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Synthesis and Structural Characterization of a Binuclear Molybdenum–Hydrazido(2–) Complex, $[Mo_2O_4(NNPh_2)\{(CH_3)_2NCH_2CH_2NHCH_2CH_2S\}_2]$

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The chemistry of complexes possessing a molybdenum–thiolate core with organohydrazine ligands provides analogies for intermediates in the protonation of coordinated dinitrogen [1]. Although exploitation of the condensation-type reaction between disubstituted organohydrazines, H_2NNRR', and molybdenum–oxo precursors allows a facile synthetic methodology for the isolation of a variety of molybdenum–hydrazido(2–) complexes, the products of these reactions depend critically upon the nature of the hydrazine substituents, reaction solvent, and the identity of the coligands [2–5]. We recently demonstrated that sterically-demanding coligands, such as *N*,*N*-bis(mercaptoethyl)-*N'*,*N'*-dimethylethylenediamine $[(SCH_2CH_2)_2NCH_2CH_2NMe_2]^{2-}$, may profoundly influence the coordination geometries of organosubstituted hydrazine derivatives prepared from precursors with the dioxomolybdenum core [5]. Extension of these investigations to reactions of organohydrazine derivatives with tridentate thiolate amine complexes of oxomolybdenum(VI) yielded the unanticipated binuclear complex $[Mo_2O_4(NNPh_2)\{(CH_3)_2NCH_2CH_2NHCH_2CH_2S\}_2]$, (I). Although mononuclear oxohydrazidomolybdenum(VI) complexes are quite common [6], there have been no reports of structurally confirmed examples of binuclear oxohydrazidomolybdenum species. In contrast, binuclear Mo(V) complexes containing the related diazenido ligand, –NNR, have been identified [7].

The reaction of $[Mo_2O_5\{(CH_3)_2NCH_2CH_2NHCH_2CH_2S\}_2]$ [8] in methanol/methylene chloride (1:1, *v*/*v*) with excess H_2NNPh_2, followed by addition of anhydrous ether and storage at 5 °C for three weeks, yields large pale yellow crystals of I†. The infrared spectrum displayed a strong band at 1582 cm^{-1} attributed to ν(N–N) of the coordinated hydrazido ligand. The pattern of medium and strong bands in the 700–900 cm^{-1} region is characteristic of the presence of both terminal and bridging oxo groups. Crystal data: monoclinic space group, $P2_1/a$ with a = 10.867(3), b = 14.932(3), c = 18.715(3) Å, β = 100.41(1)°, V = 2986.8(10) $Å^3$, D_{calc} = 1.63 g cm^{-3}, for Z = 4. The structure solution and refinement were based on 3147 reflections (345 parameters) with $F_o \geqslant 3\sigma(F_o)$ to give a final R value of 0.032.

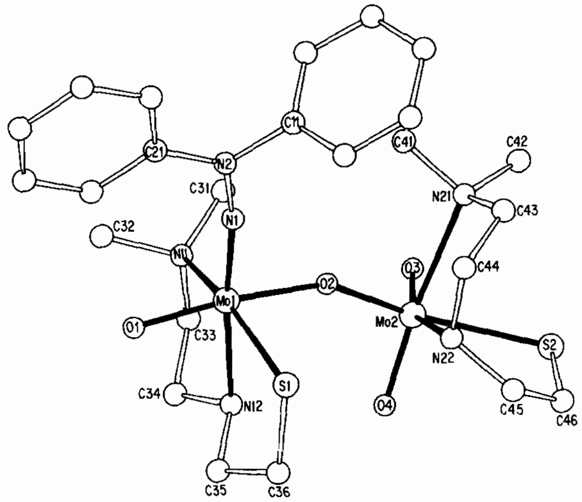

Fig. 1. ORTEP view of the structure of $[Mo_2O_4(NNPh_2)\{(CH_3)_2NCH_2CH_2NHCH_2CH_2S\}_2]$, showing the atom-labelling scheme. Selected bond lengths (Å) and angles (°): Mo1–S1, 2.411(1); Mo1–O1, 1.72(3); Mo1–O2, 2.077(3); Mo1–N1, 1.808(4); Mo1–N11, 2.305(4); Mo1–N12, 2.256(4); Mo2–S2, 2.516(1); Mo2–O2, 1.848(3); Mo2–O3, 1.711(3); Mo2–O4, 1.722(4); Mo2–N21, 2.507(4); Mo2–N22, 2.337(4); N1–N2, 1.314(5); O1–Mo1–O2, 157.5(1); O1–Mo1–N1, 101.8(2); S1–Mo1–N11, 158.9(1); N1–Mo1–N12, 174.5(2); S2–Mo2–O2, 154.5(1); O2–Mo2–O3, 105.7(1); O4–Mo2–N21, 169.3(2); O2–Mo2–N22, 81.1(2); Mo1–N1–N2, 169.3(3); Mo1–O2–Mo2, 154.0(2).

The structure of I is shown in Fig. 1, while selected bond lengths and angles are presented in the caption. As illustrated by Fig. 1, the discrete binuclear molecules of I possess C_1 symmetry as a consequence of the substitution of a single oxo group of one molybdenum center by a hydrazido(2–) ligand. The consequences of this unsymmetrical substitution pattern are evident in a number of unusual structural features. While Mo1 displays $[MoN_3O_2S]$ coordination geometry, Mo2 exhibits $[MoN_2O_3S]$ geometry, essentially identical to that of the parent complex $[Mo_2O_5\{(CH_3)_2NCH_2CH_2NHCH_2CH_2S\}_2]$.

The coordination geometry about Mo1 is considerably distorted from the octahedral limit as a consequence of bonding to the two chemically distinct amine donors and the thiolate donor of the tridentate ligand, to a single terminal oxo group, to a bridging oxo group, and to the α-nitrogen of the hydrazido(2–) ligand. A unique feature of the structure is the location of the terminal oxo group O1 *trans* to the bridging oxo group O2, as a consequence

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†*Anal.* Calc. for $C_{24}H_{40}Mo_2N_6O_4$: C, 39.38; H, 5.78; N, 11.48. Found: C, 39.68; H, 5.76; N, 11.35%.

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of which the Mo1–O2 distance is unusually long at 2.077(3) Å, as compared to the more normal Mo-bridging oxo group distance of 1.848(3) Å for Mo2–O2. The coordination sphere of Mo1 must accommodate four strongly π-bonding ligands: thiolate sulfur, the terminal and bridging oxo groups and the hydrazido unit, while satisfying the considerable steric demands of the dimethyl substituted amine donor and the diphenylhydrazine. This combination of steric and electronic effects results in the unique disposition of oxo groups.

The non-equivalence of related bond distances about the Mo centers reflects the relatvie dispositions of ligand groups. Thus, while the Mo1–S1 distance is 2.411(1) Å, the Mo2–S2 distance is 0.105 Å longer as a consequence of the *trans* influence of the bridging O2. Likewise, the Mo1–N11 bond distance of 2.305(4) Å may be compared to the Mo1–N22 distance of 2.507(4) Å, which is under the influence of a terminal oxo group O3. Although the Mo2–N21 bond length is significantly longer than the corresponding Mo1–N11 distance, the latter is still *ca.* 0.10 Å longer than that anticipated for a Mo–N single bond. This observation suggests that the hydrazido(2–) group exerts a non-negligible *trans* influence, although obviously an effect much less significant than that associated with *trans* oxo groups.

Although a symmetrically substituted binuclear complex $[\{MoO(NNR_2)(Me_2NCH_2CH_2NHCH_2CH_2S)\}_2(\mu\text{-}O)]$ might be the anticipated product of the reaction, we have found no evidence for its formation under any reaction conditions. The isolation of **I** as the unique hydrazido-containing product of the reaction argues that the structure adopted by **I** results from the steric constraints imposed by the tridentate ligand and the phenyl substituents of the hydrazido group and that these steric considerations are dominant in preventing successive substitution of oxo groups.

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