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Chemistry of Polydentate Thiolate–Amine Complexes of Molybdenum with Organosubstituted Hydrazines. Synthesis and Structural Characterization of the Six-coordinate Bis-phenyldiazenido Complex, $[Mo(N_2C_6H_5)_2\{(SCH_2CH_2)_2NCH_2CH_2N(CH_3)_2\}]$, and of the Five-coordinate Hydrazido(2–) Complex, $[MoO(NNMePh)\{(SCH_2CH_2)_2NCH_2CH_2N(CH_3)_2\}]$

SHAHID N. SHAIKH and JON ZUBIETA*

Department of Chemistry, State University of New York at Albany, Albany, N.Y. 12222, U.S.A.

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The chemistry of molybdenum with sulfur-containing ligands is of some contemporary interest in view of the potential relationship to bioinorganic chemistry [1] and to general catalysis [2]. The interactions of complexes possessing a molybdenum–thiolate core with organohydrazine have received attention as models for intermediates in the protonation of coordinated dinitrogen [3]. Although the reaction chemistry of molybdenum-oxo precursors with organosubstituted hydrazines generally proceeds via a simple condensation reaction, eqn. (1), the

$$MoO_2L_4 + 2H_2NNRR' \longrightarrow Mo(NNRR')_2L_4 + 2H_2O \qquad (1)$$

products of the reaction are not always readily predicted and may depend critically on both the nature of hydrazine substituents and the identity of the coligands, L [4–6]. Since sterically-demanding ligands have been shown to influence profoundly the geometries and reactivities of oxo-molybdenum precursors [7], we sought to investigate the chemistry of organosubstituted hydrazine derivatives with the dioxo-molybdenum(VI) core ligated to a sterically constraining ligand, *N,N*-bis(mercaptoethyl)-*N,N'*-dimethylethylenediamine. In this paper, we report the structures of the bis(phenyldiazenido) derivative, $[Mo(NNPh)_2L]$, and the unusual pseudo-trigonal bipyramidal species, $[MoO(NNMePh)L]$, $L = [(SCH_2CH)_2NCH_2CH_2N(Me)_2]^{2-}$.

Reaction of $[MoO_2L]$ [7] in methanol with excess phenylhydrazine yields microcrystals of the purple $[Mo(NNPh)_2L]$. Recrystallization from DMF/MeOH affords suitable crystals. The infrared bands at 1618 cm^{-1} and 1605 cm^{-1}, attributed to asymmetric and symmetric ν_{N-N}, confirmed the presence of the bisdiazenido-unit, $[Mo(NNC_6H_5)_2]^{2+}$, while the absence of bands of significant intensity in the 850–1000 cm^{-1} region was consistent with the absence of the terminal oxo-units.

Crystal Data [Mo(NNPh)₂L] (1)

$M = 512.4$; orthorhombic space group $P2_12_12_1$, $a = 8.572(2)$, $b = 12.535(3)$, $c = 21.175(3)$ Å, $V = 2275.3(6)$ Å^3, to give $D_c = 1.49$ g cm^{-3} for $Z = 4$. The structure solution and refinement were based on 1236 unique reflections with $I_o \geqslant 3\sigma(I_o)$ to give a final R value of 0.063.

In a similar fashion, reaction of $[MoO_2L]$ with two equivalents of $H_2NNMePh$ yields bright yellow crystals, analyzing for $[MoO(NNMePh)L]$. Characteristic infrared bands at 1595 cm^{-1} and 902 cm^{-1}, assigned to ν_{N-N} and ν_{Mo-O}, respectively, confirmed the presence of the oxo-hydrazido–molybdenum unit $[MoO(NNMePh)]^{2+}$.

Crystal Data [MoO(NNMePh)L] (2)

$M = 438.3$; monoclinic space group $P2_1/c$, $a = 13.515(2)$, $b = 8.427(2)$, $c = 17.403(3)$ Å, $\beta = 97.35(1)°$, $V = 1965.7(8)$ Å^3, $Z = 4$ to give $D_c = 1.48$ g cm^{-3}. The structure solution and refinement were based on 1609 reflections with $I_o \geqslant 3\sigma(I_o)$ to give a residual of 0.053.

The structure of $[Mo(NNPh)_2L]$ (**1**) is shown in Fig. 1, while that of $[MoO(NNMePh)L]$ (**2**) is displayed in Fig. 2, both with relevant bond lengths and angles. The overall geometry about the molybdenum in **1** is pseudooctahedral with *trans* thiolate ligands. The diazenido ligands are mutually *cis*, with the amine nitrogen donors occupying positions *trans* to these π-bonding ligands. The bond lengths in the $[Mo(NNPh)_2]^{2+}$ unit lie within the normal range (Mo–N, 1.85(2) Å (average); N–N, 1.23(2) Å (average)). The linearity of the Mo–N–N units is consistent with extensively delocalized multiple bonding throughout the grouping and with the function of the phenyldiazo-groups as three-electron donors to the metal. The considerable *trans* influence of the diazenido-groups is apparent in the long Mo–amine nitrogen distances, Mo–N(5), 2.27(2) Å and Mo–N(6), 2.36(2) Å. The significant lengthening of the Mo–N(6) bond distance is in part attributable to the steric bulk of the methyl substituents. Although complexes containing two diazenido ligands were considered relatively rare [8], it does appear that in the chemistry of molybdenum–dioxo complexes, substitution of the bis-diazenido unit for the *cis*-dioxo groups is the consistent pattern of substitution [9].

The structure of **2** contrasts dramatically with that described for **1**. In this instance, the molybdenum enjoys pseudotrigonal bipyramidal geometry, as determined by a Muetterties–Guggenberger analysis [10], with the thiolate sulfur donors and the oxo-group defining the equatorial plane and N(2) of the hydrazido ligand and the amine donor N(1) occupying the axial positions. The most unusual

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*Author to whom correspondence should be addressed.

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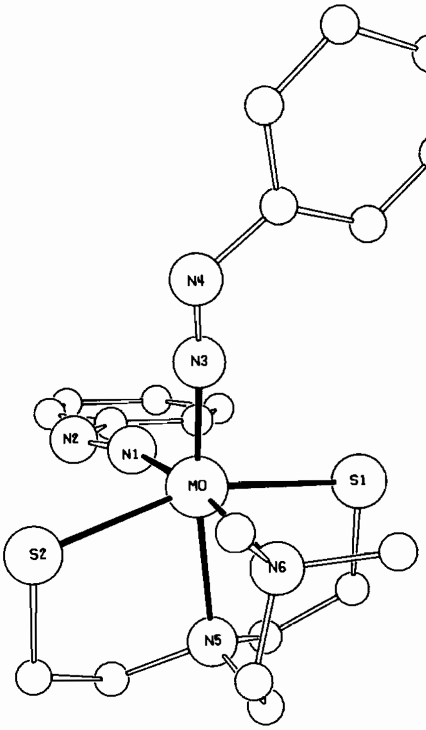

Fig. 1. ORTEP view of the structure of $[Mo(NNC_6H_5)_2\{(SCH_2CH_2)_2NCH_2CH_2N(CH_3)_2\}]$, **1**, showing the atom-labelling scheme. Selected bond lengths (Å) and angles (°): Mo–S(1), 2.456(6); Mo–S2, 2.486(7); Mo–N(1), 1.88(2); Mo–N(3), 1.82(2); Mo–N(5), 2.27(2); Mo–N(6), 2.36(2); N(1)–N(2), 1.23(2); N(3)–N(4), 1.22(2); S(1)–Mo–S(2), 160.8(2); N(1)–Mo–N(6), 170.1(7); N(3)–Mo–N(5), 170.5(7); Mo–N(1)–N(2), 162.7(15); Mo–N(3)–N(4), 173.0(15).

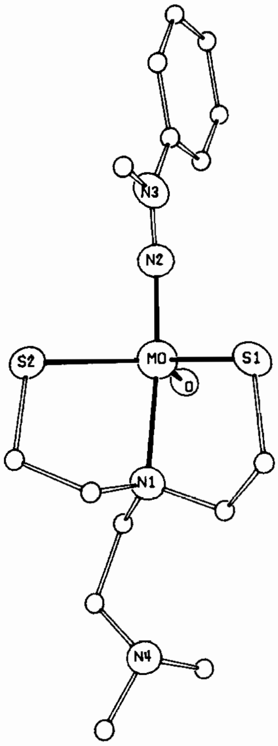

Fig. 2. ORTEP view of the structure of $[MoO(NNMePh)\{(SCH_2CH_2)_2NCH_2CH_2N(CH_3)_2\}]$, **2**, showing the atom-labelling scheme. Selected bond lengths (Å) and angles (°): Mo–S(1), 2.325(3); Mo–S(2), 2.382(3); Mo–O, 1.714(6); Mo–N(1), 2.285(8); Mo–N(2), 1.787(8); N(2)–N(3), 1.30(1); S(1)–Mo–S(2), 120.5(1); S(1)–Mo–O, 116.4(3); S(2)–Mo–O, 120.7(3); N(1)–Mo–N(2), 162.3(3); Mo–N(2)–N(3), 164.8(7).

feature of the structure is the uncoordinated amine nitrogen N(4). The Mo–N(2) and N(2)–N(3) bond distances, 1.787(8) Å and 1.30(1) Å, and the linearity of the Mo–N(2)–N(3) valence angle are consistent with the formal assignment of the ligand as a four-electron donating hydrazido(2–) group. Hence, for the amine nitrogen N(4) to coordinate, a 20-electron count would be imposed on the metal. It appears that the unusual 'dangling' amine group is a consequence of the electronic structure of the complex rather than any steric constraints imposed by the methyl substituents. The structure of the bis-diazenido species, **1**, demonstrates that the tripodal ligand may function as a tetradentate while accommodating two diazenido-substituents. On steric grounds alone, there is no reason to anticipate that the ligand should not function likewise in the presence of an oxo- and a hydrazido group, since the $[MoO(NNMePh)]^{2+}$ unit is no more sterically-demanding than the $[Mo(NNPh)_2]^{2+}$ grouping.

Although **2** is isoelectronic with $[MoO(NNMe_2)(SPh)_3]^{1-}$ [11], the latter species exhibits geometry approaching the square pyramidal limit, with the oxo-group in the apical position. On the other hand, the complex $[MoO(NNMe_2)(SCH_2CH_2SCH_2CH_2S)]$ and related species [12] displays an intermediate geometry between the trigonal bipyramidal and square pyramidal limits. The details of the five-coordinate geometries assumed by this latter class of complexes are dictated by ligand constraints, rather than electronic effects. A detailed structural analysis will appear in a subsequent publication.

References

1 J. T. Spence, *Coord. Chem. Rev., 48,* 59 (1983).
2 'Chem. Uses Molybdenum, Proc. 5th Int. Conf., Newcastle, U.K., 1985', Polyhedron Symposia in Print, 1986.
3 J. Chatt, A. J. Pearman and R. L. Richards, *J. Chem. Soc., Dalton Trans.,* 2139 (1977).
4 C. Pickett, S. Kumar, P. A. Vella and J. Zubieta, *Inorg. Chem., 21,* 908 (1982).
5 P. L. Dahlstrom, J. R. Dilworth, P. Shulman and J. Zubieta, *Inorg. Chem., 21,* 933 (1982).
6 M. D. FitzRoy, J. M. Frederiksen, K. S. Murray and M. R. Snow, *Inorg. Chem., 24,* 3265 (1985).
7 E. I. Stiefel, K. F. Miller, A. E. Bruce, J. Heinecke, N.

Pariyadath, J. L. Corbin, J. M. Berg and K. O. Hodgson, in W. E. Newton and S. Otsuka (eds.), 'Molybdenum Chemistry of Biological Significance', Plenum, New York, 1980, p. 279.
8 J. R. Dilworth, S. A. Harrison, D. R. M. Walton and E. Schweda, *Inorg. Chem., 24,* 2594 (1985).
9 T.-C. Hsieh and J. Zubieta, *Inorg. Chem., 24,* 1287 (1985); T.-C. Hsieh and J. Zubieta, *J. Chem. Soc., Chem. Commun.,* (1985) in press; T.-C. Hsieh and J Zubieta, *Polyhedron,* (1986) in press.
10 E. L. Muetterties and L. J. Guggenberger, *J. Am. Chem. Soc., 96,* 1748 (1974).
11 R. J. Burt, J. R. Dilworth, G. J. Leigh and J. Zubieta, *J. Chem. Soc., Dalton Trans.,* 2295 (1982).
12 J. R. Dilworth, J. Hutchinson, L. Throop and J. Zubieta, *Inorg. Chim. Acta, 79,* 208 (1983).