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Investigations of the Coordination Chemistry of Molybdenum with Facultative Tetradentate Ligands Possessing N_2S_2 Donor Sets. 5.[1] Crystal and Molecular Structures of the Hydrazido(2–) and Diazenido Derivatives $[MoO(N_2Ph_2)L]$ and $[Mo(N_2C_6H_4OCH_3)_2L]$

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The crystal and molecular structures of two derivatives of Mo(VI) with substituted hydrazine ligands, oxo[diphenylhydrazido(2–)][*N*,*N'*-dimethyl-*N*,*N'*-bis(mercaptoethyl)ethylenediamine]molybdenum(VI), $[MoO(N_2Ph_2)L]$, and [bis((*p*-methoxyphenyl)diazenido)][*N*,*N'*-dimethyl-*N*,*N'*-bis(mercaptoethyl)ethylenediamine]molybdenum(VI), $[Mo(N_2C_6H_4OCH_3)_2L]$, are reported. $[MoO(N_2Ph_2)L]$ crystallizes as red needles in space group $P2_1/c$ with unit cell dimensions $a = 13.248$ (2) Å, $b = 11.229$ (2) Å, and $c = 15.780$ (2) Å and with $\beta = 109.46$ (1)° and $Z = 4$. The structure has been refined to $R_1 = 0.027$ and $R_2 = 0.048$ on the basis of 2784 independent reflections. The molecule is pseudooctahedral with the hydrazido(2–) group cis to the oxo ligand. $[Mo(N_2C_6H_4OCH_3)_2L]$ crystallizes in space group Cc with unit cell dimensions $a = 22.557$ (2) Å, $b = 8.483$ (3) Å, and $c = 18.030$ (2) Å and with $\beta = 133.25$ (1)° and $Z = 4$. The structure refined to values of R_1 and R_2 of 0.043 and 0.049, respectively, on the basis of 1505 independent reflections. The diazenido ligands are mutually cis and enjoy significant multiple-bond interaction with the molybdenum, as indicated by the short average Mo–N distance of 1.81 (2) Å. In both structures, the ligand L exhibits the sterically strained configuration associated with this tetradentate ligand. The electrochemistry of a series of complexes of the type $[Mo(N_2C_6H_4X)_2L]$ is discussed and related to the geometry of the diazenido ligands.

Introduction

The physical properties and chemical reactions of the molybdenum(VI) compound $[MoO_2L]$, where L is a tetradentate N_2S_2 ligand, have been reported.[1] The reactions of $[MoO_2L]$ with substituted hydrazines produced a variety of complexes, depending on the nature of the hydrazine ligand. While disubstituted hydrazines H_2NNR_2 yielded the oxohydrazido(2–) complexes $[MoO(N_2R_2)L]$, reaction of $[MoO_2L]$ with monosubstituted hydrazines, H_2NNHR, resulted in the isolation of the bis(diazenido) species $[Mo(N_2R)_2L]$.

The chemistry of hydrazido(2–) complexes is currently of interest since they have been identified as intermediates in the protonation of coordinated dinitrogen to ammonia.[3,4] The organodiazenido group, N_2R, has been considered useful in understanding the chemistry of N_2 and NO.[5] The parallel between organodiazenido complexes and those of the diazenide ion, $HN{=}N^-$, a potential but inaccessible reduction product of ligating dinitrogen, is the basis for the current interest in these species.[6] Organodiazenido complexes have been synthesized by a variety of processes,[7] including alkylation of coordinated dinitrogen.[8] Although bis(diazenido) complexes of the type $[Mo(N_2R)_2(S_2CNR_2)_2]$ have been synthesized previously,[6] they have not been structurally characterized.

We report here the structures of an oxohydrazido(2–) complex $[MoO(N_2Ph_2)L]$ and a bis(diazenido) complex $[Mo(N_2C_6H_4OCH_3)_2L]$, together with a comparison of the coordination of the $-N_2R$ group with that of the N_2R_2 group. The geometry of the sterically strained L ligand is compared to the geometry observed in other molybdenum complexes, $[MoO_2L]$ and $[Mo_2O_3L_2]$.[9,10] The effect of the geometry of the metal–diazenido moiety on the reduction potentials of the series of complexes $[Mo(N_2C_6H_4X)_2L]$ is discussed.

Table I. Summary of Experimental Conditions and Crystal Data for $[Mo(N_2C_6H_4OCH_3)_2(S_2N_2C_8H_{18})]$

cryst: purple needle, 0.25 × 0.40 × 0.10 mm
cryst syst: monoclinic
space group: CC
$a = 22.557$ (2) Å
$b = 8.483$ (3) Å
$c = 18.030$ (2) Å
$\beta = 133.25$ (1)°

$V = 2512.8$ Å^3
$Z = 4$
fw: 572
$F(000) = 1184$
ρ(calcd) = 1.51 g cm^{-3}
ρ(obsd)^a = 1.49 g cm^{-3}

diffractometer: Hilger-Watts four circle
radiation: Mo Kα (λ 0.710 69 Å)
$\mu = 6.39$ cm^{-1}
scan technique: θ(crystal)–2θ(counter)
scan rate: 2–10° min^{-1}
data collected: $2 < 2\theta < 40°$
reflctns measd: $h,k,\pm l$
obsd reflctns: 1505 with $I(\text{obsd}) \geq 3.0\sigma(I(\text{obsd}))$

^{a} Flotation.

Experimental Section

$[Mo(NNC_6H_4OCH_3\text{-}p)_2(C_8H_{18}N_2S_2)]$. Collection and Reduction of X-ray Data. The crystal used for data collection was a shiny purple regular plate of dimensions 0.20 × 0.34 × 0.20 mm. Preliminary precession and Weissenberg photographs (λ 1.5418 Å) showed the crystal to have systematic absences *hkl* for $h + k \neq 2n$ and *h*0*l* for $l \neq 2n$, indicating the space group to be either $C2/c$ or the noncentrosymmetric equivalent Cc. Details of the data collection are given in Table I.

Structure Solution and Refinement. The structure of the compound was determined by conventional heavy-atom methods. The reflection statistics and the distribution of peaks in the Patterson map showed the space group to be Cc. The Patterson was solved for the positions

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(1) For part 4 of this series and references to previous work see: Dahlstrom, P. L.; Hyde, J. R.; Vella, P. A.; Zubieta, J. *Inorg. Chem.*, preceding paper in this issue.

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Table II. Atomic Positional and Thermal Parameters (×10^2) for [Mo($N_2C_6H_4OCH_3$)$_2$($S_2N_2C_8N_{18}$)]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	0.2500	0.0370 (1)	0.2500	3.87 (5)	3.19 (4)	3.49 (3)	0.46 (15)	2.82 (4)	0.23 (16)
S1	0.1975 (5)	−0.0039 (13)	0.0789 (5)	4.17 (35)	6.44 (41)	2.19 (29)	0.87 (33)	2.00 (28)	1.38 (37)
S2	0.2998 (5)	−0.0044 (13)	0.4206 (6)	5.27 (39)	5.09 (38)	4.28 (25)	0.08 (35)	3.51 (33)	0.76 (37)
O1	0.038 (1)	0.565 (2)	0.362 (1)	4.4 (6)	5.2 (7)	6.9 (7)	−0.2 (6)	4.1 (5)	1.7 (5)
O2	0.465 (2)	0.568 (3)	0.146 (2)	9.9 (8)	11.0 (9)	5.9 (7)	1.1 (8)	5.9 (6)	−1.6 (8)
N1	0.334 (2)	−0.178 (3)	0.285 (2)	10.7 (9)	6.9 (8)	8.2 (8)	4.8 (7)	8.7 (7)	7.7 (7)
N2	0.1739 (7)	−0.169 (2)	0.223 (1)	1.5 (4)	4.3 (6)	1.6 (5)	1.7 (5)	0.8 (4)	0.6 (5)
N3	0.170 (1)	0.179 (2)	0.202 (2)	3.7 (6)	1.3 (5)	3.6 (7)	0.8 (5)	2.1 (5)	−0.2 (5)
N4	0.111 (1)	0.276 (2)	0.154 (1)	2.9 (5)	2.7 (6)	6.0 (2)	0.4 (5)	3.4 (5)	0.4 (5)
N5	0.328 (1)	0.182 (3)	0.297 (2)	4.3 (6)	6.6 (8)	4.4 (7)	1.0 (6)	3.9 (5)	0.1 (7)
N6	0.388 (2)	0.260 (2)	0.343 (1)	9.4 (8)	5.1 (8)	2.6 (5)	−1.2 (6)	4.3 (6)	−0.6 (7)
C1	0.288 (1)	−0.107 (2)	0.121 (2)	7.1 (8)	7.3 (8)	5.2 (7)	0.1 (6)	5.0 (6)	1.6 (7)
C2	0.314 (1)	−0.226 (2)	0.189 (1)	7.2 (7)	8.8 (8)	4.9 (7)	0.1 (7)	4.5 (6)	3.4 (7)
C3	0.299 (1)	−0.311 (3)	0.302 (2)	6.6 (8)	3.7 (7)	6.8 (8)	1.1 (7)	1.7 (8)	1.4 (7)
C4	0.209 (2)	−0.317 (3)	0.235 (2)	8.9 (9)	4.5 (8)	8.5 (9)	−0.1 (8)	4.1 (7)	−2.1 (7)
C5	0.1480 (9)	−0.143 (2)	0.285 (1)	5.7 (6)	5.2 (7)	5.2 (7)	0.7 (6)	4.3 (6)	0.2 (6)
C6	0.228 (2)	−0.135 (3)	0.398 (2)	9.3 (9)	9.0 (9)	6.3 (8)	−0.5 (7)	6.3 (7)	−1.1 (8)
C7	0.412 (2)	−0.174 (4)	0.375 (2)	5.5 (8)	9.8 (10)	8.1 (9)	0.4 (8)	4.3 (7)	2.4 (9)
C8	0.083 (2)	−0.154 (3)	0.117 (2)	5.6 (8)	6.5 (9)	7.1 (9)	−1.8 (8)	3.7 (7)	−3.5 (7)
C9	0.0978 (7)	0.348 (2)	0.2182 (7)	5.5 (7)	3.5 (7)	7.0 (8)	−1.7 (7)	5.8 (6)	−0.5 (6)
C10	0.1522 (7)	0.336 (1)	0.3240 (7)	6.7 (9)	5.1 (9)	3.5 (7)	−0.3 (7)	3.0 (6)	−0.4 (8)
C11	0.1333 (7)	0.406 (1)	0.3757 (7)	3.8 (7)	5.5 (8)	6.0 (8)	0.7 (7)	3.4 (6)	2.8 (7)
C12	0.0600 (7)	0.487 (2)	0.3217 (7)	7.0 (8)	4.3 (8)	6.2 (7)	0.1 (7)	5.2 (6)	−1.1 (7)
C13	0.0056 (7)	0.498 (2)	0.2159 (7)	4.1 (7)	4.1 (8)	4.2 (7)	0.4 (6)	3.1 (6)	0.1 (6)
C14	0.0245 (7)	0.428 (2)	0.1641 (7)	2.6 (6)	1.4 (6)	1.0 (5)	0.1 (5)	0.3 (4)	−0.6 (5)
C15	0.085 (1)	0.570 (4)	0.460 (2)	4.7 (8)	9.1 (9)	5.9 (8)	−1.1 (8)	2.6 (6)	0.1 (8)
C17	0.4765 (7)	0.421 (2)	0.3470 (8)	6.0 (7)	6.0 (9)	8.0 (8)	−0.6 (7)	6.0 (6)	−1.0 (7)
C18	0.4948 (7)	0.501 (2)	0.2972 (8)	3.8 (7)	5.2 (8)	5.0 (7)	−0.2 (6)	3.6 (6)	−0.8 (7)
C20	0.3692 (7)	0.407 (2)	0.1352 (8)	5.7 (8)	5.1 (8)	3.4 (6)	0.1 (6)	3.5 (6)	1.5 (7)
C21	0.3509 (7)	0.328 (2)	0.1850 (8)	2.3 (6)	2.4 (7)	4.3 (7)	−0.7 (5)	2.7 (5)	−1.8 (5)
C22	0.399 (2)	0.588 (4)	0.030 (2)	7.2 (8)	8.8 (9)	5.4 (8)	0.7 (7)	4.8 (7)	−1.5 (7)

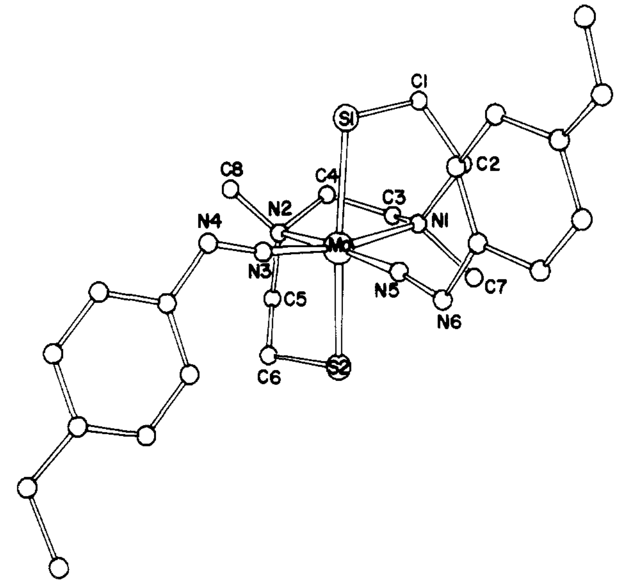

Figure 1. Structure of [Mo($N_2C_6H_4OCH_3$-p)$_2$L], showing 50% probability ellipsoids and the atom labeling scheme.

Table III. Selected Bond Lengths (Å) and Angles (Deg) for Mo($N_2C_6H_4OCH_3$-p)$_2$($S_2N_2C_8H_{18}$)

Mo–S1	2.456 (7)	N2–C4	1.47 (3)
Mo–S2	2.472 (8)	N2–C8	1.58 (3)
Mo–N1	2.37 (1)	N3–N4	1.28 (2)
Mo–N2	2.27 (1)	N5–N6	1.20 (3)
Mo–N3	1.81 (1)	N4–C9	1.51 (2)
Mo–N5	1.81 (2)	N6–C16	1.38 (2)
S1–C1	1.85 (2)	O1–C12	1.31 (2)
S2–C6	1.80 (3)	O1–C15	1.30 (3)
N1–C2	1.53 (3)	O2–C19	1.41 (2)
N1–C3	1.53 (4)	O2–C22	1.53 (3)
N1–C7	1.44 (3)	av C–C ring	1.40 (2)
N2–C5	1.57 (2)		
S1–Mo–S2	163.7 (1)	Mo–N1–C7	116.6 (21)
S1–Mo–N1	80.6 (5)	Mo–N1–C3	101.0 (15)
S1–Mo–N2	88.9 (3)	C3–N1–C7	101.7 (23)
S1–Mo–N3	91.5 (5)	N1–C3–C4	117.6 (21)
S1–Mo–N5	99.5 (6)	C3–C4–N2	113.9 (22)
S2–Mo–N1	87.7 (5)	C4–N2–Mo	111.8 (12)
S2–Mo–N2	77.7 (4)	C4–N2–C8	112.5 (18)
S2–Mo–N3	98.2 (6)	C4–N2–C5	117.2 (15)
S2–Mo–N5	92.5 (7)	Mo–N2–C8	111.3 (12)
N1–Mo–N2	79.6 (5)	Mo–N2–C5	109.6 (10)
N1–Mo–N3	169.1 (9)	C5–N2–C8	93.1 (15)
N1–Mo–N5	93.3 (9)	N2–C5–C6	106.7 (14)
N2–Mo–N3	92.8 (6)	C5–C6–S2	112.9 (16)
N2–Mo–N5	168.0 (7)	C6–S2–Mo	103.7 (8)
N3–Mo–N5	95.5 (4)	Mo–N3–N4	170.4 (17)
Mo–S1–C1	96.3 (7)	N3–N4–C9	113.8 (17)
S1–C1–C2	113.0 (16)	Mo–N5–N6	168.3 (19)
C1–C2–N1	115.7 (17)	N5–N6–C19	119.6 (17)
C2–N1–Mo	110.5 (13)	C12–O1–C15	120.2 (19)
C2–N1–C7	119.4 (24)	C19–O2–C22	116.0 (20)
C2–N1–C3	104.5 (21)		

of the molybdenum and sulfur atoms. Subsequent difference Fourier maps revealed the positions of all the remaining atoms including hydrogens. All nonhydrogen atoms were refined anisotropically; the hydrogen atoms were treated as fixed contributions in the refinement. Neutral-atom scattering factors for the nonhydrogen atoms and corrections for the anomalous dispersion effects of molybdenum and sulfur atoms were employed.[11] Scattering factors for the hydrogen atoms were those of Stewart et al.[12]

The final full-matrix least-squares refinement converged at $R_1 = 0.043$ and $R_2 = 0.049$ where $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ with $w = 4F_o^2/\sigma^2(F_o^2)$. The "goodness of fit" parameter $[\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NP})]^{1/2}$ was 1.37 for NO = 1505 and NP = 286. A final difference Fourier map showed no excursions of electron density greater than 0.3 e Å^{-3}. Refinement of the alternative, inverted structure in *Cc* led to final *R* values of 0.069 and 0.075 for R_1 and R_2, respectively. The original refinement was taken to be correct.

Atomic positional and thermal parameters, along with their standard deviations, are given in Table II. Table III lists interatomic distances

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Table IV. Summary of Crystal and Experimental Data for [$MoO(NNPh_2)L$]

cryst: red prism, 0.25 × 0.25 × 0.3 mm	$V = 2213$ Å^3
cryst syst: monoclinic	$Z = 4$
space group: $P2_1/c$	fw: 500.54
$a = 13.248$ (2) Å	$F(000) = 1032$
$b = 11.229$ (2) Å	d(calcd) = 1.502 g cm^{-3}
$c = 15.780$ (2) Å	d(measd) = 1.49 g cm^{-3}
$\beta = 109.46$ (1)°	

diffractometer: Enraf-Nonius CAD 4
radiation: Mo Kα($\bar{\lambda}$ 0.710 73 Å)
scan technique: ω–θ
scan rate: 2–20° min^{-1}
data collected: $0 < 2\theta < 45°$
reflctns measd: $h,k,\pm l$
obsd reflctns: 2784 with $F_o \geq 2.58\sigma(F_o)$

and angles for [$Mo(NNC_6H_4OCH_3)_2L$]. Relevant least-squares planes and angles between selected planes are given in Table VII. Listings of observed and calculated structure factor amplitudes and hydrogen atom parameters are provided as supplementary material. A view of the geometry of [$Mo(NNC_6H_4OCH_3)L$] is shown in Figure 1, together with the atom labeling scheme.

[$MoO(N_2Ph_2)(C_8H_{18}N_2S_2)$]. Collection and Reduction of X-ray Data. Red prismatic crystals of [$MoO(NNPh_2)L$] were obtained by slow evaporation of a solution of the compound in methylene chloride.

Data were collected by Molecular Structure Corp., College Station, TX 77840, with an Enraf-Nonius CAD 4 diffractometer. Cell constants were obtained by the computer centering of 25 reflections followed by least-squares refinement of the setting angles. Data were obtained by the authors in the form of F_o intensities. No correction for absorption was made. Relevant crystal data and experimental parameters are presented in Table IV.

Solution and Refinement of the Structure. The structure was solved with use of 2784 symmetry-independent reflections with $F_o \geq 2.58\sigma(F_o)$. The programs used in the solution of the structure are part of the X-RAY72 system.[27] The molybdenum atom was located by means of a three-dimensional Patterson function. All other nonhydrogen atoms were located by subsequent difference Fourier syntheses. Mean atomic scattering factors for neutral Mo, S, O, N, C, and H were used.[11,12] Refinement to convergence with isotropic thermal parameters for all nonhydrogen atoms gave a value for the error index, R, of 0.072. The function minimized in the least-squares refinement routines was $\sum w(|F_o| - |F_c|)^2$ where the weighting function, w, is $\sigma(F_o)^{-1}$. Real and imaginary dispersion corrections to the mean atomic scattering factors for Mo and S were introduced at this point, and the structure was refined to convergence with anisotropic thermal parameters for all nonhydrogen atoms. At this stage of refinement R was 0.047 and the positions of the hydrogen atoms were revealed by a difference Fourier synthesis. Hydrogen atoms were included in the final cycles of least-squares refinement as fixed contributors in their calculated positions with a bond distance of 0.95 Å and an isotropic thermal parameter of 0.07 Å^2. The final value for the error index, R, was 0.027, and that for the weighted error index, R_w, was 0.048. The "goodness of fit" was 1.60, and the overdetermination ratio was 11.0 for the number of observations (NO), 2784, and the number of parameters (NP), 254.

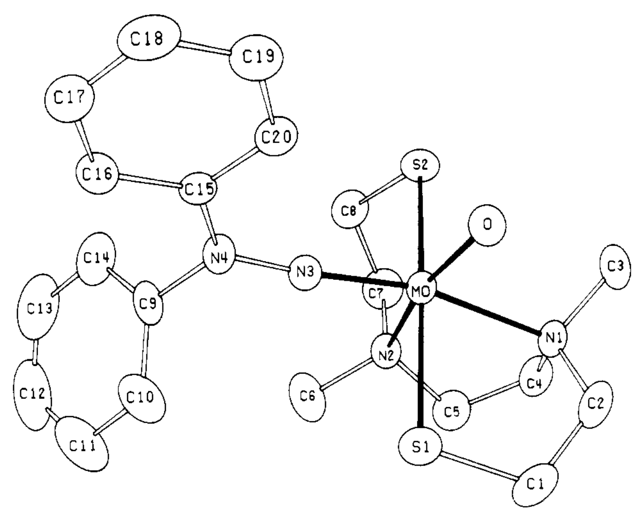

Figure 2. Structure of [$MoO(N_2Ph_2)L$], showing 50% probability ellipsoids and the atom labeling scheme.

Atomic positional and thermal parameters for [$MoO(NNPh_2)L$] are collected in Table V. Intramolecular bond distances and angles are given in Table VI. Relevant least-squares planes and angles between selected planes are listed in Table VII. Listings of observed and calculated structure factor amplitudes and calculated hydrogen

Table V. Final Positional and Anisotropic Thermal Parameters (×10^2) for [$MoO(NNPh_2)L$][a]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	0.84560 (2)	0.12626 (2)	0.24244 (2)	2.9 (3)	2.75 (3)	3.00 (3)	0.33 (1)	1.21 (2)	0.55 (1)
S(1)	0.7641 (1)	0.0088 (1)	0.1095 (1)	5.27 (7)	4.23 (6)	4.49 (6)	−0.85 (5)	1.64 (5)	−0.95 (4)
S(2)	0.9062 (1)	0.2985 (1)	0.3450 (1)	4.65 (6)	3.91 (6)	3.76 (6)	0.22 (4)	0.91 (5)	−0.38 (4)
N(1)	0.9494 (2)	0.1891 (2)	0.1548 (2)	3.28 (16)	3.26 (15)	3.41 (16)	−0.12 (13)	1.24 (14)	0.23 (13)
N(2)	0.7490 (2)	0.2953 (2)	0.1515 (2)	3.26 (16)	4.48 (18)	3.73 (16)	−0.05 (14)	1.48 (14)	1.16 (14)
N(3)	0.7400 (2)	0.0888 (2)	0.2835 (2)	3.28 (16)	3.26 (15)	3.41 (16)	−0.12 (13)	1.24 (14)	0.23 (13)
N(4)	0.6710 (2)	0.0536 (2)	0.3214 (2)	3.26 (16)	4.48 (18)	3.73 (16)	−0.05 (14)	1.48 (14)	1.16 (14)
O	0.9531 (2)	0.0458 (2)	0.3047 (2)	3.68 (14)	3.82 (13)	4.28 (14)	0.83 (11)	1.28 (11)	0.75 (11)
C(1)	0.8547 (4)	0.0300 (4)	0.0454 (3)	7.78 (31)	5.36 (24)	4.98 (24)	−0.03 (23)	3.56 (23)	−1.14 (20)
C(2)	0.9600 (3)	0.0820 (3)	0.1028 (3)	5.47 (25)	4.76 (22)	5.85 (25)	0.68 (20)	3.72 (22)	−0.09 (20)
C(3)	1.0597 (3)	0.2230 (4)	0.2124 (3)	3.20 (20)	6.40 (26)	6.19 (25)	−0.20 (19)	2.16 (19)	0.90 (21)
C(4)	0.9028 (3)	0.2920 (3)	0.0953 (2)	5.19 (23)	3.91 (21)	4.80 (22)	0.45 (18)	2.78 (19)	1.25 (17)
C(5)	0.7836 (3)	0.3006 (4)	0.0714 (2)	5.44 (25)	5.57 (24)	4.32 (22)	0.73 (20)	1.80 (20)	1.83 (19)
C(6)	0.6322 (3)	0.2761 (4)	0.1193 (3)	3.41 (21)	7.13 (29)	7.34 (27)	1.18 (21)	1.08 (21)	2.70 (24)
C(7)	0.7734 (4)	0.4116 (4)	0.2008 (3)	6.23 (27)	4.20 (22)	5.92 (26)	1.43 (21)	1.94 (22)	0.65 (19)
C(8)	0.7911 (3)	0.3947 (3)	0.2997 (3)	5.42 (25)	4.23 (21)	5.28 (24)	1.00 (19)	2.19 (21)	−0.20 (18)
C(9)	0.5614 (3)	0.0924 (4)	0.2804 (2)	2.67 (19)	5.49 (23)	4.70 (23)	−0.53 (18)	1.17 (18)	2.27 (19)
C(10)	0.5054 (3)	0.0503 (4)	0.1948 (3)	4.58 (26)	6.90 (29)	6.36 (29)	−1.20 (23)	0.09 (22)	1.91 (24)
C(11)	0.4024 (4)	0.0911 (6)	0.1515 (5)	5.51 (32)	9.56 (40)	8.43 (37)	−2.14 (31)	−0.87 (29)	3.05 (33)
C(12)	0.3583 (4)	0.1699 (6)	0.1948 (5)	4.79 (31)	8.97 (40)	12.96 (54)	1.24 (30)	3.51 (35)	6.60 (41)
C(13)	0.4126 (5)	0.2101 (5)	0.2789 (5)	7.68 (38)	9.56 (41)	11.30 (44)	2.44 (33)	5.87 (37)	4.01 (38)
C(14)	0.5169 (4)	0.1704 (4)	0.3228 (3)	5.53 (28)	7.36 (29)	7.22 (30)	1.70 (25)	3.49 (25)	2.29 (26)
C(15)	0.7031 (3)	−0.0275 (3)	0.3951 (2)	3.61 (19)	3.05 (17)	2.44 (16)	−0.65 (15)	0.84 (15)	0.17 (14)
C(16)	0.6274 (3)	−0.0731 (3)	0.4289 (2)	4.34 (22)	4.59 (21)	3.97 (20)	−1.07 (19)	1.10 (18)	0.70 (18)
C(17)	0.6601 (4)	−0.1517 (4)	0.5008 (3)	5.98 (28)	5.57 (24)	4.13 (23)	−1.78 (22)	1.69 (22)	0.78 (19)
C(18)	0.7651 (4)	−0.1835 (4)	0.5382 (2)	7.82 (32)	4.63 (23)	3.50 (21)	−0.19 (23)	1.26 (23)	0.83 (18)
C(19)	0.8406 (3)	−0.1364 (3)	0.5051 (3)	5.43 (26)	5.17 (25)	4.07 (23)	0.89 (20)	1.02 (21)	0.50 (17)
C(20)	0.8093 (3)	−0.0577 (3)	0.4321 (2)	4.35 (20)	4.13 (20)	3.27 (18)	0.12 (17)	1.27 (16)	0.36 (15)

[a] Estimated standard deviations in the least significant digits given are in parentheses. The thermal ellipsoid is of the form $\exp[-2\pi^2 \cdot (a^2U_{11} + b^{*2}U_{22} + c^{*2}U_{33} + 2a^*b^*U_{12} + 2a^*c^*U_{13} + 2b^*c^*U_{23})]$.

Table VI. Selected Bond Lengths (Å) and Angles (Deg) for [MoO(NNPh$_2$)L]

Mo-S(1)	2.408 (1)	C(8)-S(2)	1.810 (4)
Mo-S(2)	2.478 (1)	N(3)-N(4)	1.309 (4)
Mo-N(1)	2.359 (3)	N(4)-C(9)	1.446 (4)
Mo-N(2)	2.464 (3)	C(9)-C(10)	1.389 (5)
Mo-N(3)	1.778 (3)	C(10)-C(11)	1.384 (6)
Mo-O	1.696 (2)	C(11)-C(12)	1.363 (10)
S(1)-C(1)	1.823 (5)	C(12)-C(13)	1.359 (9)
C(1)-C(2)	1.506 (5)	C(13)-C(14)	1.397 (7)
C(2)-N(1)	1.489 (5)	C(14)-C(9)	1.350 (7)
N(1)-C(3)	1.490 (4)	N(4)-C(15)	1.426 (4)
N(1)-C(4)	1.487 (4)	C(15)-C(16)	1.380 (6)
C(4)-C(5)	1.501 (6)	C(16)-C(17)	1.388 (5)
C(5)-N(2)	1.483 (6)	C(17)-C(18)	1.366 (6)
N(2)-C(6)	1.475 (5)	C(18)-C(19)	1.378 (7)
N(2)-C(7)	1.499 (5)	C(19)-C(20)	1.400 (5)
C(7)-C(8)	1.511 (6)	C(20)-C(15)	1.374 (5)
S(1)-Mo-S(2)	161.89 (3)	C(5)-N(2)-C(6)	107.3 (3)
S(1)-Mo-N(1)	80.37 (7)	C(5)-N(2)-C(7)	109.4 (3)
S(1)-Mo-N(2)	85.39 (6)	Mo-N(2)-C(7)	112.9 (2)
S(1)-Mo-N(3)	90.55 (9)	C(6)-N(2)-C(7)	109.1 (3)
S(1)-Mo-O	105.00 (8)	N(2)-C(7)-C(8)	111.0 (3)
S(2)-Mo-N(1)	91.38 (7)	C(7)-C(8)-S(2)	107.7 (3)
S(2)-Mo-N(2)	76.79 (6)	C(8)-S(2)-Mo	99.2 (1)
S(2)-Mo-N(3)	93.97 (9)	Mo-N(3)-N(4)	172.9 (2)
S(2)-Mo-O	90.62 (8)	N(3)-N(4)-C(9)	117.1 (3)
N(1)-Mo-N(2)	73.7 (1)	N(3)-N(4)-C(15)	120.1 (3)
N(1)-Mo-N(3)	165.4 (1)	C(9)-N(4)-C(15)	122.6 (3)
N(1)-Mo-O	87.6 (1)	N(4)-C(9)-C(10)	117.6 (4)
N(2)-Mo-N(3)	94.3 (1)	C(14)-C(9)-C(10)	121.5 (4)
N(2)-Mo-O	157.0 (1)	C(9)-C(10)-C(11)	119.1 (5)
N(3)-Mo-O	105.9 (1)	C(10)-C(11)-C(12)	118.9 (5)
N(4)-Mo-O	102.9 (1)	C(11)-C(12)-C(13)	122.0 (5)
Mo-S(1)-C(1)	103.0 (1)	C(12)-C(13)-C(14)	119.5 (6)
S(1)-C(1)-C(2)	111.5 (3)	C(13)-C(14)-C(9)	119.0 (4)
C(1)-C(2)-N(1)	113.9 (3)	N(4)-C(15)-C(16)	119.6 (3)
C(2)-N(1)-C(3)	106.7 (3)	C(20)-C(15)-C(16)	121.1 (3)
C(2)-N(1)-C(4)	112.0 (3)	C(15)-C(16)-C(17)	118.9 (3)
Mo-N(1)-C(4)	113.8 (2)	C(16)-C(17)-C(18)	121.0 (4)
C(3)-N(1)-C(4)	107.6 (3)	C(17)-C(18)-C(19)	119.9 (4)
N(1)-C(4)-C(5)	112.9 (3)	C(18)-C(19)-C(20)	120.0 (4)
C(4)-C(5)-N(2)	112.4 (3)	C(19)-C(20)-C(15)	119.1 (4)

Table VII. Deviations of Atoms from Selected Least-Squares Planes[a]

a. [MoO(N$_2$Ph$_2$)L]

plane 1		plane 2		plane 3	
Mo	−0.001	C9	−0.004	Mo	0.001
N3	0.002	C10	0.006	N3	−0.003
N4	−0.001	C11	−0.004	N4	0.002
C9	−0.000	C12	−0.001	C15	−0.000
σ	0.001	C13	0.003	σ	0.002
P	0.045	C14	−0.001	P	0.575
Q	9.183	σ	0.004	Q	8.649
R	8.546	P	−6.883	R	9.239
S	3.270	Q	−8.524	S	3.187
		R	8.566		
		S	−2.244		

plane 4				plane	atoms
C15	−0.004	σ	0.005	5	Mo
C16	0.005	P	−0.938		S1
C17	0.000	Q	8.641		N1
C18	−0.005	R	9.815		
C19	0.006	S	2.985	6	Mo
C20	−0.001				N1
					N2
				7	Mo
					S2
					N2

Dihedral Angles (Deg) between Selected Least-Squares Planes

1-2	66.6	2-4	72.6	6-7	84.6
3-5	6.5	5-6	88.0	5-7	74.0

b. [Mo(N$_2$C$_6$H$_4$OCH$_3$)$_2$L]

plane 8		plane 9		plane 10	
Mo	0.001	C9	0.004	Mo	0.029
N3	−0.002	C10	−0.002	N5	−0.068
N4	0.001	C11	−0.001	N6	0.032
C9	0.000	C12	0.002	C16	0.007
σ	0.001	C13	−0.000	σ	0.046
P	13.887	C14	−0.003	P	13.552
Q	6.340	σ	0.003	Q	−6.507
R	−4.324	P	11.846	R	−4.465
S	2.624	Q	7.178	S	2.002
		R	−5.308		
		S	2.495		

plane 11				plane	atom
C16	0.001	σ	0.002	12	Mo
C17	0.000	P	0.581		S1
C18	−0.001	Q	−0.810		N1
C19	0.003	R	0.075		
C20	−0.003	S	1.202	13	Mo
C21	−0.001				N1
					N2
				14	Mo
					S2
					N2

Dihedral Angles (Deg) between Selected Least-Squares Planes

8-9	11.9	9-11	76.8	13-14	90.0
10-11	9.0	12-13	89.5	12-14	79.3

[a] Deviations are in Å. σ is the standard deviation of the defining atoms from the plane. P, Q, R, and S are the variables for the normal form of the equation of a plane, $Px + Qy + Rz = S$, in direct space.

atom positions are provided as supplementary material. An ORTEP representation of the molecular structure with the atom labeling scheme is shown in Figure 2.

Results and Discussion

Structure of [Mo(NNC$_6$H$_4$OCH$_3$-*p*)$_2$L]. The geometry of the monomeric complex [Mo(NNC$_6$H$_4$OCH$_3$-*p*)$_2$L] is shown in Figure 1. The molybdenum is pseudooctahedrally coordinated to the thiol sulfurs and amine nitrogens of L and to the terminal nitrogen of the diazenido ligands. The average Mo–S bond length of 2.464 (7) Å is similar to the corresponding values of 2.420 (10) and 2.443 (1) Å for the compounds [MoO$_2$L] and [MoO(NNPh$_2$)L]. The average Mo–N(diazenido) bond distance of 1.82 (1) Å is comparatively short and consistent with multiple bonding between the molybdenum and the diazenido nitrogen. The Mo–N bond length may be compared to values of 1.781 (7) Å for [Mo(N$_2$Ph)(S$_2$CNMe$_2$)$_3$] and of 1.770 (6) Å for [Mo(N$_2$-3-C$_6$H$_4$(NO$_2$))(S$_2$CNMe$_2$)$_3$].[13] The lengthening of the Mo–N distance by about 0.05 Å in [Mo(N$_2$C$_6$H$_4$OCH$_3$)$_2$L] from the average value observed for the latter two dtc complexes may be anticipated by virtue of the mutually cis orientation of the diazenido groups competing for the metal t_{2g} orbitals.

The most unusual feature of the structure of [Mo(N$_2$C$_6$H$_4$OCH$_3$)$_2$L] is the nonequivalence of the molybdenum–amine nitrogen bonds: Mo–N1, 2.37 (1) Å; Mo–N2, 2.27 (1) Å. Similar nonequivalence has been observed in the structures of [MoO(N$_2$Ph)L], [FeL]$_2$,[14] and [Zn$_2$Cl$_2$L]$_2$·2H$_2$O,[15] where steric effects have been invoked to rationalize these differences in metal–nitrogen bond distances. Since the amine nitrogens N1 and N2 are trans to structurally identical diazenido groups, the significantly different Mo–N(amine) bond lengths must

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reflect inherent ligand strain rather than differences in the magnitude of the trans influence of the multiply bonded ligands, as invoked for $[MoO(N_2Ph_2)L]$ where the difference in trans influence of the oxo relative to that of the hydrazido(2−) ligand may be the dominant effect. The average Mo–N(amine) distance, 2.32 (1) Å, is comparable to values of 2.324 (5) and 2.399 (5) Å observed for $[MoO_3(dien)]$[16] and $[Mo_2O_6EDTA]^{4-}$,[17] respectively, where the amine nitrogen is trans to an oxo group. A considerably shorter Mo–N(amine) distance, in the range 2.22–2.27 Å, is observed for $Na_2[Mo_2O_4(cys)_2]$,[18] $[Mo_2O_4(his)_2]$,[19] and $Na_2[Mo_2S_2O_2(cys)_2]$,[20] consistent with the absence of the strong trans influence of the oxo ligand on the amine group.

The ligand donor atoms assume the anticipated configuration about the molybdenum: the diazenido groups are mutually cis in order to maximize effective overlap with the metal t_{2g} orbitals, the amine nitrogens of L are trans to the multiply bonded diazenido groups, and the thiolate sulfurs are mutually trans, thus assuming a cis configuration relative to diazenido and amine nitrogen donors. The trans thiolate configuration is observed in all pseudooctahedral structures of this type, with the exception of $[MoO_2(CH_3NHCH_2C(CH_3)_2S)_2]$[22] where steric constraints impose an unusual cis thiolate geometry.

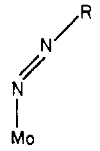
The L ligand geometry is similar to that observed for $[Zn_2Cl_2L]_2 \cdot 2H_2O$.[15] Atoms C1 and C2 are on opposite sides of the N1–Mo–S1 plane, and atoms C5 and C6 are on opposite sides of the N2–Mo–S2 plane, producing a symmetric skew conformation for the two $\overline{\text{C–N–Mo–S–C}}$ rings.[23] The two methyl groups are on opposite sides of the diamine chelate ring.

The diamine ring conformations in $[MoO_2L]$, $[MoO(N_2Ph_2)L]$, and $[Mo(N_2C_6H_4OCH_3)_2L]$ are in general agreement with calculated minimum-energy conformations of five-membered diamine chelate rings, as described by Hawkins[24] and Busch.[25] As the average Mo–N distance decreases from 2.41 Å in $[MoO(N_2Ph_2)L]$ to 2.32 Å in $[Mo(N_2C_6H_4OCH_3)_2L]$, the N–Mo–N angle increases from 73.7 to 79.9°, as predicted by these calculations.

Idealized octahedral geometry requires bond angles around the metal of 90 or 180°. The degree of strain in these complexes has been defined as the deviation of the intrachelate ring angles from the value in an idealized polyhedron divided by the idealized angle. In $[Mo(N_2C_6H_4OCH_3)_2L]$, the intraring angles are 80.6 (N1–Mo–S1), 77.7 (N2–Mo–S2), and 79.6° (N1–Mo–N2), resulting in a large accumulated strain (10.4%, 13.7%, and 11.6%, respectively) and causing the two $\overline{\text{C–N–Mo–S–C}}$ rings to fold back toward the N1–Mo–N2 ring. This folding allows the S1–Mo–S2 angle to open to a value of 163.7°, thus placing the thiolato groups in the preferred trans configuration.

The molybdenum–diazenido groups exhibit a geometry consistent with molybdenum–nitrogen multiple bonding and extensive delocalization throughout the Mo–N–N groups. Both groups are essentially linear (Mo–N_3–N4, 170.4°; Mo–N5–N6, 168.3°), while the short N–N distances of 1.20 (3) and 1.28 (2) Å for N5–N6 and N3–N4 are consistent with considerable multiple-bond character. The diazenido ligand may thus be considered a three-electron donor, with canonical form A essentially adopted, in a fashion reminiscent of the bis(hydrazido(2−)) complexes $[Mo(N_2R_2)(dtc)_2]$ where canonical form C clearly predominates.[26] It is interesting to note that whereas bis(diazenido) complexes of the type $[Mo(N_2R)_2(dtc)_2]$ or $[Mo(N_2R)_2L]$ are formally 18-electron complexes, the analogous bis(hydrazido(2−)) species are formally 20-electron species. This difference does not appear to be reflected in the structural and chemical properties of the complexes, suggesting that the electronic distribution at the molybdenum may be similar in these species.


A


B

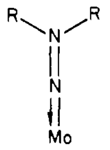

C

Table VIII. Polyhedral Edge Distances (Å)

a. $[Mo(N_2C_6H_4OCH_3\text{-}p)_2L]$

S1–N1 (bite)	3.124	S1–N5	3.302
S2–N2 (bite)	2.978	S2–N1	2.926
N1–N2 (bite)	2.848	S2–N3	3.267
N3–N5	2.687	S2–N5	3.125
S1–N2	3.300	N1–N5	3.071
S1–N3	3.096	N2–N3	2.970

b. $[MoO(N_2Ph_2)L]$

S1–N1 (bite)	3.076	S1–O	3.285
S2–N2 (bite)	3.069	S2–N1	3.462
N1–N2 (bite)	2.894	S2–N3	3.148
N3–O	2.773	S2–O	3.018
S1–N2	3.304	N1–O	2.847
S1–N3	3.007	N2–N3	3.145

Each phenyl ring of the diazenido ligands takes up a position roughly in the plane of the $\overline{\text{C–N–Mo–S–C}}$ chelate ring containing the amine nitrogen trans to the diazenido group (ring C9–C14 in the $\overline{\text{C1–N1–Mo–S1–C2}}$ plane; ring C16–C21 in the $\overline{\text{C5–N2–Mo–S2–C6}}$ plane), thus minimizing steric repulsions. Since the phenyl ring C9–C14 is twisted out of the Mo–N3–N4–C9 plane by 12°, while ring C16–C21 is 9° out of the Mo–N5–N6–C16 plane, through conjugation from the phenyl ring to Mo is not maximized. This is consistent with the correlation of σ_p of X (X = H, Me, OMe, Cl) with the redox potential of $[Mo(N_2C_6H_4X)_2L]$ (vide infra).

A significant contraction occurs in the valence angle at the molybdenum as the cis oxo groups of the parent compound $[MoO_2L]$ are successively replaced by substituted hydrazine ligands in $[MoO(N_2Ph_2)L]$ and $[Mo(N_2R)_2L]$. Thus, the valence angle exhibits decreasing values of 112.1, 105.9, and 95.5° for O1–Mo–O2, O–Mo–N3, and N3–Mo–N5, respectively, in the series $[MoO_2L]$, $[MoO(N_2R_2)L]$, $[Mo(N_2R)_2L]$. The origin of this effect is unclear but may be related to the less severe steric requirements of the monosubstituted diazenido

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Table IX. Comparison of Geometries for Molybdenum-Hydrazido(2–) and Molybdenum-Diazenido Complexes

compd	X[a]	Mo-L_{trans}[b]	Mo-L_{cis}	Mo-N	N-N	Mo-N-N	X-Mo-X′ (X, X′)	ref
$[MoO_2(S_2CNPr_2)_2]$	O	2.651 (S)	2.451 (S)	...	...	...	105.7 (O, O)	28
$[MoO(N_2Me_2)(S_2CNMe_2)_2]$	O	2.720 (S)	2.476 (S)	1.799	1.29	168.0	104.4 (O, N)	4
	N	2.576 (S)						
$[Mo(N_2Ph_2)_2(S_2CNMe_2)_2]$	N	2.680 (S)	2.493 (S)	1.790	1.31	169.9	...	26
$[Mo(N_2MePh)_2(S_2CNMe_2)_2]$	N	2.662 (S)	2.488 (S)	1.790	1.30	172.6	...	29
$[Mo(N_2PhEt)(S_2CN(CH_2)_5)_3]^+$	N	2.56 (S)	2.50 (av, S)	1.715	1.37	170.0	...	30
$[MoO_2L]$	O	2.39 (N)	2.42 (S)	...	...	...		9
		2.44 (N)	2.41 (S)	...	...	...		
$[MoO(N_2Ph_2)L]$	O	2.464 (N)	2.408 (S)	1.778	1.309	172.9	105.9 (O, N)	this work
	N	2.359 (N)	2.478 (S)					
$[Mo(N_2C_6H_4OCH_3)_2L]$	N	2.37 (N)	2.456 (S)	1.82	1.28	170.4	95.5 (N, N)	this work
		2.27 (N)	2.472 (S)	1.81	1.20	168.3		
$[Mo(N_2Ph)(S_2CNMe_2)_3]$	N	2.611 (S)	2.479 2.532 (S)	1.781	1.233	171.5	...	13
$[Mo(N_2\text{-}3\text{-}C_6H_4NO_2)(S_2CNMe_2)_3]$	N	2.574 (S)	2.515 (S)	1.770	1.262	170.6	...	13
$[Mo(N_2CO_2Et)(S_2CNMe_2)_3]$	N	2.604 (S)	2.487 2.529 (S)	1.732	1.274	178.9	...	31
$[MoO(N_2Me_2)(C_9H_6NO)_2]$	O	2.123 (O)	2.019 (O)	1.800	1.28	155.5	100.8	32
	N	2.302 (N)	2.250 (N)					

[a] X or X′ refers to the oxo group or multiply bond hydrazido(2–) or diazenido nitrogen. Distances are given in angstroms and angles in degrees. [b] L′ refers to donor groups cis or trans to X. The donor atom is given in parentheses.

ligand in contrast to those of the disubstituted hydrazido(2–) ligand and to the considerable steric requirements of the tightly bound oxo ligand.

Although the N3–Mo–N5 angle is relatively small and the N3···N5 contact is only 2.687 Å, the cis-diazenido groups are not linked to give a type of tetrazene structure. The N4···N6 distance (Table VIII) is significantly longer than the van der Waals contact radius (6.01 Å vs. ca. 3.0 Å), and the infrared spectrum of the complex exhibits strong bands at ca. 1600 cm^{-1}, the normal region for $\nu(NN)$ in singly bent diazenido complexes. This frequency is not nearly low enough to be considered characteristic of tetrazene-type ligands, an observation confirmed by the structure.

Structure of $[MoO(N_2Ph_2)(C_8H_{18}N_2S_2)]$. The pseudooctahedral geometry of the formally Mo(VI) species is illustrated in Figure 2. The major distortions from idealized octahedral geometry result from the differences in the donor groups and the steric constraints imposed by the diamine chelate ring C—N—Mo—N—C. The twist angles about the trigonal planes defined by the S(1), N(1), O and S(2), N(2), N(3) atoms, a measure of the deviation from ideal octahedral geometry, average 60 (7)°, while twist angles of 60.0° define an ideal octahedron. The two trigonal planes are not perfectly parallel but are forced apart by the bridging NCH_2CH_2N chelate ring such that they form a dihedral angle of 10.6°.

The diphenylhydrazido ligand occupies the anticipated position cis to the terminal oxo ligand. The hydrazido group is nearly linearly bonded to molybdenum in a manner similar to that of most other Mo–hydrazido(2–) complexes. The Mo–N(3) bond distance, 1.778 Å, is consistent with a substantial degree of multiple-bond character. The Mo–N(3)–N(4) angle is 172.9° with the hydrazine bent slightly toward the terminal oxo ligand as previously found for $[MoO(NNMe_2)(C_9H_6NO)_2]$[32] where the Mo–N–N angle, 155.0°, is the smallest that has been found for a "linearly" bonded hydrazido(2–) ligand. The compound $[MoO(NNMe_2)S_2CNMe_2]$[4] with an Mo–N–N angle of 168.0° has the hydrazine ligand bent slightly away from the terminal oxo ligand. All bis(hydrazido(2–)molybdenum compounds have the hydrazido groups bent slightly toward each other with Mo–N–N angles in the range 168–179°.

The L ligand folds about the molybdenum in the anticipated manner such that the two sulfur donor atoms occupy relative trans positions. The Mo–S bond distances, Mo–S(1), 2.408 Å, and Mo–S(2), 2.478 Å, are nonequivalent, an effect previously noted for $[Mo_2O_3L_2]$ and related to the inherent strain of coordinated L and to the nonequivalence of Mo–N(amine) bond lengths. The two molybdenum–amine nitrogen bond distances are substantially different with Mo–N(1), 2.359 Å, and Mo–N(2), 2.464 Å. This difference is expected since N(1) occupies a position trans to the terminal oxo ligand while N(2) occupies a position trans to the more weakly bonded hydrazido ligand. In addition, the interent steric constraints imposed by the C–N–Mo–N–C chelate ring may be responsible for the distortion in the Mo–N bond distances.

The effect of the more strongly bonded oxo ligand is illustrated by the greater trans influence exerted by the oxo ligand relative to the hydrazido ligand in $[MoO(NNPh_2)(C_6H_9NO)_2]$.[32] Thus, the Mo–O(oxinate) distance trans to the oxo group in $[MoO(NNPh_2)(C_9H_6NO)_2]$ is lengthened to 2.123 Å compared to the unperturbed Mo–O(oxinate) distances of 2.019 Å in the same complex and of 1.98 Å in the parent species, $[MoO_2(C_9H_6NO)_2]$,[33] while a distance of 2.302 Å is observed for the Mo–N(oxinate) bond trans to the hydrazido group compared to the unperturbed Mo–N(oxinate) distance of 2.250 Å. Significant differences in the relative trans influence exerted by oxo and hydrazido ligands have also been reported for $[MoO(NNMe_2)(S_2CNMe_2)_2]$[4] where Mo–S distances of 2.720 and 2.576 Å are observed for sulfur donors trans to the oxo and hydrazido ligands, respectively. Some caution must be exercised in ascribing these distortions solely to the trans influence since the large steric hindrances between the donor atoms in complexes of this type and the deformation of the Mo–ligand angles from the ideal 90° also influence the Mo–ligand distances.

Structural parameters for molybdenum–hydrazido and molybdenum–diazendio complexes are compared in Table IX. The structural parameters for the Mo–N–N moiety are remarkably similar except for the complex $[MoO(N_2Me_2)(C_9H_6NO)_2]$ where significant bending of the Mo–N–N linkage is observed. The origin of this effect is discussed elsewhere.[32]

Electrochemical Studies. The complexes of which $[Mo(N_2C_6H_5)_2L]$ is typical undergo a pseudoreversible reduction as judged by cyclic voltammetry. Table X lists the electrochemical data for the diazenido complexes. At fast scan rates (2.0–0.3 V s^{-1}) the process conformed to the criteria for a

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(32) Dahlstrom, P. L.; Dilworth, J. R.; Zubieta, J., unpublished results.

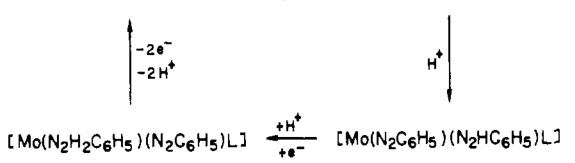
(33) Atovmyan, L. O.; Sokolova, Yu A. *J. Struct. Chem. (Engl. Transl.)* **1971**, *12*, 780–786.

Table X. Electrochemical Parameters for Molybdenum Diazenido Complexes

complex	$E_{1/2}^{\text{red}}$, V[b]	$\lvert E_p^{\text{red}} - E_p^{\text{ox}}\rvert$, mV	$i_p^{\text{ox}}/i_p^{\text{red}}$ [c]
[Mo($N_2C_6H_5$)$_2$L]	−1.40	87	0.9
[Mo(N_2-4-$C_6H_4OCH_3$)$_2$L]	−1.48	83	1.0
[Mo(N_2-4-C_6H_4Me)$_2$L]	−1.47	92	1.0
[Mo(N_2-4-$C_6H_4NO_2$)$_2$L]	−1.20	90	1.0
[Mo(N_2-4-C_6H_4Cl)$_2$L]	−1.32	84	1.0
[Mo(N_2-3-C_6H_4Me)$_2$L]	−1.40	85	1.0

[a] Cyclic voltammograms performed in 0.2 M [n-Bu_4N]PF_6/CH_2Cl_2 with 5×10^{-3} M complex at a Pt working electrode.
[b] Potentials vs. SCE and estimated from cyclic voltammetry from $E_{1/2}^{\text{red}} = (E_p^{\text{red}} + E_p^{\text{ox}})/2$. iR compensation was not employed.
[c] Peak current ratio $i_p^{\text{red}}/C\nu^{1/2}$ was similar to that observed for the ferrocene–ferrocenium couple at the same electrode at a 0.3 V s^{-1} scan rate.

pseudoreversible one-electron reduction. As the scan speed was decreased (0.2–0.01 V s^{-1}), the peak current ratio $i_p^{\text{ox}}/i_p^{\text{red}}$ deviated from unity, and the peak current function approached that for an overall two-electron reduction. These observations are consistent with the scheme



Under anaerobic conditions, reactions of H_2NNHPh with [MoO_2L] yield an intermediate complex analyzing for [Mo($N_2H_2C_6H_5$)($N_2C_6H_5$)L], whose solution properties are similar to those of the product of the electrolysis. That this is indeed an intermediate in the formation of the bis(diazenido) complexes is shown by the observation that exposure of solutions of the phenyl derivative [Mo($N_2H_2C_6H_5$)($N_2C_6H_5$)L] to air results in the formation of the bis(diazenido) complexes without further compounds being involved. Similar behavior has been observed for the related dithiocarbamate complexes [Mo(N_2Ar)$_2$(dtc)$_2$].[6]

Cyclic voltammograms recorded under the same conditions for the series of aryl-substituted complexes [Mo($N_2C_6H_4$X)$_2$L] showed similar behavior to that of the parent compound, that is, a pseudoreversible reduction in the −1.2 to −1.5 V range. If we assume that changes in solution-energy differences for the substituted series are negligible, then $E_{1/2}^{\text{red}}$ can be regarded as a measure of the energy of the LUMO of each complex. The primary reduction potentials show the expected trends: the more electron withdrawing the substituent the more positive is the reduction potential, suggesting stabilization of the LUMO. The detailed pattern emerges from the correlation of $E_{1/2}^{\text{red}}$ with σ_p indicating that there is restricted resonance stabilization of the anionic species by delocalization of charge from the aromatic ring into the diazenido nitrogens and that the influence of the substituent is essentially inductive. The structure of [Mo($N_2C_6H_4OCH_3$)$_2$L] shows that the aryl ring is twisted out of the Mo–N–N–C plane by ~10°, which demonstrates that π delocalization extending from the ring to the metal is hindered.

Concluding Remarks. The hydrazido(2−) and diazenido complexes of molybdenum with the tetradentate ligand L are sterically strained, in common with other complexes of this ligand studied to date.

The reaction of substituted hydrazines with [MoO_2L] to yield discrete, well-behaved complexes suggests that the condensation-type reaction between hydrazines and *cis*-dioxomolybdates is a general one. The nature of the product is dependent upon the nature both of the substituted hydrazine and of the coligands, as illustrated in this and previous papers.[1] Further studies of the reactivity of molybdenum–hydrazido(2−) and –diazenido complexes are in progress.

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Registry No. MoO(N_2Ph_2)L, 80228-57-5; Mo($N_2C_6H_4OCH_3$)$_2$L, 80228-56-4; Mo($N_2C_6H_5$)$_2$L, 80228-55-3; Mo(N_2-4-C_6H_4Me)$_2$L, 80228-54-2; Mo(N_2-4-$C_6H_4NO_2$)$_2$L, 80228-53-1; Mo(N_2-4-C_6H_4Cl)$_2$L, 80228-52-0; Mo(N_2-3-C_6H_4Me)$_2$L, 80228-51-9.

Supplementary Material Available: Listings of observed and calculated structure factors and calculated hydrogen atom positions (26 pages). Ordering information is given on any current masthead page.