Table IX. Comparison of the Barriers to Internal Rotation of Some Similar Molecules

molecule	barrier, kcal/mol	ref
CH_3PH_2	1.96	36
CH_3PF_2	1.74	5
CH_3PCl_2	3.37	25
CH_3POF_2	3.0 ± 0.2	3
CH_3POCl_2	4.4	25
CH_3PSF_2	3.82	this study
CH_3PSCl_2	3.2	25

CH_3PSF_2 that we prepared but disappeared when the technique of distillation followed by vacuum fractionation was utilized.

The tabulated frequency limits for the infrared absorption characteristic of the P═S stretching mode have varied widely, and it has been concluded that there are two vibrational frequencies with ranges 685–862 cm^{-1} (band I) and 550–730 cm^{-1} (band II) that are associated with the presence of this bond.[35] Although it has been suggested by some authors that the second band could originate from the presence of a second conformer, it is clear from the normal-coordinate calculations that the higher frequency band originates from the mixing of the P—C and P═S stretching modes. Also, it should be pointed out that the relative intensity of the Raman band at 643 cm^{-1} compared to the 820-cm^{-1} band indicates that the lower frequency band is more appropriately described as the phosphorus–sulfur stretch and our force field overascribes the amount of mixing between these two modes. However, it appears that all compounds with the general formula $RPSY_2$, where R is an alkyl group and the Ys are halogens, OR, NR_2, or other alkyl groups, will show such mixing, but the presence of a second conformer can be more easily detected in the Raman effect with the appearance of a second band in the 600-cm^{-1} spectral region.

In the vibrational study of CH_3PF_2,[5] the question arose as to whether the trend in barrier values observed in group 4A compounds of the type CH_3MH_3, CH_3MH_2F, CH_3MHF_2, and CH_3MF_3 would be followed for the corresponding compounds containing a group 5A element. In group 4A, carbon is unique in that substitution of fluorine for hydrogen in ethane results in an initial increase in the barrier to internal rotation followed by a very small decrease in the barrier as substitution of subsequent fluorines follows. Analogous silicon[36] and germanium[37] compounds show a decrease in the barrier to internal rotation as fluorine substitution occurs. Apparently nitrogen is unique in compounds containing group 5A elements because a dramatic increase in the barrier to internal rotation is observed with fluorine substitution whereas for the analogous phosphorus and arsenic compounds a decrease in the barrier is observed with fluorine substitution.[5]

In Table IX are summarized some barriers to internal rotation for molecules similar to CH_3PSF_2. As the barrier changes from CH_3PH_2[38] to CH_3PF_2,[5] one observes an expected decrease from 1.96 to 1.74 kcal/mol, but in CH_3PCl_2[25] a large increase to 3.37 kcal/mol is observed due to the effect of the chlorine substitution. Similarly, the barrier values for CH_3PF_2,[5] CH_3POF_2,[3] and CH_3PSF_2 are found to be 1.74, 3.0, and 3.82 kcal/mol, respectively. In comparing the barriers for CH_3POF_2[3] and CH_3POCl_2,[25] one finds an expected increase from 3.0 to 4.4 kcal/mol. However, from CH_3PSF_2 to CH_3PSCl_2[25] we see a decrease from 3.82 to 3.2 kcal/mol, which does not fit into the expected trend, and it appears that the barrier in CH_3PSCl_2 is too low. Therefore, either the earlier assignment[25] of the weak Raman line at 221 cm^{-1} to the torsional mode of CH_3PSCl_2 is in error or the barrier has a very unusual value. It is possible that this band is a two-phonon band and the torsional mode lies under one of the skeletal bends. Since the barrier value for this molecule appears to be out of line, it would be useful to verify the assignment of the 221-cm^{-1} band with deuterium substitution.

Acknowledgment. We gratefully acknowledge the financial support of this study by the National Science Foundation through Grant CHE-82-15492.

Registry No. CH_3PSF_2, 753-72-0; methylphosphonothioic dichloride, 676-98-2; antimony trifluoride, 7783-56-4.

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Notes

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Formation of Diketone Ligands by Oxidation of Macrocyclic Iron(II) Complexes with Molecular Oxygen

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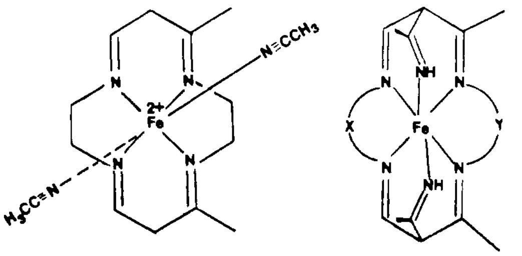
Previously we have reported that low-spin iron(II) complexes of neutral tetraaza macrocyclic ligands containing secondary amine groups (NHR_2) coordinated to iron(II) react with molecular oxygen producing, via an oxidative dehydrogenation, stable coordinated triene and tetraene ligands.[1,2] In the course of our studies concerning the reactivity of iron(II) complexes 1 and 2 containing bis(β-diimine) macrocyclic ligands,[3,4] we discovered that molecular oxygen also reacts with these com-



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2a, $X = (CH_2)_2$, $Y = (CH_2)_3$
b, $X = (C(CH_3)_2)_2$, $Y = (CH_2)_3$
c, $X = Y = (CH_2)_3$

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plexes even though the ligands contain no coordinated secondary amine groups. The purpose of this report is to describe the reactions of complexes **1** and **2** with molecular oxygen to yield complexes containing carbonyl functions on the apical carbon atoms.

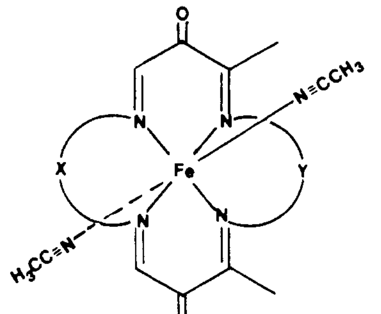
Experimental Section

Physical Measurements. Visible and ultraviolet spectra were obtained with a Cary Model 14R recording spectrophotometer. Infrared spectra were obtained from Nujol mulls applied between KBr disks on a Perkin-Elmer Model 337 recording spectrophotometer. Proton NMR spectra were obtained on a Varian HA-100 spectrophotometer in CH_3CN-d_3. Chemical shifts (δ) are reported relative to internal Me_4Si. Electrical resistances of solutions were measured by using an Industrial Instruments RC16B conductivity bridge and a conductance cell with a cell constant of 0.100 cm^{-1} at 25 °C and 1000 Hz with approximately 10^{-3} M solutions. The magnetic susceptibilities of solid samples were determined by the Faraday method. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Cyclic voltammetric measurements were performed with an Indiana Instruments and Chemical Corp. controlled potential and derivative voltammeter, Model ORNL-1988A. A Hewlett-Packard/Moseley Division X-Y recorder was used to obtain permanent records of current-potential curves. All measurements were carried out in purified acetonitrile under nitrogen in a Vacuum Atmospheres controlled-atmosphere chamber with 0.1 M n-Bu_4NBF_4 as the supporting electrolyte. For cyclic voltammetry, a platinum-wire electrode was used as the indicator electrode and a silver wire immersed in 0.1 M $AgNO_3$ (+0.36 V vs. SCE) was used as the reference electrode. Scan rates between 10 and 50 mV s^{-1} were used in the cyclic voltammetry studies.

Syntheses. The oxidation of complexes **1** and **2** was carried out by bubbling dry oxygen through solutions of the complexes (as their PF_6 or CF_3SO_3 salts) in dry acetonitrile (distilled from CaH_2 under N_2) until a deep blue solution resulted. During this period a number of color changes occurred resulting in an initial change from orange to deep gold, then green, and finally deep blue.

Oxidation of 1. Oxygen was bubbled through a solution of **1** for 24 h. By the end of this time, the deep blue product precipitated from solution in excess of 80% yield, giving compound **3d** as its bis(hexafluorophosphate) salt. Complex **3d** was also isolated as its bis(trifluoromethanesulfonate) salt by starting with the CF_3SO_3 salt of complex **1**. With both of these counterions, the product **3** is insoluble in all common solvents. Anal. Calcd for $C_{16}H_{22}F_{12}FeN_6O_2P_2$: C, 28.42; H, 3.28; N, 12.43. Found: C, 28.73; H, 3.26; N, 12.75. Calcd for $C_{18}H_{22}F_6FeN_6O_6S_2$: C, 31.59; H, 3.24; N, 12.28. Found: C, 31.32; H, 3.11; N, 12.57. The solid-state electronic spectrum was determined on a halocarbon mull. λ_{max}: 666, 315 nm.



3a, X = $(CH_2)_2$, Y = $(CH_2)_3$
b, X = $(C(CH_3)_2)_2$, Y = $(CH_2)_3$
c, X = Y = $(CH_2)_3$
d, X = Y = $(CH_2)_2$

Oxidation of 2a and 2b. From the oxidation of **2b** a crystalline blue product was obtained in the following manner. An acetonitrile solution containing 10 g of complex **2b** was allowed to react with O_2 for 4 days. After that time, the solution was evaporated to dryness and the solid was dissolved in a minimum volume of hot acetonitrile (10 mL). This solution was then eluted through a cellulose (Whatman) column (3 in. × 12 in.) with a 1:1 CH_3CN-benzene solution. The blue solution was reduced to dryness, the residue dissolved in a minimum volume (10 mL) of hot acetone, and the resultant solution stored at −20 °C for several days. Deep blue crystals of an acetone solvate formed and were collected and washed with Et_2O and dried in vacuo. The yield was 0.6 g (6%). The electronic spectrum of the mother liquor is identical with that of the crystalline product in acetonitrile. λ_{max} (ϵ): 626 (6500), 317 nm (3400). Anal. Calcd for $C_{21}H_{36}F_{12}FeN_6O_2P_2\cdot C_3H_6O$: C, 37.07; H, 4.73; N, 10.45. Found: C, 37.16; H, 4.55; N, 10.40.

In a similar fashion, the 15-membered cis hexaene complex **2a** was allowed to react with O_2 for 4 days and the product isolated initially, as described for the oxidation of **2b**. In this case, crystals of the oxidation product were not obtained, but analytically pure material could be obtained by precipitating the product from CH_3CN (after chromatography) with Et_2O. The blue product was obtained as a powder in excess of 50% yield. Anal. Calcd for $C_{17}H_{28}F_{12}FeN_6O_2P_2$: C, 33.80; H, 4.32; N, 11.26. Found: C, 33.97; H, 4.46; N, 11.01. Electronic spectrum in CH_3CN, λ_{max} (ϵ): 620 (6500), 310 nm (9000).

Oxidation of 2c. Oxygen reacts with the 16-membered ring cis complex **2c** much more slowly, requiring approximately 2 weeks for formation of the blue solution. Due to the very high solubility of the product and its instability toward chromatography support materials, we have only been able to isolate impure materials. Electronic spectrum in CH_3CN, λ_{max}: 620, 318 nm.

Results and Discussion

The identification of the products obtained from the reaction of oxygen with the iron(II) complexes of the bis(β-diimine)-containing macrocyclic ligands (**1** and **2**) was made possible by isolation and characterization of the crystalline complex **3b**. The IR spectrum of this product contains an intense absorption at 1630 cm^{-1} and a sharp absorption at 1700 cm^{-1}. The trans assignment of the structure is based on the nitromethane solution IR spectrum of **3b**, which shows only one sharp band at 2275 cm^{-1} in the $C\equiv N$ stretching region. This indicated that the coordinated acetonitrile molecules are mutually trans in this complex. The product **3b** (as well as all the products **3**) has a slight residual magnetic moment (0.5 μ_β) typical of low-spin iron(II) complexes. The molar conductance value in CH_3CN based on the above formulation for **3b** is 285 Ω^{-1} cm^2 M^{-1}, which is in the range expected for a bi-univalent electrolyte.[5] A major difficulty that hindered our attempts to purify and characterize these oxidation products is their instability to hydroxylic materials. All of the diketone products **3** are very sensitive to hydroxylic materials, including water, alcohols, and even chromatographic support material such as silica gel or alumina, giving products of unknown composition.

The structures of these oxidation products have been established from the ^1H NMR spectrum of complex **3b** (Figure 1). The ^1H NMR spectrum shows one vinyl proton resonance at δ 8.8, two types of methylene resonances (a triplet at δ 4.1 and a quintet at δ 2.7), and four methyl singlets. The integrated intensity ratios are 1:1:3:2:3:3:6. These results are consistent with structure **3b** (*trans*-$[Fe(Me_6[15]tetraenedioneN_4)(CH_3CN)_2](PF_6)_2$, *trans*-bis(acetonitrile)-(2,2,3,3,7,13-hexamethyl-1,4,8,11-tetraazacyclopentadeca-6,14-dione-4,7,12-15-tetraene)iron(II) hexafluorophosphate), in which one acetone molecule crystallizes in the lattice. This is in excellent agreement with the elemental analysis.

When crystals of the acetone solvate **3b** were ground and heated (~50–60 °C) in vacuo for 24 h, the elemental analysis of the remaining powder indiated that 1 mol of acetone was lost. Also, the methyl resonance at δ 3.0 disappeared from the ^1H NMR spectrum of the material, and the sharp infrared

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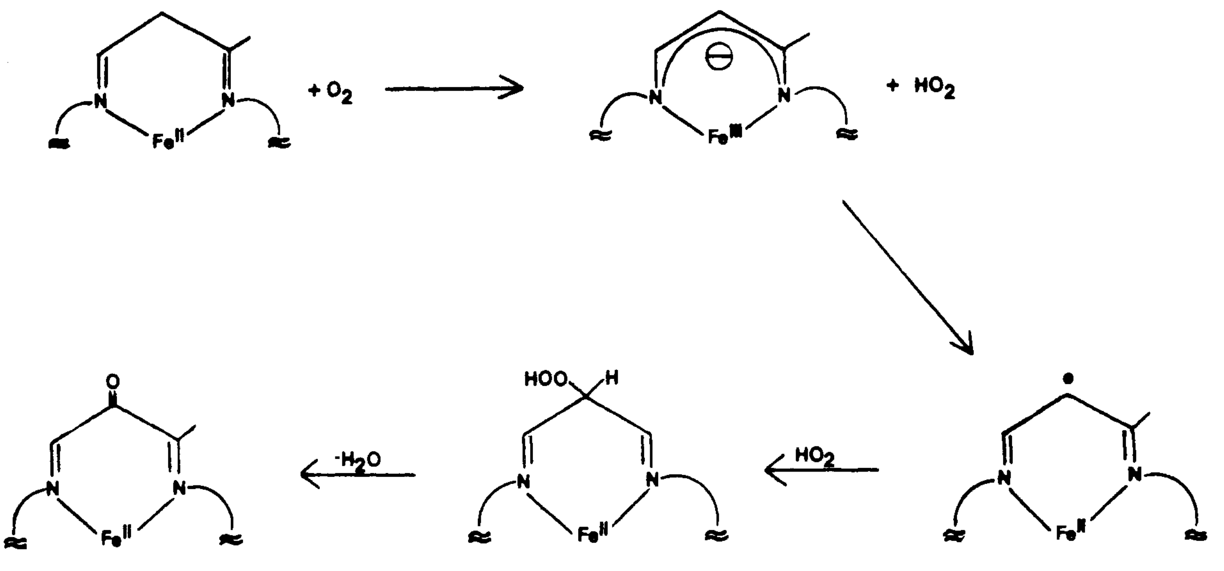
Scheme I



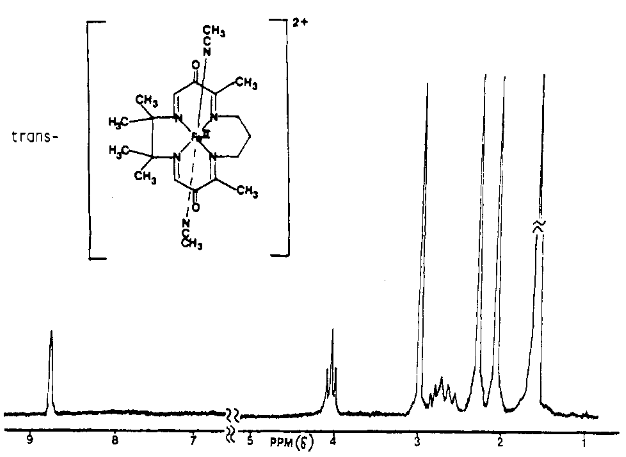


Figure 1. ^{1}H NMR spectrum of the diketone complex **3c**, *trans*-[Fe(Me$_6$[15]tetraenedioneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$, in acetonitrile-d_3.

absorption at 1700 cm^{-1} disappeared (assigned to the acetone C=O stretching mode).

The reactions of the cis hexaene complexes **2a** and **2c** with oxygen give corresponding deep blue colored products, but due to their much greater solubilities no crystalline products were isolated. An analytically pure product **3a** was isolated from the oxidation reaction of the 15-membered ring complex **2a** by precipitation from acetonitrile with diethyl ether. However, the increased solubility of the 16-membered ring product **3c** precluded isolation of a pure material. In contrast, the 14-membered ring complex **1** reacts with oxygen to yield a blue product that precipitates directly from acetonitrile and is insoluble in all common solvents. Starting with the CF$_3$SO$_3^-$ counterion instead of PF$_6^-$ did not increase the solubility of the product **3a** in any of the common solvents. Analyses of the materials isolated with both anions agree with the diketone formulation of structure **3**.

The electronic spectra of complexes **3** are especially significant. Since the 14-membered ring derivative (assigned structure **3d**) is too insoluble to permit characterization by the usual solution measurements, its electronic spectrum was determined in the solid state. The positions of the band maxima in the solid state correspond closely to the maxima observed for the solution spectra of the more soluble complexes **3a–c**. In all cases, a higher energy absorption was observed near 315 nm (32 × 10^3 cm^{-1}) and an intense lower energy absorption near 650 nm ((15–16) × 10^3 cm^{-1}). The latter is assigned to a metal (filled t_{2g} (O_h) orbitals) to ligand π^* (conjugated π-system) charge-transfer transition $M^{2+} \rightarrow \pi^*$. If this assignment is correct, then the $M^{2+} \rightarrow \pi^*$ transition of the diketone ligand lies somewhat lower in energy than that observed for the complex with a 14-membered macrocyclic bis(α-diimine) ligand bound to low-spin iron(II).[2] It follows that this macrocyclic diketone ligand structure must be a very good π-acceptor of electron density from the filled metal t_{2g} (O_h) orbitals.

The results of cyclic voltammetric studies on the diketone complex **3b** also reveal that the diketone ligand structure **3** profoundly affects the electronic environment of the iron. In acetonitrile solution, this complex exhibits three well-defined reduction waves at −0.66, −1.15, and −1.74 V. Also, only one oxidation wave was observed at a moderately high potential (+1.14 V). Both reduction and oxidation processes are irreversible, but the values indicate that these iron(II) complexes are easier to reduce and harder to oxidize than the bis(acetonitrile)iron(II) complexes of 14-membered tetraaza macrocyclic ligands containing the bis(α-diimine) structure.[6,7]

Our results (especially the similarity of the electronic spectra) suggest that the products of the oxygen reactions possess structure **3** in all cases. This conclusion is also supported by the observation of similar oxidation products formed from 14-membered macrocyclic cobalt(III) complexes. In one case the complex is formed by the reaction of oxygen with cobalt(II) acetate and the protonated salt of the bis(β-diimine) ligand. The products contain one conjugated apical ketone group.[8]

The slow reaction of the iron(II) complexes **1** and **2** with oxygen to produce the observed tetraenedione complexes **3** is reminiscent of a free-radical autoxidation in which no initiator is present.[9] It is well established that doubly allylic methylene centers are especially prone to autoxidation reactions yielding

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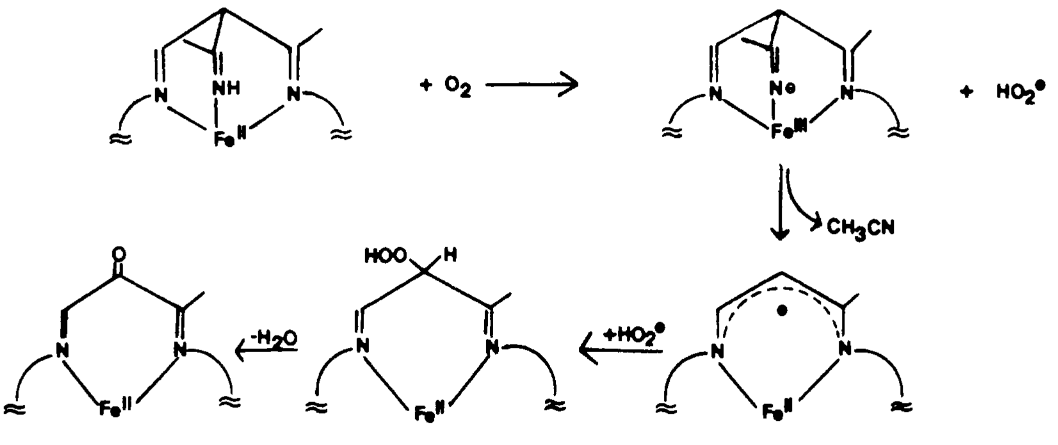
Scheme II



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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.

Acknowledgment. The support of the National Institutes of Health through Grant No. GM R0110040 is gratefully acknowledged.

Registry No. **1**, 59527-05-8; **2a**-$(PF_6)_2$, 59388-85-1; **2b**-$(PF_6)_2$, 59388-81-7; **2c**, 56689-50-0; **3a**-$(PF_6)_2$, 87639-00-7; **3b**-$(PF_6)_2$, 87614-91-3; **3d**-$(PF_6)_2$, 87614-88-8; **3d**-$(CF_3SO_3)_2$, 87614-89-9; O_2, 7782-44-7; 5,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,7,11,14-tetraene, 62133-97-5; α,α',2,2,3,3,7,13-octamethyl-1,4,8,12-tetraazacyclopentadeca-4,7,12,15-tetraene-6,14-dimethanimine, 87614-92-4; α,α',7,13-tetramethyl-1,4,8,12-tetraazacyclopentadeca-4,7,12,15-tetraene-6,14-dimethanimine, 87614-93-5; α,α',2,12-tetramethyl-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene-3,11-dimethanimine, 87614-94-6.

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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 hydrodesulfurization (HDS) catalysis. In situ molybdenum-edge EXAFS (extended X-ray absorption fine structure) studies[1] on sulfided Co/Mo/γ-Al_2O_3 catalysts have demonstrated the presence of MoS_2-like structures, although the number of molybdenum atoms in the second coordination shell is reduced from that in crystalline MoS_2. These results suggest that the MoS_2 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 MoS_2 may be structurally similar to the poorly crystalline MoS_2 prepared by the thermal decomposition of amorphous MoS_3. In this study, we have used EXAFS as a probe of the structural

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