

Crevice Co-ordination. Binding of a Ligand Molecule in a Molecular Crevice. The Crystal and Molecular Structure of μ -Oxo- μ -pyridine- μ -sulphido-bis[$(O,O$ -di-isopropyl phosphorodithioato)oxomolybdenum(v)]

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Reaction of $[\{\text{MoO}(\text{LL})_2\}_2\text{OS}]$ (LL = O,O -di-isopropyl phosphorodithioato) with pyridine gives rise to a stable 1 : 1 adduct in which the pyridine occupies a molecular crevice and is bound to both molybdenum atoms [Mo-N 2.95(2) and 2.93(2) Å]: as a result of the adduct formation the shape of the molybdenum dimer is altered.

Molybdenum(v) complexes of the general type $[\{\text{Mo}(\text{O})(\text{LL})_2\}_2\text{O}_{2-x}\text{S}_x]$ [LL = dithiocarbamato, R_2NCS_2^- , phosphorodithioate, $(\text{RO})_2\text{PS}_2^-$, $x = 0, 1, 2$] are well known.¹ The molybdenum atoms are five-co-ordinate and displaced towards the terminal oxide ligands. Although the molybdenum atoms might appear to be unsaturated these complexes are considered² to have rather little tendency to form adducts (other than by oxidative addition) presumably because of the presence of a Mo-Mo bond, the *trans* repulsive influence of the terminal oxide ligand, and the steric crowding at the sixth co-ordination position caused by the displacement of molybdenum towards the terminal oxide and by the folding in the bridge. A pyridine (py) adduct $[\text{Mo}(\text{O})(\text{S}_2\text{COEt})_2(\text{py})]$ has been reported³ with the Mo^{IV} monomer $[\text{MoO}(\text{LL})_2]$, but with the Mo^{V} dimers the adducts contain a bidentate ligand bridging the molybdenum atoms {*e.g.* acetate in the ion

$[\text{Mo}_2\text{O}_4(\text{NCS})_4(\text{CH}_3\text{CO}_2)]^{3-}$.⁴ The possibility of co-ordination number changes in molybdenum chemistry is of great interest in the context of the binding of substrates to molybdoenzymes.¹

We have now found that the title compound (1) is formed by addition of pyridine to μ -oxo- μ -sulphido-bis[O,O -di-isopropyl phosphorodithioato)oxomolybdenum(v)] (2), the structure of which we have recently reported.⁵ In (2), the molybdenum atoms are in a five-co-ordinate environment with an equatorial plane containing sulphur atoms from the bidentate phosphorodithioate ligand, bridging oxygen and sulphur atoms, and an axial terminal oxygen atom. There is a weak Mo . . . Mo bond of 2.690(2) Å. The conformation of the Mo_2SO moiety in (2) is similar to that found in the compound $[\{\text{MoO}(\text{S}_2\text{CNPr}^{\text{D}})\}_2\text{OS}]$ and therefore presumably typical of this type of bridge system.⁶ We report here the structure of the title compound (1) which is formed by the

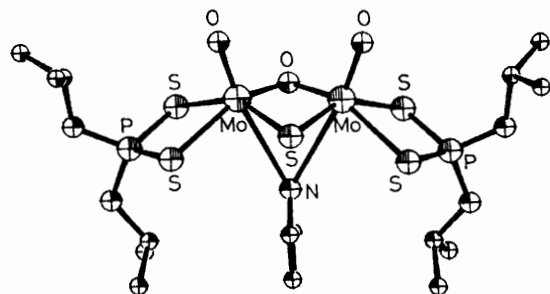


Figure 1

direct addition of one molecule of pyridine to (2). The compound $[(\text{MoO}(\text{LL})_2(\text{O})(\text{S})(\text{py}))_2]$ (1), crystallised when pyridine was added in drops to a toluene solution of (2). Crystals suitable for X-ray analysis were grown by slow evaporation at ca. 20 °C of a solution of (1) in CHCl_3 -toluene (1:1).

Crystals of (1) are monoclinic, space group $P2_1/a$ with cell dimensions $a = 17.200(10)$, $b = 12.690(11)$, $c = 15.448(9)$ Å, $\beta = 110.0(1)^\circ$, $U = 5168.9$ Å³, $\text{Mo}_2\text{S}_6\text{O}_7\text{P}_2\text{C}_{17}\text{H}_{33}\text{N}$, $M = 777.4$, $U = 3168.9$ Å³, $Z = 4$, $D_m = 1.63$ g cm⁻³, $D_c = 1.63$ g cm⁻³. The intensities of 2309 independent reflections above background have been measured on a diffractometer. The structure has been determined by heavy atom methods and refined to $R = 0.059$. The structure of (1) consists of $[(\text{MoOLL})_2(\text{O})(\text{S})(\text{py}))_2]$ molecules (Figure 1).[†] We compare its structure with that of the parent compound (2) in Table 1.³ In the adduct (1), the general structure of (2) is maintained; the pyridine molecule has approached the two molybdenum atoms from the sterically open side of the molecule, the side *trans* to the terminal oxygens. The Mo...N distances are 2.95(2) and 2.93(2) Å. The pyridine ring is almost coplanar with the bridging oxygen and sulphur atoms (0.07 and 0.13 Å respectively from the C₅N ring plane). The Mo-N-Mo angle is 53.6(2)°, while the two O-Mo-N angles are 169.8(4) and 170.6(6)°. Thus the pyridine nitrogen atom occupies the *trans*-position in both co-ordination spheres. This symmetrical position for the pyridine ring allows the pyridine molecule to approach as close as possible to both Mo atoms. The Mo...N distances in (1) are longer than expected for a Mo-N bond (*cf.* 2.23 Å in cysteine and histidine complexes)¹ even allowing for its position *trans* to the multiple Mo=O bond, but nevertheless there is an interaction between the Mo atom and the pyridine molecule because the conformations of the molybdenum co-ordination spheres are markedly changed as shown in Table 1.

The most spectacular change is that the angle of fold between the two MoO_bS_b groups (*b* denotes bridging atom) has increased by 16.9° from 146.8° in (2) to 163.7° in (1). This is concomitant with an increase in O-Mo-S bridge angles from 98.4 to 101.7° (mean) and a decrease of the Mo...Mo distances to 2.653(2) Å in (1) from 2.690(2) Å in (2). The Mo-N interaction *trans* to Mo=O has changed the molybdenum environment: the Mo atoms in (1) are now displaced 0.55 and 0.56 Å above the S₃O equatorial plane [*cf.* 0.69 Å in (2)].

[†] 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.

Table 1. Distances are in Å and angles in °.^a

	$[(\text{MoOLL})_2\text{OS}(\text{py})]$ (1)	$[(\text{MoOLL})_2\text{OS}]$ (2)
Mo...Mo	2.653(2)	2.690(2)
Mo-S _b	2.332(4), 2.328(4)	2.370(4), 2.333(4)
Mo-O _b	1.950(8), 1.966(9)	1.967(10), 2.011(10)
Mo-O _b -Mo	85.3(3)	85.1(4)
Mo-S _b -Mo	69.4(1)	69.8(1)
O _b -Mo-S _b	101.9(3), 101.5(3)	98.4(3), 98.5(3)
$\text{MoO}_b\text{S}_b \wedge \text{MoO}_b\text{S}_b$	163.7(1)	146.8(1)
Distances of Mo from:		
S ₃ O plane	0.55(1), 0.56(1)	0.69(1), 0.69(1)
Mo-S _L	2.540(4), 2.486(3)	2.503(3), 2.475(4)
	2.531(4), 2.497(5)	2.501(4), 2.472(3)
Mo-O _t	1.679(12), 1.681(9)	1.632(8), 1.654(8)

^a Subscripts: b bridging, t terminal, and L ligand.

There are no significant changes in the lengths of bonds containing molybdenum atoms and the Mo-O-Mo and Mo-S-Mo angles remain unchanged after pyridine addition. However there are enough changes of molecular dimensions caused by the presence of pyridine to indicate a significant Mo...N interaction.

Previously a compound $[\text{Mo}_2\text{O}_5(\text{NH})\{\text{S}_2\text{P}(\text{OEt})_2\}_2]\text{THF}$ (THF = tetrahydrofuran), in which a molecule of THF solvent is located asymmetrically between two molybdenum atoms, was reported.⁷ Unlike our pyridine adduct this compound loses its solvent at room temperature and the THF molecule has no structural effects despite one Mo-O distance of 2.633 Å. We have found that adducts similar to our pyridine adduct are formed by reaction of (2) with methyl-substituted pyridines, pyridazine, 1,10-phenanthroline, and 2,2'-bipyridyl. We are investigating these compounds. We speculate that binding of the adduct molecules is facilitated by the molecular crevice formed by the alkyl chains of the phosphorodithioato ligands (*cf.* Figure 1). There are no abnormally short intramolecular distances but there are several pyridine carbon to dithiophosphonate hydrogen distances of ca. 2.9 Å. The strength of interaction with the molybdenum atom will then depend on the ligand basicity (*e.g.* pyridine > THF), as well as steric factors.

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