

Fe-M-S Complexes Derived from MS_4^{2-} Anions (M = Mo, W) and Their Possible Relevance as Analogues for Structural Features in the Mo Site of Nitrogenase

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The field of bioinorganic chemistry is currently an open frontier for research in coordination chemistry. Early explorations in this area were initiated upon recognition of the fact that certain transition-metal ions, often in trace amounts, were essential for specific biological processes. With advances in protein crystallography and recent applications of X-ray absorption spectroscopy, the protein coordination environments for the metal ions in a number of metalloproteins and metalloprotein active sites have been revealed to near-atomic resolution.

Among the principal aims of current bioinorganic chemistry research are the isolation and characterization of synthetic analogues which by definition should "reproduce ligation modes and approach or achieve the stereochemistry of metalloprotein or metalloenzyme sites".¹ Success in this endeavour should eventually be very useful in understanding structure-function relationships in enzymes and metalloproteins. Furthermore, comparative studies between active-site analogue complexes and the active sites in metalloproteins should reveal the importance of the protein matrix in affecting the properties of the metal-containing active sites.

At times, the emphasis on the exactness in design of a metalloenzyme active-site analogue complex overshadows the basic and intrinsically interesting coordination chemistry that derives from the isolation and characterization of less exact analogues. It should be emphasized that new horizons in pure coordination chemistry have been unveiled as a result of active-site "modeling" studies. In this Account we offer a description of our studies in a quest for nitrogenase active-site analogue complexes and specifically recent results in the general area of tetrathiometalate chemistry.

Molybdenum in Biological Systems

As an essential trace metal, molybdenum is found incorporated in specific metalloenzymes in microorganisms,² plants,³ and animals.⁴ Of the known molybdoenzymes the more thoroughly and extensively studied are the nitrogenases and xanthine oxidase. Other enzymes such as nitrate reductase⁵ and sulfite oxidase^{6,7} do not contain nonheme iron and facilitate

the reduction of nitrate ion to nitrite ion and the oxidation of sulfite ion to sulfate ion, respectively.

Nitrogenase

In various nitrogen-fixing organisms examined thus far, the catalytic reduction of nitrogen to ammonia is carried out by molybdoenzymes generally referred to as nitrogenases. In all of these organisms, the nitrogen-fixing nitrogenases consist of two protein components, the Fe-Mo protein and the Fe protein. Those designated as the Fe-Mo proteins contain approximately 15-30 iron atoms, roughly equal amounts of acid-labile sulfur, and 1-2 molybdenum atoms, per M_r 200 000-230 000. The Fe proteins contain approximately 4 Fe and 4 S^{2-} per M_r 55 000-65 000.⁸

Recently a method for the isolation of an iron-molybdenum cofactor (Fe-Mo-co) from the Fe-Mo component protein of nitrogenase has been described.⁹ The Fe/Mo ratio in the Fe-Mo-co from *Azotobacter vinelandii* and *Clostridium pasteurianum* is approximately 8:1, and the cofactor contains 4-6 atoms of acid-labile sulfide per eight Fe atoms. The Fe-Mo-co in various nitrogen-fixing organisms seem to be very similar, and extracts of the Mo-Fe component from inactive mutant strains of different microorganisms are activated by the Fe-Mo-co.⁹

Mössbauer and EPR spectroscopic data on the cofactor have been interpreted in terms of a $S = 3/2$ center that contains a molybdenum and about six iron atoms in a spin-coupled structure.¹⁰ The EPR spectra of the Fe-Mo-co represent essentially the same type of structure as the one in the Mo-Fe protein, with small shifts in g values which probably reflect differences in the ligand environments.

Molybdenum K-edge, X-ray absorption fine structure (EXAFS) analyses of both the Fe-Mo protein of nit-

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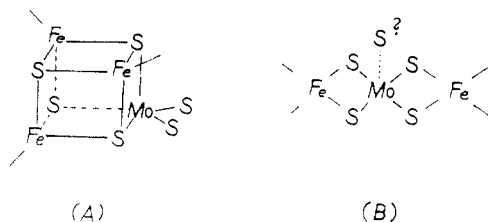


Figure 1. Possible occupancy of the first and second coordination shells around the Mo atoms in nitrogenase.

rogenase¹¹ and the Fe–Mo–co^{11,12} have shown that the sites that contain molybdenum are very similar and indicative of a Fe–Mo–S aggregate. Quantitative analysis of the X-ray absorption fine structure by a curve-fitting procedure reveals as major features 3–4 sulfur atoms in the first coordination sphere at 2.35 Å and 1–3 iron atoms further out from the Mo at ~2.7 Å. Two possible models proposed¹¹ to be consistent with the EXAFS results are shown in Figure 1.

Approaches to the Synthesis of Fe–Mo–S Complexes

Until recently, well-defined heterometallic complexes containing iron, molybdenum, and sulfur and in minimum structural compliance with the Mo EXAFS results in nitrogenase were not available. Of the two complexes that had been reported to contain Fe, Mo, and S, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}-\mu_2\text{-(S-}n\text{-C}_4\text{H}_9)_2\text{FeCl}_2$ ¹³ and $[(\text{MoS}_4)_2\text{Fe}]^{2-}$ ¹⁴ the former has been found to contain a rather long Fe–Mo distance of 3.66 Å¹⁵ while the latter appears to be a polymeric material of questionable purity.

Synthetic studies on Fe–Mo–S chemistry, guided by the nitrogenase Mo EXAFS results, not unexpectedly have intensified in the last 3 years. As a result various reports have appeared in the literature concerning the synthesis and characterization of Fe–Mo–S complexes.^{16–27} The basic approaches followed in the syntheses

of these complexes employ MoS_4^{2-} , and can be classified in two broad categories: (a) the spontaneous self-assembly reactions used extensively in the synthesis of the double cubanes with the $\text{Mo}_2\text{Fe}_6\text{S}_{11}$ framework and (b) the $\text{MoS}_4^{2-}\text{-Fe(L)}_n$ ligand exchange reactions used in the synthesis of simple Fe–Mo–S complexes containing the MoS_4 ligand. Results of the first approach appeared almost simultaneously in two independent reports concerning two quite similar complexes. The $[\text{Mo}_2\text{Fe}_6\text{S}_9(\text{SEt})_9]^{3-}$ ¹⁶ and the $[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{SPh})_9]^{3-}$ ¹⁷ complex anions reported recently possess molecular structures in which two Fe_3MoS_4 “cubane” fragments are bridged at the molybdenum sites via $(\mu\text{-S})(\mu\text{-SEt})_2$ or $(\mu\text{-SPh})_3$ units.

The EXAFS of the six-coordinate molybdenum atoms in the $[\text{Mo}_2\text{Fe}_6\text{S}_9(\text{SEt})_9]^{3-}$ and $[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{SEt})_9]^{3-}$ complexes²⁰ are quite similar to the EXAFS obtained for the Fe–Mo–co and for nitrogenase. Following the initial reports on these clusters, a number of other members of the general class of the double cubanes have been reported,¹⁸ including the $[\text{Mo}_2\text{Fe}_7\text{S}_8(\text{SR})_{12}]^{3-}$ variant¹⁹ and the one-electron reduced form of this cluster.¹⁹

In our laboratory, we have followed a stepwise approach for the eventual construction of Mo–Fe–S clusters that could serve as nitrogenase active-site analogues. As a starting point, the synthesis of simple Fe–Mo–S complexes, employing the tetrathiomolybdate anion as a ligand for iron, has been carried out. As expected, certain structural aspects of the complexes obtained are in approximate compliance with the presently accepted, elementary, features of the molybdenum site in nitrogenase. The syntheses of the analogous Fe–W–S complexes (essential for comparative studies) have been accomplished with WS_4^{2-} in parallel reactions.

The Tetrathiomolybdate Anions as Ligands

The $[\text{MS}_4]^{2-}$ complex anions are formed by the reactions of the corresponding $[\text{MO}_4]^{2-}$ oxoanions ($\text{M} = \text{Mo}, \text{W}$) with H_2S in basic aqueous solutions,²⁸ and they are members of the $[\text{MO}_x\text{S}_{4-x}]^{2-}$ series which form in these reactions. Bonding, spectroscopic, and coordination aspects of the MS_4^{2-} anions have been thoroughly studied and reviewed by Müller, Diemann, and co-workers.²⁸ Complexes of the formula $[\text{M}'(\text{MS}_4)_2]^{2-}$ ($\text{M}' = \text{Zn},^{29} \text{Ni},^{30,31} \text{Fe},^{14} \text{Co},^{32,33} \text{Pd},^{31} \text{Pt}^{31}$) have been synthesized, and structural determinations by X-ray diffraction have been reported for these complexes ($\text{M} = \text{Mo}, \text{M}' = \text{Ni};^{34} \text{M} = \text{W}, \text{M}' = \text{Zn};^{35}$ and $\text{M} = \text{W}, \text{M}' = \text{Co}^{36}$). The $[\text{MS}_4]^{2-}$ bidentate ligands in the $[\text{M}'$

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(MS₄)₂]²⁻ complexes have been placed close to the dithiophosphinate anions in the spectrochemical series.²⁸ The bonding in the 4d⁰ tetrathiometalates has been described by molecular orbital treatments,³⁷ and the principal absorptions in the electronic spectra have been assigned as S → M_d transitions.

The infrared and Raman spectra of the MS₄²⁻ anions have been studied, and absorption bands have been assigned to the symmetric M-S stretching vibrations (M = Mo, ν₁(A₁) = 458 cm⁻¹, M = W, ν₁(A₁) = 481 cm⁻¹) and the antisymmetric stretching vibrations (M = Mo, ν(T₂) = 472 cm⁻¹, M = W, ν(T₂) = 458 cm⁻¹).²⁸ In the [M'(MS₄)₂]²⁻ complexes, each of these vibrations splits into the two components as the [MS₄]²⁻ anions assume C_{2v} microsymmetry. In practice, the terminal M = S groups are characterized by one or two vibrational frequencies between 480 and 510 cm⁻¹ and the bridging M-S groups by frequencies between 430 and 460 cm⁻¹.

Evidence for the possible involvement of the MoS₄²⁻ anion as a structural component in the nitrogenase active site has been presented in recent studies by Zumft.³⁸ Thus chromatography on acid-treated, re-neutralized solutions of the Fe-Mo protein from *Clostridium pasteurianum* allows for the isolation of a fraction with a visible spectrum identical with that of aqueous MoS₄²⁻. These results are particularly interesting in view of the fact that the formation of MoS₄²⁻ from components released under the reported experimental conditions is not very likely.

Syntheses and Reactions of Fe-MS₄ Complexes

In the iron-tetrathiometalate complexes obtained thus far in our laboratory (Figure 2) the MS₄²⁻ anions serve as either bidentate chelates or bridging ligands. The infrared vibrational frequencies of the perturbed MS₄ units in these complexes can be readily interpreted in terms of the molecular structures of the Fe-MS₄ complexes (Figure 2).

The apparently simple [Fe(S₂MoS₂)₂]²⁻ dianion, member of the well-known²⁸ series of the divalent [M'(S₂MS₂)₂]²⁻ complexes, has been reported previously a number of times.^{14,39} In nearly every report, attention was brought to difficulties in obtaining this material in pure form. Upon a reinvestigation of the Fe⁺²/MoS₄²⁻ system it became apparent to us²⁶ and others⁴⁰ that the only stable, well-defined complex that could be isolated in this system was the [Fe(S₂MoS₂)₂]³⁻ trianion (5, Figure 2). Predictably, high yields of this complex could be obtained only in the presence of a reducing agent. The use of the xanthate²⁶ or dithiocarbamate⁴⁰ complexes of iron as reagents in the metathetical reaction 5 (Figure 2) allows for the concurrent presence of the 1.1 dithio ligands which serve as reducing agents.

The visible spectrum of the [Fe(S₂MoS₂)₂]³⁻ trianion²⁶ is identical with the spectrum reported for the alleged "(Fe₄Mo₄S₂₀)⁶⁻" cluster by Averill and co-workers.⁴¹ We have reproduced the reported synthesis of the "Fe₄Mo₄S₂₀" hexaanion and found that the Et₄N⁺ salt

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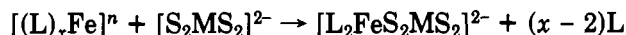
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of this material is X-ray isomorphous, and identical in all other respects to the Et₄N⁺ salt of [Fe(S₂MoS₂)₂]³⁻.

By contrast to the apparent instability of a discrete [Fe(S₂MoS₂)₂]²⁻ unit,⁴² the [Fe(S₂WS₂)₂]²⁻ dianion is reasonably stable and can be obtained as a green, paramagnetic (S = 2), microcrystalline tetraphenylphosphonium salt in analytically pure form.^{14,21} A clue regarding the origin of the instability of the [Fe(S₂MoS₂)₂]²⁻ complex may be found in the base adduct forming tendencies of the analogous tetrathiotungstate complex.²¹ Such tendencies may cause rapid polymerization of the [Fe(S₂MoS₂)₂]²⁻ complex. The [Fe(S₂WS₂)₂]²⁻ dianion appears to maintain its integrity in weakly coordinating or noncoordinating solvents (acetone, CH₂Cl₂, etc.). However, in coordinating solvents (dimethylformamide (DMF), pyridine (py), or dimethyl sulfoxide (Me₂SO)), the complex forms²¹ base adducts of the type [Fe(S₂WS₂)₂L₂]²⁻.

A single-crystal, X-ray structure determination of the bis-DMF adduct²¹ shows the iron atom located on a crystallographic center of symmetry and coordinated by two bidentate WS₄²⁻ ligands and two DMF molecules in a trans arrangement (7, Figure 2).

Rather stable mixed-ligand complexes of the type [(L)₂FeS₂MS₂]²⁻ can be obtained^{22,23} (L = PhS⁻, Cl⁻) by metathetical reactions such as



The S₂MS₂²⁻ ligands in the [L₂FeS₂MoS₂]²⁻ complexes are capable of further coordination to Lewis acids, particularly in nonpolar solvents. Addition of FeCl₂ to the [Cl₂FeS₂MS₂]²⁻ complexes results in the formation of the [(Cl₂Fe)₂S₂MS₂]²⁻ trimers²³ (3, Figure 2). For M = Mo the trimer, at least partially, resembles the proposed structure model for the first and second coordination spheres around the Mo atom in nitrogenase (Figure 1b). The reactions of organic trisulfides with the Fe(SPh)₄²⁻ complex anion have been found⁴³ to produce [Fe₂S₂(SPh)₄]²⁻ and the unusual Fe₂S₁₂²⁻ complex in which two S₆²⁻ bidentate chelates are coordinated to each of the two Fe(III) ions in a FeS₂Fe core. An apparently similar reaction, between the [(PhS)₂Fe(S₂MS₂)]²⁻ complexes and organic trisulfides, results in the generation of the S₆²⁻ ligands and formation of the [(S₆)Fe(S₂MS₂)]²⁻ complexes²⁴ (reaction 2, Figure 2).

The exceptional stability of the complexes containing the S₂FeS₂MoS₂ framework prompted us to explore the ability of MoS₄²⁻ to serve as a ligand for iron already coordinated to cysteinyl residues on a polypeptide chain. Interactions of MoS₄²⁻ with the Fe(II) complexes⁴⁴ of the Gly₂(Cys-gly)₂ octapeptide or the (Gly)₂(Cys-Gly)₄ tetradecapeptide, in DMF solution, were apparent by the characteristic absorption electronic spectra of the perturbed MoS₄²⁻ groups (Figure 3). The same (RS)₂FeS₂MoS₂ chromophore was obtained regardless of the polypeptide used, and the tetradecapeptide did not form a complex containing the (RS)₂Fe(S₂MoS₂)Fe(SR)₂ unit.⁴⁵

(42) The corresponding [Fe(S₂MoS₂)₂]³⁻ trianion undergoes an irreversible one-electron oxidation on a platinum anode.

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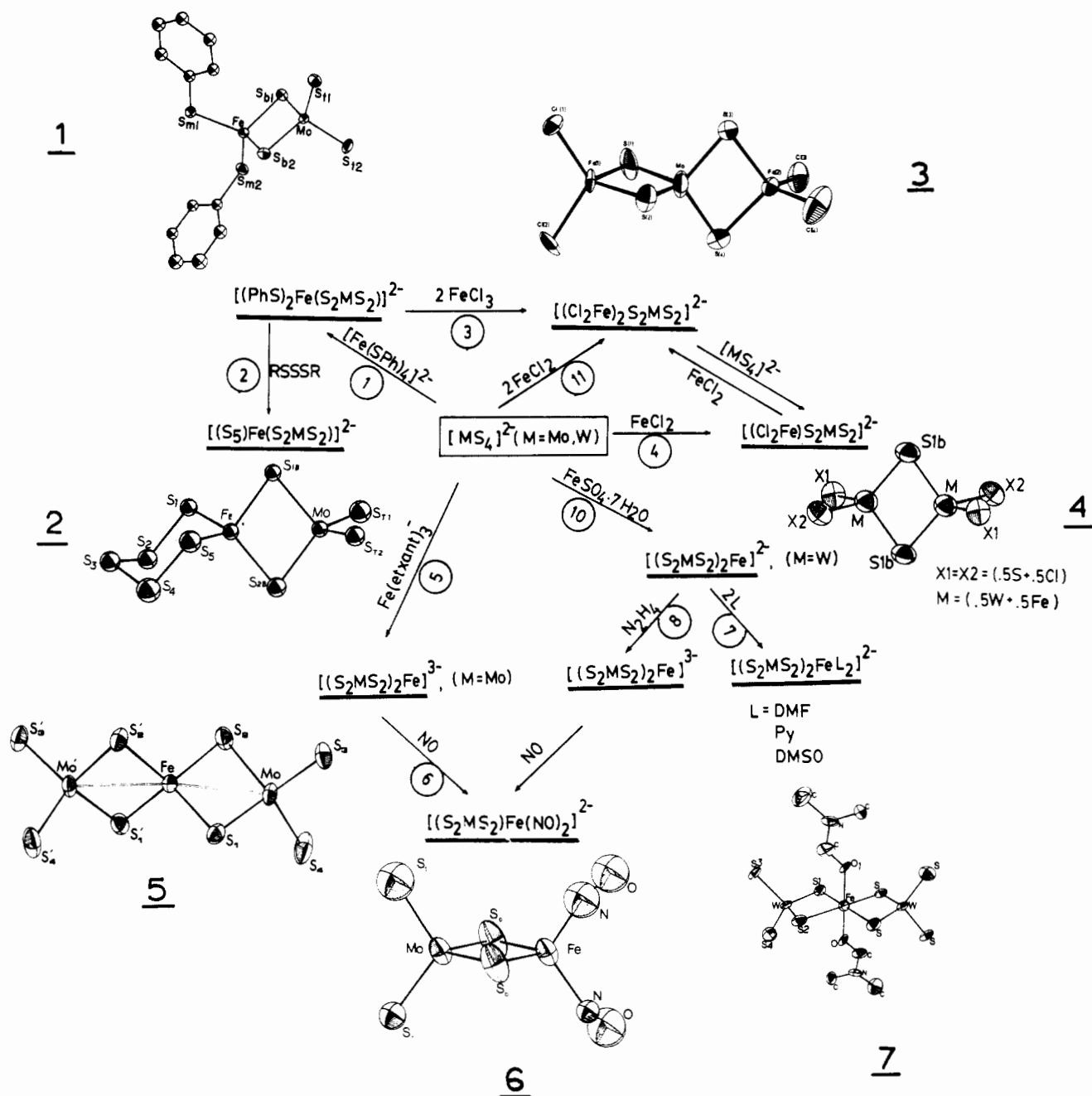


Figure 2. The MS_4^{2-} thioanions (M = Mo, W) as ligands in the synthesis of Fe- MS_4 complexes and structures of the Fe- MS_4 complexes.

Addition of KSPH to DMF solutions of the MoS_4 -Fe-peptide complexes, resulted in "extrusion" of the FeS_2MoS_2 unit as judged by the presence of the characteristic absorption spectrum of the $[(\text{SPh})_2\text{FeS}_2\text{MoS}_2]^{2-}$ complex (Figure 3). The use of PhSH in the extrusion of Fe_4S_4 cores from nonheme iron proteins has been reported by Holm⁴⁶ and by Orme-Johnson and co-workers.⁴⁷

Structures

Structures of representative types of the Fe- MS_4 complexes are depicted in Figure 2, and selected structural parameters can be found in Table I. A feature common to all of these Fe-S-M complexes is the

nearly planar FeS_2M dimetallic unit. The dimensions of this unit, in the complexes that contain tetrahedrally coordinated iron, are quite similar, and the magnitudes of the Fe-M distances and the Fe-S-M angles are found in relatively narrow ranges. Thus the mean values for the Fe-M distances and the Fe-S-M angles in complexes 1 through 6 (Figure 2, Table I) are 2.77 Å and 76°. The standard deviations⁴⁸ from these mean values are 0.04 Å and 1°, respectively. There is little doubt that at 2.77 Å, appreciable overlap can occur between the metal d orbitals of appropriate symmetry. In a convenient coordinate scheme, the d_{z^2} orbitals can be oriented along a common axis that passes through the metal ions. The existence of any M(VI)-Fe(II) bonding interactions in this configuration should depend on the overlap and relative energy matching of the d_{z^2} functions in the two metal ions.

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Table I
Selected Structural Parameters^a in the [(SPh)₂FeS₂MoS₂]²⁻ (1) [(S₂)FeS₂MoS₂]²⁻ (2), [(S₂)FeS₂WS₂]²⁻ (2'), [Cl₂FeS₂MoS₂-FeCl₂]²⁻ (3), [Cl₂FeS₂WS₂]²⁻ (4), [Fe(MoS₄)₂]³⁻ (5), [(NO)₂FeS₂MoS₂]²⁻ (6), and [(DMF)₂Fe(S₂WS₂)₂]²⁻ Complexes

	1 ²²	2 ²⁴	2' ²⁴	3 ²³	4 ²⁵	5 ²⁶	6 ²⁷	7 ²¹
Bond Lengths, Å								
Fe-M	2.750 (3)	2.731 (3)	2.753 (3)	2.775 (6)	2.821 (2) ^c	2.740 (1) ^d	2.835 (13) ^e	3.044 (1)
M-S _b	2.246 (6)	2.253 (8)	2.254 (14)			2.255 (5)	2.259 (8)	2.213 (2)
					2.204 (5)			
M-S _t	2.153 (6)	2.145 (7)	2.157 (15)			2.171 (5)	2.182 (8)	2.164 (4)
Fe-S _b	2.250 (8)	2.245 (8)	2.270 (10)	2.295 (5)		2.256 (12)	2.257 (8)	2.511 (22)
Fe-S _t	2.312 (8)	2.321 (25)	2.319 (10)	2.225 (10) ^f				
S _b -S _b	3.571 (8)	3.568 (8)	3.588 (6)	3.543 (6)		3.579 (5)		3.593 (3)
Fe(Mo)-N							1.9 (2)	
Fe(Mo)-O							2.66 (5)	
Fe(W)-S _b					2.203 (8) ^b			
Fe(W)-S _t					2.276 (8)			
Fe-O								2.075 (4)
Bond Angles, Deg								
Fe-S _b -Mo	75.5 (2)	74.3 (3)	74.9 (6)	76.1 (1)	76.4 (2)	74.77 (13)	77.7 (5)	80.0 (5)
S _b -Fe-S _b	102.9 (3)			101.0 (1)		104.9 (2)	104.5 (3)	91.35 (6)

^a For all structures the reported structural parameters are in analogous reference to the labeling shown in Figure 2, structure 1. ^b Mean values for the chemically equivalent bonds or angles. The standard deviations of the Averages were taken as the larger of the individual standard deviations or the standard deviation from the mean

$$\sigma = [\sum_{i=1}^N (X_i - \bar{X})^2 / (N - 1)]^{1/2}$$

^c The location of the [Cl₂FeS₂WS₂]²⁻ anion on a center of symmetry results in disorder. Whereas the Fe-W bond length and the Fe-S-W angle are not affected by this disorder, all M-L bonds given are average (W(Fe)-S(Cl)) values. ^d Mo-Fe-Mo = 172.64 (6)°. The iron is tetrahedrally coordinated by the two MoS₄²⁻ "ligands". ^e Independent values for the two dimers in the asymmetric unit are 2.822 (2) and 2.849 (2) Å. In these anions the same type of disorder as described in footnote c results in a twofold disorder in the location of the (NO)₂Fe and MoS₂ terminal units. ^f Fe-Cl terminal bond length.

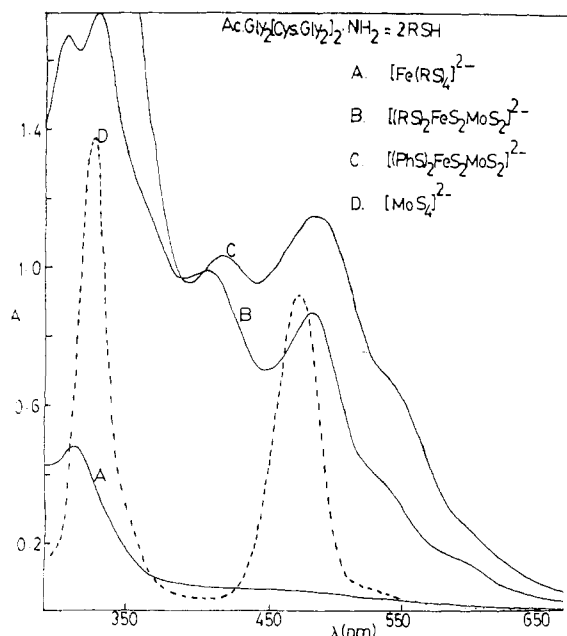


Figure 3. Visible spectra of (A) [Fe(RS)₄]²⁻, (B) [(RS)₂FeS₂MoS₂]²⁻, (C) [(PhS)₂FeS₂MoS₂]²⁻ (obtained following the addition of excess NaSPh to B), (D) MoS₄²⁻. In all cases 2RSH = AcGly₂(Cys-Gly)₂NH₂.

Unambiguous information regarding M-Fe bonding interactions in the Fe-M-S complexes cannot be obtained from the available crystallographic data. It is quite likely that the acute Fe-S-M angle, relatively invariant in all structures, determines to a large extent the length of the Fe-M separation.

Some structural trends that may tend to suggest Fe → M charge transfer are evident in the Fe-M-S complexes, when the mean values of the iron-ligand bond lengths and of the M-S bond lengths in the MS₄²⁻ ligands are considered. The Fe-S bond lengths in 1, 2, and 2' (Figure 2, Table I) at 2.281, 2.283, and 2.294 Å,

respectively, are somewhat shorter than the Fe-S bond in the ferrous [Fe(SPh)₄]²⁻ complex anion (2.353 Å).⁴⁹ If this Fe-S bond shortening is considered an indication of Fe → M charge transfer, the anticipated consequential transfer of electrons to the MS₄²⁻ units is only marginally apparent in the M-S bond lengths for 1, 2, and 2' at 2.199, 2.199, 2.205 Å, respectively. These values are only slightly longer than the M-S bonds in the MoS₄²⁻⁵⁰ and WS₄²⁻⁵¹ anions of 2.18 (1) and 2.17 (1) Å, respectively.⁵²

The insignificant influence of the electronic configuration of the M' metal ions in the MS₄-M' complexes on the dimensions of the MS₂M' rhombic units is apparent in other structural studies. The M-M' distances and the M-S-M' angles in the [(S₂MS₂)₂M']²⁻ complexes (M = Mo(VI), M' = Ni(II), 2.798 (8) Å, 77.9 (2)°;³⁴ M = W(VI), M' = Co(II), 2.796 (4) Å, 2.799 (4) Å, 77.4 (3)°, 77.2 (3)°;³⁶ M = W(VI), M' = Zn(II), 2.927 (1) Å, 78.5 (2)°)³⁵ are essentially within the range observed for the Fe-M-S complexes (Table I). The mean values of the M-S bond lengths in the MS₄²⁻ ligands also are not significantly different than the values observed in the Fe-M-S complexes.

The short M-M' distances in the [(S₂MoS₂)₂Ni]²⁻ and [(S₂WS₂)₂Zn]²⁻ complexes are particularly interesting structural features considering that extensive Ni → Mo or Zn → W charge transfer (and metal-metal bonding) are not very likely to occur in these complexes.

A conclusion that can be reached on the basis of the structural data is that the short M-Fe distances (2.8 ± 0.1 Å) in the MS₄-Fe complexes are not necessarily indicative of M-M interactions, but can be equally

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(51) K. Sasvari, *Acta Crystallogr.*, **16**, 719 (1963).

(52) Unfortunately the low accuracy in the crystallographic structure determinations for MoS₄²⁻⁵⁰ and WS₄²⁻⁵¹ makes it impossible to attach any real significance to these differences.

Table II
Mössbauer Spectra and Magnetic Properties of Fe-Tetrathiometalates^a

Complex ^d	room temp		liquid N ₂		4.2 K $\mu_{\text{eff}} \mu_B$	300 K $\mu_{\text{eff}} \mu_B$
	IS, ^b mm/s	QS, ^c mm/s	IS, mm/s	QS, mm/s		
[(PhS) ₂ FeS ₂ MoS ₂] ²⁻	0.33(1)	1.94(1)	0.44(1)	1.96(1)	4.13(6)	4.90(5)
[(PhS) ₂ FeS ₂ WS ₂] ²⁻	0.39(1)	2.20(1)	0.47(1)	2.24(1)	4.15(6)	4.88(2)
[(S ₂)FeS ₂ MoS ₂] ^{2-e}	0.22(2)	1.20(2)	0.38(2)	1.18(2)	4.43(6)	4.90(2)
[(S ₂)FeS ₂ WS ₂] ²⁻	0.38(1)	1.43(1)	0.47(1)	1.44(1)		
[(S ₂)FeS ₂ WS ₂] ²⁻	0.42(1)	1.68(1)	0.51(1)	1.66(1)	4.16(6)	4.90(1)
[Cl ₂ FeS ₂ MoS ₂ FeCl ₂] ²⁻	0.48(1)	1.96(1)	0.57(1)	1.98(1)	1.76(6)	6.58(6)
[Cl ₂ FeS ₂ WS ₂ FeCl ₂] ²⁻	0.52(1)	2.10(1)	0.63(1)	2.14(1)	3.14(6)	6.91(3)
[Cl ₂ FeS ₂ MoS ₂] ²⁻	0.48(1)	2.06(1)	0.59(1)	2.14(1)		
[Cl ₂ FeS ₂ WS ₂] ²⁻	0.54(1)	2.28(1)	0.65(1)	2.34(1)		
[S ₂ MoS ₂ FeS ₂ MoS ₂] ³⁻	0.37(1)	0.97(1)	0.42(3)	1.04(3)		3.9

^a Results obtained at the Greek Atomic Energy Commission, Research Center, Demokritos: A. Kostikas, A. Simopoulos, and V. Petrouleas. ^b Isomer shifts relative to Fe metal, with the γ -ray source at ambient temperature. ^c Quadrupole splittings. ^d Measurements on the tetraphenylphosphonium salts (Ph₄P⁺) of all anions except [S₂MoS₂FeS₂MoS₂]³⁻, for which the tetraethylammonium salt (Et₄N⁺) was used. ^e Two iron sites were detected in the spectrum.

accounted for as a structural consequence of the acute Fe-S-M angles. In the reduced Fe-Mo-S complexes, [Fe(MoS₄)₂]³⁻ and [(NO)₂Fe(MoS₄)₂]²⁻,²⁷ structural results can be used with greater confidence in arguments concerning details in the distribution of charge in the Fe-M-S complexes. The rather long Mo-S bond lengths of 2.213 Å in the trianion and of 2.220 Å in the dinitrosyl complex clearly indicate a delocalization of charge toward the tetrathiometalate units.

Magnetic Properties and Mössbauer Spectra

The magnetic properties of the dianionic Fe-M-S complexes (Table II) are characteristic of $S = 2$ ground states. The temperature dependence of the isotropically shifted proton resonances in the proton magnetic resonance spectra of the [(PhS)₂Fe(S₂MS₂)²⁻ complexes²² indicate simple Curie magnetic behavior.

The magnetic moments of the [(FeCl₂)₂S₂MS₂]²⁻ complexes (Table II) are lower than expected for two, noninteracting, high-spin ($S = 2$) Fe(II) ions. Temperature-dependence studies of the magnetic susceptibilities of these complexes show typical, weak antiferromagnetic behavior. This antiferromagnetic exchange is appreciably weaker in the W trimetallic complex than in the Mo analogue.

The only complexes in the Fe-Mo-S series which do not display magnetic properties originating from spin quintet ground states are the [Fe(MS₄)₂]³⁻ and the [(NO)₂FeS₂MoS₂]²⁻ complexes. The trianions (5, Figure 2) have magnetic moments indicative of $S = 3/2$ ground states and consistent with formally univalent tetrahedral iron with a high-spin d⁷ configuration. The dinitrosyl complexes (6, Figure 2) are diamagnetic and formally can be described as NO⁺ complexes (ν_{NO} at 1685 and 1645 cm⁻¹) of a (-2) iron with a d¹⁰ configuration. By comparison to the relative insensitivity of the crystallographic results to the changes that accompany electronic delocalization effects in the Fe-M-S complexes, Mössbauer spectroscopy has been found a very sensitive technique in probing such changes.

The ⁵⁷Fe isomer shifts of the MS₄²⁻ complexes (Table II) are intermediate in magnitude to values reported for the tetrahedral Fe(II)S₄ and Fe(III)S₄ chromophores at 0.66 and 0.25 mm/s, respectively.⁵³ By criteria estab-

lished previously for the iron-sulfur proteins and their synthetic analogues,⁵⁴ the isomer shift (IS) values observed for the Fe-M-S complexes (Table II) suggest formal oxidation states between 2 and 3 for the iron atoms and represent direct evidence for Fe → M charge transfer in these complexes.

The IS values for the [(FeCl₂)₂S₂MS₂]²⁻ complexes are close to those reported for Fe(SC₆H₅)₄²⁻⁵⁵ and the reduced rubredoxins⁵³ and suggest the two iron atoms in 3 (Figure 2) are close to a +2 formal oxidation state. This apparent reduction in charge transfer in the trimers is not surprising since the two iron atoms compete for charge transfer to the central Mo or W atoms. The delocalization of charge, hinted by the structural parameters, in the [Fe(MoS₄)₂]³⁻ complex is supported by Mössbauer spectra measurements. The ⁵⁷Fe isomer shift of 0.42 (3) mm/s is smaller than that expected for either a +1 or even a +2 oxidation state for the iron and definitely suggests extensive Fe → Mo charge transfer.

The Mössbauer results show that, in the Fe-M-S complexes, the electronic environment for the iron atoms, to a first approximation, is rather insensitive to a change from Mo to W. A closer examination of the relative IS values, however, shows that the IS values for the W complexes systematically are slightly larger than values in the corresponding Mo complexes and may indicate less extensive Fe-W charge delocalization in the WS₄²⁻ complexes.

Electronic Spectra

The electronic spectra of the Fe-M-S complexes in the visible-near-infrared regions are characterized by absorptions that can be separated into three different groups: a group of intense absorptions between 300 and 500 nm, a group of less intense absorptions between 500 and 650 nm, and an envelope of weak absorptions around 1000 nm (Figure 4).

Two intense absorptions are usually found in the 300-500-nm region. For the MoS₄²⁻ complexes (1-6 Figure 2) the separation between these two bands varies from 40 nm in 4 to 100 nm in 5 (Figure 2). The mean value of the average position of these bands for com-

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(54) T. E. Wolff, J. M. Berg, K. O. Hodgson, R. B. Frankel, and R. H. Holm, *J. Am. Chem. Soc.*, **101**, 4140 (1979).

(55) A. Kostikas, V. Petrouleas, A. Simopoulos, D. Coucovanis, and D. G. Holah, *Chem. Phys. Lett.*, **38**, 582 (1976).

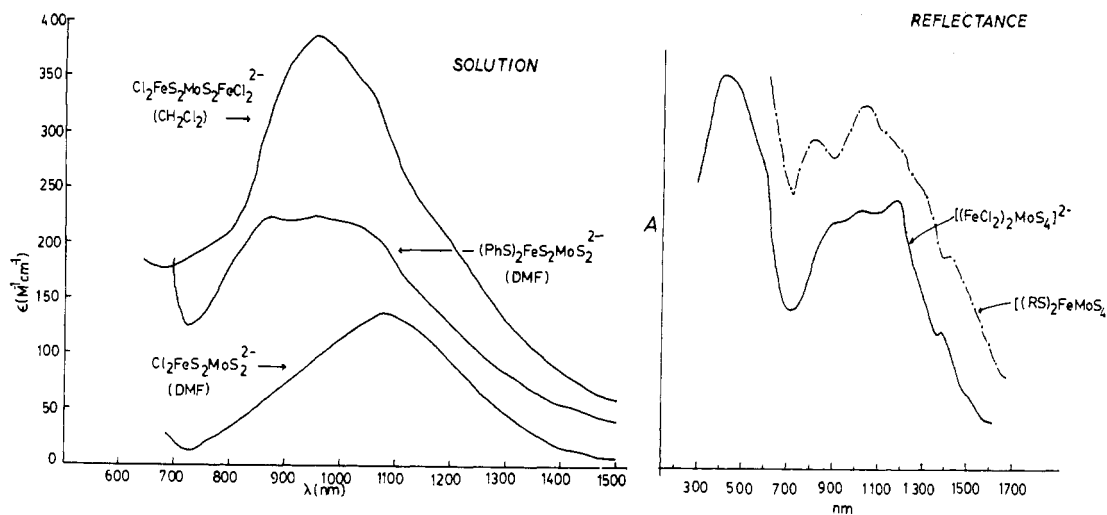


Figure 4. Solution and reflectance near-IR spectra of the Fe-MoS₄ complexes.

plexes 1 to 6 is 460 ± 40 nm. This value is quite close to the energy of the S \rightarrow Mo ($\pi(t_1) \rightarrow d(e)$) transition in the MoS₄²⁻ anion^{8c} (470 nm).

Apparently the MoS₄²⁻ S \rightarrow Mo transition in the Fe-MoS₄ complexes is split due to a lowering in local symmetry about the central atom in the MS₄²⁻ unit, from T_d to D_{2d} in the trimetallic complexes and to C_{2v} in the dimetallic species. This lowering in symmetry lifts the degeneracy in the $d_{x^2-y^2}$ and d_{z^2} orbitals. Exactly the same spectral features are observed in the 300–500-nm region for the WS₄²⁻ analogous complexes; however, relative to the MoS₄²⁻ complexes the absorptions are hypsochromically shifted. The splitting varies from 75 nm in 5' to 44 nm in 4' and the mean value of the average positions of the S \rightarrow W absorptions for complexes 1 to 6 (Figure 2) is 399 ± 14 nm, again, a value remarkably close to the energy of the S \rightarrow W ($\pi(t_1) \rightarrow d(e)$) transition in WS₄²⁻ (392 nm).

The transitions found in all complexes between 650 and 500 nm tentatively are assigned to the Fe-S chromophores since no such low-energy transitions are observed in the spectra of the MS₄²⁻ anions. Again, hypsochromic shifts are observed for these bands in the spectra of the WS₄²⁺ complexes by comparison to the MoS₄²⁻ complexes.

A unique feature in the near-infrared reflectance and solution electronic spectra of the dimeric and trimeric MS₄²⁻ adducts is the presence of a broad absorption band with considerable structure centered around 1000 nm (Figure 4). We tentatively assign these envelopes of absorptions to Fe \rightarrow Mo (W) transitions. The energies of these transitions when compared to the energies of the S \rightarrow Mo (W) transitions suggest that in the MS₄-Fe complexes the energies of the Fe d orbitals are located roughly between the primarily sulfur molecular orbitals and the empty Mo(VI) or W(VI) d orbitals. A simplified, tentative, MO diagram for the S₂MS₂-Fe complexes is shown in Figure 5.

The characteristic electronic spectra of the MoS₄-Fe complexes over a wide energy range should be useful as diagnostic indicators for the possible presence of exogenous MoS₄²⁻ ligand interactions with cysteinyl residue-protein-bound iron atoms. This contention gains credibility by the observation⁴⁵ that in the electronic spectra of the (Gly)₂(Gly₂-Cys)₂FeMoS₄ and (Gly)₂(Gly₂-Cys)₄Fe₂(MoS₄)₂ peptide complexes, ab-

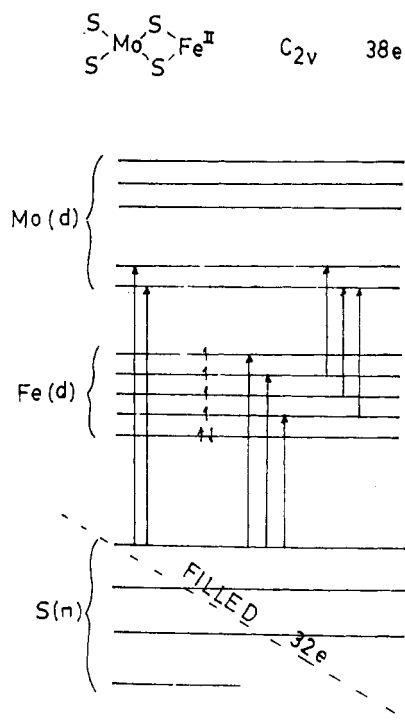


Figure 5. Proposed, schematic energy level diagram for the Fe-MoS₄ complexes.

sorptions in each of the three spectral regions, characteristic for Fe-MoS₄, are observed. The presence of (Cys)₂FeS₂MoS₂ units as a likely source of these absorptions is substantiated by the substitution of the Cys⁻ ligands with PhS⁻ ligands and the subsequent formation of [(SPh)₂FeS₂MoS₂]²⁻ (Figure 3).

Spectra similar to those observed for the [S₂FeS₂MoS₂]²⁻ or [(RS)₂FeS₂MoS₂]²⁻ complexes have been reported in the 300–500-nm range for the acid-base-treated nitrogenase solutions³⁸ and for the Fe-Mo protein isolated from *Desulfovibrio gigas*⁵⁶ (Figure 6). A strong argument could be made for the presence of Fe-MoS₄ coordination in these systems if weak absorption around 1000 nm also were observed. Unfortunately, no such absorptions were reported, perhaps

(56) J. J. Moura, A. V. Xavier, M. Bruschi, J. Legall, and J. M. P. Cabral, *J. Less Common Metals*, **54**, 555 (1977).

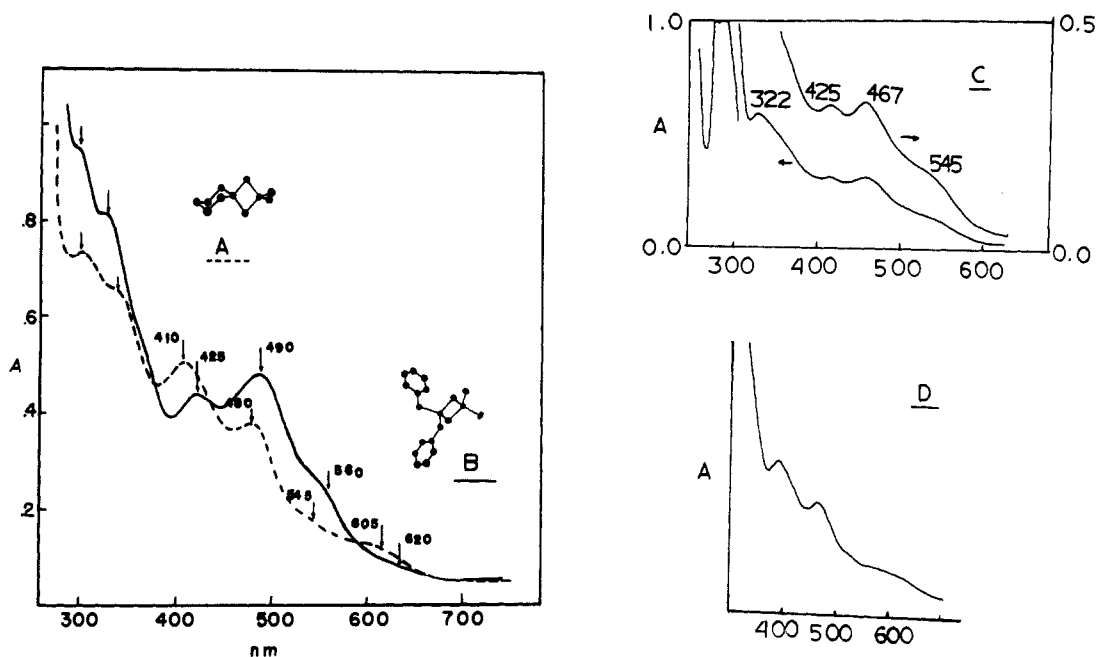


Figure 6. The visible spectra of $[S_2FeS_2MoS_2]^{2-}$ in DMF (A), $[(PhS)_2FeS_2MoS_2]^{2-}$ in DMF (B), the Fe-Mo-S protein from *Desulfovibrio gigas* (C), and solutions of acid-base treated nitrogenase, (D). Part C is reproduced with permission from ref 57. Copyright 1980, Plenum Press. Part D is reproduced with permission from ref 38. Copyright 1978, Springer, Berlin.

because this region of spectrum was not examined.

Conclusions and Directions for Future Research

In all of the Fe-Mo S_4 complexes isolated thus far, the Fe/Mo ratio falls short of the approximate 6:1 ratio suggested by Mössbauer and EPR spectroscopic studies¹⁰ for the Fe-Mo-S sites in the Fe-Mo protein of nitrogenase. The challenge in the synthesis of acceptable analogue complexes clearly is to design molecules that confirm to the known structure characteristics of nitrogenase.

An analysis of the available data on nitrogenase and on the Fe-Mo-Co indicates that most or all of the sulfur atoms in the Fe-Mo-S aggregate must be located around a four- or five-coordinate Mo atom. This conclusion finds support in (a) the analytical data on the cofactor^{9,57} (4-6 S atoms per Mo atom and no amino acids present!), (b) the apparent release of Mo S_4^{2-} following acid hydrolysis and reneutralization of the Mo-Fe protein of nitrogenase,³⁸ and (c) the Mo EXAFS analysis results^{11,12} (~3-4 sulfur atom in the first coordination sphere).

The similarity in the EPR and Mössbauer spectra of the isolated Fe-Mo-co and the Fe-Mo protein component of nitrogenase¹⁰ show (a) a lability of the peripheral ligands on the Fe-Mo-S cluster and (b) a reasonably stable Fe-Mo-S core that appears to have been extruded intact from the protein matrix. Minor differences in the properties of the cofactor isolated by different buffering procedures and the sharpening effects of thiophenol on the EPR spectra of the Fe-Mo-Co⁵⁷ further suggest that the original peripheral cluster ligands in the Fe-Mo protein (cysteinyl residues?) probably have been replaced in the cofactor by buffer anions (citrates, phosphates) and/or methylformamide (NMF)

solvent molecules during the cofactor isolation procedure.

Considering all of the available data, one is led to the conclusion that the Fe atoms in the Fe-Mo-S cluster core probably are held by oxide or hydroxide bridging ligands. Two of these iron atoms very likely are bridged to the Mo atom via sulfur atoms (Figure 1), while the rest of the iron atoms complete their coordination spheres by interactions with either the protein backbone, as in the Fe-Mo protein, or exogenous ligands, as in the Fe-Mo-co.

It is now apparent that the MS_4^{2-} anions as ligands are unique in their ability to delocalize charge in the $MS_4^{2-}-M'$ complexes by accepting electron density in low-lying, unoccupied M d orbitals. Not only is there a delocalization of charge in the $MS_4^{2-}-M'$ complexes, but very often these complexes undergo reversible reductions by one or even two electrons. Such reductions have been reported for the $[MS_4]_2M'^{2-}$ complexes ($M' = Ni, Pd, Pt; M = Mo$ or W),³¹ and for $[(WS_4)_2Co]^{2-}$.³³ In the MS_4-Fe complexes we have observed reversible one-electron reductions for the $[(FeCl_2)_2MoS_4]^{2-}$ and $[(WS_4)_2Fe]^{2-}$ complexes and have isolated the stable $[(MS_4)_2Fe]^{3-}$ trianions.

The $[(MoS_4)_2Fe]^{3-}$ complex, remarkably, shows an ^{57}Fe Mössbauer isomer shift more characteristic for Fe(III) than for Fe(I) and undergoes even further quasi-reversible reduction at -1.75 V.^{26,40} The propensity of the $[M'(MS_4)_2]^{2-}$ complexes to accept electrons also is evident in the pronounced tendency of the $[Fe-(WS_4)_2]^{2-}$ complex toward the formation of base "adducts" with σ electron donor molecules. The characterization of one such adduct (structure 7, Figure 2) demonstrate for the first time that the $[Fe(MS_4)_2]^{2-}$ complexes can function as coordinatively unsaturated species and that the MS_4^{2-} anions can serve as chelating ligands in pseudooctahedral complexes.

These observations should encourage attempts in the design and synthesis of specific, coordinatively unsaturated $M'-MS_4$ complexes as catalysts for the reduction

(57) B. E. Smith, in "Molybdenum Chemistry of Biological Significance", W. E. Newton and S. Otsuka, Eds., Plenum Press, 1980, p 179.

of substrate molecules. In such $M'-MS_4$ complexes the MS_4^{2-} ligands could serve as convenient electron storage and relay sites.

I wish to express my sincere appreciation to Professor N. C. Baenziger and Dr. D. Swenson, who as collaborators in our studies have made important contributions to our program. The solid-state physics group (A. Kostikas, A. Simopoulos, and V. Petrouleas) in the Nuclear Research Center Demokritos in Athens, Greece, have been instrumental in conducting Mössbauer and magnetic studies very important for an in-depth under-

standing of the electronic structures of the Fe-Mo-S complexes. I wish to acknowledge the immense contributions of my students, Elliot Simhon and Phil Stremple. Without their talented synthetic contributions a lot of this work would not have been possible. Also I wish to thank Rosario Neira in Professor J. P. Fackler's laboratories, who has obtained and provided the reflectance spectra of the compounds reported in this account. Financial support from the National Science Foundation (CHE-79-0389), the National Institutes of Health (GM 26671-01), and a Nato Research Grant (No. 1321) is gratefully acknowledged.