{o}-\text{Xyl})]^{2-}$ complex have apparently been successful.⁶⁴ These results are in accord with those observed²⁸ for the FeS_2Fe core, which is only stabilized by aryl or \underline{o} xylyldithiolate ligands.

5. Sodium Diethyldithiocarbamate

In order to further ascertain the variety of ligands that the FeS_2MoS_2 core will tolerate, a ligand exchange reaction between $[\text{FeMoS}_4\text{Cl}_2]^{2-}$ and two equivalents of the anhydrous sodium salt of diethyldithiocarbamic acid in MeCN was explored. Reaction was immediate, producing a deep violet solution whose optical spectrum contained features at 580, 510, 340, and 290 nm, characteristic of $[\text{Fe}(\text{MoS}_4)_2]^{3-}$ formation. It is very likely that the reductant in this case is the dithiocarbamate ligand, which can be easily oxidized to a thiuramdisulfide. Indeed, Newton and coworkers⁶⁵ prepare $[\text{Fe}(\text{MoS}_4)_2]^{3-}$ from $[\text{Fe}(\text{Et}_2\text{NCS}_2)_2]$ and MoS_4^{2-} . The above experimental results represent yet another example of formation of $[\text{Fe}(\text{MoS}_4)_2]^{3-}$ via exposure of an iron-molybdenum dimer complex to reducing conditions.

G. Reactions of $[Fe_{4}S_{4}X_{4}]^{2-}$ (X = S-t-Bu, SPh, Cl)

1. <u>t</u>-Butyl Thiolate

Considering the fact that the Fe_4S_4 core readily accommodates a variety of ligand types, such as aryl and alkyl thiols,²⁴ aryl phenols,⁵⁹ and halides,²⁹ the possibility of coordinating tetrathiomolybdate to the Fe_4S_4 center was examined. Optical spectra of an MeCN solution of $[\text{Fe}_4\text{S}_4(\text{S}-\underline{t}-\text{Bu})_4]^{2-}$ and four equivalents of MoS_4^{2-} indicated no reaction had taken place after ca. four days at

room temperature. When four equivalents of a proton donor such as trimethylpyridinium hydrochloride was added, however, the reaction mixture immediately became deep red-violet in color. Subsequent workup gave a product whose optical spectrum strongly resembled that 20a of $[Fe(MoS_4)_2]^{3-}$, even though elemental analysis results agreed with the formulation, $(Me_4N)_{3n}[Fe_2Mo_2S_{10}]_n$. Also, reaction of the product with an excess of PhSH/Et₃N in MeCN gave [FeMoS_{μ}- $(SPh)_2]^{2-}$, analogous to the results observed for a genuine sample of $[Fe(MoS_4)_2]^3$. Likewise, X-ray diffraction powder patterns of "(Et₄N)_{3n}[Fe₂Mo₂S₁₀]_n" and authentic $(Et_4N)_3[Fe(MoS_4)_2]$ were very similar. When a sample of "(Et₄N)_{3n}[Fe₂Mo₂S₁₀]_n" was further purified and reanalyzed, the molybdenum-to-iron ratio rose to 1.3. These analytical and chemical data strongly suggest that $"(R_4N)_{3n}[Fe_2Mo_2 S_{10}]_n$ ", as synthesized here, is really an impure form of $(R_4N)_3[Fe(MoS_4)_2]$. A variety of potential reductants exist in the reaction mixture, such as alkyl thiol, sulfide, and iron(II), which could account for formation of the reduced product, $[Fe(MoS_4)_2]^{3-}$.

2. Thiophenolate

The reaction between $[Fe_4S_4(SPh)_4]^{2-}$ and four equivalents of MoS_4^{2-} in MeCN was also examined. In this case, the reaction mixture turned deep maroon, and a dark microcrystalline solid precipitated after being stirred for ca. four days at room temperature. The optical spectrum of the crystalline solid in MeCN corresponded exactly to that reported²¹ for the trinuclear complex, $[Fe_2MoS_6(SPh)_2]^{3^-}$. This reaction is significant in that it indicates that aryl Fe₄S₄ centers fragment in the presence of tetrathiometallates into Fe₂S₂ centers, in contrast to the results observed for an alkyl Fe₄S₄ center both with and without a proton donor. The explanation for this difference may involve electronic effects of aryl <u>vs</u> alkyl thiols towards molybdenum-iron-sulfur cores. To date, the Fe₂MoS₆ core has not been prepared with alkyl thiol ligands.⁶²

The fragmentation of $Fe_{4}S_{4}$ to $Fe_{2}S_{2}$ may be due to the affinity of MoS_{4}^{2-} for lower formal oxidation states of iron. The $Fe_{4}S_{4}$ core is best described⁶⁶ as a delocalized system containing four iron (+2.5) atoms (rather than a localized one with two iron(II) + two iron(III) atoms). Subsequent coordination by MoS_{4}^{2-} may stabilize the ferrous iron sites, thereby disrupting the delocalized core. This perturbation may be enough to initiate fragmentation of the $Fe_{4}S_{4}$ center. Like the $[Fe_{2}MoS_{11}]^{3-}$ ion, $[Fe_{2}MoS_{6}^{-}$ $(SPh)_{2}]^{3-}$ essentially represents a partially reduced $FeS_{2}Fe$ core stabilized by MoS_{4}^{2-} . Why the reaction does not continue and form $[Fe(MoS_{4})_{2}]^{3-}$ may be related to the decreased reducing ability of aryl <u>vs</u> alkyl thiols towards the metal-sulfur core, and is supported by the fact²⁸ that only aryl or <u>o</u>-xylyldithiolate complexes of the FeS₂Fe core, which formally contains iron(III), have been prepared to date.

3. Chloride

The reaction between $[Fe_4S_4Cl_4]^{2-}$ and MoS_4^{2-} in MeCN was carried out in order to determine whether the trinuclear species, $[Fe_2MoS_6Cl_2]^{3-}$, was indeed stable, or whether the Fe_4S_4 core would degrade into the mononuclear iron complex, $[Fe(MoS_4)_2]^{3-}$. Optical spectra of a reaction solution containing $[Fe_4S_4Cl_4]^{2-}$ along with four equivalents of MoS_4^{2-} indicated the formation of $[Fe(MoS_4)_2]^{3-}$ in high yield. Attempts to prepare the $[Fe_2MoS_6Cl_2]^{3-}$ complex from reaction of $[Fe_2MoS_6(SPh)_2]^{3-}$ with two equivalents of PhCOCl in MeCN have also failed.⁶²

In view of the results discussed in the preceeding sections, the preferred product obtained upon reaction of various Fe_4S_4 centers with MoS_4^{2-} is $[Fe(MoS_4)_2]^{3-}$, which represents total degradation of a tetranuclear iron center into a mononuclear one stabilized by MoS_4^{2-} . The exception is the reaction between $[Fe_4S_4(SPh)_4]^{2-}$ and MoS_4^{2-} , which stops at a dinuclear iron species, $[Fe_2MoS_6(SPh)_2]^{3-}$, stabilized by MoS_4^{2-} and thiophenolate.

H. Reactions of $[MoS_9]^{2-}$

One of the major handicaps in trying to synthesize new iron-molybdenum-sulfur complexes has been the relative lack of well characterized molybdenum-sulfur starting materials. Therefore, the reactivity of the recently reported²⁶ $[MoS_9]^{2-}$ complex has been examined. In reactions with potential reductants such as PhS⁻ and $[Fe(CO)_4]^{2-}$, the $[MoS_9]^{2-}$ complex was simply reduced to MoS_4^{2-} in near quantitative yield. In reactions with ferrous chloride and $[Fe_4S_4(SPh)_4]^{2-}$, the $[MoS_9]^{2-}$ complex behaved like MoS_4^{2-} , yielding $[FeMoS_4Cl_2]^{2-}$ and $[Fe_2MoS_{11}]^{3-}$, respectively. The excess of sulfur present in the latter reaction undoubtedly prompts formation of $[Fe_2MoS_{11}]^{3-}$ instead of $[Fe_2MoS_6(SPh)_2]^{3-}$.

Under reaction conditions that would normally give rise to "double cubane" complexes of the type, $[Fe_6Mo_2S_8(SR)_9]^{3-}$, if MoS_4^{2-} were employed, very different results were obtained with $[MoS_9]^{2-}$. Thus, reaction of ferrous chloride, EtS⁻, and $[MoS_9]^{2-}$ in a three:twelve:one ratio resulted in a mixture of products, primarily $[Fe(MoS_4)_2]^{3-}$ and the recently synthesized $[Fe_2Mo_2S_{10}]^{4-}$ ion,²² instead of $[Fe_6Mo_2S_8(SEt)_9]^{3-}$. Reaction of ferric chloride, PhS⁻, and $[MoS_9]^{2-}$ in a three:twelve:one ratio yielded an unstable product that decomposed upon standing in solution, rather than $[Fe_6Mo_2S_8(SPh)_9]^{3-}$.

Unfortunately, these reactions suggest that the $[MoS_a]^{2-}$

complex behaves as simply an oxidized form of MoS_4^{2-} , which spontaneously converts to MoS_4^{2-} under appropriate conditions.

I. <u>Reactions of Molybdenum(III) and Molybdenum(V)</u> Compounds

Considering the lack of molybdenum-sulfur starting materials mentioned earlier, the possibility of using sources of reduced molybdenum was explored.

The first compound examined was $(\text{Et}_4\text{N})_3[\text{MoCl}_6]$. It was found to be inert towards such oxidized sources of iron and sulfur as $[\text{Fe}_2\text{S}_2(\text{SPh})_4]^{2^-}$ and ferric chloride/PhS⁻. No spectroscopic evidence for even simple ligand exchange was observed. However, $[\text{MoCl}_6]^{3^-}$ did react with PhS⁻ in refluxing MeCN to yield the recently reported²⁵ complex, $[\text{Mo}_2(\text{SPh})_9]^{3^-}$. The tetraethylammonium salt of this complex was prepared on a large scale, but it could not be isolated in crystalline form. Therefore, the extinction coefficient of the complex ion was determined by measuring the absorbance at 550 nm of a solution of known concentration of the solid in MeCN. A standard solution of $[\text{Mo}_2(\text{SPh})_9]^{3^-}$ in MeCN was prepared and used in reactions with various soluble sources of oxidized iron.

Reactions between $[Mo_2(SPh)_9]^{3-}$ and dimeric sources of iron(III) such as $[Fe_2S_{12}]^{2-}$ and $[Fe_2S_2(SPh)_4]^{2-}$ were performed. In both cases, the product obtained upon precipitation with THF or by slow cooling was an ill-defined, amorphous black solid that would not completely redissolve. Filtered solutions of the material gave featureless optical spectra and decomposed upon standing. These reaction results are suggestive of a mixture of products being formed in each case, some of which are not stable in solution and eventually decompose.

Subsequent workup of a reaction mixture containing $[Mo_2(SPh)_9]^{3-}$ and $[Fe_4S_4Cl_4]^{2-}$ gave an amorphous black solid that also would not completely redissolve. Optical spectra of the soluble material contained maxima at ca. 450 nm, suggesting that simple ligand exchange had occurred, yielding $[Fe_4S_4(SPh)_4]^{2-}$ as one product. As before, the solution decomposed on standing, preventing any isolation of a crystalline product. The reaction was not investigated further.

Thus, $[Mo_2(SPh)_9]^{3-}$ does not appear to be as useful a molybdenum staring material as originally hoped. Reactions with a variety of sources of iron give rise to impure, amorphous solids, most likely mixtures, which decompose in solution.

Lastly, the reaction between $(\text{Et}_4\text{N})[\text{MoO}(\text{SPh})_4]$ and ferrous chloride was examined. It was discovered that the $[\text{MoO}(\text{SPh})_4]^-$ complex can be conveniently prepared by exposure of an MeCN solution of $[\text{Mo}_2(\text{SPh})_9]^{3-}$ to oxygen until the solution becomes an intense blue. It can be precipitated in crystalline form by the addition of

absolute ethanol.

Reaction of the oxo complex with one equivalent of ferrous chloride in MeCN, followed by precipitation of the product with isopropanol, yielded an orange-brown amorphous solid. The optical spectrum of the solid in MeCN was simply a rising absorbance. These results are very similar to those observed by Wedd, Dance, and coworkers, 36 who explored the reaction between [MoO(SPh)₄]⁻ and ferric chloride. They likewise obtained an orange solid whose optical spectrum in MeCN was a rising absorbance with a slight shoulder at ca. 380 nm. Based on elemental analysis results, they formulated the product as $(Et_4N)[Mo_2O_2-(SPh)_6C1]$.

It had been hoped that ferrous chloride might coordinate $[MoO(SPh)_4]^-$ to form a dinuclear complex, much as it does with MoS_4^{2-} to yield $[FeMoS_4Cl_2]^{2-}$. If the actual product formulation is correct, it appears that the iron simply abstracts thiophenolate from $[MoO(SPh)_4]^-$, leading to dimerization of the latter complex to $[Mo_2O_2(SPh)_6Cl]^-$. Although no other reactions between $[MoO(SPh)_4]^-$ and other sources of iron were examined, its usefulness as a start-ing material seems quite limited.

IV. CONCLUSIONS

The heteronuclear dimeric complexes, $[FeMS_4X_2]^{2-}$ (M = Mo, W; X = SAryl, OAryl), can be prepared by ligand exchange reactions involving $[FeMS_4Cl_2]^2$ or $[Fe(MoS_4)_2]^3$, and isolated in pure form as their tetraethylammonium salts. Structural analyses indicate nearly tetrahedral sulfur or sulfur-oxygen coordination around each metal center. Mössbauer and temperature-dependent magnetic susceptibility results agree with a high-spin iron(II)molybdenum(VI) description of these complexes. A variety of other physical measurements have been performed on these complexes, including dc polarography, and optical and infrared spectroscopy. Proton NMR results show that the observed chemical shifts are primarily contact in origin. They also suggest that the iron-oxygen interaction in $[FeMS_4(OAr)_2]^{2-}$ possesses significant and unexpected covalent character. Substitution of tungsten for molybdenum has little effect on observed magnetic susceptibility and NMR results but does cause perturbations in Mössbauer and electrochemical measurements for reasons already discussed.

The reactivity of these dimeric complexes towards a variety of reagents has been explored. They demonstrate interconversion chemistry similar to that observed for

iron-sulfur centers. To date, no spectroscopic or chemical evidence supports the existence of the reduced species, $[FeMoS_{\mu}(SPh)_{2}]^{3-}$.

The trinuclear species, $[Fe_2MoS_{11}]^{3-}$, can be readily prepared from the reaction of $[Fe_2S_{12}]^{2-}$ and MoS_4^{2-} . Various results, including Mössbauer, optical, infrared, and ESR spectroscopy, suggest a structure analogous to that of $[Fe_2MoS_6(SAr)_2]^{3-}$. It was discovered that this latter complex can be conveniently prepared by reaction of MoS_4^{2-} with $[Fe_4S_4(SAr)_4]^{2-}$.

A variety of reactions involving sources of molybdenum other than MoS_4^{2-} were attempted, with little success. The complex, $[MoS_9]^{2-}$, behaved like MoS_4^{2-} in several reaction situations, while exposure of $[MoCl_6]^{3-}$, $[Mo_2(SPh)_9]^{3-}$, and $[MoO(SPh)_4]^-$ to a variety of sources of iron gave rise to apparent mixtures, from which no discreet products could be isolated in pure form.

The dimeric and trimeric complexes described by this work are certainly not models for the metal center in the cofactor of nitrogenase. Besides the obvious differences in metal atom stoichiometry, the average molybdenum-sulfur distance in the dimeric complexes (2.20 Å) is shorter than that reported for the cofactor (2.35 Å) based on EXAFS results.¹⁰ The iron-molybdenum distance for the thiolate dimer is relatively close (2.76 Å) to that calculated for the cofactor (2.71 Å). Also, the formal oxidation state

of +6 for molybdenum in the dimer is higher than that reported for the molybdenum in the cofactor.¹⁰

The FeS_2 Mo core, which effectively represents replacement of one iron in the FeS_2 Fe unit by molybdenum, possesses a unique stability similar to the double cubane complexes, which represent replacement of one iron in an Fe_4S_4 core by molybdenum. Therefore, the FeS_2 Mo unit could possibly resemble a structural portion of the cofactor.

Furthermore, preliminary EXAFS results on the dimeric and trimeric complexes discussed herein have proved extremely useful in interpreting similar data on the cofactor. The study of these complexes has also served to extend greatly the area of iron-molybdenum-sulfur chemistry in general, an area that was essentially nonexistent three years ago. REFERENCES

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