An Asymmetric Triply-bridged MoV Complex with Bridging Azido-ligand. The Structures of $[Mo_2O_2(\mu\text{-}N_3)\{S(CH_2)_3S\}_3]^-$ and its Precursor $[MoO\{S(CH_2)_3S\}_2]^-$

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The complex $[MoO(SCH_2CH_2CH_2S)_2]^-$ reacts with HN_3 in methanol to give $[Mo_2O_2(\mu\text{-}N_3)(SCH_2CH_2CH_2S)_3]^-$; *X*-ray crystallography shows the former anion to have tetragonal pyramidal co-ordination about Mo with an apical oxo-group and the latter to be an asymmetric dinuclear complex with a triple bridge comprising two dithiolate sulphurs and a bent azide group linking two distinct pseudo-octahedral molybdenums.

The implication from extended *X*-ray absorption fine structure (EXAFS) studies that the molybdenum in nitrogenase is predominantly ligated by sulphur has dramatically stimulated research in molybdenum complexes with sulphur ligands. However the majority do not interact with dinitrogen or any of the nitrogenase inhibitors or alternative substrates.

We here report our attempts to introduce the nitrogenase substrate azide ion onto a sulphur ligated molybdenum. The complex $[MoO(SPh)_4]^{-1}$ is inert to both azide ion and HN_3 and we prepared the analogues with dithiolate-ligands in the hope they would be more reactive.

$[PPh_4][MoO(SCH_2CH_2CH_2S)_2]$
(1)

$[PPh_4][Mo_2O_2(\mu\text{-}N_3)(SCH_2CH_2CH_2S)_3]$
(2)

Dark blue-green crystals of (1) were obtained as a PPh_4 salt from treatment of $[MoO_2(MeCHOHCHOMe)_2].2MeCHOHCHOHMe$[2] with propane-1,3-dithiol in methanol and addition of $[PPh_4]Br$. *Crystal data:* monoclinic, space group $P2_1/n$, $a = 9.612(2)$, $b = 21.022(4)$, $c = 15.462(3)$ Å, $\beta = 103.06(1)°$, $U = 3043.3$ Å^3, $Z = 4$, 3687 reflections were collected, of which 1957 were used (Mo-K_α radiation, final R value 5.8%).† The structure of the anion is shown in Figure 1 and reveals a tetragonal pyramidal geometry about Mo very similar to that in $[MoO(SPh)_4]^-$,[3] suggesting that the bite of the chelate ligand has little influence on the disposition of the sulphur atoms. The Mo–S average distance of 2.389(3) Å is also very close to the value of 2.403(4) Å found in the aryl thiolate complex indicating a small structural thiolate substituent effect. Cyclic voltammetry of (1) in MeCN on Pt with $[Bu^n_4N][BF_4]$ as support electrolyte revealed a reversible reduction at -1.18 V *vs.* saturated calomel electrode. This compares with a reduction potential of -1.13 V under similar conditions for $[MoO(SPh)_4]^-$.[4]

Complex (1) reacts rapidly with HN_3 in methanol (generated *in situ* from Me_3SiN_3) to give $[Mo_2O_2(\mu\text{-}N_3)(SCH_2CH_2CH_2S)_3]^-$

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

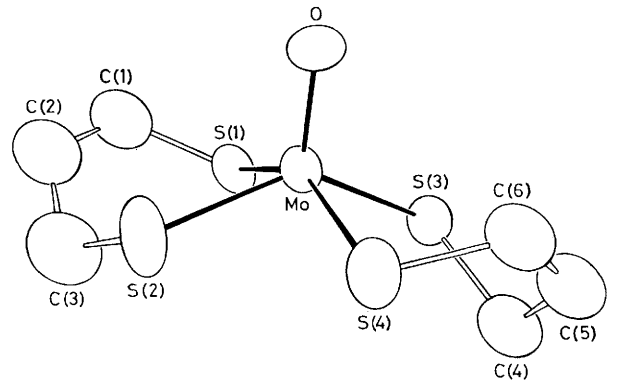

Figure 1. ORTEP representation of $[MoO(SCH_2CH_2CH_2S)_2]^-$ showing atom labelling scheme. Selected bond lengths (Å) and angles(°): Mo–O, 1.667(8); Mo–S(1), 2.398(3); Mo–S(2), 2.376(3); Mo–S(3), 2.387(3); Mo–S(4), 2.393(4); ∠S(1)–Mo–S(2), 89.0(1); ∠S(1)–Mo–S(3), 80.1(1); ∠S(2)–Mo–S(4), 80.3(1); ∠S(3)–Mo–S(4), 88.2(1); ∠S(1)–Mo–S(4), 147.9(1); ∠S(2)–Mo–S(3), 138.8(1).

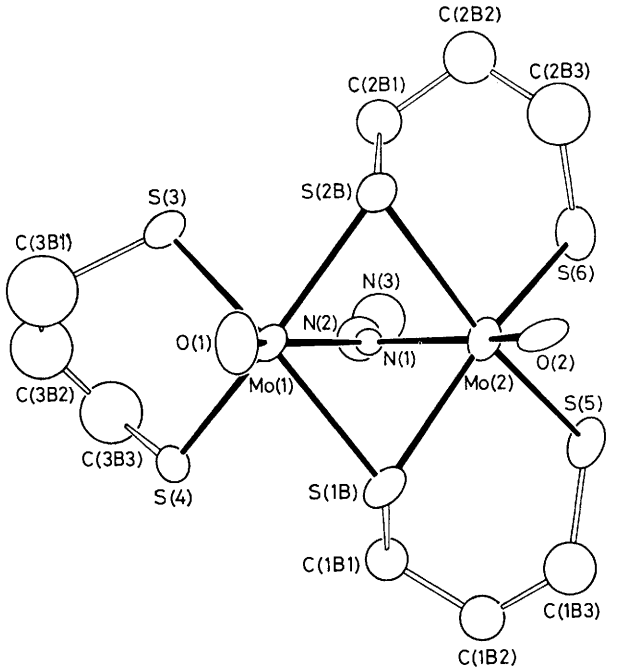

Figure 2. ORTEP representation of $[Mo_2O_2(\mu\text{-}N_3)(SCH_2CH_2CH_2S)_3]^-$ showing atom labelling scheme. Selected bond lengths (Å) and angles (°): Mo(1)–Mo(2), 2.893(3); Mo(1)–O(1), 1.67(1); Mo(2)–O(2), 1.66(1); Mo(1)–N(1), 2.21(1); Mo(2)–N(1), 2.24(1); N(1)–N(2), 1.18(2); N(2)–N(3), 1.09(4); ∠S(1B)–Mo(1)–S(3), 164.8(3); ∠S(2B)–Mo(1)–S(4), 164.2(3); ∠O(1)–Mo(1)–N(1), 153.8(8); ∠S(3)–Mo(1)–S(4), 87.6(3); ∠S(1B)–Mo(2)–S(5), 87.2(3); ∠N(1)–N(2)–N(3), 153.4(29).

isolated in good yield as its tetraphenylphosphonium salt, (**2**). The reaction presumably involves protic attack at the dithiolate sulphurs with loss of one dithiolate ligand as free dithiol. By contrast, $[MoO(SPh)_4]^-$ is inert to HN_3 under similar conditions reflecting a lower electron density on the sulphurs.

Dark red crystals of (**2**) were grown from methyl cyanide–diethyl ether. *Crystal data:* orthorhombic, space group $P2_12_12_1$, $a = 9.398(3)$, $b = 14.650(2)$, $c = 27.426(2)$ Å, $U = 3775.8$ Å^3, $Z = 4$, 2563 reflections were collected, of which 1244 were used (Mo-K_α radiation, final R value 5.8%).† An ORTEP view of the structure of the anion is shown in Figure 2, together with some bond lengths and angles. The complex is dinuclear with two non-equivalent pseudo-octahedral molybdenums. The unusual asymmetry is imposed by the odd number of dithiolate ligands, one Mo being ligated by two dithiolates which also provide bridging sulphurs for the other Mo which is also ligated by a chelated non-bridging dithiolate. This structure contrasts with that of $[Mo_2O_2(SCH_2CH_2O)_3Cl]^-$, where the chloride is terminally bound and one SCH_2CH_2O occupies a bridging site.[5] The structural parameters of the triple bridge are very similar to those of other triply-bridged Mo_2O_2 species.[6,7] The most interesting feature of the bridge is the unusual[8] non-linear conformation of the bridging azido-group which is bent at N(2) with ∠N(1)–N(2)–N(3) = 153.4(29)°. The non-linearity is caused by intermolecular interaction of the N(3) nitrogen with a methylene hydrogen of an adjacent molecule in the unit cell, and is not electronic in origin.

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