The original data set, collected with Mo $K\alpha$ radiation, resulted in too few observed reflections to complete the structure refinement (*SHELX*76; Sheldrick, 1976). A second data set, which was collected with Cu $K\alpha$ radiation, contained enough observed reflections to completely refine the structure (*SHELXL*93; Sheldrick, 1993) and resulted in a lower R value even though a large absorption correction had to be applied to the data. All non-H atoms were refined anisotropically, except for the set of F atoms with an occupancy factor of 0.3 and the atoms of the disordered acetonitrile molecule. A common isotropic U value was refined for all the bipyridine and terpyridine H atoms and a second common U value was refined for the ammine H atoms. The disordered acetonitrile molecule was refined using a model with two positions for the N atom and the methyl group, and a single atom representing the middle C atom. Weighted R factors, wR and all goodness-of-fit values, S, are based on F^2, while conventional R factors, R, are based on F, with F set to zero for negative F^2. Eight reflections were excluded from the refinement because $F_o^2 << F_c^2$. The observation criterion of $F^2 > 2\sigma(F^2)$ is used only for calculating $R_{\rm obs}$, *etc.*, and is not relevant to the choice of reflections for refinement. R factors based on F^2 are statistically about twice as large as those based on F and R factors based on all data will be even larger.

Data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1976). Cell refinement: *CAD*-4 *Operations Manual*. Data reduction: *KAPPA CRYSNET* (Berman, Bernstein, Bernstein, Koetzle & Williams, 1976). Program(s) used to solve structure: *SHELX*76. Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *ORTEP*III (Burnett & Johnson, 1996).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1275). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A 1:2 Adduct of Tetrakis(μ-thiobenzoato-*O*,*S*)dimolybdenum(II)(*Mo*—*Mo*) with Triphenylphosphine Oxide, $[Mo_2(C_7H_5OS)_4].2[(C_6H_5)_3OP]$

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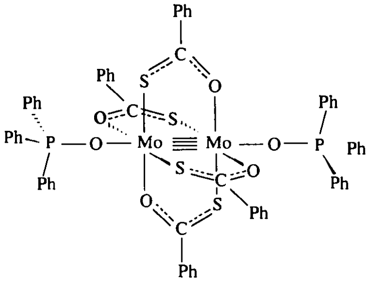
Abstract

The reaction of tetrakis(μ-thiobenzoato-*O*,*S*)dimolybdenum(II)(*Mo*—*Mo*) and triphenylphosphine oxide in a 1:2 stoichiometric ratio yields the title adduct. The dinuclear complex molecule, which has a quadruple Mo$\equiv$Mo bond bridged by four thiobenzoato ligands, is located on a centre of symmetry. This is the first structural example in which two quadruply bonded Mo atoms [2.152(1) Å] are coordinated by both O and S

donor atoms, as well as being the first adduct of an Mo≡Mo species with two axially bonded triphenylphosphine oxide molecules. The Mo—O(Ph$_3$PO) bond is relatively weak, judging by its length of 2.492 (3) Å.

Comment

Quadruply bonded molybdenum(II) dinuclear complexes have been synthesized with a wide variety of bridging ligands. However, whereas many of the $Mo_2(O_2CR)_4$ type and several of the $Mo_2(S_2CR)_4$ type have been structurally characterized (Cotton, 1986), the title complex, (I), as far as we know, is the first example of an Mo≡Mo system in which the Mo atoms are coordinated by both O and S donor atoms, *i.e.* of the $Mo_2(OSCR)_4$ type. Also, this is the first structural example of a 1:2 Mo≡Mo/R_3PO adduct with two axially bonded phosphine oxide molecules. The most closely related structures are unsymmetrical 1:1 adducts, one with triphenylphosphine oxide, $[Mo_2(S_2CNC_4H_4)_2(O_2CCH_3)_2].OPPh_3$, the other with triethylphosphine oxide $[Mo_2(S_2PEt_3)(O_2CCH_3)]BF_4.OPEt_3$. They were the result of unsuccessful attempts to prepare symmetrical 1:2 complexes (Baird, Fanwick & Barwick, 1985).



(I)

The structure of the title complex consists of discrete molecules. The dimeric molecule has a crystallographically imposed centre of symmetry at the midpoint of the Mo—Mo bond, as has been found for structurally related Mo≡Mo complexes. Selected bond lengths and angles are listed in Table 2. The Mo—Mo^i [symmetry code: (i) $-x$, $-y$, $1-z$] bond of 2.153 (1) Å agrees with the values established for such bonds in similar complexes, but is among the longest so far found (Cotton, 1986; Cotton & Walton, 1982).

Although the Mo—O bond to the axially bound triphenylphosphine oxide is quite long [2.492 (3) Å], this interaction is responsible for weakening and lengthening the Mo—Mo bond. In the 1:1 adducts with triphenylphosphine oxide and triethylphosphine oxide mentioned above, the corresponding Mo—O distances are 2.378 (7) and 2.348 (5) Å, respectively. In the title compound, the coordination polyhedron about an Mo atom is quite irregular, with *cis* angles at molybdenum varying from 87.2 (1) to 99.5 (1)°. The Mo—Mo—O(Ph$_3$PO) axial angle of 172.1 (1)° deviates significantly from linearity compared with those found in the unsymmetrical 1:1 adducts with triphenylphosphine oxide [177.9 (2)°] and with triethylphosphine oxide [178.3 (1)°]. The bond lengths and angles in the ligands are within expected ranges.

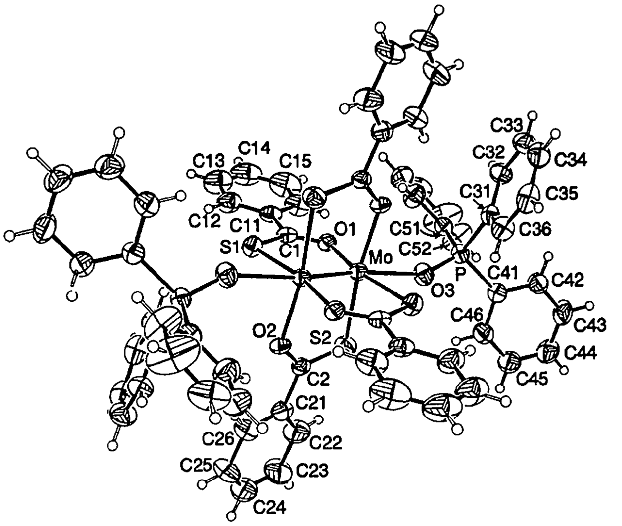


Fig. 1. A view of the title structure with the atom-labelling scheme. For clarity, only the atoms of the assymetric unit, with the exceptions of C16 and C53–C56, are labelled. Displacement ellipsoids are drawn at the 40% probability level.

Experimental

The $[Mo_2(C_7H_5OS)_4]$ complex was synthesized using the literature procedure of Steele & Stephenson (1973). Tetrahydrofuran was carefully dried and distilled prior to use. The title compound was prepared by stirring a mixture of triphenylphosphine oxide (0.23 g, 0.827 mmol) with the complex (0.3 g, 0.405 mmol) in tetrahydrofuran (5 ml) for 30 min at 310–320 K. The synthesis was carried out in an atmosphere of purified nitrogen. Well formed red crystals suitable for X-ray diffraction analysis were grown from the solution, which was left at room temperature for a period of 2–3 d (yield 0.32 g, 60.9%). Analysis found: C 59.01, H 3.75, Mo 14.59, S 9.75%; $C_{64}H_{50}Mo_2O_6P_2S_4$ requires: C 59.26, H 3.89, Mo 14.79, S 9.89%.

Crystal data

$[Mo_2(C_7H_5OS)_4].2C_{18}H_{15}OP$
$M_r = 1297.1$
Monoclinic
$P2_1/c$
$a = 11.936\ (2)$ Å
$b = 20.053\ (3)$ Å
$c = 12.306\ (3)$ Å
$\beta = 93.480\ (10)°$
$V = 2940.0\ (10)$ Å^3
$Z = 2$
$D_x = 1.465$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 48 reflections
$\theta = 7.6–12.1°$
$\mu = 0.674$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.30 × 0.25 × 0.16 mm
Red

Data collection

Philips PW1100 diffractometer updated by Stoe
$\theta/2\theta$ scans
Absorption correction: none
6043 measured reflections
5731 independent reflections
3213 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.044$
$\theta_{\rm max} = 26°$
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 24$
$l = 0 \rightarrow 15$
3 standard reflections frequency: 120 min intensity decay: 4.5%

Refinement

Refinement on F^2
$R(F) = 0.0494$
$wR(F^2) = 0.0933$
$S = 1.085$
5731 reflections
352 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0494P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 1.01$ e Å^{-3} (close to Mo)
$\Delta\rho_{\rm min} = -0.45$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Mo	0.03689 (3)	0.01148 (2)	0.42457 (3)	0.03703 (13)
S1	−0.16220 (11)	0.08577 (6)	0.55821 (11)	0.0484 (3)
S2	−0.10609 (11)	−0.05209 (7)	0.31634 (10)	0.0534 (4)
P	0.20907 (10)	0.05037 (6)	0.17535 (10)	0.0415 (3)
O1	−0.0510 (3)	0.10107 (14)	0.3834 (2)	0.0407 (7)
O2	−0.1718 (3)	−0.07237 (14)	0.5142 (2)	0.0398 (7)
O3	0.1256 (3)	0.0213 (2)	0.2470 (3)	0.0540 (9)
C1	−0.1264 (4)	0.1241 (2)	0.4431 (4)	0.0385 (11)
C2	−0.1897 (4)	−0.0822 (2)	0.4106 (4)	0.0411 (11)
C11	−0.1786 (4)	0.1890 (2)	0.4088 (4)	0.0479 (13)
C12	−0.2570 (5)	0.2206 (3)	0.4698 (5)	0.066 (2)
C13	−0.2987 (6)	0.2827 (3)	0.4387 (7)	0.088 (2)
C14	−0.2635 (7)	0.3122 (3)	0.3485 (7)	0.098 (3)
C15	−0.1867 (7)	0.2828 (3)	0.2855 (6)	0.096 (2)
C16	−0.1454 (5)	0.2197 (3)	0.3165 (5)	0.066 (2)
C21	−0.2908 (4)	−0.1232 (2)	0.3767 (4)	0.0522 (13)
C22	−0.3273 (5)	−0.1322 (3)	0.2710 (5)	0.079 (2)
C23	−0.4225 (6)	−0.1710 (4)	0.2453 (7)	0.099 (2)
C24	−0.4802 (5)	−0.1973 (4)	0.3241 (7)	0.094 (2)
C25	−0.4456 (5)	−0.1895 (3)	0.4310 (7)	0.091 (2)
C26	−0.3505 (5)	−0.1522 (3)	0.4583 (5)	0.069 (2)
C31	0.3457 (4)	0.0615 (2)	0.2441 (4)	0.0422 (11)
C32	0.4076 (4)	0.1196 (3)	0.2406 (4)	0.0544 (13)
C33	0.5123 (5)	0.1236 (3)	0.2972 (5)	0.068 (2)
C34	0.5542 (5)	0.0707 (3)	0.3567 (4)	0.067 (2)
C35	0.4940 (5)	0.0131 (3)	0.3589 (4)	0.068 (2)
C36	0.3891 (4)	0.0081 (3)	0.3040 (4)	0.0578 (14)
C41	0.2294 (4)	−0.0013 (2)	0.0591 (4)	0.0442 (12)
C42	0.3263 (4)	0.0005 (3)	0.0029 (4)	0.0600 (15)
C43	0.3345 (5)	−0.0360 (3)	−0.0913 (5)	0.075 (2)
C44	0.2459 (5)	−0.0742 (3)	−0.1313 (5)	0.072 (2)
C45	0.1517 (5)	−0.0775 (3)	−0.0762 (5)	0.076 (2)
C46	0.1427 (5)	−0.0413 (3)	0.0194 (5)	0.0629 (15)
C51	0.1646 (4)	0.1304 (2)	0.1218 (4)	0.0455 (12)
C52	0.1493 (6)	0.1416 (3)	0.0122 (5)	0.090 (2)
C53	0.1096 (8)	0.2037 (4)	−0.0243 (7)	0.133 (4)
C54	0.0879 (5)	0.2530 (3)	0.0423 (7)	0.087 (2)
C55	0.1002 (6)	0.2409 (3)	0.1512 (6)	0.081 (2)
C56	0.1375 (5)	0.1800 (3)	0.1912 (5)	0.069 (2)

Table 2. *Selected geometric parameters (Å, °)*

Mo—Mo$^{\rm i}$	2.1523 (9)	S1—C1	1.689 (5)
Mo—O1	2.126 (3)	S2—C2	1.688 (5)
Mo—O2$^{\rm i}$	2.122 (3)	P—O3	1.490 (3)
Mo—O3	2.492 (3)	O1—C1	1.283 (5)
Mo—S1$^{\rm i}$	2.4591 (13)	O2—C2	1.295 (5)
Mo—S2	2.4567 (14)		
O2$^{\rm i}$—Mo—O1	87.20 (12)	O1—Mo—O3	87.37 (11)
O2$^{\rm i}$—Mo—Mo$^{\rm i}$	99.10 (8)	Mo$^{\rm i}$—Mo—O3	172.15 (9)
O1—Mo—Mo$^{\rm i}$	99.47 (8)	S2—Mo—O3	83.32 (8)
O2$^{\rm i}$—Mo—S2	167.99 (8)	S1$^{\rm i}$—Mo—O3	81.35 (8)
O1—Mo—S2	89.59 (9)	C1—S1—Mo$^{\rm i}$	104.5 (2)
Mo$^{\rm i}$—Mo—S2	92.84 (4)	C2—S2—Mo	103.5 (2)
O2$^{\rm i}$—Mo—S1$^{\rm i}$	88.92 (9)	C1—O1—Mo	121.4 (3)
O1—Mo—S1$^{\rm i}$	168.35 (9)	C2—O2—Mo$^{\rm i}$	120.9 (3)
Mo$^{\rm i}$—Mo—S1$^{\rm i}$	91.98 (4)	P—O3—Mo	152.3 (2)
S2—Mo—S1$^{\rm i}$	91.96 (5)	O1—C1—S1	122.6 (3)
O2$^{\rm i}$—Mo—O3	84.97 (11)	O2—C2—S2	123.6 (3)

Symmetry code: (i) $-x, -y, 1 - z$.

The positions of the Mo atoms were found by the Patterson method and all other non-H atoms were found by subsequent least-squares refinement and difference electron-density synthesis. H atoms were generated geometrically and their isotropic displacement parameters taken as $1.2U_{\rm eq}$ of the parent atom.

Data collection: *STADI*4 (Stoe & Cie, 1996*a*). Cell refinement: *STADI*4. Data reduction: *XRED* (Stoe & Cie, 1996*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*96 (Sheldrick, 1996). Molecular graphics: *ORTEX*5 (McArdle, 1996). Software used to prepare material for publication: *SHELXL*96.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1284). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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