

## A Triply-bridged Binuclear Hydrazidomolybdenum(v) Complex with Terminal, Bridging, and 'Dangling' Thiolate Ligands. The Chemical and Structural Characterization of $[\text{HNET}_3]_2[\text{Mo}_2(\text{NNPh})(\text{NNHPh})(\text{SCH}_2\text{CH}_2\text{S})_3(\text{SCH}_2\text{CH}_2\text{SH})] \cdot 2/3\text{H}_2\text{NNHPh}$

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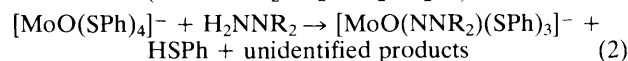
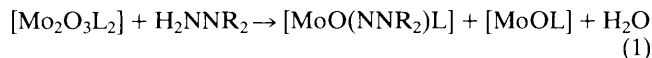
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The title compound has been obtained by treating  $[\text{Mo}(\text{NNHPh})_2(\text{butane-2,3-diolate})_2] \cdot \text{H}_2\text{NNHPh}$  with excess of dimercaptoethane in methanol; X-ray crystallography reveals the first example of a binuclear bis-hydrazido complex and a unique instance of a molybdenum(v) complex exhibiting thiolate co-ordination *trans* to a strongly  $\pi$ -bonding group.

Extended X-ray absorption fine structure (EXAFS) studies have implicated sulphur ligation as the primary co-ordination mode for molybdenum in nitrogenase and other molybdoenzymes.<sup>1</sup> However, there are few examples of molybdenum-sulphur complexes which interact with small molecules that function as nitrogenase inhibitors or alternative substrates.

Hydrazido(2-) complexes are intermediates in the protonation of co-ordinated dinitrogen<sup>2</sup> and have been extensively investigated as probes for the properties of sulphur-ligated molybdenum.<sup>3</sup> The pattern of reactivity of disubstituted hydrazines with molybdenum-thiolates is complex, with reaction generally proceeding *via* a simple condensation reaction at bound oxo-centres [equation (1)]<sup>4</sup> but occasionally involving the thiolate-sulphur sites themselves [equation (2)].<sup>5</sup>

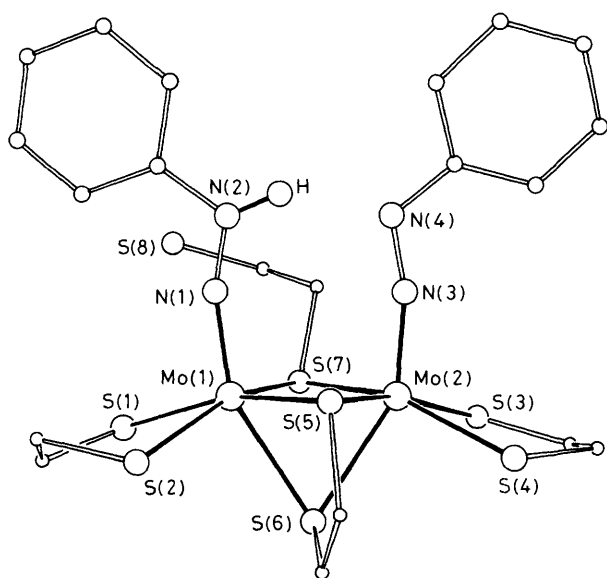
Attempts to investigate the substitution chemistries of complexes of chelating dithiolates such as  $[\text{MoO}(\text{SCH}_2\text{CH}_2\text{S})_2]^-$  have been frustrated by dealkylation



and dimerization reactions, producing  $[\text{Mo}_2\text{S}_4(\text{SCH}_2\text{CH}_2\text{S})_2]^{2-}$  and analogous species.

In an effort to circumvent these problems the complex  $[\text{Mo}(\text{NNHPh})_2(\text{butane-2,3-diolate})_2] \cdot \text{H}_2\text{NNHPh}^\dagger$  was synthesized from  $[\text{MoO}_2(\text{butane-2,3-diolate})_2] \cdot 2\text{butane-2,3-diol}$  and the parent hydrazine. Treatment of this material with excess of 1,2-dimercaptoethane in methanol yielded a bright red crystalline material analysing for  $(\text{Et}_3\text{NH})-$

<sup>†</sup> Satisfactory analytical data were obtained.



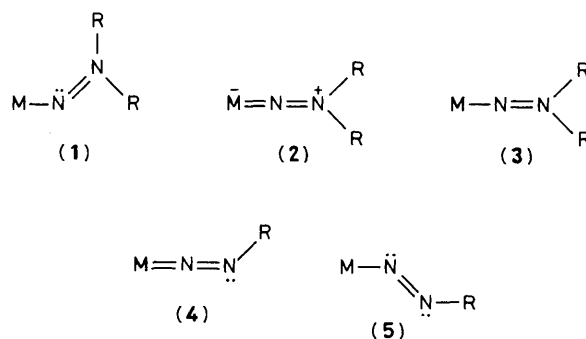
**Figure 1.** ORTEP representation of  $[\text{Mo}_2(\text{NNHPH})(\text{NNPh})(\text{SCH}_2\text{CH}_2\text{S})_3(\text{SCH}_2\text{CH}_2\text{SH})]^{2-}$  showing the atom labelling scheme. Selected bond lengths (Å) and angles ( $^\circ$ ): Mo(1)–Mo(2) 2.837(2), Mo(1)–S(1) 2.485(6), Mo(1)–S(2) 2.483(5), Mo(1)–S(5) 2.426(5), Mo(1)–S(6) 2.582(5), Mo(1)–S(7) 2.446(5), Mo(1)–N(1) 1.793(6), Mo(2)–S(3) 2.516(6), Mo(2)–S(4) 2.435(5), Mo(1)–S(5) 2.422(5), Mo(2)–S(6) 2.572(6), Mo(2)–S(7) 2.436(5), Mo(2)–N(3) 1.740(7), N(1)–N(2) 1.29(2), N(3)–N(4) 1.35(2); S(1)–Mo(1)–S(2) 81.4(2), S(1)–Mo(1)–S(5) 162.0(1), S(2)–Mo(1)–S(6) 98.8(2), S(1)–Mo(1)–S(7) 84.2(2), S(1)–Mo(1)–N(1) 101.2(1), S(2)–Mo(1)–S(5) 82.8(2), S(2)–Mo(1)–S(6) 94.9(2), S(2)–Mo(1)–S(7) 158.7(2), S(2)–Mo(1)–N(1) 101.7(1), S(5)–Mo(1)–S(6) 94.9(2), S(2)–Mo(1)–S(7) 158.7(2), S(2)–Mo(1)–N(1) 101.7(1), S(5)–Mo(1)–S(6) 74.1(2), S(5)–Mo(1)–S(7) 108.4(2), S(5)–Mo(1)–N(1) 90.3(1), S(6)–Mo(1)–S(7) 71.8(1), S(6)–Mo(1)–N(1) 155.6(1), S(7)–Mo(1)–N(1) 96.4(1), S(3)–Mo(2)–S(4) 82.2(2), S(3)–Mo(2)–S(5) 165.5(2), S(3)–Mo(2)–S(6) 101.4(2), S(3)–Mo(2)–S(7) 82.5(2), S(3)–Mo(2)–N(3) 102.3(2), S(4)–Mo(2)–S(6) 74.3(2), S(5)–Mo(2)–S(7) 108.7(2), S(5)–Mo(2)–N(3) 86.5(1), S(6)–Mo(2)–N(3) 94.0(1), Mo(1)–N(1)–N(2) 161.1(7), Mo(2)–N(3)–N(4) 162.2(6).

$[\text{Mo}(\text{NNHPH})(\text{SCH}_2\text{CH}_2\text{S})_2] \cdot 1/3\text{H}_2\text{NNHPH}^\ddagger$  and behaving as a 1 : 2 electrolyte. X-Ray crystallographic analysis revealed the title formulation and the unusual binuclear nature of this product.

**Crystal data:**  $\text{C}_{32}\text{H}_{60}\text{Mo}_2\text{N}_6\text{S}_8 \cdot 2/3\text{H}_2\text{NNHC}_6\text{H}_5$ ,  $M = 1048$ , triclinic, space group  $P1$ ,  $a = 10.224(2)$ ,  $b = 10.874(3)$ ,  $c = 35.942(8)$  Å,  $\alpha = 86.59(1)$ ,  $\beta = 88.79(1)$ ,  $\gamma = 61.96(1)^\circ$ ;  $U = 3520.5(10)$  Å<sup>3</sup>,  $Z = 3$ , based on title formulation, to give  $D_c = 1.48$  g cm<sup>-3</sup> [ $D_o = 1.46(1)$  g cm<sup>-3</sup>, flotation], 5699 reflections were used of 6219 collected (Mo- $K_\alpha$  radiation, final  $R$  value 6.2%, error of fit 1.53).§ The structure of one of three crystallographically unique anions is shown in Figure 1, together with the relevant bond lengths and angles. The complex anion is binuclear with equivalent pseudo-octahedral molybdenum atoms sharing a common face defined by three bridging thiolate donors. The co-ordination about each

‡ Satisfactory analytical data were obtained for the title compound. I.r.: strong vibrations in the 1550–1650 cm<sup>-1</sup> region due to co-ordinated hydrazido(2-) and phenyldiazenido groups.

§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



molybdenum atom is completed by the thiolate sulphur atoms of the terminal chelating dimercaptoethane ligands and by the nitrogen donor N(1) of the  $\sigma$ -hydrazido ligands.

An unusual feature of the structure is the presence of three structurally distinct types of dimercaptoethane ligands: two terminally co-ordinating chelating groups, a doubly bridging ligand, and a dimercaptoethane group bridging through a single thiolate donor and, hence, presenting a free thiol function, a situation reminiscent of the structure of  $(\text{Pr}_3\text{NH})[\text{Mo}_2\text{O}_2(\text{SCH}_2\text{CH}_2\text{O})_3(\text{SCH}_2\text{CH}_2\text{OH})]^{6-}$ .

A unique feature of the structure is the occupancy of a co-ordination site *trans* to the strongly multiply bonded hydrazido ligands by the bridging thiolate S(6). As a consequence, the Mo–S(6) distances, 2.577(8) Å (av.), are significantly elongated, as compared to the average of all other Mo–S distances in the binuclear unit, 2.457(8) Å. Strongly  $\sigma$ - and  $\pi$ -donating thiolate groups and terminal hydrazido or terminal oxo-groups occupying a S–Mo–N(O) axis are in competition for the same set of metal *p*- and *d*-orbitals, an orientation that has been considered electronically unfavourable.<sup>7</sup>

A further consequence of this competition for the metal *d*-orbitals by the mercapto-sulphur and the hydrazido-nitrogen is shown by the orientation of the NNHPH groups. Although they are bound in the usual approximately linear, end-on fashion with Mo–N–N averaging 161.7°, the NNHPH planes are rotated *ca.* 27° from the eclipsing conformation relative to the S(1)–Mo(1)–S(5) and the S(4)–Mo(2)–S(7) vector projections. This orientation is intermediate between the fully eclipsed orientation of mononuclear  $\text{NNR}_2$  complexes where metal–hydrazido bonding is maximized<sup>8</sup> and the 40° orientation that bisects the bond angles in the tetragonal plane found for the trinuclear  $[\text{Mo}_2\text{S}_8(\text{NNMe}_2)]^{2-}$  species,<sup>9</sup> where there is no net overlap of the Mo  $t_{2g}$ -type orbitals with the nitrogen *p*-orbitals. The metal–hydrazido grouping is apparently stabilized by hydrogen bonding between the terminal hydrazido(2-) nitrogen N(2) and the terminal phenyldiazenido nitrogen N(4), as illustrated in Figure 1. As a consequence, the  $\text{Mo}_2(\text{NNPh})(\text{NNHPH})$  grouping is planar, presenting a seven-membered ring Mo(1)–N(1)–N(2)–H...N(4)–N(3)–Mo(2), and there is a considerable distortion from linearity of the Mo–N–N moieties so as to bend the terminal –NPh and –NHPH groupings toward each other. The nitrogenous fragments, –NNHR and –NNR, may be considered in a formal sense to behave as hydrazido(2-) and hydrazido(3-) functionalities, respectively, and hence as four- and three-electron donors, although the –NNR grouping is conventionally treated as a cationic three electron donor, the organodiazo ligand.<sup>10</sup> Regardless of the formalism employed, the hydrazido(2-) geometry is consistent with considerable contributions from canonical forms (2) and (3), while the phenyldiazo group displays essentially the singly bent form (4) with the lone pair directed toward the

hydrazido-hydrogen. The bent hydrazido(2-) geometry (1) and 'doubly-bent' diazenido structure (5) appear to make no significant contributions to the overall geometries.

As anticipated from the structural studies, the unidentate thiol may be alkylated at the free thiol function to give a species with an unco-ordinated sulphide moiety. Attempts to protonate the co-ordinated hydrazido ligands result in a complex mixture of products, presumably as a result of competition by the mercapto-sulphur groups as protonation sites or disruption of the hydrogen-bonding framework.

The isolation of the title complex suggested that monomeric arylthiols would yield complexes of the type  $[\text{Mo}_2(\text{NNR})(\text{NNHR})(\text{SAr})_7]^{2-}$ . Attempts to synthesize these species have yielded complexes analysing for  $[\text{Mo}_2(\text{NNR})(\text{NNHR})(\text{SAr})_6(\text{OMe})]^{2-}$ , R = Ph and Ar = Ph or *p*-C<sub>6</sub>H<sub>4</sub>Me, when carried out in methanol and for  $[\text{Mo}_2(\text{NNR})(\text{NNHR})(\text{SAr})_7]^{2-}$ , Ar = *p*-C<sub>6</sub>H<sub>4</sub>Me, when carried out in tetrahydrofuran.

The study confirms the remarkable versatility of the triply-bridged co-ordination mode in stabilizing binuclear Mo<sup>V</sup>-complexes.<sup>11</sup> Furthermore, the flexibility of co-ordination modes adopted by the hydrazido ligand is illustrated by the initial observation of thiolate-sulphur co-ordination *trans* to a normally strongly  $\pi$ -bonding ligand.

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