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Synthesis, Properties, and Crystal and Molecular Structures of the Complexes $[Mo(XC_6H_4CSN_2)(XC_6H_4CSN_2H)(XC_6H_4CSNNC(CH_3)_2)]$ (X = *p*-Cl, *p*-Me). Species Possessing Three Chemically and Crystallographically Distinct Chelate Rings

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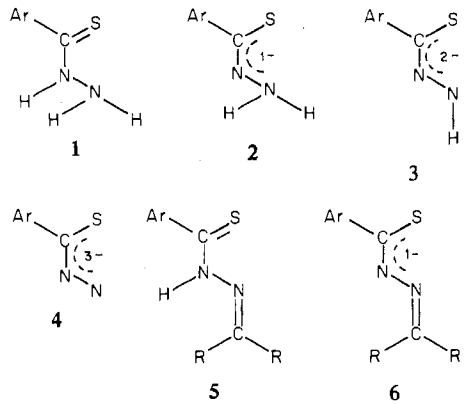
The crystal and molecular structures of the complexes $[Mo(XC_6H_4CSN_2)(XC_6H_4CSN_2H)(XC_6H_4CSNNCMe_2)]$, X = CH_3 (III) and Cl (IV), have been investigated by X-ray diffraction techniques. Compound III crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the unit cell of dimensions a = 12.505 (9) Å, b = 12.533 (10) Å, c = 10.274 (8) Å, α = 115.62 (1)°, β = 86.41 (2)°, and γ = 93.45 (1)°, while compound IV displays monoclinic symmetry, space group $P2_1/c$ with four molecules in the unit cell of dimensions a = 13.049 (1) Å, b = 12.838 (1) Å, c = 17.183 (1) Å, and β = 90.87 (1)°. The structures were solved by using 2573 and 2889 symmetry-independent reflections, respectively, with $I \geq 2.58\sigma(I)$. Refinement by full-matrix least-squares methods, using anisotropic temperature factors for all nonhydrogen atoms, gave a final R factor of 0.073 for III. Similar refinement, with the inclusion of hydrogen atoms with isotropic thermal parameters, yielded a final residual of 0.038 for IV. The structures are essentially identical with a coordination polyhedra intermediate between trigonal-prismatic and octahedral geometries with the sulfur and nitrogen donor atoms disposed on opposite triangular faces in a facial configuration. In complex IV the chelate rings exhibit Mo–N bond distances and Mo–N–N valence angles of 1.786 (5) Å and 142.8 (3)° for the diazenido(1–) ligand, 1.967 (5) Å and 131.6 (4)° for the diazene ring, and 2.216 (5) Å and 116.9 (4)° for the hydrazonido form. The Mo–S distance of 2.48 Å for the sulfur trans to the multiply bonded diazenido nitrogen is significantly longer than the average distance 2.457 (2) Å for the other Mo–S bonds and indicates a structural trans influence. The severe distortions from the trigonal-prismatic geometry are partially steric in origin, arising from the introduction of the hydrazonido group and resultant nonbonding interactions in the N1N3N5 plane.

Introduction

The current interest in complexes of molybdenum with sulfur-containing ligands as potential models for metal binding sites in the redox-active molybdoenzymes[1,2] has prompted our investigation of the structures of molybdenum complexes with thioaroylhydrazido ligands.

Thiohydrazides are capable of stabilizing molybdenum in a number of unusual geometries, including the asymmetric dimer $[Mo_2O(S_2CNEt_2)_2(ClC_6H_4CSN_2)_2]$[3] and the trigonal-prismatic species $[Mo(C_6H_5CSN_2H)_3]$.[4] It was found that treatment of the Mo(VI) complexes $[Mo(XC_6H_4CSN_2H)_3]$ (X = H, *p*-CH_3, *p*-OCH_3 or *p*-Cl) with acetone in the presence of dilute acid gave complexes possessing a single condensed hydrazone or hydrazonido ligand, $[Mo(XC_6H_4CSN_2)(XC_6H_4CSN_2H)(XC_6H_4CSNNCMe_2)]$. The complexes are unusual in possessing three chemically distinct ligand groups, and it was felt that this provided a unique opportunity for structural definition of the various coordination types available with this type of ligand. Substituted thiohydrazines may ligate as the fully protonated hydrazine **1**, the singly deprotonated hydrazide **2**, the doubly deprotonated diazene **3**, or the triply deprotonated diazenide(1–) **4**; the hydrazone may be neutral, **5**, or deprotonated, **6**. [Formal assignment of charge can be somewhat ambiguous. Charges have been assigned here according to the best interpretation for the compounds reported.] The structural parameters defining these coordination types have not been systematized.

A further feature of considerable interest is the overall coordination geometry of the molybdenum atom in these complexes. The parent compounds $[Mo(XC_6H_4CSN_2H)_3]$ are isomorphous with the species $[Mo(C_6H_5CSN_2H)_3]$, which displays distorted trigonal-prismatic geometry about the Mo. Trigonal-prismatic geometry has been observed for a number of Mo(VI) d^0 complexes with ligands capable of providing extensively delocalized chelate systems. We anticipated that introduction of the sterically bulky hydrazone ligand might



produce significant geometric distortions, arising from both steric and electronic effects.

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Table I. Molybdenum Thiohydrazonido Complexes

complex	color	anal.,[a] % C	H	N	^{1}H NMR[b]
$[Mo(C_6H_5CSN_2)(C_6H_5CSN_2H)(C_6H_5CSNNC(CH_3)_2)]$ (I)	yellow-brown	48.8 (49.2)	4.1 (4.6)	14.2 (14.3)	
$[Mo(p\text{-}CH_3OC_6H_4CSN_2)(p\text{-}CH_3OC_6H_4CSN_2H)(p\text{-}CH_3OC_6H_4CSN_2C(CH_3)_2)]$ (II)	yellow-brown	48.0 (48.1)	4.2 (4.2)	12.3 (12.4)	2.52, 2.58 (d, acetone methyls), 3.85, 3.89, 2.1 (d, p-CH_3O groups), 6.8–7.0, 7.9–8.2 (m, phenyl protons)
$[Mo(p\text{-}CH_3C_6H_4CSN_2)(p\text{-}CH_3C_6H_4CSN_2H)(p\text{-}CH_3C_6H_4CSN_2C(CH_3)_2)]$ (III)	yellow-brown	51.5 (51.4)	4.6 (4.2)	12.9 (13.3)	2.43, 2.45 (d, p-CH_3 groups), 2.55, 2.60 (d, acetone methyls), 7.2–7.4, 7.9–8.2 (m, phenyl protons)
$[Mo(p\text{-}ClC_6H_4CSN_2)(p\text{-}ClC_6H_4CSN_2H)(p\text{-}ClC_6H_4CSN_2C(CH_3)_2)]$ (IV)	yellow-brown	42.6 (41.9)	2.9 (2.6)	12.4 (12.2)	2.56, 2.59 (d, acetone methyls), 7.3–7.5, 7.9–8.4 (m, phenyl protons)

[a] Calculated values in parentheses. [b] $CDCl_3$ solution; chemical shifts are in ppm relative to tetramethylsilane as an internal standard; d = doublet, m = multiplet.

Table II. Experimental Data for the X-ray Diffraction Study of $[Mo(CH_3C_6H_4CSN_2)(CH_3C_6H_4CSN_2H)(CH_3C_6H_4CSNNCMe_2)]$ and $[Mo(ClC_6H_4CSN_2)(ClC_6H_4CSN_2H)(ClC_6H_4CSNNCMe_2)]$

	$[Mo(CH_3C_6H_4CSN_2)(CH_3C_6H_4CSN_2H)(CH_3C_6H_4CSNNCMe_2)]$	$[Mo(ClC_6H_4CSN_2)(ClC_6H_4CSN_2H)(ClC_6H_4CSNNCMe_2)]$
	(A) Crystal Parameters at 22 + 1 °C	
space group	$P\bar{1}$	$P2_1/c$
a, Å	12.505 (9)	13.049 (1)
b, Å	12.533 (10)	12.838 (1)
c, Å	10.274 (8)	17.193 (1)
α, deg	115.62 (1)	90.00
β, deg	86.41 (2)	90.87 (1)
γ, deg	93.45 (1)	90.00
V, Å^3	1448.1	2879.9
Z	2	4
mol wt	629.7	689.9
ρ(calcd), g cm^{-3}	1.44	1.59
ρ(obsd), g cm^{-3}	1.42 (2)	1.57 (2)
	(B) Measurement of Intensity Data	
instrument	Siemens AED quarter-circle diffractometer	Enraf-Nonius CAD-4
radiatn	Mo Kα (λ = 0.710 69 Å), Zr foil filter	Mo Kα, graphite monochromator; 2.5° takeoff angle
attenuators	used for counts > 5000/s	used for counts > 5000/s
scan mode	coupled θ(cryst)–2θ(counter)	ω scans
scan speed	1°/min	variable, max θ = 10°/min, min θ = 1.2°/min
range	$3.7 < 2\theta < 42°$	$0° < 2\theta < 45°$
scan length	from $2\theta(K\alpha_1) + 0.8°$ to $2\theta(K\alpha_2) - 0.8°$	$0.70 + 0.347 \tan\theta$
bkgd measmt	stationary cryst, stationary counter 160 s at beginning and end of each 2θ range	stationary cryst, stationary counter, 10 s at beginning and end of each 2θ range
std reflctns	3 measd every 40 reflctns	4 measd every 100 reflctns
reflctns collected	3188 total to give 2573 with $I > 2.58\sigma(I)$	4087 total to give 2889 with $I > 2.58\sigma(I)$
	(C) Reduction of Intensity Data	
F(000)	646.0	1384.0
abs coeff (μ, cm^{-1})	6.8	9.6

For elucidation of the chelate bonding parameters for the various ligand types and the effects of bulky substituents on the metal-bound nitrogen on the overall coordination geometry, the X-ray crystallographic analysis of the structure of $[Mo(p\text{-}CH_3C_6H_4CSN_2)(p\text{-}CH_3C_6H_4CSN_2H)(p\text{-}CH_3C_6H_4CSNNCMe_2)]$ (III) was undertaken. Although this analysis provided identification and structural parameterization of the various ligand types, hydrogen atoms were not located. In order to provide unambiguous data on the degree of ligand protonation, the structure of an analogous compound providing significantly better quality crystals, $[Mo(p\text{-}ClC_6H_4CSN_2)(p\text{-}ClC_6H_4CSN_2H)(p\text{-}ClC_6H_4CSNNCMe_2)]$ (IV), was investigated. Although the crystal habits of III and IV were not isomorphous, the structure analyses discussed herein confirm that the complexes are structurally analogous, with some minor angular distortions of the order of magnitude associated with differences in crystal packing forces.

The unusual magnetic properties associated with these complexes are discussed in light of their established structures.

Experimental Section

Preparation of Complexes. The preparations were carried out by using reagent grade solvents with no precautions to exclude oxygen. Analytical and spectroscopic data are summarized in Table I. The numbers in the table are used throughout the text.

$[Mo(C_6H_5CSN_2)(C_6H_5CSN_2H)(C_6H_5CSNNC(CH_3)_2)]$ (I). $[Mo(PhCSN_2H)_3]$ (1.0 g) in acetone (40 mL) was treated with 4 N HCl (1.0 mL) dropwise. The resulting yellow-brown solution was evaporated to dryness and the residue recrystallized from dichloromethane–methanol. $[Mo(p\text{-}MeOC_6H_4CSN_2)(p\text{-}MeOC_6H_4CSN_2H)(p\text{-}MeOC_6H_4CSNNC(CH_3)_2)]$ (II), $[Mo(p\text{-}MeC_6H_4CSN_2)(p\text{-}MeC_6H_4CSN_2H)(p\text{-}MeC_6H_4CSNNC(CH_3)_2)]$ (III), and $[Mo(p\text{-}ClC_6H_4CSN_2)(p\text{-}ClC_6H_4CSN_2H)(p\text{-}$

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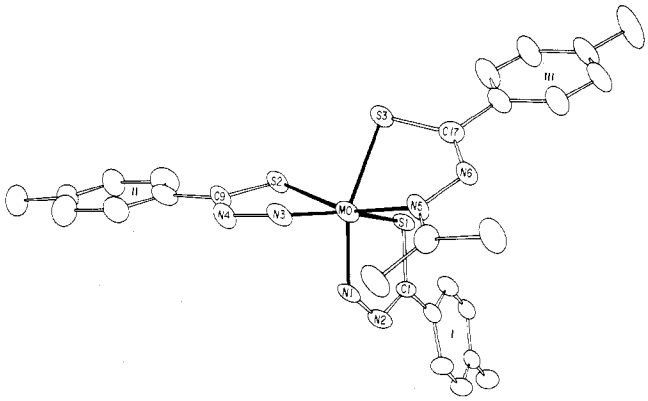

Figure 1. Perspective view of the molecule $[Mo(CH_3C_6H_4CSN_2)(CH_3C_6H_4CSNNH)(CH_3C_6H_4CSNNCMe_2)]$ showing the atom labeling scheme.

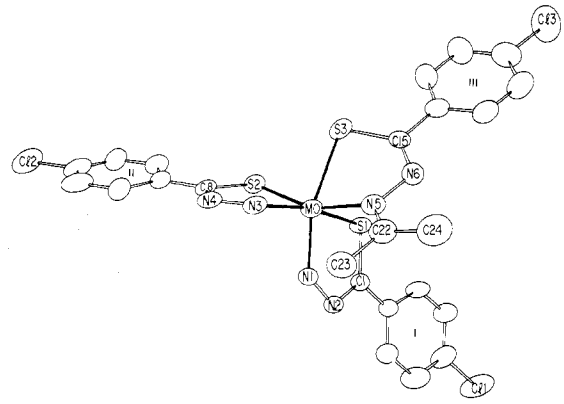

Figure 2. Perspective view of the molecule $[Mo(ClC_6H_4CSN_2)(ClC_6H_4CSN_2H)(ClC_6H_4CSNNCMe_2)]$, showing the atom labeling scheme.

$ClC_6H_4CSNNC(CH_3)_2)]$ (IV) were prepared similarly. Analytical and spectroscopic data are given in Table I.

Collection and Reduction of X-ray Data. Green-brown needles of both III and IV were obtained by slow evaporation of solvent from methylene chloride–methanol solution. Approximate unit cell parameters and space groups were determined from Weissenberg and precession photographs by using Ni-filtered Cu Kα radiation (λ = 1.5418 Å).

With use of a Siemens AED paper-type-driven diffractometer, data were collected on a crystal of III mounted along the needle axis and with dimensions 0.11 × 0.54 × 0.16 mm. The details of the data collection are given in Table II. The apparatus and data reduction were as described previously.[4] The orientation matrix used for data collection and the lattice parameters were computed from least-squares refinement of the χ, ϕ, and 2θ settings of 18 carefully centered reflections.

A crystal of IV mounted along its needle axis and with dimensions 0.15 × 0.32 × 0.15 mm was employed for data collection on a Nonius CAD-4 diffractometer. The details of the data collection are also given in Table II.

Determination of the Structures. In both cases the initial Patterson map revealed the position of the molybdenum atom. Subsequent difference Fourier maps revealed the positions of all nonhydrogen atoms for III and all atoms, including hydrogens, for IV.

Full-matrix least-squares refinement was based on F, and the function was minimized as $\sum w(|F_o| - |F_c|)^2$. The weights, w, were taken as $\sigma(F_o)^{-1}$, and $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. Atomic scattering factors for nonhydrogen atoms were taken from Cromer and Waber.[27] Scattering factors for hydrogen were those of Stewart, Davidson, and Simpson.[28] The anomalous dispersion corrections for molybdenum, sulfur, and chlorine were included. The programs used in the refinements were those compiled in the 1972 version of the X-ray system of Stewart et al.[9] and operated on the UNIVAC 1110 computer.

Refinement of positional parameters and individual anisotropic temperature factors for all nonhydrogen atoms of III converged at values of 0.078 and 0.087 for R and R_w, respectively, where $R = \sum||F_o| - |F_c||/\sum|F_c|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$. The error in an observation of unit weight was 1.05. A final difference Fourier map showed no region of electron density greater than 0.8 e Å^{-3} on a scale where the average value for a carbon atom is 5.5 e Å^{-3}. Although a number of these peaks were consistent with hydrogen atom positions, the quality of the map lacked sufficient definition to merit a systematic attempt to locate hydrogen atoms.

Upon refinement of positional and anisotropic thermal parameters for nonhydrogen atoms, structure IV converged to a conventional R factor of 0.063. A difference Fourier map at this stage of refinement disclosed the positions of all hydrogen atoms. Refinement on all atomic positional parameters, anisotropic temperature factors for nonhydrogen atoms, and isotropic temperature factors for hydrogen atoms converged to R = 0.038 and R_w = 0.040, with an error in an observation of unit weight of 1.35. Final atomic positional parameters and temperature factors for both III and IV are given in Table III. Table IV contains relevant bond lengths and valence angles for the complexes, and Table V lists the significant nonbonding interactions. Coefficients of selected least-squares planes and dihedral angles between planes are presented in Table VII. Perspective views of the molecular geometries giving the atom labeling schemes are presented in Figures 1 and 2 for III and IV, respectively. Figure 3 illustrates the packing of the symmetry-related molecules in the unit cell of III while Figure 4 reveals the packing for the monoclinic cell of complex IV.

Results and Discussion

Structures. Reference to Tables IV and VI and Figures 1 and 2 establishes that the structures of III and IV are analogous as regards overall coordination geometry about the molybdenum atoms and that they possess identical ligand types in terms of the ligand charge formalism described in the introduction. The discussion will focus on the structural aspects of $[Mo(p\text{-}ClC_6H_4CSN_2)(p\text{-}ClC_6H_4CSN_2H)(p\text{-}ClC_6H_4CSNNCMe_2)]$ (IV) since the nature of the coordinated ligands has been determined unambiguously in this case. The conclusions to be drawn apply with equal validity to complex III. Where significant differences do occur in valence angles and dihedral angles, crystal packing forces will be invoked to explain these effects.

The structure of IV consists of monomeric molecules of geometry intermediate between octahedral and trigonal prismatic with the sulfur and nitrogen donor atoms disposed on opposite triangular faces in a facial configuration. The two triangular faces are almost parallel to one another, the dihedral angle between them measuring 0.9°. The molybdenum atom lies 1.53 and 0.900 Å from the triangular faces defined by the sulfur and nitrogen atoms, respectively. Comparison to the displacement of the Mo from the faces generated by sulfur and nitrogen donors for $[Mo(NHC_6H_4S)_3]$,[29] 1.525 and 1.227 Å, and for $[Mo(C_6H_5CSN_2H)_3]$,[4] 1.53 and 1.24 Å, respectively, reveals a significant shift of the molybdenum atom toward the N1N3N5 face.

The distortion from regular octahedral symmetry about the molybdenum is demonstrated in Table VI where the structural parameters are compared to those for ideal polytopal forms[12] and for molybdenum diazenido complexes of approximate trigonal-prismatic geometry. The inherent distortions that arise from the effects of ligation through different donor atoms (S and N) in the chelate rings are also considered in terms of idealized polyhedra of C_3 and C_{3v} symmetries whose shape-determining angles have been calculated from average values for the polyhedral edges as derived from the structures of $[Mo_2O(S_2CNEt_2)_2(ClC_6H_4CSN_2)_2]$[3] and $[Mo(C_6H_5CS-$

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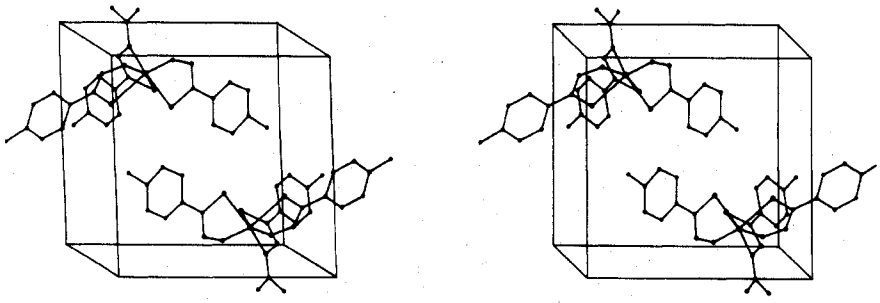

Figure 3. Stereoscopic pair of the symmetry-related molecules in the unit cell of $[Mo(CH_3C_6H_4CSN_2)(CH_3C_6H_4CSN_2H)(CH_3C_6H_4CSNNCMe_2)]$.

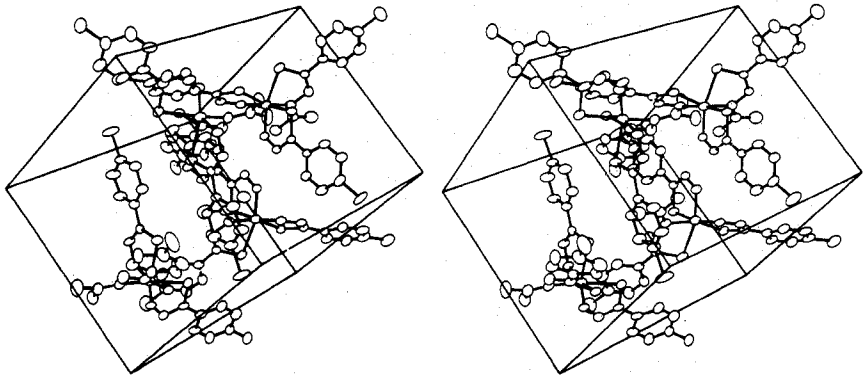

Figure 4. Stereoscopic pair showing the unit cell packing for $[Mo(ClC_6H_4CSN_2)(ClC_6H_4CSN_2H)(ClC_6H_4CSNNCMe_2)]$.

$N_2H)_3]$.[4] An average shape-determining angle, δ_1, of 52.3° suggests a structure intermediate between octahedral and trigonal-prismatic geometries for which δ_1 would have values of 70.5 and 0.0°, respectively.

Another useful descriptor of distortion in tris(chelate) complexes is the twist angle defining the chelate projection angle onto the mean plane defined by the triangular faces S1S2S3 and N1N3N5. The observed angles of 45° for α(S1, N1), 31° for α(S2, N3), and 40° for α(S3, N5) fall between the limits of 60° for idealized octahedral geometry and 0° for the ideal trigonal prism. This trigonal twist angle, α, has been shown to correlate with chelate bite distances and angles.[30] Thus the expected coordination geometry may be calculated by minimizing the total donor atom repulsion energy, taking into account the constraints imposed by the chelate bite.[31,32] The average bite angle of 74.7° observed for IV predicts a chelate projection angle, α, of about 40–45°. Although this value is close to those observed for IV (Table VI), the model does not take into account the steric effects imposed by the condensed hydrazone ring. Since the model is also inadequate in correlating the geometries of maleonitriledithiolates, $[M(S_2C_2R_2)_3]^{x\pm}$, a class of compounds to which the thioaroylhydrazides are clearly related, the agreement between calculated and observed twist angles may be fortuitous.

Inspection of Table VI demonstrates that the hydrazonido derivatives III and IV have undergone considerable distortion from the trigonal-prismatic geometry observed for the parent species, $[Mo(C_6H_5CSN_2H)_3]$,[4] for example. Since it has been argued that a low number of d electrons (d^0–d^2) is optimal for trigonal-prismatic geometry,[6] the results previously reported for $[Mo(C_6H_5CSN_2H)_3]$ were anticipated. It is apparent that the condensation with acetone results not only in the disruption of the delocalized ring system of the hydrazone but also in a considerable distortion from the trigonal-prismatic geometry usually associated with d^0 complexes of molybdenum with thiobenzoyldiazenido ligands.

This distortion toward octahedral geometry may be rationalized in terms of steric and electronic effects, discussed below.

The distorted geometry of the hydrazonido derivative is characterized by irregular polyhedral edges (Table V) arising from a constrained chelate bite, from the chemical nonequivalence of the three chelate rings, and from significant steric interactions of the hydrazonido carbon atoms with donor groups. Thus, there are three crystallographically distinct S···N intraligand or bite distances of 2.776 (8), 2.552 (11), and 2.837 (11) Å. Although variation in the edge lengths of the triangular faces defined by S1S2S3 and N1N3N5 is anticipated on the basis of the differences in the van der Waals radii of sulfur and nitrogen, giving rise to a tapered polyhedron, there is also a significant contribution to these interligand interactions from the hydrazonido substituent. While the parent complex $[Mo(C_6H_5CSN_2H)_3]$ displays fairly regular triangular faces, S1S2S3 with an average edge length of 3.292 Å (3.228 (7)–3.337 (7)-Å range) and N1N3N5 with an average edge length of 2.75 (2) Å (2.74 (2)–2.77 (2)-Å range), the hydrazonido derivative IV exhibits a fairly regular S1S2S3 face with an average edge length of 3.344 Å (3.292 (3)–3.442 (3)-Å range) but an N1N3N5 face with significantly different N···N distances: 2.727 (8), 3.169 (8), and 3.289 (6) Å. The N···N nonbonding distance involving the unsubstituted donors N1 and N3 is similar to that observed for N···N distances in $[Mo(C_6H_5CSN_2H)_3]$ and consistent with the result anticipated from the sum of the van der Waals radii.[17] The N5···N1 and N5···N3 distances are significantly expanded, presumably as a result of steric interaction with the hydrazone carbon atoms. With assumption of approximate values of 1.5 and 2.0 Å for the van der Waals radii of nitrogen and the methyl group,[17] respectively, the N1···C23 and N3···C23 distances presented in Table V are short and indicate some steric interaction. Any contraction of the N1···N5 or N3···N5 distances to produce equivalent N···N edges would only decrease the nonbonded distances N1···C23 and N3···C23 and hence increase the unfavorable interaction.

A unique feature of the structure is the presence of the three crystallographically and chemically nonequivalent chelate ring

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Table III

(a) Final Positional and Thermal Parameters[a, b] for $[Mo(CH_3C_6H_4CSN_2)(CH_3C_6H_4CSNNH)(CH_3C_6H_4CSNNCMe_2)]$

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	0.2862 (1)	0.3826 (1)	0.2415 (1)	7.8 (1)	5.8 (1)	6.7 (1)	−1.74 (5)	−1.58 (6)	2.83 (2)
S1	0.4193 (2)	0.2268 (2)	0.1201 (3)	7.4 (2)	5.2 (2)	5.7 (3)	−1.8 (2)	−2.0 (2)	1.5 (2)
S2	0.1897 (2)	0.2435 (2)	0.3196 (3)	8.4 (3)	5.6 (2)	6.3 (3)	−2.1 (2)	−1.0 (2)	2.6 (2)
S3	0.1935 (3)	0.2752 (3)	0.0149 (3)	7.7 (3)	7.2 (2)	6.3 (3)	−2.6 (2)	−2.0 (2)	3.1 (2)
N1	0.4109 (8)	0.4370 (8)	0.3704 (10)	6.8 (7)	5.8 (6)	5.1 (7)	−0.5 (6)	−2.0 (6)	2.7 (5)
N2	0.5101 (8)	0.3961 (8)	0.3468 (11)	7.9 (8)	4.3 (6)	6.1 (8)	−1.5 (6)	−2.2 (6)	1.8 (6)
N3	0.1929 (8)	0.4647 (8)	0.3857 (11)	8.6 (8)	5.9 (7)	5.8 (8)	−2.4 (6)	−2.1 (6)	3.2 (6)
N4	0.1327 (9)	0.4629 (8)	0.4925 (12)	9.4 (8)	5.8 (7)	6.8 (8)	−1.3 (6)	0.0 (7)	3.4 (6)
N5	0.3254 (8)	0.4851 (8)	0.1185 (11)	8.5 (8)	6.7 (7)	5.2 (8)	−2.0 (6)	−0.7 (6)	3.4 (6)
N6	0.3430 (8)	0.4178 (9)	−0.0309 (12)	7.6 (8)	7.6 (7)	6.7 (8)	−1.3 (6)	−1.6 (6)	4.8 (7)
C1	0.5250 (9)	0.2949 (10)	0.2333 (10)	6.2 (9)	5.5 (8)	7.2 (10)	−2.1 (7)	−2.0 (7)	3.5 (8)
C2, I	0.6272 (10)	0.2390 (11)	0.2082 (13)	7.5 (9)	6.9 (9)	5.2 (9)	−1.6 (8)	−0.7 (7)	3.1 (7)
C3, I	0.7205 (10)	0.3015 (11)	0.2851 (14)	7.2 (9)	6.0 (8)	8.6 (11)	−1.8 (7)	−1.2 (8)	1.1 (8)
C4, I	0.8148 (10)	0.2482 (11)	0.2736 (14)	5.9 (8)	7.6 (9)	7.5 (10)	−1.3 (7)	−0.9 (8)	1.0 (8)
C5, I	0.8264 (11)	0.1265 (11)	0.1840 (14)	7.9 (10)	7.4 (9)	7.3 (10)	−1.8 (8)	−0.7 (8)	3.9 (8)
C6, I	0.7390 (11)	0.0635 (11)	0.0972 (14)	7.6 (10)	6.7 (9)	6.1 (10)	−1.1 (8)	−0.4 (8)	2.5 (8)
C7, I	0.6417 (11)	0.1167 (11)	0.1105 (14)	9.0 (10)	5.5 (8)	5.6 (9)	−1.1 (7)	−1.3 (8)	1.4 (7)
C8, I	0.9267 (11)	0.0635 (12)	0.1749 (16)	6.2 (9)	9.1 (10)	11.5 (13)	0.4 (8)	−0.7 (9)	3.6 (10)
C9	0.1227 (10)	0.3518 (11)	0.4699 (12)	7.3 (9)	9.4 (10)	5.2 (9)	−2.3 (8)	−0.7 (7)	3.6 (8)
C10, II	0.0584 (11)	0.3222 (12)	0.5794 (14)	8.9 (10)	10.4 (11)	6.7 (10)	−3.2 (9)	−2.6 (8)	4.5 (9)
C11, II	0.0561 (12)	0.1987 (12)	0.5585 (18)	11.4 (13)	8.9 (11)	13.4 (15)	−2.6 (10)	−1.4 (11)	6.2 (11)
C12, II	−0.0045 (12)	0.1777 (15)	0.6739 (17)	10.5 (12)	15.6 (15)	10.4 (14)	−2.16 (11)	0.7 (11)	9.0 (12)
C13, II	−0.0511 (12)	0.2746 (12)	0.7923 (17)	6.7 (11)	20.4 (23)	7.5 (12)	−0.7 (12)	−0.1 (9)	9.8 (14)
C14, II	−0.0489 (12)	0.3924 (14)	0.8087 (20)	9.7 (13)	12.7 (14)	15.1 (16)	−0.3 (10)	2.2 (11)	8.5 (13)
C15, II	0.0079 (11)	0.4115 (12)	0.7002 (17)	7.9 (10)	10.3 (11)	10.4 (13)	0.3 (9)	−0.4 (9)	4.8 (10)
C16, II	−0.1051 (13)	0.2396 (19)	0.9152 (20)	9.7 (13)	22.0 (22)	11.2 (16)	−0.3 (13)	2.8 (11)	9.7 (16)
C17	0.2882 (10)	0.3172 (10)	−0.0854 (15)	6.4 (9)	6.7 (8)	10.4 (12)	−1.0 (7)	−2.0 (8)	5.8 (8)
C18, III	0.3104 (11)	0.2400 (11)	−0.2439 (13)	9.4 (11)	6.8 (9)	5.9 (10)	−0.5 (8)	−1.3 (8)	3.1 (8)
C19, III	0.2831 (13)	0.1187 (12)	−0.2982 (18)	14.4 (14)	6.2 (9)	7.1 (12)	−1.4 (9)	−0.4 (11)	2.4 (9)
C20, III	0.3115 (13)	0.0491 (13)	−0.4374 (19)	15.1 (16)	7.2 (10)	9.3 (14)	−0.9 (10)	−0.9 (11)	4.5 (1)
C21, III	0.3699 (12)	0.0914 (13)	−0.5319 (16)	14.0 (14)	8.7 (11)	7.3 (11)	−0.8 (9)	−1.8 (10)	4.0 (9)
C22, III	0.3935 (13)	0.2093 (12)	−0.4740 (14)	14.4 (14)	7.8 (10)	5.2 (10)	−1.6 (9)	−1.6 (9)	3.1 (8)
C23, III	0.3642 (12)	0.2831 (12)	−0.3371 (15)	11.4 (12)	9.5 (11)	7.4 (11)	−2.5 (9)	−1.2 (9)	4.9 (9)
C24, III	0.4019 (17)	0.0121 (14)	−0.6882 (18)	24.6 (24)	10.0 (12)	7.0 (12)	0.3 (14)	2.6 (14)	4.1 (11)
C25	0.3460 (10)	0.6001 (11)	0.1686 (16)	7.3 (9)	6.6 (9)	11.0 (13)	−1.8 (7)	−0.8 (9)	5.8 (9)
C26	0.3460 (10)	0.6001 (11)	0.0609 (16)	13.1 (13)	6.2 (9)	8.7 (12)	−1.2 (9)	0.2 (10)	4.1 (11)
C27	0.3321 (12)	0.6778 (12)	0.3244 (15)	11.6 (12)	6.3 (9)	6.1 (11)	−1.2 (8)	0.3 (9)	0.3 (8)

(b) Final Thermal and Positional Parameters for $[Mo(ClC_6H_4CSN_2)(ClC_6H_4CSN_2H)(ClC_6H_4CSNNCMe_2)]$

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	−0.20588 (5)	0.15866 (5)	0.06088 (4)	4.63 (4)	4.30 (4)	4.91 (5)	0.01 (3)	0.41 (2)	−0.04 (3)
S1	−0.0839 (1)	0.3071 (1)	0.0232 (1)	4.5 (1)	3.4 (1)	6.1 (1)	0.07 (8)	0.76 (9)	0.05 (8)
S2	−0.3040 (1)	0.2056 (1)	−0.0595 (1)	4.9 (1)	4.1 (1)	4.9 (1)	0.28 (9)	−0.29 (9)	0.00 (9)
S3	−0.3068 (1)	0.3117 (1)	0.1148 (1)	4.3 (1)	4.8 (1)	5.5 (1)	−0.54 (9)	−0.08 (9)	1.08 (9)
N1	−0.0871 (4)	0.0930 (4)	0.0201 (3)	4.7 (3)	2.7 (3)	5.3 (4)	−0.42 (26)	0.36 (29)	−0.17 (26)
N2	0.0088 (5)	0.1256 (4)	0.0014 (3)	4.4 (4)	3.9 (3)	5.2 (4)	0.13 (29)	0.18 (29)	−0.38 (28)
N3	−0.2910 (4)	0.0618 (4)	0.0446 (3)	4.1 (3)	4.2 (3)	4.9 (4)	0.14 (28)	1.2 (28)	0.47 (28)
N4	−0.3539 (4)	0.0213 (4)	−0.0069 (3)	4.4 (3)	4.2 (3)	5.1 (4)	0.89 (29)	0.60 (29)	0.46 (29)
N5	−0.1575 (4)	0.1742 (5)	0.1849 (3)	5.4 (3)	4.6 (3)	4.6 (3)	0.54 (32)	−0.07 (27)	0.19 (31)
N6	−0.1574 (5)	0.2737 (5)	0.2215 (3)	6.5 (4)	5.3 (4)	4.4 (4)	0.38 (33)	−0.22 (31)	−0.46 (30)
C1	0.0189 (5)	0.2274 (5)	0.0025 (4)	4.5 (4)	3.9 (4)	3.0 (4)	0.14 (34)	0.07 (31)	0.51 (31)
C2, I	0.1216 (5)	0.2705 (5)	−0.125 (4)	4.5 (4)	3.8 (4)	4.0 (4)	−0.22 (33)	0.48 (33)	0.08 (32)
C3, I	0.1437 (6)	0.3754 (6)	−0.0046 (4)	4.9 (5)	4.2 (4)	6.5 (5)	0.85 (36)	0.66 (39)	0.97 (37)
C4, I	0.2431 (6)	0.4133 (6)	−0.0010 (5)	6.1 (5)	4.4 (5)	7.7 (6)	−0.35 (4)	0.23 (4)	0.40 (40)
C5, I	0.3215 (6)	0.3419 (7)	−0.0251 (5)	5.0 (4)	6.1 (6)	7.4 (5)	−1.5 (4)	−0.05 (39)	1.5 (5)
C6, I	0.3023 (6)	0.2370 (7)	−0.0335 (5)	5.7 (5)	7.0 (6)	9.4 (7)	−0.84 (44)	1.7 (5)	0.83 (48)
C7, I	0.2027 (6)	0.2026 (6)	−0.0284 (4)	5.6 (5)	5.0 (5)	6.7 (5)	−1.1 (4)	0.68 (41)	0.04 (37)
C8	−0.3698 (5)	0.0885 (5)	−0.0649 (4)	3.3 (4)	4.6 (4)	4.8 (4)	−0.32 (32)	0.93 (31)	0.13 (34)
C9, II	−0.4395 (5)	0.0711 (5)	−0.1296 (4)	4.0 (4)	5.1 (4)	5.1 (4)	−0.66 (35)	1.1 (3)	−0.57 (36)
C10, II	−0.4662 (6)	0.1321 (6)	−0.1866 (5)	5.4 (5)	5.9 (5)	7.1 (5)	1.1 (4)	−0.67 (42)	0.41 (43)
C11, II	−0.5301 (6)	0.1018 (7)	−0.2487 (5)	6.7 (6)	8.9 (7)	6.6 (6)	−0.11 (51)	−0.83 (47)	0.27 (51)
C12, II	−0.5681 (6)	0.0030 (8)	−0.2520 (5)	5.0 (5)	8.8 (7)	5.6 (5)	1.5 (5)	0.42 (41)	2.5 (5)
C13, II	−0.5435 (6)	−0.0676 (7)	−0.1962 (5)	6.1 (5)	7.4 (6)	6.9 (5)	3.1 (5)	0.69 (46)	2.1 (5)
C14, II	−0.4793 (6)	−0.0393 (6)	−0.1349 (4)	5.7 (5)	6.2 (5)	6.0 (5)	−1.1 (4)	0.93 (41)	0.08 (41)
C15	−0.2225 (5)	0.3382 (5)	0.1934 (4)	4.5 (4)	4.6 (4)	4.4 (4)	−0.35 (36)	1.1 (3)	−0.78 (35)
C16, II	−0.2261 (5)	0.4448 (5)	0.2291 (4)	5.1 (4)	5.0 (4)	4.1 (4)	0.94 (36)	0.57 (35)	0.48 (33)
C17, II	−0.1664 (6)	0.4686 (6)	0.2943 (4)	5.7 (5)	6.5 (5)	6.4 (5)	−0.15 (42)	−0.15 (42)	0.84 (43)
C18, II	−0.1647 (7)	0.5678 (7)	0.3244 (5)	8.8 (7)	7.6 (6)	5.7 (5)	1.1 (5)	−1.9 (5)	2.1 (5)
C19, II	−0.2236 (7)	0.6437 (6)	0.2909 (5)	9.8 (7)	5.3 (5)	5.3 (5)	1.1 (5)	0.58 (48)	0.88 (40)
C20, II	−0.2850 (7)	0.6213 (6)	0.2282 (5)	10.1 (7)	4.6 (4)	5.6 (5)	−1.1 (5)	0.20 (49)	0.52 (41)
C21, II	−0.2860 (6)	0.5223 (6)	0.1977 (5)	8.1 (6)	5.7 (5)	4.2 (4)	−0.46 (45)	−0.29 (41)	0.29 (38)
C22	−0.1199 (6)	0.0996 (4)	0.2276 (4)	6.6 (5)	6.3 (5)	4.5 (5)	0.99 (43)	−0.10 (38)	0.38 (39)
C23	−0.0775 (8)	0.1165 (8)	0.3074 (5)	13.2 (9)	9.9 (7)	6.8 (6)	3.4 (7)	−2.3 (6)	0.80 (56)
C24	−0.1216 (7)	−0.0079 (6)	0.1978 (5)	9.8 (7)	6.2 (5)	5.5 (5)	2.0 (5)	−0.43 (48)	1.0 (4)
Cl1	0.4472 (2)	0.3857 (2)	−0.0308 (2)	5.1 (1)	8.8 (2)	16.0 (3)	−2.4 (1)	−0.07 (15)	0.97 (18)
Cl2	−0.3524 (2)	−0.0337 (2)	−0.3297 (2)	7.4 (2)	13.1 (2)	7.6 (2)	1.7 (2)	−1.4 (1)	3.6 (2)
Cl3	−0.2211 (3)	0.7707 (2)	0.3264 (2)	18.4 (3)	5.3 (2)	7.9 (2)	0.15 (2)	−2.1 (2)	2.0 (1)

Table III (*Continued*)

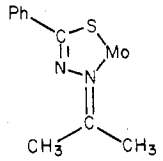
atom	x	y	z	U, Å²	atom	x	y	z	U, Å²
HC3	0.089 (4)	0.417 (4)	0.0103 (3)	2.1 (17)	HC20	−0.323 (7)	0.672 (7)	0.205 (5)	8.2 (30)
HC4	0.266 (5)	0.497 (5)	−0.008 (4)	3.4 (20)	HC21	−0.328 (4)	0.510 (5)	0.154 (3)	2.3 (17)
HC6	0.315 (5)	0.263 (6)	0.452 (4)	14.1 (23)	HC23A	−0.117 (7)	0.154 (8)	0.336 (5)	6.5 (30)
HC7	0.186 (5)	0.129 (5)	−0.037 (4)	3.5 (22)	HC23B	−0.058 (7)	0.064 (7)	0.316 (5)	12.3 (28)
HC10	−0.438 (4)	0.199 (4)	−0.185 (33)	2.2 (16)	HC23C	−0.038 (8)	0.156 (9)	0.311 (6)	6.3 (39)
HC11	−0.548 (4)	0.145 (4)	−0.281 (3)	3.9 (14)	HC24A	−0.089 (6)	−0.016 (6)	0.156 (4)	4.2 (22)
HC13	−0.572 (5)	−0.131 (5)	−0.204 (3)	3.8 (19)	HC24B	−0.106 (6)	−0.050 (6)	0.232 (5)	5.2 (26)
HC14	−0.464 (4)	−0.083 (4)	−0.1992 (3)	1.4 (20)	HC24C	−0.184 (9)	−0.023 (9)	0.180 (7)	14.1 (5)
HC17	−0.125 (4)	0.416 (4)	0.312 (3)	0.3 (15)	HN1	−0.090 (4)	0.031 (4)	0.012 (3)	2.1 (14)
HC18	−0.130 (4)	0.585 (4)	0.356 (3)	2.8 (14)					

[a] Estimated standard deviations are given in parentheses. [b] $U_{ij} \times 10^2$. The vibrational coefficients relate to the expression $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

systems. The structural dimensions of the chelate rings are compared to those reported for a number of complexes of thiobenzoylhydrazine and thiosemicarbazone derivatives in Table VIII, while the equations of the least-squares planes for the chelate rings are presented in Table VII.

Hydrazonido Ligand. The extensive delocalization which is common to thiobenzoylhydrazide chelate rings is apparently disrupted upon condensation with acetone to form the hydrazonido ligand. The effects are most pronounced in the lengthening of the N5–N6 bond distance to 1.424 (9) Å, similar to the value of 1.47 Å generally cited for an sp^2–sp^2 single bond between nitrogen atoms, and in the opening of the chelate "bite" distance to 2.880 (6) Å from values of approximately 2.55–2.75 Å for the extensively delocalized systems. While it is clear from the deviations of the atoms from the best plane through MoS3C15N6N5 (Table VII) that this chelate ring is somewhat puckered, closer examination reveals that the ligand group S3C15N6N5 is indeed planar, the distortion arising from the folding of the ligand plane along the S3···N5 vector. Similar deviations from planarity have been observed for trigonal-prismatic tris(dithiolate) complexes[29,33,34] and for tris(catecholato) compounds,[35] although the magnitude of the bending for IV, 30.4°, is somewhat larger than values previously reported.

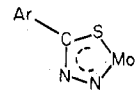
The planarity of ligand grouping for the hydrazonido ligand, together with the contraction of the C15–N6 bond distance to 1.277 (9) Å, compared to the 1.324 (9) Å average for C1–N2 and C8–N4, and the significantly lengthened N5–N6 bond distance of 1.424 (9) Å, comparable to N–N single-bond distance, suggest that canonical form **7** makes a significant contribution to the overall ligand structure.



7

Although the Mo–N5 distance of 2.216 Å (Table IV) is considerably longer than the average value of 1.98 Å usually observed for thioaroyldiazene derivatives of molybdenum, this bond length is comparable to Mo–N single-bond distances in $[Mo_2O_4(His)_2]$ of 2.23 Å,[19] in $[Mo_2O_4(CysOEt)_2]$ of 2.219 (3) Å,[20] in $[Mo_2O_2S_2(CysOEt)_2]$ of 2.24 (3) Å,[21] in $[Mo_2O_2S_2(His)_2]$ of 2.254 (9) Å,[22] and of 2.23 (2) Å in $[Na_2Mo_2O_4(Cys)_2]$,[24] when hybridization differences at the nitrogen are taken into account. The Mo–N5–N6 angle of 116.9 (4)° is also consistent with the absence of significant Mo–N multiple bonding which may be expected to expand the valence angle at the metal-bound nitrogen.

Diazenido(1−) Ring. Although the chelate ring MoS2C8N4N3 displays unexceptional bond lengths for C8–S2, C8–N4, and N3–N4 (Table IV and VIII), the Mo–N3 distance of 1.785 (5) Å is extremely short and indicative of a significant multiple-bonding interaction. Concomitant with the decrease in the Mo–N distance are the contraction of the chelate "bite" S2···N3 to 2.575 (6) Å and the expansion of the N4–N3–Mo angle to 142.8 (3)°. These structural parameters are consistent with the formulation of the ligand as the diazenido(1−) or completely deprotonated species **8**. The



8

contraction of the valence angle at N4 to 109.7 (6)° is required to maintain the planarity of the ring and the consequent extensive delocalization of charge. The internal bond lengths and angles (Table VIII) may be compared to those reported for the diazenido(1−) chelate rings in the dimeric $[Mo_2O(S_2CNEt_2)_2(ClC_6H_4CSN_2)_2]$ complex which show a similar general trend, although the steric and electronic constraints imposed on the bridging nitrogen donor groups of the latter would be expected to cause expansion of the chelate bite and of the Mo–N distances.

The lengthening of the Mo–S1 bond distance to 2.480 (2) Å, from an average of 2.457 (2) Å for Mo–S2 and Mo–S3 in IV and an average of 2.400 (2) Å in $[Mo(C_6H_5CSN_2H)_3]$,[4] suggests a structural trans influence resulting from the presence of the multiply bonded N3 in a pseudo-trans configuration (S1–Mo–N3 angle of 155.63 (6)°).

Diazene Ring. The remaining chelate ring, MoS1C1N2N1, exhibits structural parameters consistent with formulation of the ligand as a diazene or hydrazido(2−) group, **3**. The internal parameters of the chelate ring (Table IV and VIII) are nearly identical with those for the ring geometries in $[Mo(C_6H_5CSNNH)_3]$. The Mo–N1 bond distance, 1.967 (5) Å, is significantly shorter than that observed for Mo–N5, 2.216 (5) Å, where a single-bond interaction must dominate, indicating an Mo–N1 bond order greater than 1. The proton of the NH group lies in the plane of the ligand (Table VII), consistent with sp^2 hybridization at N1.

A general feature of the structure of IV of some interest is the folding of the ligand planes along the S···N vectors. A similar effect has been observed for $[Mo(NHC_6H_4S)_3]$[29] and for a number of trigonal-prismatic dithiolates[33,34] and thioaroylhydrazides.[3] Intermolecular packing forces (Table IX) may be responsible to some degree for these irregular ligand

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Table IV. Selected Bond Lengths and Angles

(a) $[Mo(CH_3C_6H_4CSN_2)(CH_3C_6H_4CSN_2H)(CH_3C_6H_4CSNNCMe_2)]$

Bond Lengths, Å

Molybdenum Coordination Sphere			
Mo-S1	2.482 (3)	Mo-N1	2.00 (1)
Mo-S2	2.446 (3)	Mo-N3	1.80 (1)
Mo-S3	2.453 (3)	Mo-N5	2.18 (1)
Diazene Ligand			
S1-C1	1.74 (1)	C-C(av), I	1.41 (2)
N2-C1	1.31 (1)	C5-C8	1.50 (2)
N1-N2	1.34 (1)		
C1-C2	1.45 (2)		
Diazenido(1−) Ligand			
S2-C9	1.76 (1)	C-C(av), II	1.42 (2)
N4-C9	1.31 (2)	C12-C16	1.54 (3)
N3-N4	1.30 (1)		
C9-C10	1.50 (2)		
Hydrazonido Ligand			
S3-C17	1.73 (1)	N5-C25	1.32 (2)
N6-C17	1.31 (2)	C25-C26	1.52 (2)
N5-N6	1.41 (1)	C25-C27	1.48 (2)
C17-C18	1.51 (2)		
C-C(av), III	1.39 (2)		
C21-C24	1.52 (2)		

Bond Angles, Deg

Molybdenum Coordination Sphere			
S1-Mo-S2	86.7 (1)	S3-Mo-N1	156.6 (3)
S1-Mo-S3	82.9 (1)	S3-Mo-N3	110.5 (4)
S2-Mo-S3	85.3 (1)	S3-Mo-N5	75.3 (3)
S1-Mo-N1	75.7 (3)	N1-Mo-N3	92.9 (4)
S1-Mo-N3	153.4 (4)	N1-Mo-N5	98.2 (4)
S1-Mo-N5	97.8 (3)	N3-Mo-N5	107.6 (5)
S2-Mo-N1	102.4 (3)		
S2-Mo-N3	72.2 (4)		
S2-Mo-N5	159.4 (3)		
Diazene Ligand			
Mo-S1-C1	98.2 (4)	C-C-C(av), I	119.9 (12)
S1-C1-C2	121.1 (8)	C4-C5-C8	122.8 (12)
S1-C1-N2	119.2 (10)	C6-C5-C8	119.8 (11)
N2-C1-C2	119.6 (11)		
C1-N2-N1	116.3 (9)		
N2-N1-Mo	121.6 (6)		
Diazenido(1−) Ligand			
Mo-S2-C9	95.7 (5)	C-C-C(av), II	120.0 (14)
S2-C9-C10	122.1 (11)	C12-C13-C16	114.3 (20)
S2-C9-N4	119.7 (11)	C14-C13-C16	121.1 (15)
N4-C9-C10	118.1 (11)		
C9-N4-N3	106.0 (10)		
N4-N3-Mo	144.6 (10)		
Hydrazonido Ligand			
Mo-S3-C17	193.8 (5)	N5-C25-C26	117.5 (12)
S3-C17-C18	121.4 (9)	N5-C25-C27	120.5 (15)
S3-C17-N6	122.7 (10)	C26-C25-C27	122.0 (12)
N6-C17-C18	115.8 (13)	C-C-C(av), III	120.0 (14)
C17-N6-N5	114.8 (12)	C20-C21-C24	123.5 (14)
N6-N5-Mo	115.1 (8)	C22-C21-C24	120.9 (16)
N6-N5-C25	116.5 (13)		
Mo-N5-C25	127.9 (10)		

(b) $[Mo(ClC_6H_4CSN_2)(ClC_6H_4CSN_2H)(ClC_6H_4CSNNCMe_2)]$

Bond Lengths, Å

Molybdenum Coordination Sphere			
Mo-S1	2.480 (2)	Mo-N1	1.967 (5)
Mo-S2	2.463 (2)	Mo-N3	1.785 (5)
Mo-S3	2.451 (2)	Mo-N5	2.216 (5)
Diazene Ligand			
S1-C1	1.729 (7)	C-C(av), I	1.39 (1)
N2-C1	1.315 (9)	C-H(av), I	0.96 (7)
N1-N2	1.362 (8)	C5-Cl1	1.738 (8)
N1-HN1	0.87 (5)		
C1-C2	1.48 (1)		
Diazenido(1−) Ligand			
S2-C8	1.733 (7)	C-C(av), II	1.38 (1)
N4-C8	1.333 (9)	C-H(av), II	0.88 (5)
N3-N4	1.305 (8)	C12-Cl2	1.743 (8)
C8-C9	1.469 (9)		
Hydrazonido Ligand			
S3-C15	1.763 (7)	C-H(av), III	0.87 (5)
N6-C15	1.277 (9)	C19-Cl3	1.742 (8)
N5-N6	1.424 (8)	C23-HC23A	0.86 (9)
N5-C22	1.30 (1)	C23-HC23B	0.79 (9)
C22-C23	1.49 (1)	C23-HC23C	0.73 (11)
C22-C24	1.47 (1)	C24-HC23A	0.85 (8)
C15-C16	1.50 (1)	C24-HC23B	0.82 (8)
C-C(av), III	1.37 (1)	C24-HC24C	0.88 (12)

Bond Angles, Deg

Molybdenum Coordination Sphere			
S1-Mo-S2	88.27 (5)	S3-Mo-N1	159.4 (2)
S1-Mo-S3	84.94 (5)	S3-Mo-N3	107.4 (2)
S2-Mo-S3	84.15 (2)	S3-Mo-N5	76.0 (1)
S1-Mo-N1	75.0 (2)	N1-Mo-N3	93.2 (3)
S1-Mo-N3	155.63 (6)	N1-Mo-N5	98.3 (3)
S1-Mo-N5	93.1 (2)	N3-Mo-N5	110.1 (3)
S2-Mo-N1	101.4 (2)		
S2-Mo-N3	72.7 (2)		
S2-Mo-N5	159.9 (2)		
Diazene Ligand			
Mo-S1-C1	97.6 (3)	C-C-C(av), I	120.0 (7)
S1-C1-C2	121.6 (5)	C4-C5-Cl1	119.4 (6)
S1-C1-N2	121.0 (5)	C6-C5-Cl1	118.7 (6)
N2-C1-C2	117.5 (6)	C-C-H(av), I	119.4 (44)
C1-N2-N1	113.2 (6)		
N2-N1-Mo	131.6 (4)		
N2-N1-HN1	107.6 (42)		
Mo-N1-HN1	122.3 (43)		
Diazenido(1−) Ligand			
Mo-S2-C8	97.4 (2)	N4-N3-Mo	142.8 (4)
S2-C8-N4	116.8 (5)	C-C-C(av), II	120.0 (7)
S2-C8-C9	123.3 (5)	C11-C12-Cl2	119.7 (6)
C9-C8-N4	119.9 (6)	C13-C12-Cl2	119.6 (6)
C8-N4-N3	109.7 (6)	C-C-H(av), II	120.7 (41)
Hydrazonido Ligand			
Mo-S3-C15	95.8 (2)	N5-C22-C23	123.1 (6)
S3-C15-N6	124.7 (5)	N5-C22-C24	119.4 (8)
S3-C15-C16	117.8 (4)	C23-C22-C24	117.5 (9)
C16-C15-N6	117.5 (5)	C-C-C(av), II	120.0 (9)
C15-N6-N5	114.7 (6)	C18-C19-Cl3	120.9 (7)
N6-N5-Mo	116.9 (4)	C20-C19-Cl3	118.8 (8)
N6-N5-C22	114.5 (4)	C-C-H(av), III	120.2 (43)
No-N5-C22	128.3 (4)		

foldings. However, the magnitude of the bending at the hydrazonido ligand cannot be explained by packing forces alone and may result from the intramolecular contacts (Table V) brought about by the bulky substituent on N5 and the inherent ligand folding of highly delocalized ligand systems in nonoctahedral environments.[29]

The overall irregularity of the coordination geometry in species III and IV may be attributed to the combination of the steric effects discussed previously and to electronic effects stabilizing trigonal-prismatic geometry. Although a d^0 electronic configuration is important in stabilizing trigonal-prismatic geometries,[6] molecular orbital descriptions[36] also emphasize that ligand π interactions can contribute significantly: (1) the lone pair of the coordinated ligand in the chelate plane, π_h, may interact with the metal d_{z^2} orbital; (2) the delocalized orbitals perpendicular to the chelate plane, π_v, may interact with metal d_{xy} and $d_{x^2-y^2}$ orbitals. The interaction of the metal

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Table V. Selected Intramolecular Nonbonding Distances and Polyhedral Edge Lengths (Å)

(a) $[Mo(CH_3C_6H_4CSN_2)(CH_3C_6H_4CSN_2H)(CH_3C_6H_4CSNNCMe_2)]$

S1···S2	3.384 (5)	S2···N1	3.477 (11)
S1···S3	3.266 (6)	S3···N3	3.511 (10)
S2···S3	3.320 (6)	N1···N3	2.756 (16)
S1···N1(bite)	2.776 (8)	N1···N5	3.159 (18)
S2···N3(bite)	2.552 (11)	N3···N5	3.214 (17)
S3···N5(bite)	2.837 (11)	N1···C27	3.46 (2)
S1···N5	3.516 (12)	N3···C27	3.36 (2)

(b) $[Mo(ClC_6H_4CSN_2)(ClC_6H_4CSN_2H)(ClC_6H_4CSNNCMe_2)]$

S1···S2	3.442 (3)	S3···N3	3.436 (5)
S1···S3	3.329 (3)	N1···N3	2.729 (8)
S2···S3	3.293 (3)	N1···N5	3.169 (8)
S1···N1(bite)	2.752 (5)	N3···N5	3.289 (6)
S2···N3(bite)	2.575 (6)	N1···C23	3.36 (1)
S3···N5(bite)	2.880 (6)	N3···C23	3.53 (1)
S1···N5	3.413 (6)	Mo···HN1	2.48 (5)
S2···N1	3.443 (5)		

d_{z^2} orbital with the π_h orbital of the diazene and the hydrazonido ligands cannot be significant since the π_h orbitals of the nitrogens N1 and N5 are involved in bonding to HN1 and to C22, respectively. Furthermore, the π_v orbital of N5 of the hydrazonido group is utilized in π bonding to C22, further disrupting the metal–ligand π interactions required for stabilization of trigonal-prismatic geometry. The diazenido(1−) ligand, however, enjoys strong π interaction with the metal, favoring trigonal-prismatic geometry. The distorted geometry adopted by the complexes may be a balance of the various electronic and steric effects produced by the unusual ligand types.

Comparison of the structures of III and IV confirms the basic identity of the species, although the complexes crystallize in different space groups. The small differences in corresponding bond lengths and valence and dihedral angles, although statistically significant in some instances, may be attributed to differences in crystal packing forces. Inspection of Table IX suggests that N5 and N6 of the hydrazonido ligand of III participate in significant nonbonded contacts with the centrosymmetrically related pair of nitrogen atoms in the cell. In the case of IV, however, there is no such close approach, inter-ring contacts providing the most significant interaction. Thus, the intermolecular interactions appear to be qualitatively different in the two cases.

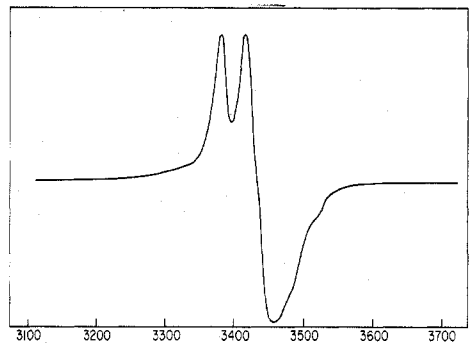

Figure 5. EPR spectrum of a polycrystalline sample of $[Mo(CH_3C_6H_4CSN_2)(CH_3C_6H_4CSN_2H)(CH_3C_6H_4CSNNCMe_2)]$ at room temperature and at 9.195 GHz.

Magnetic Properties. The hydrazonido derivatives III and IV were found to exhibit weak room-temperature paramagnetism, with the details of magnetic behavior dependent upon substituents on the aryl group. Thus, while the complexes crystallizing in the triclinic space group $P\bar{1}$, $[Mo(XC_6H_4CSN_2)(XC_6H_4CSN_2H)(XC_6H_4CSNNCMe_2)]$, X = p-CH_3 and p-OCH_3, displayed room-temperature ESR signals and temperature-dependent susceptibilities, illustrated in Figures 5 and 6, respectively, the magnetism associated with the species exhibiting the monoclinic crystal habit, IV with X = Cl, was essentially independent of temperature. Consequently, no room-temperature ESR spectrum was observed in this instance. Since the structural and other chemical evidence unambiguously identifies these complexes as Mo(VI) species with d^0 electronic configuration, the origin of observed magnetism may reside either in a paramagnetic impurity or in a paramagnetic state localized on the diazene ligand, with the ground state essentially diamagnetic. Such a ligand-localized paramagnetic state must be thermally accessible for the derivatives X = CH_3 and OCH_3. The absence of Mo hyperfine splitting in the room-temperature and liquid-nitro-

Table VI. Ideal and Observed Dihedral Angles (Deg) for Six-Coordinate Complexes

complex	δ_1[a]	δ_2	δ_3	α, twist angle[b]
ideal octahedron	70.5, 70.5, 70.5	70.5, 70.5, 70.5	70.5, 70.5, 70.5, 70.5, 70.5, 70.5	60
ideal MS_3N_3, C_3[d]	68.4, 68.4, 68.4	68.4, 68.4, 68.4	69.0, 69.0, 69.0, 76.3, 76.3, 76.3	60
$[Mo(CH_3C_6H_4CSN_2)(CH_3C_6H_4CSNNH)(CH_3C_6H_5CSNNC(CH_3)_2)]$[c]	41.2, 48.8, 54.9	84.9, 85.5, 89.0	69.0, 70.4, 72.5, 72.7, 73.7, 81.0	29, 37, 40
$[Mo(ClC_6H_4CSN_2)(ClC_6H_4CSNNH)(ClC_6H_4CSNNCMe_2)]$	44.8, 50.8, 61.3	82.9, 86.4, 86.8	66.7, 68.7, 70.3, 70.4, 73.3, 82.2	31, 40, 45
$[Mo_2O(S_2CNEt_2)_2(C_6H_5CON_2)_2]CH_2Cl_2$	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
$[Mo_2O(S_2CNEt_2)_2(ClC_6H_4CSN_2)_2]CH_2Cl_2$	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
$[Mo(C_6H_5CSN_2H)_3]DMF$	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
$[Mo(NHC_6H_4S)_3]$	17.7, 18.6, 19.6	132.1, 132.1, 133.2	80.1, 80.3, 81.2, 84.9, 85.3, 86.2	11, 13, 13
ideal MS_3N_3, C_{3v}[d]	0, 0, 0	119.7, 119.7, 119.7	86.7, 86.7, 86.7, 93.3, 93.3, 93.3	0
ideal trigonal prism	0, 0, 0	120, 120, 120	90, 90, 90, 90, 90, 90	0

[a] The dihedral angles δ_1, δ_2, and δ_3 are defined in ref 12. For trigonal-prismatic geometry, the δ_1's define the retangular faces and the δ_3's are the dihedral angles between rectangular faces and triangular faces of the prism. [b] The twist angles define the relative orientation of the parallel triangular faces of the polyhedron. The angles are calculated by taking the average of the projection angles on the plane normal to the line generated through the metal and the centroid of the top and bottom triangular faces. [c] The δ_1's are the angles between the planes N1S1S2 and N1N3S2, N3S2S3 and N3N5S3, and N5S1S3 and N1N5S1. The δ_2's refer to the angles between the sets of planes N1N3S2 and N3S2S3, N5S1S3 and N3N5S3, and N1S1S2 and N1N5S1. The δ_3's are the interplanar angles between the planes defined by N1N3N5 and the planes N1N3S1, N3N5S2, and N1N5S3 and by S1S2S3 and the planes S1S2N1, S2S3N3, and S1S3N5. [d] The idealized geometries are based on polyhedra generated about a central Mo atom by chelating ligands and have the following shape-determining parameters: S···N(intraligand), 2.75 Å; S···S(edge nonbonding distances), 3.20 Å; N···N(edge nonbonding distances), 2.75 Å.

Table VII

(a) Equations of Least-Squares Planes for $[Mo(CH_3C_6H_4CSN_2)(CH_3C_6H_4CSN_2H)(CH_3C_6H_4CSNNCMe_2)]$

atom	dev from plane, Å	atom	dev from plane, Å
Plane 1. $-3.081x - 7.684y + 9.441z + 1.789 = 0$; $\sigma = 0.067$			
C1	0.108	C5	0.009
C2	−0.013	C6	−0.058
C3	−0.055	C7	−0.042
C4	−0.046	C8	0.098
Plane 2. $10.845x - 1.073y + 5.304z - 3.376 = 0$; $\sigma = 0.048$			
C9	0.070	C13	−0.022
C10	−0.015	C14	−0.038
C11	−0.019	C15	−0.018
C12	−0.041	C16	0.082
Plane 3. $11.342x - 4.639y + 4.555z - 1.331 = 0$; $\sigma = 0.042$			
C17	0.077	C21	0.018
C18	−0.035	C22	0.002
C19	−0.029	C23	−0.050
C20	−0.018	C24	0.036
Plane 4. $3.252x + 9.880y - 8.315z - 2.651 = 0$; $\sigma = 0.057$			
Mo	0.053	N1	−0.077
S1	−0.045	N2	0.038
C1	0.031		
Plane 5. $9.866x - 2.332y + 6.661z - 3.478 = 0$; $\sigma = 0.065$			
Mo	0.062	N3	−0.090
S2	−0.046	N4	0.032
C9	0.042		
Plane 6. $10.246x - 7.540y + 1.654z - 0.202 = 0$; $\sigma = 0.275$			
Mo	0.250	N5	−0.324
S3	−0.267	N6	0.118
C17	0.223		
Plane 7. $2.415x + 10.287y - 8.611z - 2.306 = 0$; $\sigma = 0.013$			
C1	0.006	N2	0.015
N1	−0.007	C1	−0.013
Plane 8. $10.540x - 2.007y + 6.054z - 3.441 = 0$; $\sigma = 0.009$			
S2	0.005	N4	0.010
N3	−0.006	C9	−0.009
Plane 9. $8.993x - 7.956y + 4.859z + 0.367 = 0$; $\sigma = 0.019$			
S3	−0.009	N6	−0.022
N5	0.010	C17	0.021

(b) Selected Dihedral Angles between Least-Squares Planes

plane 1	plane 2	angle, deg	plane 1	plane 2	angle, deg
1	4	15.6	5	6	129.7
2	5	9.5	7	MoS1N1	8.3
3	6	28.4	8	MoS2N3	9.8
4	5	103.1	9	MoS3N5	36.0
4	6	99.0			

(c) Equations of Least-Squares Planes for $[Mo(ClC_6H_4CSN_2)(ClC_6H_4CSN_2H)(ClC_6H_4CSNNCMe_2)]$

atom	dev from plane, Å	atom	dev from plane, Å
Plane 10. $1.637x - 1.758y + 16.859z + 0.494 = 0$; $\sigma = 0.006$			
C2	0.008	C5	−0.004
C3	−0.004	C6	0.007
C4	0.002	C7	−0.009
Plane 11. $10.474x - 3.638y - 9.231z + 3.634 = 0$; $\sigma = 0.005$			
C9	0.004	C12	−0.002
C10	−0.008	C13	−0.002
C11	0.007	C14	0.001
Plane 12. $-10.097x - 2.912y + 10.370z - 3.410 = 0$; $\sigma = 0.040$			
C16	−0.047	C19	−0.011
C17	0.061	C20	0.0249
C18	−0.036	C21	0.007
Plane 13. $4.241x - 0.220y + 16.170z - 0.0126 = 0$; $\sigma = 0.066$			
Mo	0.062	S1	−0.061
N1	−0.078	C1	0.057
N2	0.020		
Plane 14. $9.704x - 5.477y - 9.043z + 3.510 = 0$; $\sigma = 0.040$			
Mo	0.038	S2	−0.028
N3	−0.055	C8	−0.024
N4	0.117		
Plane 15. $9.460x + 6.768y - 7.808z + 1.484 = 0$; $\sigma = 0.221$			
Mo	0.202	S3	0.157
N5	−0.201	C15	−0.206
N6	0.117		
Plane 16. $2.932x - 0.608y + 16.673z + 0.035 = 0$; $\sigma = 0.038$			
S1	−0.011	N2	−0.008
N1	0.058	C1	−0.007
		HN1	−0.048
Plane 17. $10.120x - 5.199y - 8.528z + 3.641 = 0$; $\sigma = 0.007$			
S2	0.004	N4	0.009
N3	−0.005	C8	−0.008
Plane 18. $-9.075x - 4.172y + 11.198z - 2.771 = 0$; $\sigma = 0.003$			
S3	−0.002	N6	−0.004
N5	0.002	C15	0.004

(d) Selected Dihedral Angles between Least-Squares Planes

plane 1	plane 2	angle, deg	plane 1	plane 2	angle, deg
10	13	13.5	14	15	122.7
11	14	8.9	16	MoS1N1	10.5
12	15	19.5	17	MoS2N3	5.8
13	14	103.7	18	MoS3N5	30.4
13	15	101.1			

gen-temperature ESR spectra of these species is consistent with extensive delocalization of electron density on the ligand, an effect that appears to be not uncommon for thiohydrazide ligands.[37-39] The hydrazonido complexes I–IV give sharp-line ^1H NMR spectra (see Table I).

Electrochemical Properties. The electrochemical behavior of the hydrazonido complexes is entirely different from that observed for the parent complexes $[Mo(XC_6H_4CSN_2H)_3]$,[41] reflecting the disruption of the delocalized ring system by formation of the hydrazone. The complexes of the type $[Mo(XC_6H_4CSN_2H)_3]$ undergo two successive reversible one-electron reductions as shown in Figure 7a.

$$[Mo(CH_3C_6H_4CSN_2H)_3] \xrightleftharpoons{-0.315\ V} [Mo(CH_3C_6H_4CSN_2H)_3]^- \xrightleftharpoons{-0.95\ V} [Mo(CH_3C_6H_4CSN_2H)_3]^{2-}$$

This behavior is characteristic of systems where ligand-based redox properties have been established,[42] since successive reduction involving predominantly metal orbitals would necessitate considerable reorganization of the metal coordination sphere and hence irreversible behavior.[43] The absence of Mo hyperfine structure in the variable-temperature EPR spectrum of $[Mo(XC_6H_4CSN_2H)_3]^-$, generated electrochemically in the

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Table VIII. Comparison of Average Structural Features[a] of Five-Membered Rings of the Type $M(RCSNH_nNH_m)$[b] and the Free Ligand

compd	ring type	M–S	M–N	S···N	C–S	C–N	N–N	M–S–C	S–C–N	C–N–N	N–N–M	S–M–N	ref
$NH_2CSNHNH_2$	free thiosemicarbazone			c	1.685	1.337	1.399		121.5	122.5			36
$[Ni(NH_2CSNHNH_2)]^{2+}$ d	hydrazine ($n = 1, m = 2$)	2.16	1.90	2.88	1.75	1.29	1.44	114.9	119.4	118.1	91.2	90.0	37
$[Ni(NH_2CSNNH_2)]$	hydrazido(1–) ($n = 0, m = 2$)	2.155	1.911	2.67	1.746	1.247	1.537	102.9	120.9	109.8	123.2	81.7	38
$[Cu(C_6H_5CSNHNH_2)_2](NO_3)_2$	hydrazine ($n = 1, m = 2$)	2.293 (3)	1.981 (8)	2.93 (1)	1.70 (1)	1.30 (1)	1.44 (1)	95.6 (3)	112.3 (7)	119.9 (8)	113.4 (6)	86.3 (2)	11
$[Mo(C_6H_5CSNNH)_3]$	diazene ($n = 0, m = 1$)	2.400 (5)	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)	76.5 (4)	39
$[Mo_2O(S_2CNEt_2)(ClC_6H_4CSN_2)_2]$[e]	diazenido(1–) ($n = 0, m = 0$)	2.398 (7)	1.91 (2)	2.67 (2)	1.73 (2)	1.29 (2)	1.39 (2)	99.5 (8)	119.7 (17)	111.4 (16)	134.3 (11)	75.8 (6)	10
$[Mo(CH_3C_6H_4CSN_2)(CH_3C_6H_4CSN_2H)(CH_3C_6H_4CSNNCMe_2)]$	diazene ($n = 0, m = 0$)	2.482 (7)	2.00 (1)	2.776 (8)	1.74 (1)	1.31 (1)	1.34 (1)	98.2 (4)	119.2 (10)	116.3 (9)	129.6 (6)	75.3 (3)	40
	diazenido(1–) ($n = 0, m = 0$)	2.446 (4)	1.80 (1)	2.552 (11)	1.76 (1)	1.31 (1)	1.30 (1)	95.7 (5)	119.7 (11)	106.0 (10)	144.6 (10)	72.2 (4)	
	hydrazonido	2.453 (3)	2.18 (1)	2.837 (11)	1.73 (1)	1.31 (1)	1.41 (1)	93.8 (5)	122.7 (10)	114.8 (12)	115.1 (8)	75.3 (3)	
$[Mo(ClC_6H_4CSN_2)(ClC_6H_4CSN_2H)(ClC_6H_4CSNNCMe_2)]$	diazene ($n = 0, m = 0$)	2.480 (2)	1.967 (5)	2.752 (5)	1.729 (2)	1.315 (9)	1.362 (8)	97.6 (2)	121.0 (5)	113.2 (6)	131.6 (4)	75.5 (2)	41, 40
	diazenido(1–) ($n = 0, m = 0$)	2.463 (2)	1.785 (5)	2.575 (6)	1.733 (9)	1.333 (9)	1.305 (8)	97.4 (2)	116.8 (5)	109.7 (6)	142.8 (3)	72.7 (2)	
	hydrazonido	2.451 (2)	2.216 (5)	2.880 (6)	1.763 (7)	1.277 (9)	1.424 (9)	95.8 (2)	124.7 (5)	114.7 (6)	116.9 (4)	76.0 (1)	

[a] Distances in Å; angles in deg; esd's in parentheses. [b] For $n = 1, m = 2$; $n = 2, m = 2, 1$, or 0; X = H, CH_3, or Cl. [c] The structure is for the trans configuration of the S and N donors. With use of 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. [d] $Cu_3Cl_5^{2-}$ as counterion. [e] Parameters for the distorted trigonal-prismatic site. Note that the terminal diazenido nitrogen bridges the two molybdenum atoms.

Table IX. Selected Intermolecular Contacts (Å)

atoms	dist, Å	atoms	dist, Å
(a) $[Mo(CH_3C_6H_4CSN_2)(CH_3C_6H_4CSN_2H)(CH_3C_6H_4CSNNCMe_2)]$			
C3′···N3	3.57 (2)	N5′···N5	3.35 (1)
C3′···N4	3.37 (2)	N6′···N6	3.11 (1)
C4′···N4	3.42 (1)		
(b) $[Mo(ClC_6H_4CSN_2)(ClC_6H_4CSN_2H)(ClC_6H_4CSNNCMe_2)]$			
N3′···C13	3.395 (9)	C4′···C21	3.367 (8)
N3′···C14	3.407 (8)	C5′···C21	3.449 (9)

Table X. Voltammetric Data for the Reduction of Complexes $[Mo(ArCSNNR)_3]$ and $[Mo(XC_6H_4CSN_2)(XC_6H_4CSN_2H)(XC_6H_4CSNNCMe_2)]$

complex	potentials, $E_{p/2}$[a] E_1	E_2
$[Mo(C_6H_5CSNNH)_3]$	−0.27	−0.77
$[Mo(CH_3C_6H_4CSNNH)_3]$	−0.26	−0.87
$[Mo(XC_6H_4CSN_2)(XC_6H_4CSN_2H)(XC_6H_4CSNNCMe_2)]$		
X = CO_2CH_3	−0.34	
X = Cl	−0.43	
X = H	−0.51	
X = OCH_3	−0.55	
X = CH_3	−0.56	

[a] Potentials vs. saturated calomel electrode (KCl). Voltammograms were recorded at a vitreous carbon electrode in 0.1 M $(C_4H_9)_4NPF_6$ in dichloromethane, degassed with argon, at 200 mV/s.

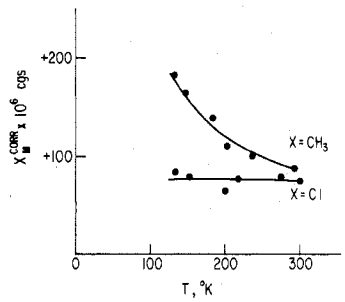

Figure 6. Variation of susceptibility with temperature for $[Mo(XC_6H_4CSN_2)(XC_6H_4CSN_2H)(XC_6H_4CSNNCMe_2)]$, X = CH_3 and Cl.

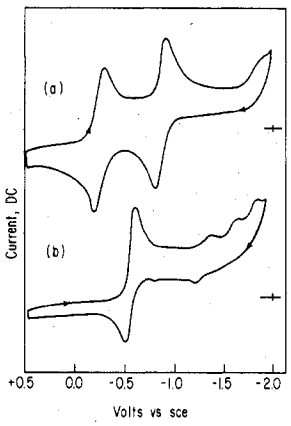

Figure 7. Cyclic voltammograms of 10^{-3} M complex in 0.1 M $(C_4H_9)_4NPF_6$ in dichloromethane (scan rate 200 mV/s, vitreous carbon electrode): (a) $[Mo(CH_3C_6H_4CSN_2H)_3]$ and (b) $[Mo(CH_3OC_6H_4CSN_2)(CH_3OC_6H_4CSN_2H)(CH_3OC_6H_4CSNNCMe_2)]$.

EPR tube, tends to reinforce this argument.

The hydrazonido derivatives III and IV are considerably more difficult to reduce to the monoanionic complex than the

$$[Mo(XC_6H_4CSN_2)(XC_6H_4CSN_2H)(XC_6H_4CSNNCMe_2)] \overset{1e^-}{\rightleftharpoons} [Mo(XC_6H_4CSN_2)(XC_6H_4CSN_2H)(XC_6H_4CSNNCMe_2)]^- \quad (1)$$

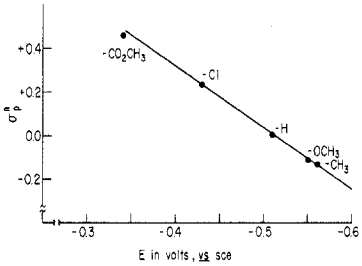

Figure 8. Effect of substituents on the primary cathodic couple $[Mo(XC_6H_4CSN_2)(XC_6H_4CSN_2H)(XC_6H_4CSNNCMe_2)]/[Mo(XC_6H_4CSN_2)(XC_6H_4CSN_2H)(XC_6H_4CSNNCMe_2)]^-$. Relationship between the reduction potential and the Hammett constant σ_p^n.[40]

unsubstituted precursors $[Mo(XC_6H_4CSN_2H)_3]$, as shown in Table X and Figure 7. The initial cathodic process is quasi-reversible, the degree of reversibility dependent on the aryl substituent. The electrode process is described by eq 1. The reduction product has been generated by controlled potential electrolysis in an EPR tube, yielding a one-line spectrum centered at $g = 2.01$. The substituent effect on the reversible one-electron reduction is illustrated in Figure 8. The correlation with σ_p^n establishes that the trend is related to simple inductive effects. Thus, the more electron-withdrawing groups stabilize the reduced form relative to the neutral complex and yield more positive redox potentials for the reductive couple. Conversely, the electron-donating methyl substituent provides the most negative redox potential. A similar substituent dependence of redox potential has been observed in the electrochemical oxidation of the complexes $[Mo(N_2C_6H_4X)(S_2CNR_2)_3]$.[44]

A number of successive irreversible cathodic processes occur in the range −1.5 to −2.0 V for the hydrazonido derivatives. The nature of these processes has not been established, controlled potential electrolysis at these potentials yielding nonintegral values for electrons transferred and producing insoluble materials.

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Registry No. I, 74998-59-7; II, 74998-60-0; III, 74998-61-1; IV, 72664-35-8; $Mo(p\text{-}CH_3O_2CC_6H_4CSN_2)(p\text{-}CH_3O_2CC_6H_4CSN_2H)(p\text{-}CH_3O_2CC_6H_4CSNNCMe_2)$, 74998-62-2; $Mo(PhCSN_2H)_3$, 53449-66-4; $Mo(CH_3C_6H_4CSN_2H)_3$, 74998-63-3; acetone, 67-64-1.

Supplementary Material Available: Listings of calculated and observed structure factors (65 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of Tricyclopropylaluminum Dimer

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The crystal and molecular structure of tricyclopropylaluminum dimer has been determined at 22 °C and at −62 °C. The molecule crystallizes in the space group $P2_1/c$ with four molecules per unit cell. The cell dimensions are $a = 14.573$ (3) Å, $b = 9.422$ (2) Å, $c = 13.719$ (6) Å, $\beta = 98.12$ (2)°, and $V = 1864.8$ Å^3 at 22 °C and $a = 14.470$ (2) Å, $b = 9.319$ (2) Å, $c = 13.431$ (2) Å, $\beta = 99.06$ (1)°, and $V = 1788.5$ (5) Å^3 at −62 °C. Conventional discrepancy factors of 0.091 at 22 °C and 0.072 at −62 °C were obtained for a disordered model. The observed bond distances show normal Al–C terminal distances (1.944 Å average) and normal bridge Al–C distances (2.074 Å average). Both the terminal and bridging cyclopropyl groups have relatively long C_α–C_β bonds and short C_β–C_β bond distances. The severe distortion of the longer C–C distances observed in the bridging cyclopropyl groups are interpreted in terms of nonbonding metal orbital α-carbon p-orbital overlap yielding increased stability for the cyclopropyl-bridged aluminum dimer.

Introduction

The structures of organoaluminum derivatives have been of great interest over the years because of the early discovery that these systems contain bridging, five-coordinate carbon atoms. Since the initial work several structural determinations have been carried out with most of these recently reviewed in detail.[1] The solid-state structures determined include Al_2Me_6,[2] $Ph_2NAl_2Me_5$,[3] Al_2Ph_6,[4] $Al_2Ph_2Me_4$,[5] $Al_2(\mu\text{-}trans\text{-}CH{=}CH\text{-}(t\text{-}Bu))_2(i\text{-}Bu)_4$,[6] and preliminarily reported $Al_2(\mu\text{-}C{\equiv}CPh)_2Ph_4$[7] and $Al_2(c\text{-}Pr)_6$.[8] In addition, the structure of $Al_2(C{\equiv}C{-}Me)_2Me_4$ determined in the gas phase has recently appeared.[9] Prior to these structural determinations a bonding model was proposed on the basis of the unusual stability of the bridged dimer Ga_2Vi_6,[10] which involved the overlap of the hybrid orbital of the bridging carbon atom with the two metal orbitals, as suggested for Al_2Me_6, with additional stabilization arising from the interaction of the π system with the vacant nonbonding orbitals centered on the metal atom. This model has since been extended to account for the stability of the vinyl-bridged aluminum compounds,[11] of the arylaluminum

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