two Cu—Cl distances show a difference of 0·1 Å; even more pronounced is the difference between the angles $(N_1/N_2)^*$—Cu—Cl (143·0°) *vs* $(N_1/N_2)^*$—Cu—Cl′ (117·6°).

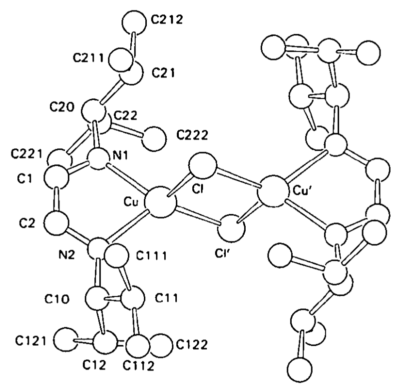

Fig. 1. *SCHAKAL* plot and numbering scheme of (2*b*).

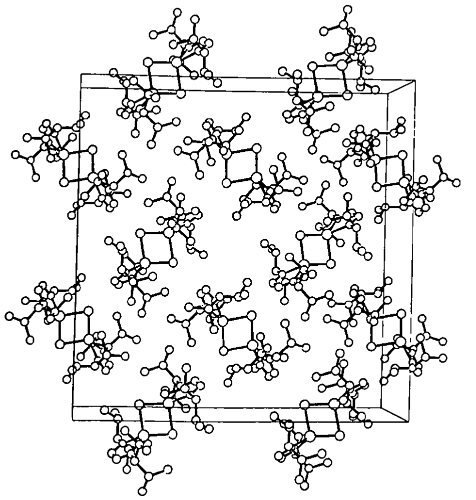

Fig. 2. View of the unit cell along the *c* axis.

The observed structure (Fig. 2) is in agreement with the observed dissociation of (2*b*) in solution into two three-coordinate species (dad)CuCl. Solid (2*b*) is a red crystalline material with $\lambda_m = 510$ nm, while in all solvents $\lambda_m \simeq 375$ nm. The molecular weight in dichloromethane or acetone was determined as 360 ± 20 (calculated for the monomer: 351·4); the solution in acetone showed no conductivity. The steric requirements of the *N*-alkyl substituent in (2*b*) are obviously responsible for the reduced interaction between two such species also in the solid state and (1*b*) avoids completely the complex type $[(dad)_2Cu]^+[CuCl_2]^-$ encountered for (2*a*) (*R* = *tert*-butyl). The half width of the solid state CT band (metal-to-ligand type charge-transfer transition) of (2*b*) ($5500\ cm^{-1}$) is, in agreement with this structure, about 50% greater than for (2*a*) ($3500\ cm^{-1}$).

We thank Dr J. Kopf and Mr D. Melzer for valuable discussion in the course of the structural work.

---

* (N_1/N_2) means the intersection of the line through N(1),N(2) and the plane through Cu, Cl, Cl′.

References

AYRANCI, H., DAUL, C., ZOBRIST, M. & VON ZELEWSKY, A. (1975). *Helv. Chim. Acta*, **58**, 1732–1735.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

KITAGAWA, S. & MUNAKATA, M. (1981). *Inorg. Chem.* **20**, 2261–2267.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J. P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain-la-Neuve, Belgium.

SHELDRICK, G. M. (1977). *SHELX77.* Program for crystal structure determination. Univ. of Cambridge, England.

SVOBODA, M., TOM DIECK, H., KRÜGER, C. & ZSAY, Y.-H. (1981). *Z. Naturforsch. Teil B*, **36**, 814–822.

TOM DIECK, H. & RENK, I. W. (1971). *Chem. Ber.* **104**, 92–109.

TOM DIECK, H., SVOBODA, M. & GREISER, T. (1981). *Z. Naturforsch. Teil B*, **36**, 823–832.

TOM DIECK, H., SVOBODA, M. & KOPF, J. (1978). *Z. Naturforsch. Teil B*, **33**, 1381–1385.

Acta Cryst. (1983). C**39**, 843–845

Structure of μ-Oxo-(pyrimidine)-μ-sulphido-bis{[(*O*,*O*′-diisopropylphosphorodithioato)-*S*,*S*′]oxomolybdenum(V)}, $Mo_2(C_4H_4N_2)(C_6H_{14}O_2PS_2)_2O_3S$

BY PABLO J. BARICELLI, MICHAEL G. B. DREW AND PHILIP C. H. MITCHELL

Department of Chemistry, University of Reading, Whiteknights, Reading RG6 2AD, England

(*Received* 10 *December* 1982; *accepted* 23 *March* 1983)

Abstract. $M_r = 778{\cdot}4$, *Aa*, $a = 11{\cdot}854\ (8)$, $b = 9{\cdot}000\ (7)$, $c = 28{\cdot}849\ (13)$ Å, $\beta = 93{\cdot}27\ (6)°$, $U = 3072{\cdot}7\ Å^3$, $Z = 4$, $D_m = 1{\cdot}67\ (1)$, $D_x = 1{\cdot}68\ g\ cm^{-3}$, Mo *Kα*, $\lambda = 0{\cdot}7107$ Å, $\mu = 12{\cdot}51\ cm^{-1}$, $F(000) = 1568$, $T = 298$ K, $R = 0{\cdot}065$ for 2250 independent reflections. This molecule (II) is the 1:1 adduct of

0108-2701/83/070843-03$01.50

$[(MoOB)_2(O)(S)]$ (*B*=*O,O'*-diisopropylphosphorodithioato) (I) with pyrimidine. The structure of (I) persists in (II) with the pyrimidine molecule located asymmetrically between the two molybdenum atoms and weakly bound to one [Mo—N 2·86 (2), 3·26 (2) Å]. The pyrimidine plane is approximately perpendicular to the Mo···Mo vector.

Introduction. Binuclear molybdenum(V) complexes of the type $[(MoOB)_2O_{2-x}S_x]$ (*B* = dithiocarbamate, $R_2NCS_2^-$, phosphorodithioate, $(RO)_2PS_2^-$, $x = 0,1,2$) are well known (Spivack & Dori, 1975; Stiefel, 1977). Each molybdenum atom is five-coordinate and displaced towards the terminal oxide. The complex $[(MoOB)_2(O)(S)]$ $[B{=}(\text{i-PrO})_2PS_2]$ (I) has been prepared and its structure reported (Drew, Mitchell, Read & Colclough, 1981). The parent compound (I) forms 1:1 adducts with potential ligands such as pyridine, pyridazine, methyl-substituted pyridines and purines. We have reported the crystal structures of the adducts with pyridine (III) and pyridazine (IV) (Drew, Baricelli, Mitchell & Read, 1983) which are similar in that the structure of the parent compound persists but differ in the way in which the pyridine and pyridazine bind to the metal atoms. In (III) the pyridine molecule binds both molybdenum atoms weakly through nitrogen at distances of 2·97 (2), 2·93 (2) Å and the pyridine plane is approximately perpendicular to the Mo···Mo vector. In (IV), the pyridazine is parallel to the Mo···Mo vector with one nitrogen bound to each molybdenum at distances of 2·59 (2), 2·58 (2) Å. In this paper, we report on the structure of another molecule in the series, namely the 1:1 adduct with pyrimidine (II).

Experimental. Pyrimidine (0·20 g, 2·5 m mol) was added dropwise to a solution of $[\{Mo(\text{i-PrO})_2PS_2\}_2(O)(S)]$ (I) (0·50 g, 0·7 m mol) in 1:1 toluene:petroleum ether (6 cm^3). Within a few seconds a yellow solid separated. The solid was recrystallized from 1:1 chloroform:toluene. Analysis: found C 25·0; H 4·05; N 3·53%. Calc. for $C_{16}H_{32}Mo_2N_2O_7P_2S_5$: C 24·7; H 4·11; N 3·60%.

D_m by flotation, crystal 0·2 × 0·2 × 0·5 mm mounted on a Stoe STADI2 diffractometer to rotate around *b* axis, cell dimensions obtained by measurement of high-angle axial reflections, intensity data collected *via* variable-width ω scan, background counts 20s, scan rate 0·033°s^{-1}, scan width $(1{\cdot}5 + \sin\mu/\tan\theta)°$, maximum $2\theta = 50°$, systematic absences for (II) were hkl, $k+l = 2n+1$, $h0l$, $h{=}2n+1$, absorption and extinction corrections not applied, standard reflections measured after every 20 measurements for each layer: no significant change in intensity observed, 2880 independent reflections, $2\theta < 50°$, 2250 with $I > 3\sigma(I)$ included in subsequent calculations.

Positions of Mo determined from Patterson map; these conformed to *A*2/*a* but the first Fourier map indicated that the true space group was *Aa*, and so it proved; non-hydrogen atoms successively located and refined by least squares with *SHELX*76 (Sheldrick, 1976), weighting scheme chosen to give equivalent values of $w\Delta^2$ over ranges of F_o and $\sin\theta/\lambda$, $w = 1/[\sigma^2(F) + 0{\cdot}003\,F^2]$, where $\sigma(F)$ was taken from counting statistics; all atoms refined anisotropically, hydrogen atoms positioned in tetrahedral or trigonal positions, thermal parameters refined but those on the same atom were constrained to be equivalent, methyl groups refined as rigid groups with a common thermal parameter. For pyrimidine ligand, N(1), C(5) had large U_{33} terms but no disorder detected in difference Fouriers; assuming that N(1) is a nitrogen atom, we were unable to say whether C(3) or C(5) is the other nitrogen atom in the ligand. Scattering factors from *International Tables for X-ray Crystallography* (1974). Calculations performed on the CDC7600 computer at the University of Manchester Computer Centre. $R = 0{\cdot}065$ (R_w 0·067).*

Discussion. Coordinates are listed in Table 1 and interatomic distances in Table 2.

Table 1. *Atomic coordinates* (×10^4, Mo×10^5) *with e.s.d.'s in parentheses*

$$U = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	*U*(Å^2×10^3)
Mo(1)	57870	97321 (14)	67780	65 (1)
Mo(2)	53739 (13)	96978 (12)	58638 (5)	51 (1)
S(1)	3708 (4)	9623 (4)	5288 (2)	65 (4)
P(1)	4630 (4)	8331 (4)	4886 (1)	56 (4)
S(2)	6033 (4)	7868 (5)	5280 (2)	65 (4)
S(3)	6815 (4)	7745 (5)	7239 (2)	81 (5)
P(4)	5703 (4)	8032 (5)	7731 (2)	66 (4)
S(5)	4549 (5)	9446 (6)	7445 (2)	95 (5)
S*B*	4104 (3)	10461 (3)	6394 (2)	64 (3)
O*B*	6461 (8)	8690 (9)	6277 (4)	58 (9)
O(1)	6001 (11)	11257 (12)	5697 (5)	75 (12)
O(2)	6541 (13)	11275 (16)	6901 (5)	85 (16)
N(1)	4450 (13)	7032 (16)	6228 (11)	149 (28)
C(1)	5125 (16)	5838 (18)	6215 (7)	79 (19)
C(2)	4622 (18)	4420 (14)	6261 (7)	72 (18)
C(3)	3497 (17)	4372 (17)	6274 (7)	71 (20)
C(4)	2814 (15)	5546 (18)	6270 (7)	69 (18)
C(5)	3341 (16)	6853 (20)	6247 (11)	131 (28)
O(11)	3960 (10)	6934 (13)	4696 (4)	61 (12)
C(12)	3454 (15)	5870 (20)	5013 (6)	70 (18)
C(13)	3818 (23)	4331 (28)	4887 (13)	114 (36)
C(14)	2231 (18)	6024 (20)	4975 (9)	100 (24)
O(21)	6240 (14)	8502 (14)	8213 (5)	79 (16)
C(22)	6976 (22)	9778 (23)	8268 (7)	72 (23)
C(23)	6494 (31)	11063 (37)	8523 (13)	130 (46)
C(24)	8106 (22)	9211 (45)	8496 (10)	98 (40)
O(31)	4885 (11)	9023 (12)	4417 (4)	68 (12)
C(32)	5487 (23)	10433 (18)	4348 (8)	83 (23)
C(33)	4789 (31)	11454 (54)	4103 (14)	183 (62)
C(34)	6597 (25)	10117 (37)	4139 (13)	123 (44)
O(41)	5132 (12)	6557 (15)	7905 (5)	71 (14)
C(42)	4392 (21)	5616 (26)	7564 (11)	80 (29)
C(43)	4886 (27)	4114 (34)	7624 (15)	110 (49)
C(44)	3192 (29)	5810 (38)	7656 (14)	125 (50)

---

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and some bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38460 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Dimensions* (Å,°) *in the coordination sphere*

Mo(1)–Mo(2)	2·655 (2)	Mo(2)–S*B*	2·310 (5)
Mo(1)–S(3)	2·504 (5)	Mo(2)–O*B*	1·931 (10)
Mo(1)–S(5)	2·498 (6)	Mo(2)–O(1)	1·671 (11)
Mo(1)–S*B*	2·320 (4)	Mo(2)–N(1)	2·861 (18)
Mo(1)–O*B*	1·934 (10)	S(1)–P(1)	2·008 (6)
Mo(1)–O(2)	1·678 (15)	P(1)–S(2)	2·004 (6)
Mo(2)–S(1)	2·508 (5)	S(3)–P(4)	2·006 (7)
Mo(2)–S(2)	2·512 (5)	P(4)–S(5)	2·010 (7)
Mo(2)–Mo(1)–S(3)	125·18 (12)	S(5)–Mo(1)–O*B*	144·2 (3)
Mo(2)–Mo(1)–S(5)	132·89 (13)	S*B*–Mo(1)–O*B*	99·2 (3)
S(3)–Mo(1)–S(5)	78·84 (17)	Mo(2)–Mo(1)–O(2)	106·6 (5)
Mo(2)–Mo(1)–S*B*	54·83 (12)	S(3)–Mo(1)–O(2)	104·0 (5)
S(3)–Mo(1)–S*B*	146·59 (15)	S(5)–Mo(1)–O(2)	104·6 (5)
S(5)–Mo(1)–S*B*	82·55 (17)	S*B*–Mo(1)–O(2)	107·4 (5)
Mo(2)–Mo(1)–O*B*	46·56 (29)	O*B*–Mo(1)–O(2)	108·8 (5)
S(3)–Mo(1)–O*B*	80·9 (3)		
Mo(1)–Mo(2)–S(1)	138·75 (13)	S(1)–Mo(2)–O(1)	100·3 (4)
Mo(1)–Mo(2)–S(2)	128·82 (11)	S(2)–Mo(2)–O(1)	101·4 (4)
S(1)–Mo(2)–S(2)	78·57 (15)	S*B*–Mo(2)–O(1)	105·0 (4)
Mo(1)–Mo(2)–S*B*	55·20 (11)	O*B*–Mo(2)–O(1)	106·2 (5)
S(1)–Mo(2)–S*B*	85·89 (16)	Mo(1)–Mo(2)–N(1)	72·4 (5)
S(2)–Mo(2)–S*B*	151·40 (14)	S(1)–Mo(2)–N(1)	85·2 (4)
Mo(1)–Mo(2)–O*B*	46·7 (3)	S(2)–Mo(2)–N(1)	80·6 (5)
S(1)–Mo(2)–O*B*	150·32 (28)	S*B*–Mo(2)–N(1)	74·3 (4)
S(2)–Mo(2)–O*B*	83·3 (3)	O*B*–Mo(2)–N(1)	68·6 (4)
S*B*–Mo(2)–O*B*	99·7 (3)	O(1)–Mo(2)–N(1)	174·4 (6)
Mo(1)–Mo(2)–O(1)	102·5 (4)		
Mo(2)–S(1)–P(1)	87·92 (21)	S(3)–P(4)–S(5)	104·53 (29)
S(1)–P(1)–S(2)	104·79 (27)	Mo(1)–S*B*–Mo(2)	69·97 (12)
Mo(2)–S(2)–P(1)	87·90 (20)	Mo(1)–O*B*–Mo(2)	86·8 (3)
Mo(1)–S(3)–P(4)	87·93 (22)	Mo(2)–N(1)–C(1)	114·8 (13)
Mo(1)–S(5)–P(4)	88·01 (26)	Mo(2)–N(1)–C(5)	121·1 (13)

Table 3. *Interatomic distances* (Å) *and angles* (°) *in the parent phosphorodithioato complex and adducts*

B = $(\text{i-PrO})_2PS_2$; pym = pyrimidine; py = pyridine; pyz = pyridazine.

	(MoO*B*)$_2$(O)(S) (I)	pym adduct (II)	py adduct (III)	pyz adduct (IV)
Mo—N	— —	3·26 (2), 2·86 (2)	2·93 (2), 2·97 (2)	2·58 (2), 2·59 (2)
Mo—(OS_3)	0·69 (1), 0·69 (1)	0·64 (1), 0·53 (1)	0·55 (1), 0·56 (1)	0·47 (1), 0·48 (1)
Mo(1)–Mo(2)	2·690 (2)	2·654 (2)	2·671 (2)	2·655 (1)
Dihedral angle MoO_bS_b–MoO_bS_b	146·8 (1)	155·8 (1)	164·0 (1)	163·0 (1)
O_b—Mo—S_b	98·4 (3), 98·5 (3)	99·2 (3), 99·7 (3)	101·6 (2), 102·1 (3)	106·5 (3), 104·9 (3)

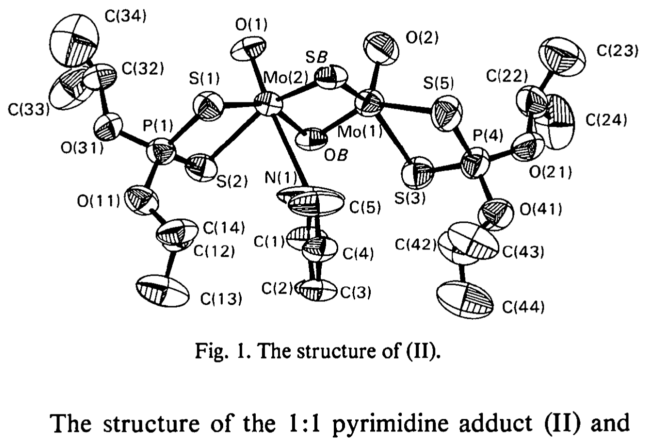

Fig. 1. The structure of (II).

The structure of the 1:1 pyrimidine adduct (II) and the atomic numbering scheme are shown in Fig. 1. The structure of the binuclear unit is similar to that of the parent compound (I), the pyridine adduct (III) and the pyridazine adduct (IV). We discuss the effect of the pyrimidine molecule on the coordination about molybdenum. Although one might imagine that the shorter Mo—N distance [2·86 (2) Å] is too long for a bonding interaction, we find that the coordination about molybdenum is affected by the Mo···N interaction. We present data for the parent compound (I) and the adducts (II), (III), (IV) in Table 3.

The most significant dimension is the distance of a molybdenum atom from the plane of the four equatorial (S_3O) atoms. This distance, when plotted against Mo—N distances, shows a linear correlation between the Mo—(OS_3) distance and Mo—N. This shows the effect of the adduct molecule, which, we might imagine, is pulling the Mo atom into the (OS_3) plane. On this basis the interaction of pyrimidine [with Mo(2)] and pyridine with Mo are similar and weaker than the interaction of pyridazine. Other dimensions which are especially affected by the adduct molecules (see Table 3) are the dihedral angle between the two MoO_bS_b planes, the O_b—Mo—S_b angle and the Mo···Mo distance. Again, the effects of pyrimidine and pyridine are similar and weaker than pyridazine.

One other structural feature worth noting is the conformation of the isopropyl groups of the dithiophosphate ligands. In the projection of the structure of the pyrimidine adduct shown in Fig. 1 the isopropyl groups can be described as 'pointing towards the pyrimidine'. The conformation of the isopropyl groups is similar in the pyridine adduct (III) and in the parent compound (I) but in the pyridazine adduct (IV), where the plane of the ring is parallel with the Mo···Mo vector, the isopropyl groups swing away from the pyridazine. That the isopropyl conformations are similar in the pyridine and pyrimidine adducts confirms our earlier view (Drew, Mitchell & Read, 1982) that the molecular crevice formed by the $(\text{i-PrO})_2PS_2$ groups can adjust to accommodate adduct molecules bound to the Mo atoms.

There are no intermolecular distances of note in the unit cell.

We thank A. W. Johans for his assistance with the crystallographic investigations. PJB thanks the University of Carabobo, Venezuela, for support.

References

Drew, M. G. B., Baricelli, P. J., Mitchell, P. C. H. & Read, A. R. (1983). *J. Chem. Soc. Dalton Trans.* pp. 649–655.

Drew, M. G. B., Mitchell, P. C. H. & Read, A. R. (1982). *J. Chem. Soc. Chem. Commun.* pp. 238–239.

Drew, M. G. B., Mitchell, P. C. H., Read, A. R. & Colclough, T. (1981). *Acta Cryst.* **B37**, 1758–1760.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Sheldrick, G. M. (1976). *SHELX76*. A program for crystal structure determination. Univ. of Cambridge, England.

Spivack, B. & Dori, Z. (1975). *Coord. Chem. Rev.* **17**, 99–151.

Stiefel, E. I. (1977). *Prog. Inorg. Chem.* **22**, 1–45.