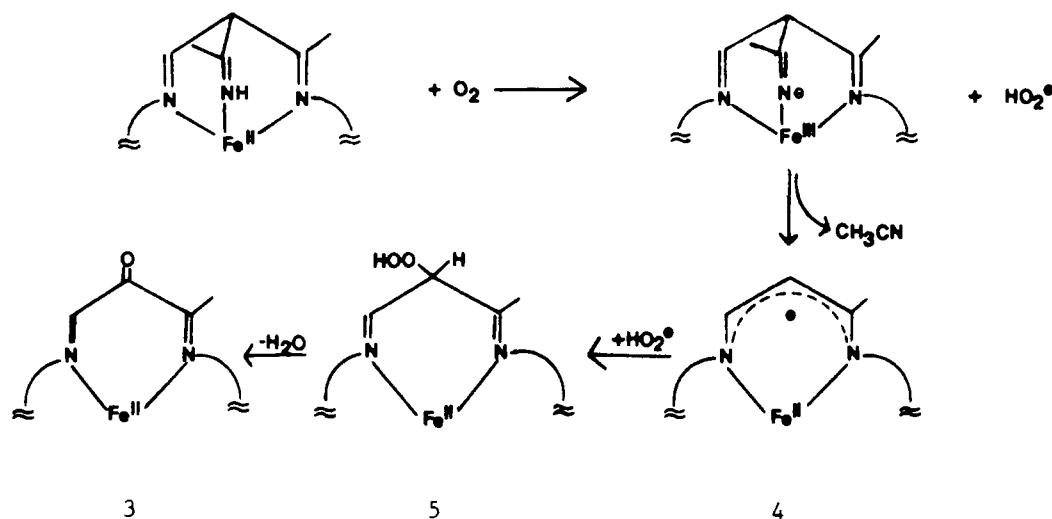


Scheme II



hydroperoxides^{10,11} that can decompose to yield ketones.¹² We believe that the most likely mechanism involves an initial slow oxidation of the iron(II) center producing iron(III) and superoxide, accompanied by proton transfer. This first step is analogous to the oxidative-dehydrogenation chemistry observed previously with other iron(II) macrocyclic amine complexes.¹ The subsequent steps would then yield the apical-C hydroperoxide species which could undergo base induced (acetonitrile solvent) dehydration to yield the observed ketone product.¹² This is shown in Scheme I for compound 1.

The mechanism for the *cis* hexaene complexes **2** would be expected to be similar to that described above for the bis(β -diimine) complex **1**. This case could proceed by essentially the same sequence of steps (Scheme II), but involving formation of an iron(III) complex from which acetonitrile could be eliminated. Alternatively, the reaction could proceed by a preequilibrium in which acetonitrile is dissociated from the hexaene yielding a bis(β -diimine) complex that could then react via the pathway suggested for the 14-membered ring derivative.

Finally, the oxidation pathway may not require autoxidation of the metal ion along the way. Since the doubly allylic methylene hydrogen atoms are susceptible to direct H atom abstraction,⁹ it is possible that oxygen could directly abstract a hydrogen atom and then recombine to yield the apical-C hydroperoxide **5**. Closely related reactions could be invoked that involve free-radical chains.

The extreme insolubility of the iron derivative of the 14-membered macrocycle does raise the possibility that a different structure may be present in this case. For example, it is known that the reaction of oxygen with a 13-membered tetraaza macrocyclic nickel(II) complex containing a single β -diimine linkage yields a dimer coupled by a C=C double bond at the apical carbon.¹³ Thus, it is possible that the iron(II) bis(β -diimine) complex **1** oxidizes to form a dimeric or even higher oligomeric complex. This would account for its extreme insolubility.

These reactive and unusual tetraenedione macrocyclic iron(II) complexes have a reactive and easily reducible counterpart in organic chemistry: namely, the *p*-quinone structure. Thus, both the structure and electronic properties of complexes **3** are suggestive of an inorganic analogue of the

p-quinone moiety. The ready reducibility described above supports this analogy.

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Registry No. **1**, 59527-05-8; **2a**-(PF₆)₂, 59388-85-1; **2b**-(PF₆)₂, 59388-81-7; **2c**, 56689-50-0; **3a**-(PF₆)₂, 87639-00-7; **3b**-(PF₆)₂, 87614-91-3; **3d**-(PF₆)₂, 87614-88-8; **3d**-(CF₃SO₃)₂, 87614-89-9; O₂, 7782-44-7; 5,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,7,11,14-tetraene, 62133-97-5; $\alpha,\alpha',2,2,3,3,7,13$ -octamethyl-1,4,8,12-tetraazacyclopentadeca-4,7,12,15-tetraene-6,14-dimethanimine, 87614-92-4; $\alpha,\alpha',7,13$ -tetramethyl-1,4,8,12-tetraazacyclopentadeca-4,7,12,15-tetraene-6,14-dimethanimine, 87614-93-5; $\alpha,\alpha',2,12$ -tetramethyl-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene-3,11-dimethanimine, 87614-94-6.

Contribution from the Baker Laboratory of Chemistry and the School of Chemical Engineering, Cornell University, Ithaca, New York 14853

An EXAFS Study of the Thermal Decomposition of Molybdenum Trisulfide

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The structures and properties of amorphous molybdenum sulfides are of special interest because of their possible role in hydrosulfurization (HDS) catalysis. In situ molybdenum-edge EXAFS (extended X-ray absorption fine structure) studies¹ on sulfided Co/Mo/ γ -Al₂O₃ catalysts have demonstrated the presence of MoS₂-like structures, although the number of molybdenum atoms in the second coordination shell is reduced from that in crystalline MoS₂. These results suggest that the MoS₂ may be present as very small (~10 Å) crystallites or islands dispersed on the alumina support. However, the reduced coordination may also be due to a large number of molybdenum atom vacancies. This amorphous MoS₂ may be structurally similar to the poorly crystalline MoS₂ prepared by the thermal decomposition of amorphous MoS₃. In this study, we have used EXAFS as a probe of the structural

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Table I

spectrum	$T, ^\circ\text{C}$	t, min	$R, \text{Å}$	N	$10^3 \Delta\sigma^2$	ΔE_0	$R, \text{Å}$	N	$10^3 \Delta\sigma^2$	ΔE_0	$R, \text{Å}$	N	$10^3 \Delta\sigma^2$	ΔE_0
1	25	0	2.41	5.4	-1.9	2.7	2.74	1.4	-2.3	-2.0	3.17	1.6	-1.2	-2.0
2	350	30	2.40	6.1	-4.2	3.4	3.03	1.1	-0.85	8.1	3.17	1.6	-0.95	2.4
3	350	30 + 3	2.39	6.9	-4.5	2.9	3.02	1.1	-0.85	12.9	3.17	2.2	-0.95	2.2
4	350	30 + 10	2.39	7.0	-4.5	3.2					3.16	5.2	-5.6	0.59
5	350	30 + 16	2.39	6.1	-3.5	4.4					3.16	5.4	-6.0	-0.89
6	350	30 + 91	2.39	6.2	-3.9	3.9					3.16	5.0	-5.0	-0.59
7	25	30 + 120	2.39	6.1	-1.0	0.82					3.16	4.0	-0.4	-1.8

changes during this irreversible decomposition. Preliminary catalysis measurements indicate that the amorphous molybdenum disulfide so prepared has a high activity for hydrodesulfurization.

Experimental Section

The amorphous MoS_3 samples used for the EXAFS study were prepared by the thermal decomposition of ammonium tetrathiomolybdate, $(\text{NH}_4)_2\text{MoS}_4$. The $(\text{NH}_4)_2\text{MoS}_4$ was obtained by saturating an ammoniacal solution (pH ~ 12) of ammonium heptamolybdate (CERAC 99.9%) with H_2S at room temperature. The red-brown precipitate was filtered, rinsed with methanol, and dried under vacuum. The $(\text{NH}_4)_2\text{MoS}_4$ was analyzed by using powder X-ray diffraction.

A small portion of the $(\text{NH}_4)_2\text{MoS}_4$ sample was heated to 200°C in an argon flow to produce amorphous MoS_3 . This black powder was analyzed by powder X-ray diffraction but showed only one broad reflection. Chemical analysis of the sample yielded a nominal stoichiometry of $\text{MoS}_{3.10}$. The amorphous MoS_3 samples were stored in a helium-atmosphere Dri-Lab.

The EXAFS samples were prepared by diluting amorphous MoS_3 with fine-mesh Al_2O_3 to obtain a sample of proper thickness. A 0.1-g sample was placed in a small reactor cell equipped with aluminum windows and heated to 350°C under nitrogen flow. When the sample reached 350°C , the gas stream was changed to a 10% mixture of H_2S in H_2 . The sample was heated for ~ 2 h during which seven EXAFS spectra were obtained. The nominal composition of the final product was $\text{MoS}_{2.5}$. This material showed no X-ray powder diffraction pattern.

The EXAFS spectra were obtained at the Cornell High Energy Synchrotron Source (CHESS) using the molybdenum K absorption edge (20002 eV). After appropriate background subtraction, the data were multiplied by a k^3 factor to prevent the larger oscillations at low k values from dominating the smaller oscillations at higher k values. The Fourier transforms of the data are shown in Figure 1. Spectrum 1 shows MoS_3 . Spectrum 2 shows the reaction at intermediate conversion, and spectrum 6 shows the final product. Also included in Figure 1 is a spectrum of polycrystalline MoS_2 prepared by reaction of high-purity elements at 1000°C . The main peak is due to the first coordination shell of sulfur about molybdenum; the subsidiary peak to the right of the main peak is attributed to Mo-Mo. Peaks at low R values ($< 1.5 \text{Å}$) are probably due to low-frequency oscillations in the background that were not completely subtracted. All peaks in the Fourier transform plot have been displaced to lower R because of phase shifts.

The EXAFS results are summarized in Table I. These parameters were obtained by curve-fitting procedures using a polycrystalline MoS_2 spectrum for model amplitude and phase functions. The curve fitting was done with four floating parameters for each coordination shell: the bond length R , the coordination number N , the difference in Debye-Waller factor $\Delta\sigma^2$, and the difference in threshold energy ΔE_0 . A maximum of a two-shell (eight-parameter) fit was performed; for spectra with more than two peaks, the peaks were fitted independently.

To ensure transferability of the phase and amplitude functions of the room-temperature model compound to the high-temperature (350°C) compounds, EXAFS spectra of the final product were taken at $-196, 25,$ and 350°C . Each of these spectra was fitted to the same 25°C model MoS_2 spectrum. The results of these fits are summarized in Table II. There is no significant difference in the bond lengths or the coordination numbers calculated from the various temperature spectra. This indicates that the phase and amplitude functions extracted from the room-temperature MoS_2 spectrum are reliable model

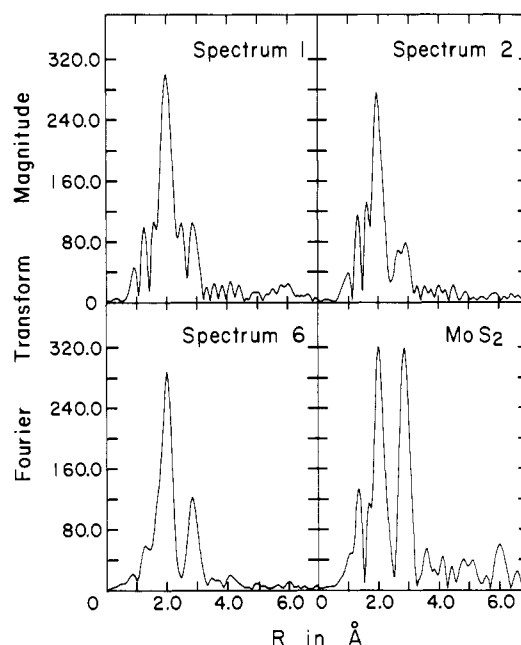


Figure 1. Magnitude of the Fourier transforms of EXAFS spectra of MoS_3 after background subtraction and multiplication by k^3 : spectrum 1, at 25°C ; spectrum 2, after heating to 350°C and holding for 30 min; spectrum 6, after 90 min in $\text{H}_2\text{S}/\text{H}_2$ at 350°C . The large peak is due to Mo-S; the subsidiary peak to the right of the main peak is due to Mo-Mo. The MoS_2 spectrum was taken at 25°C . The indicated Fourier transform magnitudes in this spectrum should be multiplied by a factor of 1.5 to obtain the correct magnitudes.

Table II

$T, ^\circ\text{C}$	$R, \text{Å}$	N	$\Delta\sigma^2$	ΔE_0	$R, \text{Å}$	N	$\Delta\sigma^2$	ΔE_0
-196	2.41	5.9	-0.01	0.0	3.15	4.5	0.7	-2.0
25	2.39	6.1	-1.0	0.8	3.16	4.0	-0.4	-0.6
350	2.39	5.8	-3.3	2.3	3.16	4.4	-4.7	0.8

functions for all of the amorphous MoS_3 spectra.

The largest errors in the EXAFS data are in the coordination numbers and Debye-Waller factors. The Debye-Waller factor is a measure of the standard deviation of the bond length distribution. This has been approximated by a Gaussian distribution function, which is not wholly adequate for disordered systems. This oversimplification affects the bond length and the coordination number, but the error in coordination number is relatively much greater.²

Discussion

The structure of amorphous molybdenum trisulfide has been the subject of several recent investigations.³⁻⁵ On the basis of evidence from high-resolution X-ray radial distribution function analysis and X-ray photoelectron spectroscopy, Liang et al.³ proposed a chain structure similar to that of the crys-

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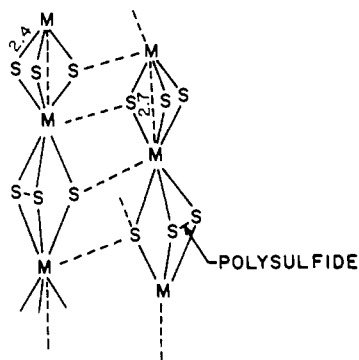


Figure 2. Proposed MoS₃ structure from Liang et al.⁴

talline group 4 and 5 trichalcogenides. Their results suggested that, in amorphous molybdenum trisulfide, the metal atoms are each coordinated by six sulfur atoms in a trigonal-prismatic environment, where each triangular face is shared by two metal atoms (see Figure 2). The results also indicated pairing of adjacent molybdenum atoms along the chain and presence of polysulfide bonds. EXAFS studies⁴ have shown the molybdenum is present in a pentavalent state, although magnetic susceptibility measurements⁴ have indicated that MoS₃ is diamagnetic. These results are consistent with the formation of metal dimers. Infrared and Raman spectroscopy experiments⁸ have provided further evidence for the presence of polysulfide bonds. The proposed molecular formula is Mo^V-(S²⁻)₂(S₂²⁻)_{1/2}.

The EXAFS results on MoS₃ indicate that each molybdenum is coordinated to an average of 5.4 sulfur atoms at 2.41 Å. There are two different molybdenum-molybdenum coordination shells: the first at 2.74 Å with an average coordination of 1.4 and the second at 3.17 Å with an average coordination of 1.6. These results are in agreement with those reported elsewhere.⁴

The structural evolution of MoS₂ from MoS₃ would involve the breaking of the metal-metal bonds present in MoS₃ and formation of sheets like those in MoS₂. The molybdenum is also reduced from a pentavalent to a tetravalent state. The EXAFS results presented here indicate the presence of a small amount of an intermediate state with a molybdenum-molybdenum bond length of 3.02 Å (Table I). A simple model is to assume that the disulfide sulfur is lost, donating 1 mol of electrons/mol of molybdenum. The sulfur is lost on heating, resulting in a reduction of the molybdenum and lengthening of the metal-metal bond. As the sulfur is lost, the molybdenum atoms become coordinatively unsaturated, allowing the chains to rearrange into sheets. The molybdenum-sulfur coordination does not seem to change significantly, which is consistent with a low concentration of the intermediate state. The increase in coordination number of the Mo-Mo 3.16-Å distance reflects the formation of a two-dimensional MoS₂-like structure. The final Mo-Mo coordination number is reduced relative to crystalline MoS₂, suggesting the presence of small crystallites.

It is interesting to note the similarity between the poorly crystalline MoS₂ produced by thermal decomposition of MoS₃ and sulfided HDS catalysts. Figure 3 compares these two materials to crystalline MoS₂. All spectra were measured at 77 K, and data sets extend to 17.7 in *k*-space, yielding higher resolution Fourier transforms than those shown in Figure 1. The HDS catalyst is American Cyanamide HDS-2A sulfided in situ at 400 °C for 4 h with H₂S/H₂.⁹ The sulfide catalyst structure is remarkably similar to that of amorphous MoS₂. Calculated coordination numbers are 4.0 for Mo-S coordi-

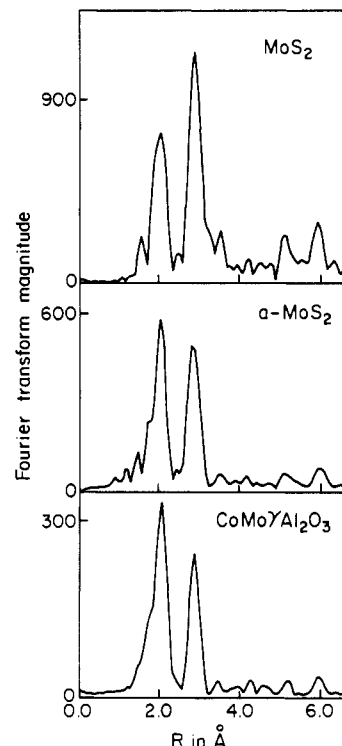


Figure 3. Magnitude of the Fourier transforms of EXAFS spectra after background subtraction and multiplication by k^3 . All spectra were recorded at 77 K. The MoS₂ spectrum is the polycrystalline model compound; the amorphous MoS₂ spectrum is the product of the decomposition of MoS₃; the Co/Mo/ γ -Al₂O₃ spectrum is the sulfide HDS catalyst.

nation at 2.41 Å and 2.5 for Mo-Mo coordination at 3.16 Å. These reduced coordination numbers suggest the catalyst is composed of smaller crystallites than the amorphous MoS₂.

Both poorly crystalline MoS₂ and sulfided Co/Mo/ γ -Al₂O₃ show the 6.32-Å Mo-Mo shell. The amplitude of this peak in crystalline MoS₂ is twice that predicted by a single-scattering EXAFS model due to a multiple-scattering effect.⁹ It is this amplitude increase that allows observation of this peak even in amorphous MoS₂. Its presence in sulfided Co/Mo/ γ -Al₂O₃ strongly suggests that Mo is present as small relatively ordered MoS₂ crystallites.

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Registry No. MoS₃, 12033-29-3; MoS₂, 1317-33-5.

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High-Pressure Kinetic Evidence for Dissociative Activation during Substitution Reactions of Some Cobalt(III), Rhodium(III), and Chromium(III) Porphyrin Complexes in Aqueous Solution

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In a series of papers²⁻⁷ it was demonstrated that axial-ligand substitution reactions of Co(III), Rh(III) and Cr(III) por-

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