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Tetraphenylphosphonium *cis*-Tetrabromobis(pyridine)molybdate(III)

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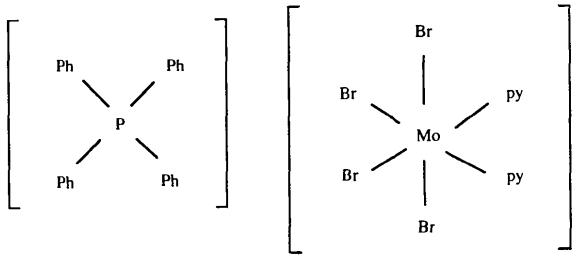
Abstract

The title compound, $(C_{24}H_{20}P)[MoBr_4(C_5H_5N)_2]$, contains a *cis*-$[Mo^{III}Br_4(C_5H_5N)_2]^-$ anion in which Br and N atoms define a slightly distorted octahedron with average Mo—Br and Mo—N(pyridine) distances of 2.580 (5) and 2.220 (5) Å, respectively.

Comment

Several salts of the $[MoBr_4py_2]^-$ anion (where py is pyridine) with univalent cations have been prepared recently (Brenčič, Leban & Modec, 1994). Because chemical and spectroscopic methods do not show unambiguously whether the pyridine ligands are *cis* or *trans*, crystal structure analysis remains the best method of identification.

In the title compound (I) (see Fig. 1, Tables 1 and 2), the pyridine ligands are found to be *cis* with respect to each other. Mo—Br and Mo—N(pyridine) distances are close to the respective values of 2.58 (1) and 2.22 (1) Å found in the crystal structure of the pyridinium salt of *trans*-$[MoBr_4py_2]^-$ (Brenčič, Čeh, Leban, Modec & Rotar, 1993). Each pyridine ring is rotated about its Mo—N bond so as to minimize contacts between the H atoms and the Br(1) and Br(2) atoms. The result of this is seen in the dissymmetry of the *cis*-$[MoBr_4py_2]^-$ anion. The unit cell contains two enantiomorphic pairs of anions. No information is available as to the possibility of separating the optical isomers.



(I)

Bond lengths and angles of the cation are comparable to those found for the crystal structure of $(PPh_4)[MoCl_4(bipy)]$ (Richards, Shortman, Povey & Smith, 1987).

The shortest contact between the anion and the cation is 3.622 (6) Å and occurs between atoms Br(2) and C(42)$(x-1, \frac{3}{2}-y, \frac{1}{2}+z)$.

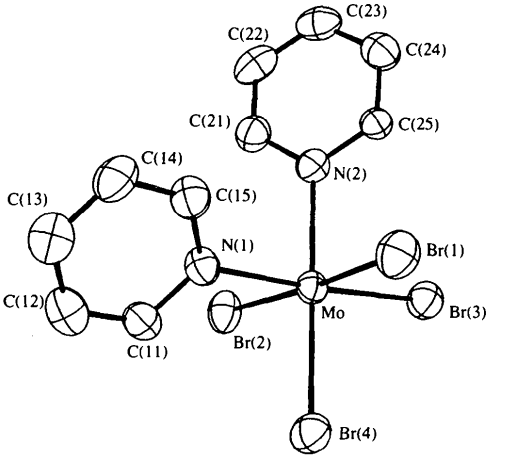


Fig. 1. The structure of the *cis*-$[MoBr_4py_2]^-$ anion with displacement ellipsoids drawn at the 50% probability level.

Experimental

Crystal data

$(C_{24}H_{20}P)[MoBr_4(C_5H_5N)_2]$
$M_r = 913.18$
Monoclinic
$P2_1/c$
$a = 9.439$ (1) Å
$b = 21.600$ (3) Å
$c = 16.678$ (3) Å
$\beta = 94.71$ (1)°
$V = 3388.8$ (9) Å^3
$Z = 4$
$D_x = 1.79$ Mg m^{-3}
$D_m = 1.78$ (2) Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 14$–16°
$\mu = 5.123$ mm^{-1}
$T = 293$ (1) K
Needle
0.48 × 0.22 × 0.18 mm
Red

Data collection

Nicolet *P*3 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (ψ scan)
$T_{min} = 0.844$, $T_{max} = 0.999$
3592 measured reflections
3349 independent reflections
3221 observed reflections $[I \geq 3\sigma(I)]$
$R_{int} = 0.019$
$\theta_{max} = 23.0°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 24$
$l = -19 \rightarrow 19$
3 standard reflections
frequency: 500 min
intensity variation: none

Refinement

Refinement on F
$R = 0.0248$
$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{max} = 0.03$

$wR = 0.0348$
$S = 0.82$
3221 reflections
469 parameters
Only coordinates of H atoms refined
$\Delta\rho_{max} = 0.34$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
Mo	0.04243 (3)	0.50954 (2)	0.76046 (2)	2.540 (8)
Br(1)	0.19767 (5)	0.44411 (3)	0.86280 (3)	3.71 (1)
Br(2)	−0.11811 (6)	0.56335 (2)	0.64844 (3)	3.99 (1)
Br(3)	0.04615 (6)	0.60681 (3)	0.85065 (3)	3.88 (1)
Br(4)	0.26687 (6)	0.54136 (3)	0.69257 (3)	3.90 (1)
N(1)	0.0201 (4)	0.4258 (2)	0.6838 (2)	2.98 (8)
N(2)	−0.1489 (4)	0.4798 (2)	0.8198 (2)	2.95 (8)
C(11)	0.0486 (6)	0.4274 (3)	0.6062 (3)	3.5 (1)
C(12)	0.0406 (6)	0.3752 (3)	0.5583 (3)	4.3 (1)
C(13)	−0.0010 (6)	0.3198 (3)	0.5898 (3)	4.5 (1)
C(14)	−0.0321 (6)	0.3174 (3)	0.6687 (3)	4.2 (1)
C(15)	−0.0191 (6)	0.3712 (2)	0.7134 (3)	3.7 (1)
C(21)	−0.2750 (5)	0.4673 (2)	0.7772 (3)	3.5 (1)
C(22)	−0.3969 (6)	0.4543 (3)	0.8130 (4)	4.4 (1)
C(23)	−0.3927 (6)	0.4514 (2)	0.8956 (4)	4.0 (1)
C(24)	−0.2657 (6)	0.4624 (3)	0.9402 (3)	3.9 (1)
C(25)	−0.1481 (5)	0.4773 (2)	0.9000 (3)	3.3 (1)
P	0.4239 (1)	0.76538 (6)	0.04856 (8)	2.67 (3)
C(30)	0.2455 (5)	0.7492 (2)	0.0740 (3)	2.8 (1)
C(31)	0.1871 (5)	0.7890 (2)	0.1289 (2)	3.4 (1)
C(32)	0.0499 (6)	0.7782 (3)	0.1496 (3)	4.1 (1)
C(33)	−0.0254 (3)	0.7287 (3)	0.1183 (3)	4.2 (1)
C(34)	0.0329 (6)	0.6893 (3)	0.0663 (3)	3.9 (1)
C(35)	0.1684 (5)	0.6989 (2)	0.0435 (3)	3.1 (1)
C(40)	0.5368 (5)	0.7629 (2)	0.1406 (3)	3.0 (1)
C(41)	0.6254 (5)	0.8113 (3)	0.1643 (3)	3.5 (1)
C(42)	0.7090 (6)	0.8065 (3)	0.2365 (3)	4.8 (1)
C(43)	0.7040 (6)	0.7553 (3)	0.2824 (4)	5.4 (2)
C(44)	0.6181 (9)	0.7064 (3)	0.2587 (4)	6.8 (2)
C(45)	0.5317 (8)	0.7103 (3)	0.1876 (3)	5.2 (1)
C(50)	0.4346 (5)	0.8395 (2)	0.0003 (3)	2.8 (1)
C(51)	0.5575 (6)	0.8533 (3)	−0.0365 (3)	4.2 (1)
C(52)	0.5691 (6)	0.9099 (3)	−0.0739 (3)	4.6 (1)
C(53)	0.4602 (6)	0.9513 (2)	−0.0765 (3)	3.9 (1)
C(54)	0.3392 (6)	0.9377 (3)	−0.0395 (3)	4.0 (1)
C(55)	0.3261 (5)	0.8822 (2)	−0.0013 (3)	3.4 (1)
C(60)	0.4761 (5)	0.7079 (2)	−0.0204 (3)	3.1 (1)
C(61)	0.5944 (6)	0.6706 (3)	−0.0022 (3)	4.2 (1)
C(62)	0.6274 (8)	0.6257 (3)	−0.0565 (4)	5.7 (2)
C(63)	0.5454 (8)	0.6176 (3)	−0.1264 (4)	5.9 (2)
C(64)	0.4288 (6)	0.6539 (3)	−0.1453 (3)	4.8 (1)
C(65)	0.3966 (6)	0.6998 (3)	−0.0924 (3)	4.1 (1)

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

Mo—Br(1)	2.5781 (7)	Mo—N(2)	2.224 (4)
Mo—Br(2)	2.5831 (7)	P—C(30)	1.803 (5)
Mo—Br(3)	2.5825 (7)	P—C(40)	1.796 (5)
Mo—Br(4)	2.5761 (7)	P—C(50)	1.799 (5)
Mo—N(1)	2.215 (4)	P—C(60)	1.789 (5)
Br(1)—Mo—N(1)	87.5 (1)	Br(4)—Mo—N(1)	90.4 (1)
Br(1)—Mo—N(2)	89.2 (1)	Br(1)—Mo—Br(2)	173.33 (2)
Br(1)—Mo—Br(3)	94.62 (2)	N(1)—Mo—Br(3)	175.3 (1)
Br(1)—Mo—Br(4)	89.66 (2)	N(2)—Mo—Br(4)	178.6 (1)
Br(2)—Mo—N(1)	85.8 (1)	C(30)—P—C(40)	107.0 (2)
Br(2)—Mo—N(2)	90.1 (1)	C(30)—P—C(50)	111.4 (2)
Br(2)—Mo—Br(3)	91.96 (2)	C(30)—P—C(60)	109.2 (2)
Br(2)—Mo—Br(4)	90.96 (2)	C(40)—P—C(50)	111.0 (2)
N(1)—Mo—N(2)	88.8 (1)	C(40)—P—C(60)	110.7 (2)
N(2)—Mo—Br(3)	87.0 (1)	C(50)—P—C(60)	107.6 (2)
Br(3)—Mo—Br(4)	93.82 (2)		

The displacement parameters of the H atoms were fixed at 1.3 times those of the C atoms to which they were connected. The *SDP* (Enraf–Nonius, 1985) and *NRCVAX* programs (Gabe, Le Page, Charland, Lee & White, 1989) were used for computing and graphics.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1097). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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{2,2-Bis[(diphenylphosphino)methyl]-1-phenylthiopropane-*P*,*P*′,*S*}tricarbonyltungsten(0)

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Abstract

The title complex, $[W(CO)_3(C_{35}H_{34}P_2S)]$, has an octahedral coordination geometry about the W atom, which is surrounded by three carbonyl ligands in a facial arrangement, two P atoms and one S atom.