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## Preparation and Crystal and Molecular Structure of a Tris(thiobenzoyldiazene)molybdenum Complex: An Example of Distorted Trigonal-Prismatic Coordination

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Received July 26, 1978

Molybdenum dioxobis(acetylacetonate),  $[\text{MoO}_2(\text{acac})_2]$ , or sodium molybdate reacts with the thioaroylhydrazines  $\text{RNHNHCSR}'$  ( $\text{R} = \text{H}$ ,  $\text{R}' = \text{C}_6\text{H}_5$ ,  $p\text{-MeC}_6\text{H}_4$ ,  $p\text{-MeOC}_6\text{H}_4$ ;  $\text{R} = \text{Ph}$ ,  $\text{R}' = \text{PhCH}_2$ ,  $1\text{-C}_{10}\text{H}_7$ ,  $p\text{-MeC}_6\text{H}_4$ ,  $p\text{-MeOC}_6\text{H}_4$ ) to give the dark green or black complexes  $[\text{Mo}(\text{RN}_2\text{CSR}')_3]$ . The structure of tris(thiobenzoyldiazene)molybdenum(VI)-dimethylformamide,  $[\text{Mo}(\text{C}_6\text{H}_5\text{CSN}_2\text{H})_3] \cdot (\text{CH}_3)_2\text{NCHO}$ , has been determined in a single-crystal X-ray diffraction study. The coordination geometry of the molybdenum is a distorted trigonal prism of sulfur and nitrogen donor atoms contributed by three chelating diazene ligands disposed in a facial configuration. The distortion may be expressed in terms of an average twist angle of  $7^\circ$ , compared to the value of  $\alpha = 0^\circ$  for a regular trigonal prism. The average molybdenum-sulfur bond distance is  $2.400(5) \text{ \AA}$  and the average molybdenum-nitrogen bond distance is  $2.03(1) \text{ \AA}$ . The bond lengths in the chelate ring systems  $\text{Mo-N-N-C-S}$  are intermediate between single- and double-bond distances, suggesting considerable delocalization of charge:  $\text{N-N}(\text{av}) = 1.32(2)$ ,  $\text{N-C}(\text{av}) = 1.35(2) \text{ \AA}$ ,  $\text{C-S}(\text{av}) = 1.69(2) \text{ \AA}$ . The complex crystallizes in the orthorhombic system, space group  $Pbca$ , with  $a = 17.458(8) \text{ \AA}$ ,  $b = 17.541(9) \text{ \AA}$ , and  $c = 17.896(9) \text{ \AA}$ . The measured density of  $1.51 \pm 0.03 \text{ g/cm}^3$  requires eight molecules per unit cell ( $\rho_{\text{calcd}} = 1.50 \text{ g/cm}^3$ ). The structure was solved by conventional Patterson and Fourier synthesis methods from 1456 independent reflections with  $I > 2.58\sigma(I)$ . Full-matrix least-squares refinement of all atoms, excluding hydrogens, converged at values for  $R_1 = 0.071$  and  $R_2 = 0.077$ .

### Introduction

The coordination chemistry of molybdenum with sulfur- and nitrogen-containing ligands has received a great deal of attention because of the possible relationship of these species to the redox-active molybdo enzymes.<sup>1,2</sup> In particular, molybdenum is believed to be involved at the active site of the enzyme complex responsible for biological nitrogen fixation. Since the initial step of the fixation process may be binding of dinitrogen, followed by protonation, complexes containing direct molybdenum-nitrogen bonds or the Mo-N-N grouping are of some interest. Consequently, the coordination chemistry of molybdenum with substituted hydrazines may have clear relevance to nitrogen fixation. Substituted hydrazines and their derivatives are versatile ligands, forming diazene, hydrazido, and hydrazine complexes depending on the number of protons retained upon coordination. The synthetic scope is increased by the ability of second- and third-row metals to form multiple bonds to nitrogen to yield complexes containing imido, diazenido, and nitrido ligands.<sup>3</sup>

In previous communications, the syntheses, physical properties, and molecular structures of the unusual, asymmetric dimers  $[\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_2(\text{C}_6\text{H}_5\text{CON}_2)_2]$  and  $[\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_2(\text{ClC}_6\text{H}_4\text{CSN}_2)_2]$ , formed in the reaction of  $[\text{MoO}_2(\text{S}_2\text{CNEt}_2)_2]$  with the appropriate hydrazine, have been described.<sup>4</sup> One molybdenum site in each of the dimers displays distorted trigonal-prismatic geometry, suggesting that the diazenido ligand may stabilize this unusual coordination type. Here we describe the full details<sup>5</sup> of the preparation of the complexes  $[\text{Mo}(\text{RN}_2\text{CSR}')_3]$  ( $\text{R} = \text{H}$ ,  $\text{R}' = \text{C}_6\text{H}_5$ ,  $p\text{-MeOC}_6\text{H}_4$ ;  $\text{R} = \text{Ph}$ ,  $\text{R}' = \text{PhCH}_2$ ,  $1\text{-C}_{10}\text{H}_7$ ,  $p\text{-MeC}_6\text{H}_4$ ,  $p\text{-MeOC}_6\text{H}_4$ ), by reaction of  $\text{MoO}_4^{2-}$  or  $[\text{MoO}_2(\text{acac})_2]$  ( $\text{acac} = \text{acetylacetonate}$ ) with the appropriate thioaroylhydrazine. The electrochemical behavior of some of these complexes is discussed and compared with that of analogous complexes. In view of the general interest in the factors determining the geometries and structures of molybdenum complexes with sulfur ligands, we have investigated the structure of the complex  $[\text{Mo}(\text{PhCSN}_2\text{H})_3] \cdot \text{DMF}$ .

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### Experimental Section

The reactions and recrystallizations were carried out in air using reagent grade solvents. Molecular weights were determined with a Hitachi Perkin-Elmer Model 115 osmometer, and IR spectra were recorded as Nujol mulls using a Pye Unicam SP 200G spectrometer.  $^1\text{H}$  NMR spectra were measured in deuteriochloroform at 100 MHz using a Jeol P.S. 100 spectrometer with tetramethylsilane as an internal standard. Microanalyses were carried out by Mr. and Mrs. Olney at the University of Sussex and by the A. G. Bernhardt Microanalytical Laboratories, West Germany.

The complex  $[\text{MoO}_2(\text{acac})_2]$  was supplied by the Climax Molybdenum Co., and the thioaroylhydrazines were prepared by the literature method.<sup>28</sup>

**Tris(thiobenzoyldiazene)molybdenum (I).** (a) Bis(acetylacetonato)dioxomolybdenum(VI) (1.0 g) and thiobenzoylhydrazine (1.5 g) were stirred in reagent grade methanol (25 mL) at room temperature to give a deep green solution and a purple microcrystalline precipitate of the complex (1.1 g, 72%). The complex can be recrystallized as purple prisms from dichloromethane-methanol or dimethylformamide-methanol.

(b) Sodium molybdate (1.0 g) in 1 N HCl (25 mL) was treated with a solution of thiobenzoylhydrazine (2.6 g) in methanol (25 mL), giving an immediate pale green precipitate of the complex, which was dried in vacuo at  $10^{-2}$  torr at room temperature and recrystallized from dimethylformamide-methanol as purple prisms.

The following complexes were prepared analogously in similar yields using the appropriate thioaroylhydrazines: tris(*p*-methoxythiobenzoyldiazene)molybdenum (II), tris[*N*-phenyl-*N'*-(*p*-methoxythiobenzoyl)diazene-*N,S*]molybdenum (III), tris[*N*-phenyl-*N'*-(*p*-methylthiobenzoyl)diazene-*N,S*]molybdenum (IV), tris[*N*-phenyl-*N'*-(*m*-chlorothiobenzoyl)diazene-*N,S*]molybdenum (V), tris[*N*-phenyl-*N'*-(1-thionaphthoyl)diazene-*N,S*]molybdenum (VI), tris[*N*-phenyl-*N'*-(1-thionaphthoyl)diazene-*N,S*]molybdenum (VII), tris[*N*-phenyl-*N'*-(benzylthiocarbonyl)diazene-*N,S*]molybdenum (VIII).

**Electrochemical Studies.** The electrolyte was dichloromethane-methanol (10:1 v/v) containing 0.1 N  $\text{Et}_4\text{NBF}_4$ , and all solutions were about 1 mM in complex. The working electrode was vitreous carbon (0.46  $\text{cm}^2$ ) with a platinum foil counterelectrode separated from the sample compartment by a sintered glass disk. The reference electrode was saturated potassium chloride-calomel separated from the sample by a glass frit and a salt bridge which contained 0.4 M  $\text{Bu}_4\text{NI}$  in methanol water (1:1 v/v). The potential of the working electrode was controlled by a Chemical Electronics TR 70/2A potentiostat. Potential sweeps were generated by a Chemical Electronics RB1

**Table I.** Summary of Crystal Data for  $[\text{Mo}(\text{C}_6\text{H}_4\text{CSN}_2\text{H}_3)_3]\cdot\text{DMF}$ 

fw = 618.9	$\rho_{\text{calcd}} = 1.50 \text{ g/cm}^3$
$a = 17.458 (8) \text{ \AA}$	$\rho_{\text{found}} = 1.51 (3) \text{ g/cm}^3$
$b = 17.541 (9) \text{ \AA}$	$F(000) = 2528.00$
$c = 17.896 (9) \text{ \AA}$	$\lambda(\text{Mo}): \text{K}\alpha, 0.7107 \text{ \AA}$
$V = 5480.3 \text{ \AA}^3$	cryst dimensions:
cryst system: orthorhombic	0.15 × 0.17 × 0.14 mm
systematic absences:	$\mu(\text{Mo K}\alpha) = 17.17 \text{ cm}^{-1}$
$0kl, k = 2n + 1; h0l, l = 2n + 1;$	1456 symmetry-independent
$hk0, h = 2n + 1$	reflections with $I > 2.58\sigma(I)$
space group: <i>Pbca</i>	in the range $4^\circ < 2\theta < 52^\circ$ ;
$Z = 8$	of 2479 collected

waveform generator, and the current-potential curves were displayed on a Bryans X-Y recorder (Model 2600A3).

**Crystal Preparation.** The complex  $[\text{Mo}(\text{PhCSNNH})_3]$  was recrystallized from dimethylformamide-methanol at room temperature. The  $^1\text{H}$  NMR spectrum of the recrystallized material exhibited a resonance consistent with the presence of a dimethylformamide molecule of crystallization, which was confirmed by the crystal density and solution of the structure.

**Collection and Reduction of Diffraction Data.** Preliminary cell dimensions were obtained from Weissenberg and precession photographs of the crystals taken with  $\text{Cu K}\alpha$  ( $\lambda 1.5418 \text{ \AA}$ ) radiation. The approximate cell dimensions from these film measurements were used to accurately center 12 reflections with  $15^\circ \leq 2\theta \leq 22^\circ$  in the counter window of a Seimens AED quarter-circle automated diffractometer. A least-squares procedure was used to obtain a best fit between the observed and calculated values of  $\chi$ ,  $\phi$ , and  $2\theta$  for these reflections. The cell parameters and relevant crystal data are presented in Table I.

Intensity data were collected on the Seimens AED using  $\text{Mo K}\alpha$  radiation filtered through zirconium foil. A scan speed of  $1^\circ/\text{min}$  was employed in measuring each reflection by the moving-crystal, moving-counter ( $\omega/2\theta$ ) scan method with a scan range of  $1.5^\circ$  in  $2\theta$ . A five-value measurement was performed on each reflection in the following fashion: the angles are set to the center of the reflection which is then scanned through  $0.7^\circ$  toward negative  $\theta$  and the count  $I_1$  is recorded; the background is measured for 1.5 min and recorded as  $I_2$ ; the reflection is scanned through  $1.5^\circ$  and the count  $I_3$  is recorded; the background  $I_4$  on the second side of the peak is counted for 1.5 min; finally, the peak is scanned back through  $0.8^\circ$  and the count

$I_5$  is recorded. Since the counting times  $t_2 + t_4 = t_1 + t_3 + t_5$ , the net count is given by the relationship  $I_{\text{net}} = 1/2[(I_1 + I_3 + I_5) - (I_2 + I_4)]$ . Three standard reflections were employed to monitor diffractometer and crystal stability. The fluctuations in the integrated intensities of the standards totaled 1.5% over the period of data collection.

The observed intensities were corrected for background, Lorentz, and polarization effects. Only reflections with  $I > 2.58\sigma(I)$  were included in the refinement. The observed data were not corrected for secondary extinction.

**Solution and Refinement of the Structure.** A sharpened Patterson map was computed using the corrected data and solved for the coordinates of the molybdenum atom ( $R = 43\%$ ). The positional coordinates of the remaining nonhydrogen atoms were obtained from subsequent difference Fourier calculations. Five cycles of refinement on the positional and isotropic temperature factors of the 31 atoms led to convergence at values of 0.145 and 0.160 for the discrepancy factors  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$  and  $R_2 = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$ , respectively, where the weights,  $w$ , were taken as  $4F^2/\sigma^2(F^2)$ . Scattering factors for the zerovalent Mo, S, N, O, and C atoms were taken from ref 13, with the effects of anomalous dispersion being included in the contributions of Mo and S to the calculated structure factors.

A Fourier synthesis at this stage of the refinement clearly revealed the position of the dimethylformamide molecule of crystallization. These atomic positions and anisotropic temperature factors for all noncarbon atoms were introduced. Five cycles of full-matrix least-squares refinement converged to  $R_1 = 0.071$  and  $R_2 = 0.077$ . The error in an observation of unit weight was 1.86. A final difference Fourier map showed no regions of electron density greater than  $1.2 \text{ e \AA}^{-3}$ , on a scale where the average value for a carbon atom is  $7 \text{ e \AA}^{-3}$ . No attempt to locate hydrogen atom positions was made.

## Discussion

**Preparation, Reactions, and Spectra of Complexes.** The tris(thioaroyldiazene) complexes were prepared in good yield by reaction of  $[\text{MoO}_2(\text{acac})_2]$  with the thioaroylhydrazines in methanol. Although the complexes could also be readily prepared from sodium molybdate, the route from molybdenyl acetylacetonate was preferred as it removed the necessity to dry in vacuo prior to recrystallization. The complexes prepared

**Table II.** Complexes of the Type  $[\text{Mo}(\text{RCSN}_2\text{R}')_3]$ 

no.	complex	color	analysis <sup>b</sup>				$M_r^b$	$^1\text{H NMR}^c$		cyclic voltammetry <sup>d</sup>	
			% C	% H	% N	% S		obsd resonances, <sup>e</sup> ppm	assignt	$E_{\text{pc}}^1, \text{V}$	$E_{\text{pc}}^2, \text{V}$
I	$[\text{Mo}(\text{PhCSNNH})_3]$	purple <sup>a</sup>	45.8 (46.2)	4.5 (4.3)	14.8 (15.3)	17.6 (17.6)	528 (546)	6.9–7.4 m	phenyl protons	-0.30	-0.79
II	$[\text{Mo}(p\text{-MeOC}_6\text{H}_4\text{CSNNH})_3]$	purple <sup>a</sup>	45.3 (45.3)	3.9 (4.2)	13.1 (13.2)	15.3 (15.1)				-0.36	-0.82
III	$[\text{Mo}(\text{PhCSNNPh})_3]$	black	60.6 (60.6)	3.9 (3.7)	10.5 (10.6)	11.9 (12.4)	748 (774)	6.10 d (2) 6.9–7.4 m 7.9 m (2)	5,6 phenyl protons phenyl protons 3,4 phenyl protons	-0.30	-0.95
IV	$[\text{Mo}(p\text{-MeOC}_6\text{H}_4\text{CSNNPh})_3]$	black	58.3 (58.3)	4.3 (4.2)	9.7 (9.6)			3.85 s (3) 6.10 d (2) 6.85 d (2) 7.0–7.2 m 8.00 d (2)	<i>p</i> -MeO protons 5,6 phenyl protons phenyl protons 3,4 phenyl protons	-0.42	-1.04
V	$[\text{Mo}(p\text{-MeC}_6\text{H}_4\text{CSNNPh})_3]$	black	61.8 (61.7)	4.7 (4.4)	10.4 (10.3)		835 (816)	2.35 s (3) 6.05 d (2) 7–7.2 m 7.90 d (2)	<i>p</i> -Me protons 5,6 phenyl protons phenyl protons 3,4 phenyl protons	-0.31	-0.95
VI	$[\text{Mo}(m\text{-ClC}_6\text{H}_4\text{CSNNPh})_3]$	black	53.4 (53.4)	3.2 (3.1)	9.7 (9.6)			6.23 d (2) 7.1–7.4 m 7.8–8.1 m	5,6 phenyl protons phenyl protons 3,4 protons		
VII	$[\text{Mo}(1\text{-C}_{10}\text{H}_7\text{CSNNPh})_3]$	black	66.2 (66.2)	3.8 (3.9)	9.0 (9.1)						
VIII	$[\text{Mo}(\text{PhCH}_2\text{CSNNPh})_3]$	black	61.1 (61.6)	5.8 (4.4)	9.8 (10.2)		801 (815)	4.15 s (2) 5.75 d (2) 6.8–7.2 m	$\text{CH}_2$ protons 5,6 phenyl protons phenyl protons		

<sup>a</sup> Green when finely crushed or in solution. <sup>b</sup> Calculated values in parentheses. <sup>c</sup> Recorded in  $\text{CDCl}_3$  solution, preventing integration of resonances in phenyl region. <sup>d</sup> Measured in 10:1  $\text{CH}_2\text{Cl}-\text{MeOH}$  which was 0.1 M in  $\text{Et}_4\text{NBF}_4$ , under  $\text{N}_2$  at room temperature, using a vitreous carbon electrode at a scan rate of 60 mV/s. Potentials are in volts relative to an aqueous saturated potassium chloride-calomel electrode. <sup>e</sup> Abbreviations: d, doublet; m, multiplet; s, singlet.

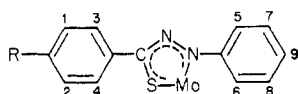


Figure 1. Numbering scheme for diazene phenyl group protons.

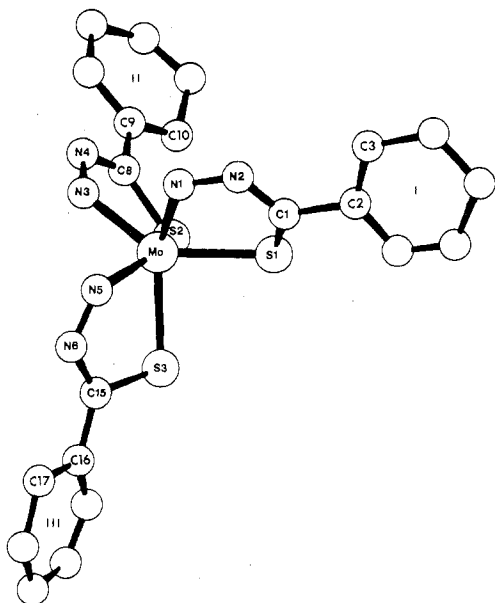


Figure 2. Molecular structure of  $[\text{Mo}(\text{C}_6\text{H}_5\text{CSN}_2\text{H})_3]$  showing the atom labeling scheme.

in this manner are indicated in Table II, together with analytical and spectroscopic data.

The complexes of the type  $[\text{Mo}(\text{ArCSNNH})_3]$  react with bases such as triethylamine in methanol to give brown anionic species which could be precipitated as tetrabutylammonium salts. These could not be obtained analytically pure but probably contain the  $[\text{Mo}(\text{ArCSNNH})_2(\text{ArCSN}_2)]^-$  anion. In the presence of an excess of dilute acid one of the diazene ligands of  $[\text{Mo}(\text{ArCSNNH})_3]$  undergoes a condensation with acetone to give the hydrazone derivatives  $[\text{Mo}(\text{ArCSNHNH}(\text{CMe}_2)(\text{ArCSNNH})_2)]$  and  $[\text{Mo}(\text{ArCSN}_2\text{H})(\text{ArCSNHNH}(\text{CMe}_2))]$ . The formulations of these two complexes have been confirmed by X-ray structural analyses, and full details will be given in a subsequent publication.

The IR spectra of the complexes  $[\text{Mo}(\text{PhCSNNH})_3]$  show a sharp medium-intensity band at  $3240\text{ cm}^{-1}$  assigned to  $\nu(\text{N-H})$ . The  $^1\text{H}$  NMR spectra of some of the complexes are summarized in Table II, with assignments, the numbering corresponding to that of Figure 1. The spectra in the region for phenyl protons in complexes III–VI are unusual in showing well-defined doublets in addition to the broad multiplets usually observed. The complexes  $[\text{Mo}(\text{ArCSNNH})_3]$  and  $[\text{Mo}$

$(\text{ArCSNNH})_2(\text{ArCSNHNH}(\text{CMe}_2))]$  do not show this well-defined splitting out of doublets. The higher field doublet is assigned to the 5,6 protons as it is maintained in benzyl complex VIII and the 7,8,9 protons would give rise to more complex multiplets. The lower field doublet is assigned to the 3,4 protons as in the *m*-chloro-substituted complex there is still a multiplet in the same region integrating as two protons.

**Electrochemical Studies.** The peak potentials observed in the cyclic voltammograms for certain of the complexes are summarized in Table II. The complexes  $[\text{Mo}(\text{ArCSNNH})_3]$  exhibit two one-electron reduction steps but no oxidation was observed. The separation between cathodic and anodic peak potentials ranged from 59 to 62 mV for the various complexes and remained substantially constant at different sweep rates. The reductive processes are therefore reversible under the conditions employed.

The *p*-methoxy-substituted complex, II, is more difficult to reduce than I at both steps, this effect being more marked for the first step. A somewhat analogous substituent dependence of redox potentials has been observed for the complexes  $[\text{Mo}(p\text{-RC}_6\text{H}_4\text{N}_2)(\text{S}_2\text{CNMe}_2)_3]$  where the oxidation potential is linearly dependent on the Hammett  $\sigma$  value for the para substituent R.<sup>29</sup>

Controlled-potential reduction of complex I or II at potentials 0.05 V more negative than the first reduction results in discharge of the characteristic emerald green color of the solution, producing a light violet solution characteristic of the anionic species  $[\text{Mo}(\text{ArCSNNH})_3]^-$ .

Only one *g* value is observed with  $g_{\text{iso}} = 1.96$  for frozen dichloromethane/methanol glasses of this species, the *g* value being similar to that observed for the structurally related complex  $[\text{Mo}\{o\text{-SC}_6\text{H}_4(\text{NH})\}_3]^-$ .<sup>30</sup>

The complexes III–VIII containing 1,2-disubstituted diazenes show a larger dependence of the first reduction potential on the substituent in the thioaroyl group. Comparison of the reduction potentials for I and III shows that introduction of a phenyl group causes no shift in the first reduction potential although the second step becomes more difficult.

**Structure.** Final positional and thermal parameters for the complex  $[\text{Mo}(\text{C}_6\text{H}_5\text{CSN}_2\text{H})_3] \cdot \text{DMF}$  are given in Table III. Table IV contains the relevant bond lengths and valence angles for the complex, and Table V presents the coefficients of the least-squares planes and the dihedral angles between planes. A perspective view of the molecular geometry giving the atom labeling scheme is presented in Figure 2. Figure 3 illustrates the packing of the symmetry-related molecules in the unit cell.

The structure consists of monomeric tris(thiobenzoyldiazene)molybdenum(VI) molecules of approximate trigonal-prismatic symmetry and an associated solvent molecule,  $(\text{CH}_3)_2\text{NCHO}$ . The distortion from regular trigonal-prismatic symmetry about the molybdenum is demonstrated both by the average twist angle,  $7^\circ$ , between the S1–S2–S3 and N1–N3–N5 planes and by the analysis and comparison of the structure to the idealized polytopal forms provided in Table

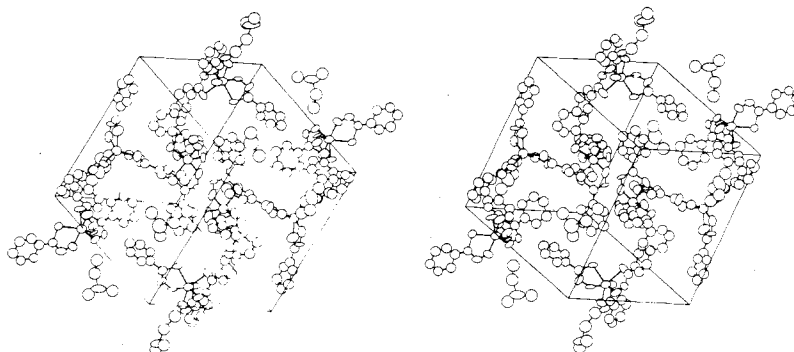


Figure 3. Stereoscopic view of the packing of the symmetry-related molecules in the unit cell.

Table III. Final Atomic Positional and Thermal Parameters for  $[\text{Mo}(\text{C}_6\text{H}_5\text{CSN}_2\text{H})_3]\cdot\text{DMF}^{a-c}$ 

atom	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Mo	0.00669 (9)	0.29011 (9)	0.51346 (8)	5.64 (9)	3.69 (8)	3.22 (7)	-0.27 (10)	0.14 (9)	-0.37 (9)
S1	0.0462 (3)	0.1723 (3)	0.4587 (3)	5.4 (3)	3.4 (3)	3.3 (3)	0.37 (28)	-0.70 (27)	-1.81 (2)
S2	-0.0492 (3)	0.3148 (3)	0.3926 (3)	5.2 (4)	5.0 (4)	3.7 (3)	-0.15 (30)	-2.3 (3)	-0.32 (26)
S3	-0.1105 (3)	0.2279 (3)	0.5473 (3)	5.3 (3)	3.5 (4)	3.1 (3)	-1.3 (3)	0.46 (26)	-0.47 (26)
N1	0.1225 (8)	0.2878 (8)	0.5355 (7)	4.9 (9)	1.5 (8)	2.4 (8)	-1.4 (9)	-0.82 (66)	-0.68 (77)
N2	0.1666 (8)	0.2269 (8)	0.5290 (8)	4.9 (9)	2.3 (10)	3.7 (11)	0.28 (82)	-0.01 (74)	-1.2 (75)
N3	0.0205 (7)	0.4027 (7)	0.4992 (8)	3.9 (9)	2.8 (8)	4.5 (11)	-0.66 (70)	0.39 (83)	-1.7 (82)
N4	0.0267 (8)	0.4382 (8)	0.4349 (7)	5.5 (11)	2.3 (8)	1.6 (8)	-1.2 (7)	-0.17 (70)	0.81 (70)
N5	-0.0040 (10)	0.3128 (8)	0.6230 (7)	5.5 (9)	4.4 (10)	2.1 (7)	-0.06 (99)	0.35 (93)	0.28 (67)
N6	-0.0653 (10)	0.3050 (8)	0.6653 (8)	6.3 (11)	3.3 (10)	3.0 (9)	-0.21 (93)	-0.08 (91)	-0.68 (79)
N7	0.1973 (14)	0.0266 (13)	0.2188 (13)	12.6 (20)	9.0 (19)	7.6 (16)	0.65 (15)	2.7 (15)	-3.6 (14)
O1	0.1247 (9)	0.0882 (9)	0.1351 (8)	6.2 (10)	7.1 (11)	6.6 (11)	1.6 (10)	-1.1 (9)	1.3 (9)

atom	x	y	z	$U, \text{Å}^2$	atom	x	y	z	$U, \text{Å}^2$
C1	0.1311 (12)	0.1658 (12)	0.5004 (12)	6.1 (6)	C13, II	0.0072 (15)	0.4235 (13)	0.1706 (12)	7.1 (7)
C2, I	0.1833 (11)	0.0961 (11)	0.4894 (11)	4.8 (5)	C14, II	-0.0218 (12)	0.3921 (11)	0.2423 (11)	5.5 (6)
C3, I	0.1449 (12)	0.0285 (12)	0.4727 (11)	5.3 (6)	C15	-0.1254 (10)	0.2657 (10)	0.6365 (9)	3.2 (5)
C4, I	0.1904 (14)	-0.0327 (13)	0.4658 (12)	6.5 (7)	C16, III	-0.1956 (11)	0.2490 (10)	0.6731 (11)	4.6 (5)
C5, I	0.2771 (11)	-0.0289 (11)	0.4615 (11)	5.0 (6)	C17, III	-0.2623 (11)	0.2241 (11)	0.6484 (10)	4.7 (6)
C6, I	0.3127 (12)	0.0436 (12)	0.4727 (11)	5.6 (6)	C18, III	-0.3257 (14)	0.2116 (14)	0.6822 (13)	7.2 (7)
C7, I	0.2647 (10)	0.1050 (10)	0.4853 (10)	4.5 (5)	C19, III	-0.3244 (13)	0.2179 (13)	0.7628 (13)	6.9 (7)
C8	-0.0060 (11)	0.3999 (10)	0.3786 (9)	3.8 (5)	C20, III	-0.2566 (12)	0.2382 (12)	0.7938 (11)	5.1 (6)
C9, II	0.0069 (13)	0.4338 (11)	0.3053 (11)	5.6 (6)	C21, III	-0.1881 (11)	0.2594 (11)	0.7567 (10)	4.4 (5)
C10, II	0.0371 (11)	0.5039 (12)	0.3002 (11)	5.0 (6)	C22, sol	0.1601 (21)	0.0813 (21)	0.2765 (22)	14.8 (14)
C11, II	0.0525 (15)	0.5384 (14)	0.2265 (14)	8.1 (8)	C23, sol	0.1664 (24)	0.0439 (24)	0.1549 (24)	14.6 (15)
C12, II	0.0225 (13)	0.4931 (15)	0.1605 (14)	7.8 (8)	C24, sol	0.2347 (24)	-0.0403 (23)	0.2498 (23)	16.6 (15)

<sup>a</sup> Estimated standard deviations are given in parentheses. <sup>b</sup>  $U_{ij} \times 10^2$ . The vibrational coefficients relate to the expression  $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ . <sup>c</sup> Numbering scheme as given in Figure 2. Roman numerals identify the ring to which the carbon atoms belong. Sol identifies the carbon atoms of the DMF molecule of crystallization. N7 and O1 are also atoms of the solvent molecule.

VI;<sup>14</sup> in addition, the planes defined by S1-S2-S3 and N1-N3-N5 are not perfectly parallel, making an angle of 178.5°. A number of molybdenum structures with approximate trigonal-prismatic coordination have been reported:  $[\text{Mo}(\text{S}_2\text{C}_2\text{H}_2)_3]$ ,<sup>9</sup>  $[\text{Mo}(\text{Se}_2\text{C}_2(\text{CF}_3)_2)_3]$ ,<sup>15</sup> and  $[\text{Mo}(\text{S}_2\text{C}_6\text{H}_4)_3]$ ,<sup>27</sup> where the twist angle is 0° by crystallographic symmetry;  $[\text{Mo}(\text{mnt})_3]^{2-}$  ( $\text{mnt} = \text{S}_2\text{CC}(\text{CN})_2$ ),<sup>2-</sup> where the twist angle is 28°; and the unusual asymmetric dimers  $[\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_2(\text{C}_6\text{H}_5\text{CON}_2)_2]$ <sup>4</sup> and  $[\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_2(\text{C}_6\text{H}_4\text{CSN}_2)_2]$  for which the geometries about the Mo atoms ligated to the diazenido ligands are defined in Table VI and shown to possess average twist angles of 10.8 and 4.3°, respectively. Since it has been argued that a low number of d electrons ( $d^0$ - $d^2$ ) is optimum for trigonal-prismatic geometry,<sup>16</sup> the results are not totally unexpected. Although any assignment of formal oxidation state to these complexes possessing highly delocalized orbitals is artificial, it has some value in practice in rationalizing the observed trends. Thus,  $[\text{Mo}(\text{S}_2\text{C}_2\text{H}_2)_3]$ ,  $[\text{Mo}(\text{Se}_2\text{C}_2(\text{CF}_3)_2)_3]$ , and  $[\text{Mo}(\text{S}_2\text{C}_6\text{H}_4)_3]$  are formally  $d^0$  complexes and exhibit regular trigonal-prismatic geometry about the Mo atom, while  $[\text{Mo}(\text{mnt})_3]^{2-}$ , being formally a  $d^2$  complex, exhibits a structure intermediate between octahedral and trigonal-prismatic types. Photoelectron spectroscopy supports the Mo(VI) formulation for the former species.<sup>23</sup> On the other hand, the formally  $d^0$  complex  $[\text{Zr}(\text{S}_2\text{C}_6\text{H}_4)_3]^{2-}$ <sup>25</sup> exhibits considerable distortion from regular trigonal-prismatic geometry, suggesting that stability arguments based on  $d^0$  formalism are of limited utility and that metal d-orbital-ligand  $\pi$ -orbital overlap may be the determining factor.<sup>25</sup>

The distortion from regular geometry observed in the dimer structures  $[\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_2(\text{C}_6\text{H}_5\text{CON}_2)_2]$  and  $[\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_2(\text{C}_6\text{H}_4\text{CSN}_2)_2]$ , arises from constraints inherent in dimer formation and the mixed-ligand environment about the Mo atoms. Major sources of the distortion from perfect trigonal-prismatic symmetry observed for  $[\text{Mo}(\text{C}_6\text{H}_5\text{CSN}_2\text{H})_3]$  are the constraints imposed on the geometry of the molecule by the five-membered chelate ring and the more severe effects of ligating through different donor groups (S

Table IV. Selected Interatomic Distances and Valence Angles<sup>a,b</sup> for  $[\text{Mo}(\text{C}_6\text{H}_5\text{CSN}_2\text{H})_3]\cdot\text{DMF}$ 

		Distances	
Mo-S1	2.390 (5)	S3-C15	1.72 (2)
Mo-S2	2.412 (5)	C15-N6	1.36 (2)
Mo-S3	2.397 (6)	C15-C16	1.45 (3)
Mo-N1	2.06 (1)	N5-N6	1.32 (2)
Mo-N3	2.01 (1)	S1...N1(bite)	2.78 (1)
Mo-N5	2.01 (1)	S2...N3(bite)	2.74 (1)
S1-C1	1.66 (2)	S3...N5(bite)	2.74 (2)
C1-N2	1.34 (3)	C-C(av, ring)	I 1.42 (3)
C1-C2	1.54 (3)		II 1.42 (3)
N1-N2	1.32 (2)		III 1.40 (3)
S2-C8	1.69 (2)	O...N1	2.81 (2)
C8-N4	1.34 (2)	O...N3	3.04 (2)
C8-C9	1.48 (3)	O...N5	2.85 (2)
N3-N4	1.31 (2)		

		Angles	
S1-Mo-S2	84.5 (2)	S1-C1-C2	121.7 (16)
S1-Mo-S3	87.5 (2)	S1-C1-N2	122.0 (16)
S2-Mo-S3	87.9 (2)	C2-C1-N2	114.2 (17)
S1-Mo-N1	77.1 (4)	C1-N2-N1	114.2 (15)
S1-Mo-N3	139.9 (4)	Mo-N1-N2	124.8 (11)
S1-Mo-N5	126.8 (4)	S2-C8-C9	124.2 (14)
S2-Mo-N1	124.9 (4)	S2-C8-N4	121.4 (13)
S2-Mo-N3	76.0 (4)	C9-C8-N4	114.0 (16)
S2-Mo-N5	143.3 (5)	C8-N4-N3	112.8 (14)
S3-Mo-N1	141.3 (4)	Mo-N3-N4	126.1 (11)
S3-Mo-N3	125.7 (4)	S3-C15-C16	118.1 (14)
S3-Mo-N5	76.4 (5)	S3-C15-N5	115.1 (13)
N1-Mo-N3	85.8 (5)	C16-C15-N5	126.7 (16)
N1-Mo-N5	84.8 (6)	C15-N5-N5	117.5 (14)
N3-Mo-N5	86.6 (6)	Mo-N5-N6	128.0 (12)
Mo-S1-C1	97.6 (8)	C-C-C(av, ring)	I 119.9 (19)
Mo-S2-C8	96.4 (6)		II 119.5 (19)
Mo-S3-C15	100.7 (6)		III 119.6 (18)

<sup>a</sup> Distances in Å; angles in deg. <sup>b</sup> Estimated standard deviations in parentheses.

and N atoms), as illustrated in Figure 4. Whereas the dimensions of the nearly ideal trigonal-prismatic structures exhibited by  $[\text{Re}(\text{S}_2\text{C}_2\text{Ph}_2)_3]$ ,<sup>6</sup>  $[\text{Mo}(\text{S}_2\text{C}_2\text{H}_2)_3]$ ,<sup>9</sup>  $[\text{Mo}(\text{S}_2\text{C}_6\text{H}_4)_3]$ ,<sup>27</sup> and  $[\text{V}(\text{S}_2\text{C}_2\text{Ph}_2)_3]$  are quite regular as shown in Table

Table V

(a) Equations of Least-Squares Planes for  $[\text{Mo}(\text{C}_6\text{H}_5\text{CSN}_2\text{H})_3]\cdot\text{DMF}$

- $-7.015X - 5.172Y + 15.515Z - 5.928 = 0$   
S1 -0.027 (49) N1 0.032 (49)  
C1 0.059 (49) N2 -0.063 (49)
- $15.123X - 8.211Y - 3.128Z + 4.557 = 0$   
S2 0.0007 (14) N3 -0.0009 (14)  
C8 -0.0015 (14) N4 0.0017 (14)
- $-6.528X + 14.682Y - 7.150Z - 0.159 = 0$   
S3 -0.0044 (89) N5 0.0059 (89)  
C15 0.0094 (89) N6 -0.0110 (89)
- $0.556X - 3.135Y + 17.599Z - 8.368 = 0$   
C2 0.025 (37) C5 -0.002 (37)  
C3 -0.037 (37) C6 -0.012 (37)  
C4 0.035 (37) C7 -0.009 (37)
- $15.880X - 7.283Y - 2.93Z + 3.172 = 0$   
C9 0.033 (36) C12 -0.001 (36)  
C10 0.002 (36) C13 -0.038 (36)  
C11 0.025 (36) C14 -0.021 (36)
- $-5.019X + 16.724Y - 1.630Z - 4.020 = 0$   
C16 0.027 (42) C19 0.009 (42)  
C17 -0.064 (42) C20 -0.042 (42)  
C18 0.042 (42) C21 0.028 (42)

(b) Selected Dihedral Angles in  $[\text{Mo}(\text{C}_6\text{H}_5\text{CSN}_2\text{H})_3]\cdot\text{DMF}$ 

plane A <sup>a</sup>	plane B	angle, deg	plane A	plane B	angle, deg
S1-C1-N2- N1	S2-C8- N4-N3	111.2	Mo-S1-N1	Mo-S2-N3	117.1
S1-C1-N2- N1	S3-C15- N6-N5	116.3	Mo-S1-N1	Mo-S3-N5	119.3
S2-C8-N4- N3	S3-C15- N6-N5	130.2	Mo-S2-N3	Mo-S3-N5	119.6
S1-C1-N2 N1	C2→C7 (ring I)	26.8	Mo-S1-N1	S1-C1-N2- N1	16.3
S2-C8-N4- N3	C9→C14 (ring II)	9.9	Mo-S2-N3	S2-C8-N4- N3	23.1
S3-C15-N6- N5	C16→C21 (ring III)	19.6	Mo-S3-N5	S3-C15-N6- N5	13.0

<sup>a</sup> Plane-generating atoms are listed; labeling refers to Figure 2.Table VI. Ideal and Observed Angles (deg) for  $\text{ML}_6$  Complexes<sup>a</sup>

complex	$\delta_1$	$\delta_2$	$\delta_3$	$\alpha$ , twist angle
ideal octahedron <sup>b</sup>	70.5, 70.5, 70.5	70.5, 70.5, 70.5	70.5, 70.5, 70.5	60
$[\text{Mo}_2\text{O}(\text{S}_2\text{CNEt})_2(\text{C}_6\text{H}_5\text{CON}_2)_2]\cdot\text{CH}_2\text{Cl}_2$	1.9, 5.2, 8.3	111.6, 112.6, 124.9	82.5, 86.8, 88.8 86.5, 88.5, 88.7	10.8
$[\text{Mo}_2\text{O}(\text{S}_2\text{CNEt})_2(\text{ClC}_6\text{H}_4\text{CSN}_2)_2]\cdot\text{CHCl}_3$	0.6, 2.4, 11.2	112.5, 117.7, 123.4	85.6, 86.8, 88.5 85.0, 87.1, 89.9	4.3
$[\text{Mo}(\text{C}_6\text{H}_5\text{CSN}_2\text{H})_3]\cdot\text{DMF}$	14.3, 16.3, 18.0	129.3, 131.3, 131.3	79.8, 80.9, 82.9 85.4, 86.9, 87.3	7.2 (av)
ideal trigonal prism <sup>b</sup>	0, 0, 0	120, 120, 120	90, 90, 90 90, 90, 90	0

<sup>a</sup> The dihedral angles enclose the edges represented in Figure 4. <sup>b</sup> The values for the idealized polytopal forms are given in ref 14.Table VII. Comparison of the Dimensions of Tris(1,2-dithiolene) Complexes of Trigonal-Prismatic Geometry with the Tris(diazene) Complex  $[\text{Mo}(\text{C}_6\text{H}_5\text{CSN}_2\text{H})_3]$ <sup>a</sup>

complex	L	M-L	L	L'	L-L' (bite)	L-L' (interligand)	S-M-S	S-M-N	twist angles, $\alpha$	ref
$[\text{Re}(\text{S}_2\text{C}_2\text{Ph}_2)_3]$	S	2.325 (4)	S	S	3.032 (10)	3.050 (8)	81.4 (4)		>1	6
$[\text{V}(\text{S}_2\text{C}_2\text{Ph}_2)_3]$	S	2.338 (4)	S	S	3.060 (6)	3.065 (av) <sup>f</sup>	81.6 (1)		8.5	7
$[\text{Zr}(\text{S}_2\text{C}_6\text{H}_4)_3]^{2-}$ <sup>e</sup>	S	2.544 (2)	S	S	3.264 (5)	3.586 (5)	79.78 (7)		37	8, 25
$[\text{Nb}(\text{S}_2\text{C}_6\text{H}_4)_3]$	S	2.441 (2)	S	S	3.150 (3)	3.231 (3)	80.35 (7)		0.7	8, 26
$[\text{Mo}(\text{S}_2\text{C}_6\text{H}_4)_3]$	S	2.367 (2)	S	S	3.110 (8)	3.091 (15)	82.1 (4)		0	8, 27
$[\text{Mo}(\text{S}_2\text{C}_2\text{H}_2)_3]$	S	2.33 (1)	S	S	3.10	3.11	<i>b</i>		0.0	9
$[\text{Mo}(\text{S}_2\text{C}_2(\text{CN})_2)_3]^{2-}$ <sup>d</sup>	S	2.373 (4)	S	S	3.127	3.188	82.2 (2)		28	10
$[\text{Mo}(\text{C}_6\text{H}_5\text{CSN}_2\text{H})_3]$	S	2.400 (5)	S	N	2.75 (1)	3.292 (7)		76.5 (5)	7.0	<i>c</i>
	N	2.03 (1)								

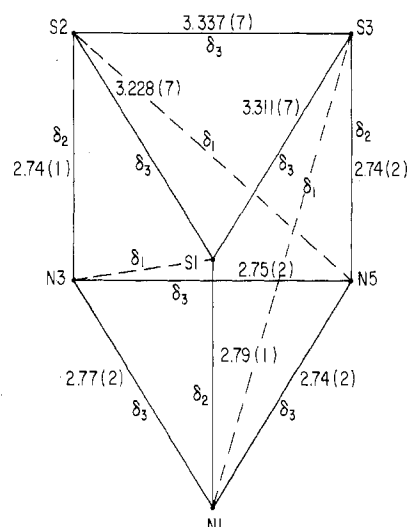
<sup>a</sup> Bond lengths in Å; angles in deg. <sup>b</sup> Value not reported. <sup>c</sup> This work. <sup>d</sup> Geometry intermediate between regular trigonal prismatic and octahedral types. <sup>e</sup> Distorted octahedral. <sup>f</sup> Reported values exhibit considerable spread: 2.927 (5), 3.088 (5), and 3.178 (5) Å.

Figure 4. Schematic representation of the coordination polyhedron. The labeled edges define the shape-determining dihedral angles tabulated in the text and characterized in ref 14.

VII, the diazene complex  $[\text{Mo}(\text{C}_6\text{H}_5\text{CNS}_2\text{H})_3]$  is characterized by irregular polyhedral edges arising from a constrained chelate bite ( $\text{S}\cdots\text{N}$  intraligand) of 2.76 (1) Å (average) and from the significant variations in the interligand distances: S-S with values of 3.228 (7), 3.311 (7), and 3.337 (7) Å and an average N-N distance of 2.75 (2) Å. An additional source of distortion is intermolecular in nature, arising from the close approach of the dimethylformamide molecule to the plane defined by the nitrogen donor atoms and resulting in a distance of 2.43 Å from the oxygen atom of the DMF molecule to the centroid of the N1-N3-N5 plane. The O-N1 and O-N5 distances (2.81 and 2.85 Å, respectively) are well within the sum of the van der Waals radii for oxygen and nitrogen, ca. 2.90 Å, and suggest appreciable intermolecular hydrogen bonding about the N-H $\cdots$ O axes. Although the quality of the final Fourier map precluded location of the hydrogen atoms, reasonable positional parameters could be assigned to the

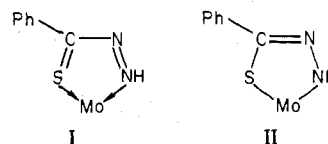
Table VIII. Comparison of Average Structural Features<sup>d</sup> of Five-Membered Rings of the Type M(RCXXNH<sub>n</sub>NH<sub>m</sub>)<sup>b</sup> and the Free Ligands

compd	M-X	X	M-N	X-N	C-X	C-N	N-N	M-X-C	X-C-N	C-N-N	N-N-M	ref
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> NCONHNH <sub>2</sub>		O		2.84	1.23	1.33	1.41		122	121		17
[Co(N <sub>2</sub> H <sub>4</sub> )(OCONHNH <sub>2</sub> ) <sub>2</sub> ]	2.064 (2)	O	2.198 (2)		1.287 (3)	1.372 (3)	1.425 (2)	116.0 (2)	117.8 (2)	118.6 (2)	104.7 (1)	18
[Cu(PhCONHNH <sub>2</sub> ) <sub>2</sub> ] <sup>2+</sup> c	1.94	O	2.01	2.61	1.26	1.33	1.44	114	120	106	117	19
[Mo <sub>2</sub> O(S <sub>2</sub> CNEt <sub>2</sub> ) <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> CON <sub>2</sub> ) <sub>2</sub> ] <sup>d</sup>	2.05 (1)	O	1.91 (1)	2.36 (2)	1.30 (2)	1.28 (2)	1.38 (2)	114.9 (10)	120.5 (16)	107.6 (15)	123.7 (10)	4
NH <sub>2</sub> CSNHNH <sub>2</sub>		S		f	1.685	1.337	1.399		121.5	122.5		20
[Ni(NH <sub>2</sub> CSNHNH <sub>2</sub> ) <sub>2</sub> ] <sup>2+</sup> e	2.16	S	1.90	2.88	1.75	1.29	1.44	114.9	119.4	118.1	91.2	21
[Ni(NH <sub>2</sub> CSNHNH <sub>2</sub> ) <sub>2</sub> ]	2.155	S	1.911	2.67	1.746	1.247	1.537	102.9	120.9	109.8	123.2	22
[Mo <sub>2</sub> O(S <sub>2</sub> CNEt <sub>2</sub> ) <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> CSN <sub>2</sub> ) <sub>2</sub> ] <sup>d</sup>	2.398 (7)	S	1.91 (2)	2.67 (2)	1.73 (2)	1.29 (2)	1.39 (2)	99.5 (8)	119.7 (17)	111.5 (16)	134.3 (11)	4
[Mo(C <sub>6</sub> H <sub>5</sub> CSNHNH <sub>2</sub> ) <sub>3</sub> ]	2.400 (5)	S	2.03 (1)	2.76 (1)	1.69 (2)	1.35 (2)	1.32 (2)	98.2 (7)	119.5 (14)	114.8 (15)	126.3 (13)	g

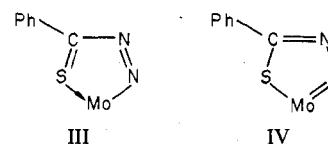
<sup>a</sup> Distances in Å; angles in deg. <sup>b</sup> For  $n = 1$ ,  $m = 2$ ;  $n = 0$ ,  $m = 2$ , 1, or 0. <sup>c</sup> Cu<sub>3</sub>Cl<sub>3</sub><sup>2-</sup> as counterion. <sup>d</sup> Parameters for the pseudo-trigonal-prismatic coordination site. <sup>e</sup> SO<sub>4</sub><sup>2-</sup> as counterion. <sup>f</sup> The structure is for the trans configuration of the S and N donors. Using the structural parameters given, a reasonable estimate of the free-ligand bite distance in the cis or ligating configuration is 3.10–3.20 Å. <sup>g</sup> This work.

nitrogen-bound hydrogens by assuming sp<sup>2</sup> hybridization for the metal-bound nitrogen and a N–H bond distance of 1.02 Å. This results in an average oxygen–hydrogen contact distance of 1.81 Å, as compared to a value of 2.6 Å for the sum of the van der Waals radii,<sup>31</sup> and an approximately linear O...H–N bond (within 10°).

The distances within the chelate rings are intermediate between single- and double-bond lengths, and comparison with C–N and N–N bond lengths in the structures of other complexes of substituted hydrazines illustrates the dependence of these distances on the degree of protonation of the ligand (Table VIII). The contraction of the N–N bond distance in the diazene groups of [Mo(C<sub>6</sub>H<sub>5</sub>CSN<sub>2</sub>H<sub>3</sub>)<sub>3</sub>], as compared to the values observed for other structures in Table VIII, suggests a large contribution to the overall structure of the ligand from a canonical form with an N–N double bond, such as I. The



relatively short C–N and Mo–N distances also indicate some contribution from resonance form II. Upon deprotonation to give formally the diazenido(1–) derivative, as in [Mo<sub>2</sub>O(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>(ClC<sub>6</sub>H<sub>4</sub>CSN<sub>2</sub>)<sub>2</sub>], a significant contraction in the C–N and Mo–N bond distances, accompanied by an increase in the N–N distance, is observed. The data indicate a significantly greater contribution by resonance form IV to the



structure of the diazenido chelate than the corresponding form II to the protonated diazene–metal ring system. Although structural parameters are not available for the parent ligand C<sub>6</sub>H<sub>5</sub>CSNHNH<sub>2</sub>, the structure of the related thiosemicarbazide is known,<sup>20</sup> and it is apparent that in the free ligand itself the C–S, C–N, and N–N bond distances are intermediate between the usual single- and double-bond values. In the absence of further structural information, a detailed analysis and comparison of the chelate systems for the hydrazine, diazene, and diazenido(1–) derivatives will not be attempted.

### Conclusion

By the conventionally applied criteria, the coordination geometry of the complex [Mo(C<sub>6</sub>H<sub>5</sub>CSN<sub>2</sub>H<sub>3</sub>)<sub>3</sub>]-DMF is best described as distorted trigonal prismatic. The result is consistent with the formal d<sup>0</sup> electronic configuration of the metal and with the highly delocalized nature of the chelate ring structure, establishing the structural analogy of the diazene complexes to those of the dithiolene derivatives.

**Acknowledgment.** Support for the crystallographic investigation by a grant from the National Institutes of Health (No. GM 22566) to J.A.Z. is gratefully acknowledged. We also thank the Climax Molybdenum Co. for the provision of molybdenyl acetylacetonate.

**Registry No.** I-DMF, 68366-08-5; II, 53480-19-6; III, 53480-20-9; IV, 53480-23-2; V, 53480-22-1; VI, 68344-02-5; VII, 68307-55-1; VIII, 53480-21-0; MoO<sub>2</sub>(acac)<sub>2</sub>, 17524-05-9.

**Supplementary Material Available:** A listing of structure factors (15 pages). Ordering information is given on any current masthead page.

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## Crystal and Molecular Structure of the Five-Coordinate Mn(III) Macrocyclic Complex (7,16-Dihydro-6,8,15,17-tetramethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecinato)-(isothiocyanato)manganese(III)

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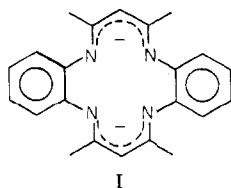
Received August 4, 1978

The crystal and molecular structure of the high-spin, five-coordinate Mn(III) complex  $[\text{Mn}(\text{C}_{22}\text{H}_{22}\text{N}_4)(\text{NCS})]$  containing the dibenzotetraaza[14]annulene macrocyclic ligand 7,16-dihydro-6,8,15,17-tetramethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecinato has been determined from three-dimensional X-ray diffraction data. The complex crystallizes in the orthorhombic space group  $D_{2h}^{14}$ -*Pbcn* with the cell dimensions  $a = 14.678$  (4),  $b = 8.704$  (2), and  $c = 16.093$  (4) Å with  $Z = 4$ , each molecule lying on a crystallographic dyad. The structure was refined by Fourier and least-squares techniques to conventional and weighted  $R$  values of 0.041 and 0.054, respectively, based on 1999 data with  $|F_o| \geq 3\sigma(F_o)$ . The average Mn(III)-N(macrocycle) bond distance is 1.958 (6) Å, while the Mn(III)-N(axial) bond distance is 2.115 (4) Å. The Mn(III) is displaced by 0.356 Å from the  $\text{N}_4$  donor plane, and the macrocyclic ligand has the usual saddle conformation. Comparisons are made with related Mn(III) structures containing porphyrin, macrocyclic, and tetradentate ligands as well as with other five-coordinate complexes containing the title macrocycle.

### Introduction

In the not too distant past, stable Mn(III) complexes were thought to be confined largely to the oxides.<sup>2</sup> The more notable exceptions were Mn(III) complexes of acetate, 2,4-pentanedione, and a few Schiff bases—all of which are strong oxidants.<sup>3-5</sup> More recently, it has been found that Mn(III) can be generated chemically<sup>6</sup> or electrochemically<sup>7</sup> with a number of ligands, particularly macrocyclic ligands, and that for some of these, especially porphyrins, Mn(III) appears to be the preferred oxidation state. It must be concluded that Mn(III) is not an uncommon oxidation state and considerably more effort is warranted in elucidating its structural and reactivity preferences.

A five-coordinate square-pyramidal geometry has been shown to be the preferred stereochemistry for the simple complexes of the dihydro-6,8,15,17-tetramethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecinato ligand, I. The



preponderance of structural data suggests that the ligand induces, partially as a consequence of its steric interactions, a tendency toward five-coordination with a preference for the metal to be displaced from the macrocyclic  $\text{N}_4$  plane. As described previously,<sup>9-11</sup> the saddle conformation of the ligand allows maximum bonding interactions while minimizing the peripheral steric interactions: (1) maximization of overlap between the N(equatorial) lone-pair electrons with the appropriate metal orbitals, (2) maintenance of planarity in the 2,4-pentanediiimino chelate rings, and (3) relief of steric interaction at the periphery.

The structure of the title complex was determined as part of our program of studying the relationships between the structure and reactivity patterns of I with a number of first- and second-row transition metals. The structural parameters associated with the Mn(III) complex are expected to be consistent with the systematic trend of values established by the study of the Mn(II), Fe(III), and Co(III) five-coordinate complexes containing the same macrocyclic ligand. Thus the structure of  $[\text{Mn}(\text{C}_{22}\text{H}_{22}\text{N}_4)(\text{NCS})]$  is discussed in light of the previous results obtained for  $[\text{Mn}(\text{C}_{22}\text{H}_{22}\text{N}_4)(\text{N}(\text{C}_2\text{H}_5)_3)_3]$ ,  $[\text{Fe}(\text{C}_{22}\text{H}_{22}\text{N}_4)\text{Cl}]$ , and  $[\text{Co}(\text{C}_{22}\text{H}_{22}\text{N}_4)\text{I}]$ . Comparisons are made with other five- and six-coordinate high-spin Mn(III) complexes, especially the porphyrin counterparts  $[\text{Mn}(\text{TP-P})\text{Cl}]$ <sup>12-14</sup> and  $[\text{Mn}(\text{TPP})\text{N}_3]$ .<sup>12</sup> Some contrasts are noted