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Synthesis and Structure of [(dmmp)OMo(μO,μS)-MoO(MeOH)(dmmp)], where dmmpH = 4,6-dimethylpyrimidine-2-thione; a Dinuclear Molybdenum(V) Complex Containing both 5- and 6-Coordinate Molybdenum

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Molybdenum(V) complexes of the type [{Mo(O)-L}$_2$O$_x$S$_{2-x}$], where L is a dithiochelating ligand and x = 0, 1, or 2, are well known [1]. The molybdenum atoms generally adopt a square-pyramidal geometry, with the metal atom displaced towards the terminal oxide ligands. Coordination number changes in such compounds are of interest in connection with the binding of substrates to molybdenum centres, *e.g.* in molybdoenzymes.

Although the molybdenum atoms in such compounds appear to be coordinatively unsaturated, adduct formation (other than by oxidative addition) has been considered to be hindered by a number of factors [2]: Mo–Mo bond formation, *trans*-repulsive influence of the terminal oxide ligands, and steric crowding at the sixth coordination site caused by the displacement of the molybdenum towards the terminal oxide and by the folding in the bridge.

Adducts with mono- and bi-dentate ligands, however, are known [2, 6]. The structures of a particularly interesting series, $Mo_2O_3S[S_2P(OC_3H_7)_2]_2 \cdot L$ (where L = pyridine, pyridazine, or pyrimidine) have recently been described [2, 3]. In the pyridine and pyridazine adducts the bases are coordinated essentially symmetrically to both Mo atoms of the dimeric unit, with relatively long Mo–N bonds (2.97 and 2.93 Å) in the case of pyridine, but with Mo–N bonds of 2.59 and 2.58 Å in the case of the pyridazine bridge. In contrast, the base in the pyrimidine adduct is located asymmetrically between the two molybdenum atoms being bound to one of them preferentially, albeit with a rather long (2.86 Å) Mo–N bond.

Asymmetrical adduct bonding has also been reported [6] in the compound $Mo_2O_3(NH)[S_2P(OC_2H_5)_2]_2 \cdot THF$. However the Mo–THF interaction in that complex is very weak, as the tetrahydrofuran was reported [6] to be lost at room temperature and differences between the coordination geometries of each molybdenum atom in the dinuclear unit are small.

As part of a study of the binding of pyrimidine-2-thiones to molybdenum, we have isolated the title compound which contains a relatively firmly held methanol molecule asymmetrically bonded to one molybdenum atom of an MoO(S)Mo dinuclear unit.

Experimental

The complex was formed by refluxing MoO$_2$-(acac)$_2$ with an excess of 4,6-dimethyl-2-mercaptopyrimidine (dmmpH) in dry methanol, under nitrogen, for 30 min. The reaction mixture darkened to give a deep red solution, which was allowed to cool to room temperature and then stored in a stoppered flask for two days. The orange crystals which formed were suitable for X-ray analysis without further purification. The solid complex is diamagnetic.

The crystals were air-stable for an apparently indefinite period at room temperature.

Crystal Data

$Mo_2C_{13}H_{18}N_4O_3S_3$, M = 566.3, orthorhombic, a = 7.484(1), b = 16.267(5), c = 34.023(9) Å, U = 4142.0 Å^3 (at 18 °C), space group *Pbnb* (No. 56), Z = 8, D_c = 1.81 g cm^{-3}. X-Ray diffraction data were collected on a Nicolet R3m/Eclipse S140 diffractometer system using an ω scan technique with graphite-monochromated Cu-Kα radiation. A total of 2327 independent reflections were measured (to θ = 52°), of which 510 were 'unobserved'. The structure was solved by Patterson and Fourier methods, and least-squares refinement has now reached R = 0.042. The program system SHELXTL was used throughout the calculation [7].

Results and Discussion

The complex is dinuclear, the molybdenum atoms being linked by one oxo- and one sulphido-bridge (Fig. 1). Each molybdenum is also bound to one terminal oxygen and to one deprotonated thione ligand molecule, coordinated via sulphur and nitrogen. Additionally, in each dinuclear unit there is a molecule of methanol coordinated to one molybdenum atom.

The Mo(1)–Mo(2) distance of 2.660(1) Å, together with the angles Mo–μO–Mo, 87.6(2)°, and Mo–μS–Mo, 70.0(1)°, indicate the presence of a metal–metal bond, and this is in agreement with the observed diamagnetism of the solid. The observed Mo–Mo distance is similar to those found [2]

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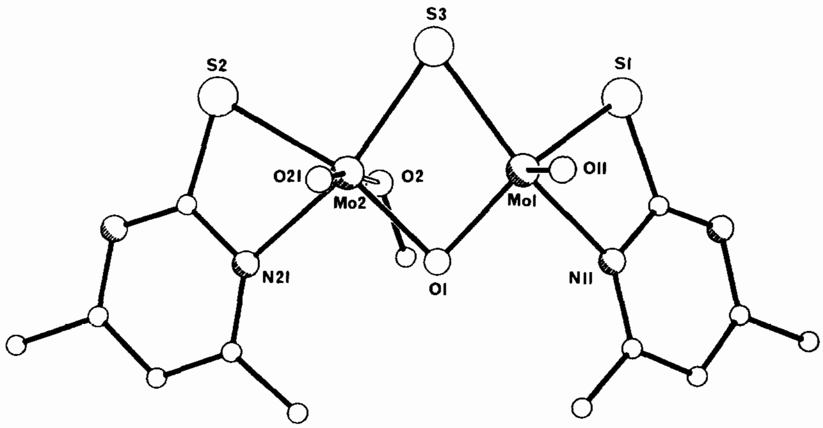

Fig. 1. Molecular structure of [(dmmp)OMo(μO,μS)MoO(MeOH)(dmmp)]. Important bond lengths are: Mo(1)–O(11) 1.664(6); Mo(1)–N(11) 2.180(7); Mo(1)–S(1) 2.435(3); Mo(1)–S(3) 2.319(2); Mo(1)–O(1) 1.911(5); Mo(2)–O(21) 1.670(6); Mo(2)–N(21) 2.209(7); Mo(2)–S(2) 2.489(2); Mo(2)–S(3) 2.321(3); Mo(2)–O(1) 1.933(5); Mo(2)–O(2) 2.535(6) Å.

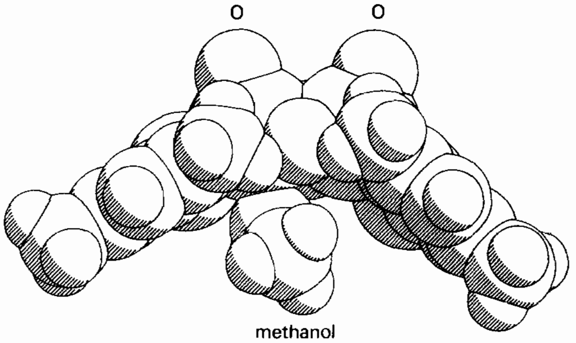

Fig. 2. Spacefilling diagram of the structure of the title compound showing the lack of steric hindrance to methanol coordination.

in other adducts of dinuclear complexes involving the Mo–μ(O,S)–Mo bridging unit.

One of the molybdenum atoms, Mo(1), lies in a distorted square pyramidal environment, with a terminal oxygen atom at the axial site and with the metal atom lying 0.68 Å above the mean plane of the basal donor atoms. The other molybdenum, Mo(2), has the methanol bonded in the sixth coordination site and is only 0.51 Å above the corresponding plane, so that it more closely approaches octahedral geometry.

Although the sulphido bridge is symmetrically disposed between the molybdenum atoms, the oxo-bridge lies marginally closer to Mo(1): Mo(1)–μO = 1.911(5) Å, Mo(2)–μO = 1.933(5) Å. The five coordinate molybdenum atom, Mo(1), also has shorter bonds to the donor atoms of the thione ligand. This difference is more marked for the bonds to thione sulphur (Mo(1)–S(1) = 2.435(3) Å, Mo(2)–S(2) = 2.489(2) Å) than for the bonds to the nitrogen atoms (Mo(1)–N(11) = 2.180(7) Å, Mo(2)–N(21) = 2.209(7) Å).

Coordination of methanol to Mo(2) causes no significant lengthening of the Mo–terminal oxygen bond compared with that for the five coordinate molybdenum. The terminal oxygen atoms remain eclipsed.

The formation of the mixed μ(O,S) bridge under the reaction conditions employed requires that the molybdenum centres have abstracted sulphur from the excess thione ligand. The complex MoO[$S_2P(OC_2H_5)_2$] has been shown [6] to abstract NH from HN_3 to give $Mo_2O_3(NH)[S_2P(OC_2H_5)_2]$, and the reducing properties of the thione ligand used here make feasible the formation of an analogous species MoO(dmmp)$_2$ from MoO$_2$(acac)$_2$. This intermediate may then react with further ligand, abstracting sulphur to give the title compound.

We attribute the relative thermal stability of this methanol adduct to the planarity of the thione ligands and their consequently favourable steric requirements. Factors such as the *trans*-influence of the terminal oxygen atoms, and steric interactions between the atoms within the primary coordination spheres of the molybdenum atoms would be expected to be similar to those in the previously reported structures. Apart from the relatively small size of the methanol molecule, the major difference here is the lack of steric crowding beneath the basal plane of the molybdenum by the thione ligands, thus allowing the solvent molecule to approach a vacant coordination site more easily (Fig. 2).

In discussing the structural features found [2, 3] for the compounds $Mo_2O_3S[S_2P(OC_3H_7)_2]_2L$ (L =

pyridine, pyrimidine, or pyridazine), Drew and his co-workers suggested that adduct formation was facilitated by 'crevice coordination' induced by the spatial disposition of the alkyl chains of the –O(C_3H_7) groups.

The results obtained for the title compound show that such a factor need not be invoked for non-oxidative addition adduct formation. Indeed, the Mo–O(methanol) distance (2.535(6) Å) observed here is shorter than those found [2, 3] for the adducts with the more basic N-heterocycles referred to above. This shortening follows naturally from the smaller steric interactions conferred by the planar thione ligands compared with the $S_2P(OR)_2$ units.

We conclude that dimeric Mo(V) complexes of this general type can form stable adducts by non-oxidative addition reactions without the need for 'crevice coordination' stabilization. Indeed, a suitable choice of the combination of intrinsic Mo-adduct bond strength and the steric requirements of the other ligands may lead to an interesting range of Mo-adduct bond lengths and stabilities.

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References

1 E. I. Stiefel, *Progr. Inorg. Chem., 22,* 1 (1977) and references therein.
2 M. G. B. Drew, P. J. Baricelli, P. C. H. Mitchell and A. R. Read, *J. Chem. Soc., Dalton Trans.,* 649 (1983).
3 P. J. Baricelli, M. G. B. Drew and P. C. H. Mitchell, *Acta Crystallogr., Sect. C:, 39,* 843 (1983).
4 T. Glowiak, M. Sabat, H. Sabat and M. F. Rudolf, *J. Chem. Soc., Chem. Commun.,* 712 (1975).
5 T. Glowiak, M. F. Rudolf, M. Sabat and B. Jeżowska-Trzebiatowska, in P. C. H. Mitchell (ed.), in 'Proc. Climax 2nd Int. Conf. Chem. Uses Molybdenum', Climax Molybdenum, London, 1977, p. 17.
6 A. W. Edelblut, B. L. Haymore and R. A. D. Wentworth, *J. Am. Chem. Soc., 100,* 2250 (1978).
7 G. M. Sheldrick, 'SHELXTL' – an Integrated System for Solving, Refining, and Displaying Crystal Structures for Diffraction Data, Revision 4, Nicolet Instruments, Warwick, England, 1983.