Crevice Co-ordination: Binding of a Ligand Molecule in a Molecular Crevice. Crystal and Molecular Structures of μ-Oxo-μ-pyridine-μ-sulphido-bis[(*OO'*-di-isopropyl phosphorodithioato)oxomolybdenum(V)] and μ-Oxo-μ-pyridazine-μ-sulphido-bis[(*OO'*-di-isopropyl phosphorodithioato)oxomolybdenum(V)][†]

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Reaction of $[\{Mo(O)(X)\}_2(O)(S)]$ (1) (X = *OO'*-di-isopropyl phosphorodithioate) with various potential ligands L, in particular pyridine (py) and pyridazine (pydz), gives rise to 1 : 1 adducts. The crystal structures of two such adducts have been determined and are reported here, namely $[\{Mo(O)(X)\}_2(O)(S)(py)]$ (2) and $[\{Mo(O)(X)\}_2(O)(S)(pydz)]$ (3). Compound (2) is monoclinic, space group $P2_1/a$, with cell dimensions a = 17.200(10), b = 12.690(11), c = 15.448(9) Å, β = 110.0(2)°, and Z = 4. Compound (3) is monoclinic, space group $P2_1/n$, with a = 17.316(8), b = 14.560(11), c = 12.150(9) Å, β = 93.0(1),° and Z = 4. The structure for (2) has been refined to R 0.057 for 2 309 observed data and for (3) to R = 0.097 for 2 316 data. The two structures are similar in that the basic core of the parent compound (1) is maintained but there are major differences in the way in which the py and pydz are bonded to the metal atoms. In (2), the py molecule is weakly bonded to both molybdenum atoms through the nitrogen with Mo–N distances of 2.97(2) and 2.93(1) Å. The pyridine plane is approximately perpendicular to the Mo · · · Mo vector. In (3) the pydz is held parallel to this vector with each molybdenum being bonded to just one nitrogen [Mo–N 2.59(2) and 2.58(1) Å]. The preparative chemistry and i.r., u.v.–visible, and ^{31}P n.m.r. spectra of the complexes are described.

Molybdenum(V) complexes of the general type $[\{Mo(O)(X)\}_2(O)_x(S)_{2-x}]$ [X = dithiocarbamate, $S_2CNR_2^-$, or phosphorodithioate, $S_2P(OR)_2^-$; x = 0—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 considered [2] to have little tendency to form adducts (other than by oxidative addition) presumably because of the combined effects of the Mo–Mo bond, the *trans* repulsive influence of the terminal oxide ligand, and the folding in the bridge.

The complex $[\{Mo(O)(X)\}_2(O)(S)]$ [1; X = $S_2P(OPr^i)_2$] [3] was originally prepared during an investigation of molybdenum–sulphur compounds of possible value as soluble friction- and wear-reducing additives to lubricating oils.[4,5] Our interest in this type of complex and the possibility of binding a sixth ligand derives from the following considerations. In tribological applications, molybdenum phosphorodithioato-complexes like (1) are incorporated in lubricating oil packages which contain substances such as amines which could, in principle, bind to the molybdenum phosphorodithioate and affect its lubricating and antioxidant properties. The adverse effect of amines on zinc phosphorodithioates is well known.[6] We therefore investigated the interaction of molybdenum phosphorodithioates with amines and N-donor ligands generally and succeeded in isolating crystalline adducts with pyridine and pyridazine.

The possibility of changing co-ordination number in molybdenum chemistry is also of great interest in the context of the binding of substrates to molybdoenzymes and subsequent product release, and of molybdenum catalysts generally. For example, the mechanism of xanthine oxidase involves binding of xanthine (and other substrates) directly to molybdenum at the active site.[7] The substrate binding sites in various molybdenum-containing heterogeneous catalysts, *e.g.* MoS_2,[8] also may be regarded as unsaturated molybdenum atoms. The binding of N-donor compounds is of particular interest because they can behave as substrates (hydrodenitrogenation [9]) and poisons at Mo centres of heterogeneous catalysts.[10] We shall see that the work reported in the present paper does describe new and unexpected modes of weak binding of pyridine and pyridazine at unsaturated molybdenum centres and does indeed extend our knowledge of substrate binding at molybdenum. We have found that the 1 : 1 adducts can be formed by addition of various ligands to μ-oxo-μ-sulphido-bis[(*OO'*-di-isopropyl phosphorodithioato)oxomolybdenum(V)] (1), the structure of which we have recently reported.[3]

In (1), the molybdenum atoms are in a five-co-ordinate environment consisting of an equatorial plane containing two sulphur atoms from the bidentate phosphorodithioate ligand, a bridging oxygen, a bridging sulphur, and an axial terminal oxygen atom. There is a weak Mo · · · Mo bond of 2.690(2) Å. The conformation of the $Mo_2(S)(O)$ moiety in (1) is similar to that found in the compound $[\{Mo(O)(S_2CNPr^n)\}_2(O)(S)]$ and is therefore presumably typical of this type of bridge system.[11] We report here the preparation and properties of adducts of (1) with N-donor ligands and also the crystal and molecular structures of the 1 : 1 adducts with pyridine (2) and with pyridazine (3). The structure of (2) has been reported in a preliminary communication.[12]

Results and Discussion

Preparative Chemistry.—Preparation of the adducts (2) and (3) is apparently straightforward, the pyridazine (pydz) adduct (3) crystallising immediately when pyridazine is added to a solution of the phosphorodithioate (1) and the pyridine (py) adduct (2) forming crystals during 12 h. In fact, although the crystal of the pyridine adduct selected for *X*-ray crystallography is obviously (2), the chemical analysis of the product (see Experimental section) corresponded more to a di-μ-sul-

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[†] *Supplementary data available* (No. SUP 23506, 32 pp.): observed and calculated structure factors, thermal parameters, H-atom positions, dimensions of OPr^i groups, least-squares planes. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Spectra [a] of the compounds $[\{Mo(O)(X)\}_2(O)(S)]$ (1), $[\{Mo(O)(X)\}_2(O)(S)(py)]$ (2), and $[\{Mo(O)(X)\}_2(O)(S)(pydz)]$ (3) [b]

Spectrum	Compound (1)	 (2)	 (3)
(*a*) I.r. (ν/cm^{-1})			
ν(Mo=O) + ν_{asym}(P–O)	985vs, 961 (sh)	980s, 963vs	990 (sh), 980 (sh)
ν_{sym}(P–O)	767s	767m	*c*
ν(MoOMo)	715m, 514m	715 (sh), 512m	715m, 514m
ν(P–S)	636s, 550s	613s, 550w	640m, 550m
ν(MoSMo)	458m, 372m	450m, 373m	462m, 372 (sh)
(*b*) U.v.–visible [d]			
$\lambda_{max.}$/nm	237 (13 700) 290 (20 500) 335 (5 000) 400 (1 100)	237 (15 000) 289 (20 500) 335 (5 600) 402 (800) 440 (350)	
(*c*) ^{31}P n.m.r. (δ/p.p.m.) [e]	103.2	103.2	103.2

[a] Characteristic transitions. [b] X = $S_2P(OPr^i)_2$. [c] Covered by pyridazine bands. [d] For solution in Et_2O; ε values (dm^3 mol^{-1} cm^{-1}) are in parentheses. [e] In $CDCl_3$, downfield relative to 85% H_3PO_4.

phido-compound, *i.e.* $[\{Mo(O)[S_2P(OPr^i)_2]\}_2(S)_2]$ (4). The molybdenum phosphorodithioate complexes are unstable in solution slowly undergoing redox equilibria, ligand dissociation, and further sulphurisation.[5] The presence of (μ-O)(μ-S) and (μ-S)$_2$ complexes in the solutions can be shown by ^{31}P n.m.r. spectroscopy.[5] Replacement of O by S in the bridge is quite easy, the sulphur coming from the phosphorodithioate (or an oxidation product of it). It is therefore likely that the reaction with pyridine (12 h) would give a mixture of products and there is an element of chance in the selection of a crystal for the structure determination as (1) and (2) were indistinguishable by eye. Indeed, the first crystal selected was compound (1) (no pyridine). With pyridazine, the rapid formation of crystals ensured a pure sample of (3).

We have also obtained precipitates by adding ethanolic solutions of methyl-substituted pyridines, adenine and xanthine, 1,10-phenanthroline, and 2,2′-bipyridine. From the analytical data, they appear to be similar to the pyridine or pyridazine adducts but we have not yet obtained suitable crystals for *X*-ray crystallography.

Spectra.—The i.r., u.v.–visible, and ^{31}P n.m.r. spectra of the phosphorodithioate (1) and the pyridine (2) and pyridazine (3) adducts are reported in Table 1. The significant feature is that the spectra are hardly, if at all, changed by the addition of pyridine or pyridazine. This is in contrast to the effect of an additional ligand such as pyridine in, for example, VO^{2+} complexes: both the i.r. spectra [ν(V=O)] and the electronic spectra (*d–d* transitions) are shifted.[13] We thought at first that the pyridine and pyridazine were merely incorporated in the crystal lattice but, as we shall see from the crystal structures, pyridine and pyridazine are interacting with the molybdenum atoms, albeit at long distances and evidently too weakly for the spectroscopic properties to be affected.

Magnetic Properties.—All three compounds are diamagnetic and e.s.r.-inactive as expected for two molybdenum(V) atoms interacting through oxide and sulphide bridges and/or a Mo–Mo bond.

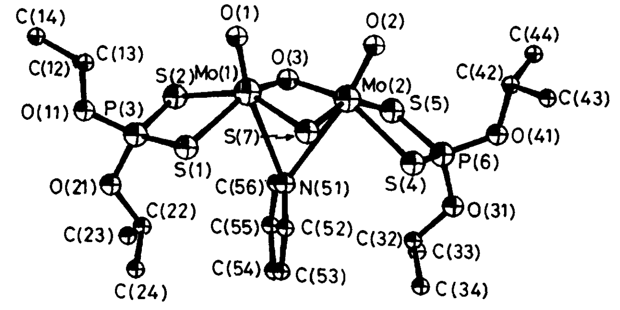

Figure 1. Molecular structure of (2)

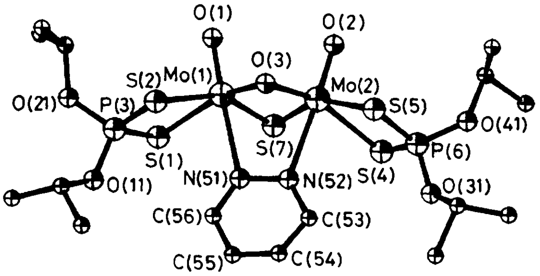

Figure 2. Molecular structure of (3); only one position for C(42), C(43), C(44) is shown

Crystal and Molecular Structures.—The unit cells of (2) and (3) contain discrete molecules of the 1 : 1 adducts, and the molecular geometry is shown in Figures 1 and 2, together with the (common) atomic numbering scheme. In the two structures the essential skeleton (below) is maintained. However, the ligand molecules are attached (albeit weakly) to the metal atoms and, as described below, alter the dimensions of the molybdenum co-ordination spheres. As is clear from Figures 1 and 2, the mode of attachment of the two ligands is totally different in the two structures. In (2), py is weakly bonded to both molybdenum atoms through the single ring nitrogen atom with Mo(1)–N(51) 2.967(19) Å and Mo(2)–N(51) 2.931(13) Å. The pyridine ring is almost coplanar with the bridging oxygen and sulphur atoms [0.07 (O) and 0.13 Å (S) from the C_5N ring plane]. The Mo–N–Mo angle is 53.5(3)°, while the two O=Mo–N angles are 169.7(4) and 170.8(5)°. Thus the pyridine nitrogen atom occupies the *trans* position in both co-ordination spheres. Its symmetrical position enables the pyridine molecule to approach as close as possible to both Mo atoms. The Mo ··· N distances in (2) are longer than expected for a Mo–N bond (*cf.* 2.23 Å in Mo^V cysteine and histidine complexes [1]) even allowing for the *trans* repulsive effect on the N-donor ligands of the multiple Mo–O(terminal) bond. Nevertheless, there is an interaction between the molybdenum atom and the py molecule because the conformations

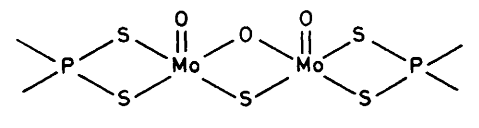

Table 2. Dimensions in the binuclear core of (1), (2), and (3) [a]

	(2)	(3)	(1)
Mo $\cdots$ Mo	2.654(2)	2.671(2)	2.690(2)
Mo–S$_b$	2.336(2), 2.329(8)	2.329(8), 2.308(8)	2.370(4), 2.333(4)
Mo–O$_b$	1.950(8), 1.974(8)	2.174(8), 2.147(13)	1.967(10), 2.011(10)
Mo–O$_b$–Mo	85.1(3)	76.4(5)	85.1(4)
Mo–S$_b$–Mo	69.3(1)	70.3(2)	69.8(1)
O$_b$–Mo–S$_b$	101.6(2), 102.1(3)	106.5(3), 104.9(3)	98.4(3), 98.5(3)
MoO$_b$S$_b$/MoO$_b$S$_b$ [b]	164.0(1)	163.0(1)	146.8(1)
Distances of Mo from S$_3$O plane	0.56(1), 0.55(1)	0.48(1), 0.47(1)	0.69(1), 0.69(1)
Mo–S$_L$	2.484(4), 2.537(3), 2.494(4), 2.530(3)	2.524(4), 2.514(5), 2.508(6), 2.524(7)	2.503(3), 2.475(4), 2.501(3), 2.472(3)
Mo–O$_t$	1.664(11), 1.680(9)	1.660(15), 1.652(16)	1.632(8), 1.654(8)

[a] Subscripts: b = bridging, t = terminal, and L = ligand. [b] Angle between MoO$_b$S$_b$ planes.

of the molybdenum co-ordination spheres are markedly changed by the presence of py, as shown in Table 2.

In (3), the pydz ligand is more strongly bound with both nitrogens bonded, each to one of the metal atoms. The Mo(1)–N(51) and Mo(2)–N(52) distances [2.593(16) and 2.582(14) Å] are much shorter than the Mo–N(py) distances in (2) but still rather long for a Mo–N bond. Evidently, a distance of 2.58—2.59 Å is as close to the molybdenum atoms (and the bridging sulphur and oxygen atoms) as the pydz can approach. The O=Mo–N angles are 176.9(6) and 175.9(6)°, so like (2) the positions *trans* to the Mo=O bond are occupied but in this compound two N atoms are involved, one to each Mo atom. The orientation of the pydz ligand is totally different from that of py in (2); instead of being perpendicular to the Mo–Mo vector, it is parallel and so in the obvious position for the ligand with two adjacent donor nitrogen atoms. The geometry is not ideal for bonding as the two Mo–N–N angles are 104.8(10) and 104.6(10) Å and the Mo–N–C angles are 134.9(14) and 135.1(14) Å. The two molybdenum atoms are close to the plane of the pyridazine ring [deviations: Mo(1) 0.29 Å, Mo(2) 0.09 Å]. The Mo–N–N–Mo torsion angle is $-3.9°$. The N–N bond length is 1.352(22) Å, so it probably still maintains considerable double-bond character (*cf.* N–N single bond 1.45 Å, double bond 1.25 Å).* We could find no other structure in the Cambridge Data Centre files with the pydz bonded in this way.

If the dimensions of the molybdenum core in (2) and (3) are compared with that in the parent compound (1) (Table 2), it is apparent that despite the comparatively weak nature of the Mo $\cdots$ N contacts, the formation of the adduct has had a considerable effect upon the geometry of the binuclear core.

In both (2) and (3), rather surprisingly, the Mo $\cdots$ Mo distance is significantly decreased despite the extra ligand and additional bonding. In (2), the bond lengths to the O and S ligands are similar to those in (1). In (3) compared with (1), Mo–O$_b$ (b = bridging) [2.174(8) and 2.147(13) Å] are greater by *ca.* 0.2 Å. Concomitantly the Mo–O$_b$–Mo angle is reduced from 85.1(3)° in (2) and 85.1(4)° in (1) to 76.4(5)° in (3). The other bond lengths in (3) remain unchanged. The Mo–S$_b$–Mo angles are equivalent in all three molecules. In both structures the mean O$_b$–Mo–S$_b$ angle is increased from the value in (1). These are (mean) 101.9 (2), 105.7 (3), and 98.4° (1).

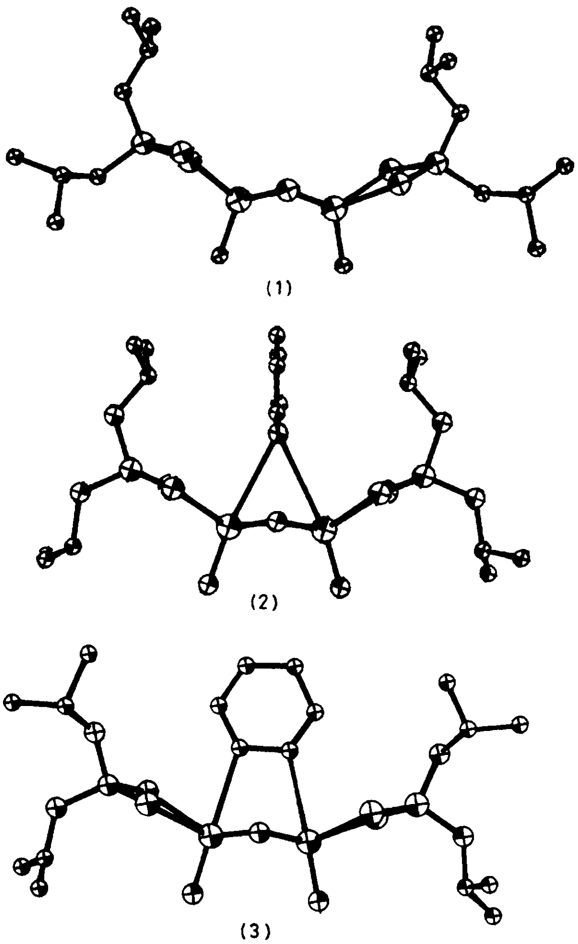

Figure 3. Projection of (1), (2), and (3) down the O$_b$ $\cdots$ S$_b$ vector

Perhaps the most spectacular change is the increase of the angle of fold between the two MoO$_b$S$_b$ groups from 146.8° in (1) to 164.0° in (2) and 163.0° in (3). The Mo–N interaction *trans* to Mo=O has also changed the molybdenum environment: the Mo atoms in (2) and (3) are displaced 0.55 and 0.56 Å and 0.48 and 0.47 Å respectively above the plane compared to 0.69 and 0.69 Å in (1). The smaller Mo displacement in (3) is consistent with our deduction from the Mo–N bond lengths that pydz in (3) is more strongly held than py in (2).

In our preliminary communication [12] of the structure of (2) we pointed out that the incorporation of the pyridine molecule might well be facilitated by the molecular crevice formed by the alkyl chains of the phosphorodithioato-ligands. Figure 3 shows the three molecules projected down the S$_b$ $\cdots$ O$_b$ vector. It is immediately obvious that the conformation of the phosphorodithioato-ligands is equivalent in (1) and (2) but that in (3) is different. Thus in (2) the py can occupy the crevice and approach both molybdenum atoms without requiring the isopropyl groups to change orientation. In (3) the approach of the two nitrogen atoms of pydz does require change in the isopropyl position from that in (1) apparently to permit approach of the pydz to the Mo centres. But in neither structure are there any abnormally short intramolecular distances. Not surprisingly in view of the different orientation of the adduct molecules in the two structures, their closest contacts with the isopropyl groups are different. In (2), the

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* From a survey of bond lengths on the Cambridge Crystal Data Centre Files, January 1982 version.

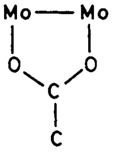
Table 3. Crystal data and refinement details

	(2)	(3)
Formula	$C_{17}H_{33}Mo_2NO_7P_2S_5$	$C_{16}H_{32}Mo_2N_2O_7P_2S_5$
M	777.4	778.4
Crystal class	Monoclinic	Monoclinic
Space group	$P2_1/a$	$P2_1/n$
Absences	$0k0, k = 2n + 1$ $h0l, h = 2n + 1$	$0k0, k = 2n + 1$ $h0l, h + l = 2n + 1$
a/Å	17.200(10)	17.316(8)
b/Å	12.690(11)	14.560(11)
c/Å	15.448(9)	12.150(9)
β/°	110.0(2)	93.0(1)
U/Å^3	3 168.9	3 058.1
Z	4	4
F(000)	1 568	1 568
μ/cm^{-1}	12.26	12.71
D_m/g cm^{-3}	1.63	1.69
D_c/g cm^{-3}	1.63	1.69
λ/Å	0.7107	0.7107
Crystal size (mm)	0.2 × 0.3 × 0.4	0.2 × 0.3 × 0.4
Rotation axis	*a*	*b*
$2\theta_{max.}$/°	50	50
No. of independent data	4 413	4 238
Criteria for data inclusion	$I > 3\sigma(I)$	$I > 2\sigma(I)$
No. of data used in refinement	2 309	2 316
No. of parameters	376	354
R	0.057	0.097
R'	0.061	0.102

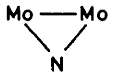
closest contacts (3.70—4.00 Å) are between the isopropyl carbons, C(32), C(33), C(34) and C(22), C(23), C(24), and all six atoms in the pyridine ring. Also, there are several C(py) $\cdots$ H(phosphorodithioate) distances of *ca.* 2.9 Å. In (3), the shortest contacts are O(11) $\cdots$ H(56) and O(31) $\cdots$ H(53) (2.60 and 2.68 Å respectively; *cf.* 3.48 and 3.58 Å to the carbons). There are no contacts between the pydz ligand and the isopropyl carbons of less than 4.3 Å.

A possible explanation of the weakness of the Mo–N bonds in both structures is found in the contacts between the donor nitrogen atoms and the bridging S(7) and O(3) atoms. Thus N(51) is 3.17 and 2.78 Å from S(7) and O(3) respectively in (2); N(51) is 3.07 and 2.92 Å from S(7) and O(3) and N(52) is 3.11 and 2.87 Å from S(7) and O(3), in (3).

We can find no precedent for these two structures and these modes of binding of pyridine and pyridazine. We note that in the compound [{Mo(O)[$S_2P(OEt)_2$]}$_2$(NH)(O)$_2$]·thf (thf = tetrahydrofuran), a molecule of thf solvent is located asymmetrically between two molybdenum atoms.[14] Unlike pyridine and pyridazine in our adducts, thf is lost from this compound at room temperature and the thf molecule has no structural effects despite one Mo–O distance of 2.633 Å. There are some other structures which also involve a bridging group between two molybdenum atoms; for example, in μ-acetato-di-μ-oxo-bis[bis(isothiocyanato)oxomolybdate(v)][15] there is an acetate group bridging the two molybdenum atoms in addition to the two bridging oxygens. The Mo–O(acetate) bond lengths are 2.277(7) and 2.335(6) Å (*i.e.* significantly less than Mo–N in our adducts). This suggests that the five-membered acetate ring (A) is less sterically strained than the three-membered pyridine ring (B) or the four-membered pyridazine ring (C). Incidentally, in the acetate adduct the Mo–O_b distances are normal [1.954(6), 1.933(5), 1.961(5), and 1.931(6) Å] and there is no lengthening, in contrast to (3), despite the strong Mo–acetate bonds. This makes the increase in bond lengths in (3) even more mysterious. There is a report of a structure with a bridging propylenediamine[16] but the Mo–N distance is not published. We would guess that propylenediamine forming a six-membered ring (D) would be as strongly bound to the molybdenum atoms as bridging acetate.



(A)



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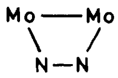
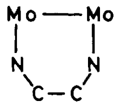


(C)



(D)

Conclusions

The molybdenum phosphorodithioato-complex [{Mo(O)(X)}$_2$(O)(S)] [1; X = $S_2P(OPr^i)_2$] forms 1 : 1 adducts with pyridine and pyridazine [{Mo(O)(X)}$_2$(O)(S)(L)] (L = py or pydz). The adduct molecules L are bound weakly to both Mo atoms of the binuclear structure. Examination of the molecular structures suggests that the phosphorodithioato-ligands may be considered to form a ' molecular crevice ' within which the adduct molecules may be located. The different mode of binding of pydz (the molecular plane parallel to the Mo–Mo vector, Figure 2, rather than at 90° as for the py adduct, Figure 1) causes the isopropyl groups to rotate away from the Mo centres (Figure 2). These weak interactions of N-donor ligands with Mo centres are of interest in connection with substrate binding to unsaturated Mo centres in molybdoenzymes and heterogeneous catalysts. A number of other molecules (methylpyridines, purines, *etc.*) apparently form similar adducts to that of py. We use the term ' crevice co-ordination ' to describe these weak interactions.

Experimental

Preparations.—*μ-Oxo-μ-pyridine-μ-sulphido-bis*[(*OO'-di-isopropyl phosphorodithioato*)*oxomolybdenum*(v)] (2). Pyridine (1.1 g, 14 mmol) was added dropwise to a solution of [{Mo(O)-[$S_2P(OPr^i)_2$]}$_2$(O)(S)] (1)[3] (5.0 g, 7.2 mmol) in toluene (10 cm^3) to which heptane (10 cm^3) had been added. The mixture was allowed to stand for 12 h. The yellow-orange crystals which formed were filtered off, washed with heptane, and dried *in vacuo*. Yield 5.6 g, 99% (Found: C, 25.2; H, 4.4; Mo, 26.2; N, 2.0; P, 7.9; S, 26.0. Calc. for $C_{17}H_{33}Mo_2NO_7P_2S_5$: C, 26.3; H, 4.25; Mo, 24.7; N, 1.80; P, 8.0; S, 20.6%).

μ-Oxo-μ-pyridazine-μ-sulphido-bis[(*OO'-di-isopropyl phosphorodithioato*)*oxomolybdenum*(v)] (3). The procedure was similar to that for the pyridine complex. Crystals formed immediately when pyridazine was added to a toluene–heptane (1 : 1) solution of (1). Yield 5.6 g, 99% (Found: C, 24.7; H, 4.1; N,3.8. Calc. for $C_{16}H_{32}Mo_2N_2O_7P_2S_5$: C, 24.7; H, 4.1; N, 3.6%).

Physical Measurements.—Infrared spectra were determined for the compounds in KBr discs using a Perkin-Elmer 683 spectrophotometer, u.v.–visible spectra using a Unicam SP1800 spectrophotometer, and ^{31}P n.m.r. spectra on a Jeol FX90Q (90 MHz for ^{1}H) n.m.r. spectrometer with 85% aqueous H_3PO_4 as external reference.

Carbon, hydrogen, and nitrogen analyses were determined by standard microanalytical procedures and Mo, P, and S by *X*-ray fluorescence at the Esso Chemical Centre, Abingdon.

Table 4. Fractional atomic co-ordinates ($\times 10^4$) for (2) with estimated standard fractional deviations in parentheses

Atom	*x*	*y*	*z*
Mo(1)	2 824(1)	1 006(1)	1 229(1)
Mo(2)	2 353(1)	1 032(1)	−595(1)
S(7)	3 155(2)	−288(3)	338(3)
S(1)	4 067(3)	298(3)	2 449(2)
S(2)	3 237(3)	2 578(3)	2 305(3)
P(3)	4 099(3)	1 643(3)	3 166(3)
S(4)	3 000(2)	337(3)	−1 699(2)
S(5)	2 205(2)	2 597(2)	−1 653(2)
P(6)	2 631(2)	1 675(3)	−2 439(2)
O(2)	1 391(5)	533(7)	−1 006(7)
O(1)	2 051(6)	506(8)	1 515(7)
O(3)	2 343(5)	2 107(7)	324(5)
N(51)	3 974(8)	1 964(9)	393(13)
C(53)	4 622(9)	3 583(11)	394(10)
C(55)	5 339(8)	2 001(14)	430(10)
C(52)	3 967(9)	3 041(9)	372(11)
C(54)	5 325(9)	3 086(12)	410(10)
C(56)	4 667(11)	1 489(11)	438(14)
O(11)	4 028(7)	1 501(10)	4 134(7)
O(21)	4 983(6)	2 157(8)	3 534(6)
O(31)	3 330(5)	2 207(7)	−2 733(6)
O(41)	2 010(6)	1 494(8)	−3 419(6)
C(12)	3 319(16)	985(23)	4 262(16)
C(13)	3 155(24)	1 674(39)	4 992(20)
C(14)	3 342(27)	−190(30)	4 360(29)
C(22)	5 429(11)	2 409(12)	2 911(11)
C(23)	5 604(16)	3 611(14)	2 990(15)
C(24)	6 169(14)	1 735(20)	3 133(18)
C(32)	4 079(8)	2 624(11)	−2 067(11)
C(33)	4 164(12)	3 742(13)	−2 322(14)
C(34)	4 767(10)	1 943(15)	−2 105(14)
C(42)	1 188(11)	974(18)	−3 582(10)
C(43)	1 239(14)	−87(18)	−4 095(15)
C(44)	551(13)	1 742(23)	−4 114(15)

Table 5. Fractional atomic co-ordinates ($\times 10^4$) for (3) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Mo(1)	1 080(1)	2 061(1)	4 943(2)
Mo(2)	2 619(1)	2 115(1)	4 876(1)
S(1)	64(3)	2 925(4)	5 942(5)
S(2)	11(3)	2 219(4)	3 472(5)
S(4)	3 664(3)	3 102(5)	5 758(5)
S(5)	3 537(3)	2 278(5)	3 342(5)
S(7)	1 927(4)	2 661(7)	6 312(7)
P(3)	−638(3)	2 769(4)	4 601(5)
P(6)	4 240(3)	2 951(5)	4 382(6)
O(1)	904(8)	999(10)	5 358(14)
O(2)	2 881(8)	1 074(11)	5 291(14)
O(3)	1 789(6)	1 819(8)	3 547(13)
N(51)	1 387(9)	3 684(11)	4 201(13)
N(52)	2 161(9)	3 686(10)	4 103(13)
C(53)	2 498(13)	4 390(19)	3 648(23)
C(54)	2 068(14)	5 092(16)	3 286(23)
C(55)	1 310(14)	5 132(15)	3 369(18)
C(56)	988(12)	4 367(18)	3 888(17)
O(11)	−967(7)	3 714(9)	4 327(11)
O(21)	−1 387(7)	2 203(11)	4 769(13)
O(31)	4 462(10)	3 904(14)	4 056(19)
O(41)	5 047(9)	2 490(16)	4 535(16)
C(12)	−1 467(13)	3 922(21)	3 289(22)
C(13)	−1 142(20)	4 691(30)	2 714(32)
C(14)	−2 256(16)	4 147(26)	3 668(35)
C(22)	−1 447(13)	1 215(20)	4 854(22)
C(23)	−1 849(19)	932(23)	5 789(25)
C(24)	−1 864(15)	935(21)	3 716(23)
C(32)	4 904(22)	4 163(28)	3 205(37)
C(33)	5 741(19)	4 254(28)	3 315(35)
C(34)	4 548(22)	5 134(29)	2 875(46)
C(42A)	5 211(48)	1 583(37)	4 872(55)
C(42B)	5 313(50)	1 776(50)	5 283(81)
C(43A)	5 630(51)	1 735(55)	6 002(57)
C(43B)	6 053(35)	2 089(44)	5 960(50)
C(44B)	5 271(79)	884(73)	4 565(98)
C(44A)	5 587(43)	1 071(55)	3 954(59)

Structure Determination.—Crystals of both compounds were obtained as described above. Crystal data are given in Table 3. The two crystals were mounted in turn on a Stoe STADI2 diffractometer and data were collected *via* variable-width ω scan. Background counts were 20 s and the scan rate of 0.033° s^{-1} was applied to a width of (1.5 + sinμ/tanθ). Absorption and extinction corrections were not applied.

Both structures were solved by the Patterson method (with some difficulty, as in both structures the *y* co-ordinates of the Mo atoms were equivalent). The positions of the remaining non-hydrogen atoms were obtained from Fourier syntheses. One of the isopropyl groups in (3) was disordered and two positions were refined with occupancies 0.5 for C(42), C(43), and C(44). The unique hydrogens on atoms C(*n*2) were placed in tetrahedral positions and their thermal parameters were refined. We attempted to locate the positions of the methyl groups through rigid group refinement. Sets of three hydrogen atoms were given a common thermal parameter which was then refined. In (2) all eight groups were located in this way. In (3) only two of the eight groups could be found.

The structure was then refined by full-matrix least squares using SHELX 76.[17] The weighting scheme used was chosen to give equivalent values of $w\Delta^2$ over ranges of F_o and $(\sin\theta)/\lambda$. For both structures this was $w = 1/[\sigma^2(F) + 0.003F^2]$ where $\sigma(F)$ was taken from counting statistics. All non-hydrogen atoms were refined anisotropically. Scattering factors were taken from international tables.[18] Calculations were made using SHELX 76 on the CDC 7600 computer at the University of Manchester Computer Centre. Crystal data and refinement details are given in Table 3. The *R* values were 0.057 for (2) and 0.097 for (3). The rather high value in (3) is due to the poor quality of the data. In addition, some of the isopropyl groups have very large thermal parameters and may also be disordered but an appropriate model could not be found. Atomic co-ordinates are listed in Tables 4 and 5. Details of interatomic distances and angles are listed in Table 6.

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Table 6. Bond lengths (Å) and angles (°) in (2) and (3) with estimated standard deviations in parentheses

	(2)	(3)		(2)	(3)
(*a*) Distances					
Mo(1)-Mo(2)	2.654(2)	2.671(2)	S(2)-P(3)	2.007(5)	1.986(7)
Mo(1)-S(1)	2.484(4)	2.524(6)	S(4)-P(6)	2.025(5)	2.003(10)
Mo(1)-S(2)	2.537(4)	2.514(5)	S(5)-P(6)	1.997(5)	1.969(9)
Mo(1)-S(7)	2.336(4)	2.329(8)	P(3)-O(11)	1.552(12)	1.519(15)
Mo(1)-O(1)	1.664(11)	1.660(15)	P(3)-O(21)	1.571(10)	1.560(15)
Mo(1)-O(3)	1.950(8)	2.174(8)	P(6)-O(31)	1.576(11)	1.499(22)
Mo(1)-N(51)	2.967(19)	2.593(16)	P(6)-O(41)	1.542(8)	1.551(18)
Mo(2)-S(4)	2.494(4)	2.508(6)	N(51)-Y(52) [b]	1.367(16)	1.352(22)
Mo(2)-S(5)	2.530(3)	2.524(7)	N(51)-C(56)	1.317(23)	1.259(28)
Mo(2)-S(7)	2.329(3)	2.308(8)	C(53)-Y(52) [b]	1.311(21)	1.32(3)
Mo(2)-O(2)	1.680(9)	1.652(16)	C(53)-C(54)	1.356(23)	1.33(3)
Mo(2)-O(3)	1.974(8)	2.147(13)	C(55)-C(54)	1.378(23)	1.32(3)
Mo(2)-N(5x) [a]	2.931(13)	2.582(14)	C(55)-C(56)	1.329(24)	1.41(3)
S(1)-P(3)	2.026(5)	1.994(8)			
(*b*) Angles					
S(1)-Mo(1)-S(2)	79.19(12)	77.91(19)	O(2)-Mo(2)-O(3)	106.4(4)	102.0(6)
S(7)-Mo(1)-S(1)	82.69(13)	84.18(24)	S(4)-Mo(2)-N(5x) [a]	86.1(4)	81.3(3)
S(7)-Mo(1)-S(2)	150.38(15)	152.31(28)	S(5)-Mo(2)-N(5x) [a]	83.5(3)	80.9(3)
S(1)-Mo(1)-O(1)	102.7(3)	100.1(5)	S(7)-Mo(2)-N(5x) [a]	73.23(26)	78.9(4)
S(2)-Mo(1)-O(1)	101.3(3)	99.2(5)	O(2)-Mo(2)-N(5x) [a]	170.8(5)	175.9(6)
S(7)-Mo(1)-O(1)	105.4(3)	104.6(5)	O(3)-Mo(2)-N(5x) [a]	65.6(4)	73.9(4)
S(1)-Mo(1)-O(3)	147.94(26)	153.1(3)	Mo(1)-S(1)-P(3)	88.01(17)	87.76(27)
S(2)-Mo(1)-O(3)	82.06(24)	83.4(3)	Mo(1)-S(2)-P(3)	86.97(17)	88.21(26)
S(7)-Mo(1)-O(3)	102.13(27)	104.9(3)	Mo(2)-S(4)-P(6)	87.84(17)	87.71(29)
O(1)-Mo(1)-O(3)	106.3(4)	101.9(6)	Mo(2)-S(5)-P(6)	87.46(15)	88.0(3)
S(1)-Mo(1)-N(51)	87.09(29)	82.7(3)	Mo(1)-S(7)-Mo(2)	69.34(11)	70.34(25)
S(2)-Mo(1)-N(51)	83.4(3)	80.0(3)	S(1)-P(3)-S(2)	105.06(21)	105.5(3)
S(7)-Mo(1)-N(51)	72.44(29)	76.9(4)	S(1)-P(3)-O(11)	115.7(5)	106.4(6)
O(1)-Mo(1)-N(51)	169.7(4)	176.9(6)	S(2)-P(3)-O(11)	115.0(5)	115.7(6)
O(3)-Mo(1)-N(51)	65.0(3)	75.1(4)	S(1)-P(3)-O(21)	113.0(4)	115.4(6)
S(4)-Mo(2)-S(5)	78.82(12)	78.03(21)	S(2)-P(3)-O(21)	113.5(4)	112.5(6)
S(7)-Mo(2)-S(4)	81.99(13)	82.59(25)	O(11)-P(3)-O(21)	94.9(5)	101.6(7)
S(7)-Mo(2)-S(5)	150.72(14)	153.83(29)	S(4)-P(6)-S(5)	104.93(22)	105.8(3)
S(4)-Mo(2)-O(2)	102.7(3)	102.4(5)	S(4)-P(6)-O(31)	113.5(3)	105.3(9)
S(5)-Mo(2)-O(2)	100.6(3)	97.9(5)	S(5)-P(6)-O(31)	113.6(4)	116.7(9)
S(7)-Mo(2)-O(2)	105.1(3)	103.3(6)	S(4)-P(6)-O(41)	114.1(4)	115.6(8)
S(4)-Mo(2)-O(3)	148.46(27)	151.1(3)	S(5)-P(6)-O(41)	114.2(4)	112.5(8)
S(5)-Mo(2)-O(3)	84.15(25)	83.5(3)	O(31)-P(6)-O(41)	97.0(5)	101.0(11)
S(7)-Mo(2)-O(3)	101.60(23)	106.5(3)	Mo(1)-O(3)-Mo(2)	85.1(3)	76.4(5)

Dimensions (°) of py ligand in (2)		Dimensions (°) of pydz ligand in (3)	
Mo(1)-N(51)-Mo(2)	53.46(26)	Mo(1)-N(51)-N(52)	104.8(10)
Mo(1)-N(51)-C(52)	114.7(12)	Mo(1)-N(51)-C(56)	134.9(14)
Mo(2)-N(51)-C(52)	113.0(8)	N(52)-N(51)-C(56)	120.1(16)
Mo(1)-N(51)-C(56)	121.1(11)	Mo(2)-N(52)-N(51)	104.6(10)
Mo(2)-N(51)-C(56)	121.7(9)	Mo(2)-N(52)-C(53)	135.1(14)
C(52)-N(51)-C(56)	117.4(14)	N(51)-N(52)-C(53)	120.2(16)
C(52)-C(53)-C(54)	120.7(13)	N(52)-C(53)-C(54)	119.0(21)
C(54)-C(55)-C(56)	118.7(15)	C(53)-C(54)-C(55)	123.5(23)
N(51)-C(52)-C(53)	121.5(14)	C(54)-C(55)-C(56)	114.7(20)
C(53)-C(54)-C(55)	118.3(14)	N(51)-C(56)-C(55)	122.4(20)
N(51)-C(56)-C(55)	123.4(14)		

x = 1 in (2) and 2 in (3). [b] Y = C in (2) and N in (3).

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