Synthesis and *X*-Ray Crystal Structure of a Novel Dimeric Molybdenum(III) Cyano Complex: $[(PPh_4)_4][Mo_2(\mu_4\text{-}S_2)(\mu_2\text{-}SO_2)(CN)_8].6H_2O$

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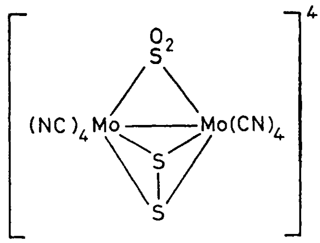
Summary *X*-Ray crystallographic analysis shows that the diamagnetic dimeric title complex has a structure in which the molybdenum atoms are bridged by a sulphur-bonded SO_2 ligand and by S_2^{2-}, the metal atoms have distorted pentagonal bipyramidal co-ordination.

MOLYBDENUM is one of the most important transition metals to function in redox enzymes. There have been many studies on molybdenum(V) systems, and some molybdenum(III) dimers have been characterized.[1,2] We present here a structural study on a novel complex (**1**) in which the bridging ligands are SO_2 and S_2^{2-}, this is the first complex to be reported in which these two ligands have a mutually bridging role.



(1)

The complex was made by aerial oxidation of $K_6[Mo_2S_2(CN)_8]$ $4H_2O$[1] (2 g) dissolved in water (20 cm^3). On passage of O_2 (or air) the aqueous solution changed colour from dark blue *via* dark green to purple. Potassium cyanide and other by-products were extracted with methanol and a purple oil was obtained. The tetraphenylphosphonium salt $[PPh_4]_4[Mo_2^{III}(\mu_4\text{-}S_2)(\mu_2\text{-}SO_2)(CN)_8]$ $6H_2O$ was made by addition of an aqueous solution of PPh_4Cl, and characterised by elemental analysis (Mo, C, H, N, P, and S), magnetic measurements, i.r. and Raman spectra, and *X*-ray structural analysis. The salt is diamagnetic at room temperature ($\chi_M = -751 \times 10^{-6}$ c.g.s.u.) and the main i.r. absorption bands of the anion occur at 2120s, 2127s, 2135s [ν(CN)], 1167s, 1040s [ν(SO) of the SO_2 bridging], 520s[ν(SS)], 458m[$\nu_s Mo_2S$], 370s, 350m, and 340m[ν_{as}-Mo_2S] cm^{-1}. Crystals suitable for *X*-ray diffraction study were obtained from oxygen-free water–methanol mixtures by slow evaporation.

Crystal data: $C_{104}H_{92}Mo_2N_8O_8P_4S_3$, $M = 1993{\cdot}9$, space group $P\bar{1}$, triclinic, $a = 25{\cdot}197$, $b = 16{\cdot}400$, $c = 12{\cdot}737$ Å, $\alpha = 109{\cdot}95$, $\beta = 89{\cdot}13$, $\gamma = 95{\cdot}04°$, $U = 4927{\cdot}5$ Å^3, $Z = 2$, $D_m = 1{\cdot}36$ g cm^{-3}, $D_c = 1{\cdot}34$ g cm^{-3}, $F(000) = 2056$, $\mu(\text{Mo-}K_\alpha) = 4{\cdot}26$ cm^{-1}. Intensity data were collected on a Philips PW1100 four-circle diffractometer with Mo-K_α radiation, absorption being neglected. The structure was solved by normal heavy atom Patterson and Fourier procedures and refined by full-matrix least-squares methods to an R value of 0·078 for 4254 reflections ($2\theta \leqslant 44°$) with $F_0 > 6\sigma(F_0)$. All atoms of the dimeric anion and the phosphorus atoms of the counter-anion were refined anisotropically. The phenyl rings of the $[PPh_4]^+$ cation were considered as rigid groups, each individual carbon atom was assigned an isotropic thermal parameter and allowed to vary during the refinement. Four of the six water molecules were clearly located and refined isotropically, the two others being disordered. They were statistically distributed over five positions with partial site occupation factors and their thermal parameter was kept fixed.†

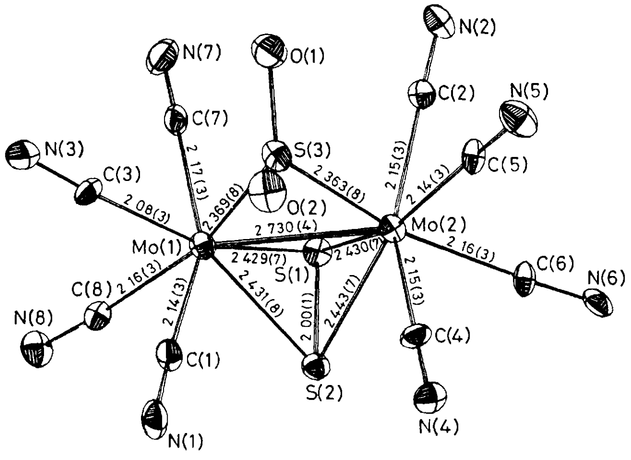


FIGURE A perspective view of the $[Mo_2(\mu_4\text{-}S_2)(\mu_2\text{-}SO_2)(CN)_8]^{4-}$ anion including the atom numbering scheme and some pertinent bond lengths.

The molecular structure of the anion and some important bond lengths are shown in the Figure. This anion is the first example of a molybdenum(III) complex triply bridged together with a disulphur S_2^{2-} ligand and a bridged SO_2 molecule. The co-ordination stereochemistry of each molybdenum atom is best described as distorted pentagonal bipyramid, both metal atoms being bound to four cyanide groups. The bridging μ_4-S_2^{2-} anion together with the C(1), C(3), and C(7) carbon atoms are coplanar within 0·18 Å, similarly the same disulphur ligand, C(4), C(5), and C(2) are coplanar within 0·16 Å. The girdle axes of these planes are respectively S(3)–Mo(1)–C(8) and S(3)–Mo(2)–C(6). The average Mo–S distance of 2·433 Å is within the average values reported for such bond lengths with the S_2^{2-} anion.[3–5] The S–S bond distance of 2·00(1) Å corresponds

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† 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.

to a normal single bond and is in general agreement with the S–S distances already observed in molybdenum complexes containing bridging S_2^{2-} anions. The sulphur dioxide ligand symmetrically bridges the two Mo atoms with a dihedral angle between Mo(1), S(3), Mo(2), and S(3), O(1), O(2) planes of 89·8°. The anion has approximate C_s symmetry with the mirror plane containing S(1), S(2), S(3), O(1), and O(2). The symmetrical nature of the bridging ligands accounts for the formal oxidation number of molybdenum atoms.

Many bridged Mo–Mo single bond distances in compounds containing bridged disulphur groups are in the range 2·70—2·85 Å.[3–6] The $Mo^{III} \ldots Mo^{III}$ distance of 2·730(4) Å in this complex suggests the presence of a direct metal–metal bond, and the existence of such a bond is further indicated by the small angle: 69° (average value) at the bridging sulphur atoms and the obtuse angle: 105·3° (average value) subtended by the bridging sulphur atoms at the molybdenum atoms. This possibility is also in accord with the observed diamagnetism of the complex, although this diamagnetism is equally compatible with a model involving superexchange *via* bridging ligands.

It appears that the sulphide ligand has been partly oxidised to S_2^{2-} in the formation of this complex. Other complexes can also be isolated from oxidation of $[Mo_2S_2(CN)_8]^{6-}$.

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