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Structure of Tetraphenylphosphonium (Bipyridine)tetrachloromolybdate(III) [PPh₄][MoCl₄(bpy)]

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Abstract. [P(C₆H₅)₄][MoCl₄(C₁₀H₈N₂)], $M_r = 733.34$, triclinic, $P\bar{1}$, $a = 9.211(1)$, $b = 12.840(1)$, $c = 14.441(2)$ Å, $\alpha = 104.31(1)$, $\beta = 101.77(2)$, $\gamma = 90.91(1)^\circ$, $V = 1616.1(8)$ Å³, $Z = 2$, $D_x = 1.51$ Mg m⁻³, D_m not measured, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 8.04$ cm⁻¹, $F(000) = 742$, $T = 272$ K, $R = 0.035$ for 4891 reflexions with $I \geq 3\sigma(I)$. Reaction of [MoCl₄(bpy)] with Li₂S₂ in tetrahydrofuran gives Li[MoCl₄(bpy)]. Metathesis using PPh₄Br forms the deep purple title complex, which has been structurally characterized by X-ray crystallography. The Mo atom is surrounded by four Cl ions and a bipyridine ligand in a distorted octahedral arrangement. Average Mo–Cl distance of 2.43 Å is consistent with values found in other Mo^{III} complexes. Two C–C distances of 3.37 and 3.38 Å occur between bipyridine ligands across the centre of symmetry.

Introduction. The EXAFS data on nitrogenase and other molybdoenzymes (Cramer, Hodgson, Gillum & Mortenson, 1978; Cramer *et al.*, 1978) has stimulated intense research interest in the preparation of Mo–S complexes. We have studied the reaction of molybdenum complexes with various sulfur-containing reagents (Povey & Richards, 1984; Povey, Richards & Shortman, 1986) and in continuation of this work lithium sulfide was investigated as a potential source of sulfur ligation.

With the aim of metathesising chloride for sulfide, the complex [MoCl₄(bpy)] was treated with Li₂S₂, but reduction of the Mo centre occurred with the elimination of S to yield the red moisture-sensitive complex Li[MoCl₄(bpy)]. Subsequent treatment by PPh₄Br in methanol converted the lithium complex to the deep

purple tetraphenylphosphonium analogue which is the subject of this structural investigation.

Experimental. Accurate unit-cell parameters were measured on a CAD-4 diffractometer using 25 accurately centred reflexions ($21 \leq \theta \leq 23^\circ$) from a crystal of dimensions $0.3 \times 0.02 \times 0.15$ mm. A full hemisphere of reciprocal space was measured ($0 \leq h \leq 11$, $-15 \leq k \leq 15$, $-17 \leq l \leq 17$), θ limit 26° , $\omega/2\theta$ scan, scan speed $3.3^\circ \text{ min}^{-1}$, 002 reflexion monitored hourly. Variation of its intensity was insignificant during the data-collection period and after data reduction from a total of 6343 unique reflexions 4891 had $I \geq 3\sigma(I)$. Intensity statistics indicated a centrosymmetric distribution and space group $P\bar{1}$ was assumed.

The solution to the structure was not straightforward. Routine application of the direct-methods program *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) failed to produce a refinable structure in the first six solutions although all the heavy-atom peaks satisfied the vector distribution in the Patterson map. Reducing the space group to $P1$, *MULTAN* then produced the correct structure from which the centre of symmetry was deduced. The correct solution in space group $P\bar{1}$ proved to be the eighth solution.

From an electron density map phased upon Mo, four Cl and P the coordinates of the four phenyl groups were obtained and refinement of structure amplitudes converged at $R = 0.105$ with H atoms at calculated positions ($d_H = 1.0$ Å). An absorption correction by *DIFABS* (Walker & Stuart, 1983) reduced R to 0.076 with minimum and maximum corrections 0.661 and 1.215 respectively. Full-matrix anisotropic refinement

first for heavy atoms, then for all atoms converged at $R = 0.035$, $wR = 0.043$, $S = 1.110$ for 4891 reflexions using a weighting scheme $w = [\sigma^2(I) + (0.05F^2)^2]^{-1/2}$. The largest shift/e.s.d. was 0.17 and the highest peak in

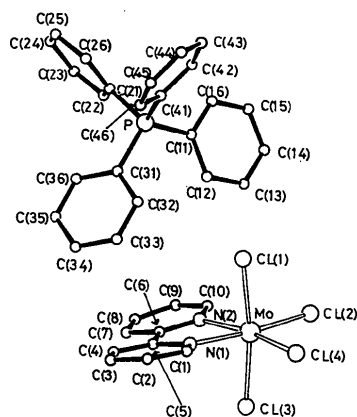


Fig. 1. Structure of [PPh₄][MoCl₄(bpy)] showing the numbering scheme used.

Table 1. Fractional atomic coordinates with e.s.d.'s in parentheses and equivalent isotropic thermal parameters (Å²)

The B_{eq} values are calculated according to the equation

$$B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i \cdot a_j$$

	x	y	z	B_{eq}
Mo	0.49225 (3)	0.38824 (2)	0.24568 (2)	2.432 (5)
Cl(1)	0.49672 (9)	0.58013 (6)	0.31981 (6)	3.52 (2)
Cl(2)	0.66083 (9)	0.41369 (8)	0.14164 (7)	4.42 (2)
Cl(3)	0.4513 (1)	0.19562 (7)	0.17006 (8)	4.27 (2)
Cl(4)	0.68778 (9)	0.36189 (8)	0.37646 (7)	4.31 (2)
P	0.16016 (9)	0.90244 (7)	0.27951 (7)	3.06 (2)
N(1)	0.3144 (3)	0.3717 (2)	0.3187 (2)	2.60 (5)
N(2)	0.2907 (3)	0.3973 (2)	0.1407 (2)	2.63 (5)
C(1)	0.3331 (4)	0.3731 (3)	0.4134 (2)	3.39 (7)
C(2)	0.2158 (4)	0.3614 (3)	0.4567 (3)	3.94 (8)
C(3)	0.0741 (4)	0.3480 (3)	0.4014 (3)	3.97 (8)
C(4)	0.0521 (3)	0.3491 (3)	0.3039 (3)	3.41 (7)
C(5)	0.1739 (3)	0.3613 (2)	0.2643 (2)	2.75 (6)
C(6)	0.1617 (3)	0.3709 (2)	0.1629 (2)	2.74 (6)
C(7)	0.0278 (4)	0.3560 (3)	0.0944 (3)	3.78 (8)
C(8)	0.0272 (4)	0.3715 (3)	0.0034 (3)	4.53 (9)
C(9)	0.1587 (5)	0.4022 (3)	-0.0177 (3)	4.35 (9)
C(10)	0.2881 (4)	0.4136 (3)	0.0518 (2)	3.55 (8)
C(11)	0.2901 (4)	0.8595 (2)	0.2025 (3)	3.11 (7)
C(12)	0.3362 (4)	0.7553 (3)	0.1847 (3)	3.42 (7)
C(13)	0.4409 (4)	0.7273 (3)	0.1276 (3)	4.35 (9)
C(14)	0.4974 (4)	0.8012 (3)	0.0873 (3)	4.70 (9)
C(15)	0.4523 (4)	0.9046 (3)	0.1054 (3)	5.13 (9)
C(16)	0.3485 (4)	0.9340 (3)	0.1616 (3)	4.40 (9)
C(21)	0.0210 (4)	0.9733 (3)	0.2185 (3)	3.65 (8)
C(22)	-0.0320 (4)	0.9376 (3)	0.1184 (3)	4.72 (9)
C(23)	-0.1461 (5)	0.9886 (4)	0.0725 (3)	6.0 (1)
C(24)	-0.2080 (5)	1.0731 (4)	0.1267 (4)	5.8 (1)
C(25)	-0.1581 (4)	1.1081 (3)	0.2259 (4)	5.6 (1)
C(26)	-0.0422 (4)	1.0585 (3)	0.2728 (3)	4.8 (1)
C(31)	0.0721 (3)	0.7880 (3)	0.3016 (2)	2.95 (6)
C(32)	0.1561 (4)	0.7249 (3)	0.3553 (3)	3.60 (8)
C(33)	0.0898 (4)	0.6351 (3)	0.3707 (3)	4.07 (8)
C(34)	-0.0617 (4)	0.6089 (3)	0.3332 (3)	4.07 (8)
C(35)	-0.1449 (4)	0.6723 (3)	0.2816 (3)	3.88 (8)
C(36)	-0.0795 (4)	0.7616 (3)	0.2652 (3)	3.46 (7)
C(41)	0.2515 (4)	0.9903 (3)	0.3951 (3)	3.89 (8)
C(42)	0.3586 (5)	1.0698 (3)	0.3987 (3)	5.0 (1)
C(43)	0.4209 (5)	1.1407 (3)	0.4886 (4)	6.3 (1)
C(44)	0.3789 (6)	1.1326 (4)	0.5717 (4)	6.6 (1)
C(45)	0.2740 (6)	1.0546 (4)	0.5683 (4)	7.1 (1)
C(46)	0.2088 (5)	0.9828 (4)	0.4798 (3)	5.5 (1)

Table 2. Selected bond lengths (Å) and angles (°) with e.s.d.'s in parentheses

Mo—Cl(1)	2.428 (1)	C(11)—C(12)	1.388 (5)
Mo—Cl(2)	2.440 (1)	C(11)—C(16)	1.395 (6)
Mo—Cl(3)	2.433 (1)	C(12)—C(13)	1.389 (6)
Mo—Cl(4)	2.432 (1)	C(13)—C(14)	1.375 (7)
Mo—N(1)	2.156 (3)	C(14)—C(15)	1.376 (6)
Mo—N(2)	2.169 (2)	C(15)—C(16)	1.376 (6)
N(1)—C(1)	1.338 (4)	C(21)—C(22)	1.383 (5)
N(1)—C(5)	1.355 (3)	C(21)—C(26)	1.391 (5)
N(2)—C(6)	1.351 (4)	C(22)—C(23)	1.387 (6)
N(2)—C(10)	1.347 (5)	C(23)—C(24)	1.378 (6)
C(1)—C(2)	1.378 (5)	C(24)—C(25)	1.367 (7)
C(2)—C(3)	1.368 (5)	C(25)—C(26)	1.395 (6)
C(3)—C(4)	1.384 (5)	C(31)—C(32)	1.393 (5)
C(4)—C(5)	1.383 (5)	C(31)—C(36)	1.392 (4)
C(6)—C(7)	1.391 (4)	C(32)—C(33)	1.383 (6)
C(7)—C(8)	1.376 (6)	C(33)—C(34)	1.393 (5)
C(8)—C(9)	1.382 (6)	C(34)—C(35)	1.375 (5)
C(9)—C(10)	1.372 (5)	C(35)—C(36)	1.380 (6)
C(5)—C(10)	1.482 (5)	C(41)—C(42)	1.391 (6)
P—C(11)	1.798 (4)	C(41)—C(46)	1.382 (2)
P—C(21)	1.795 (4)	C(42)—C(43)	1.393 (6)
P—C(31)	1.794 (4)	C(43)—C(44)	1.360 (9)
P—C(41)	1.798 (4)	C(44)—C(45)	1.365 (8)
		C(45)—C(46)	1.389 (6)
Cl(1)—Mo—Cl(2)	92.88 (3)	Cl(2)—Mo—N(2)	95.25 (8)
Cl(1)—Mo—Cl(3)	172.17 (3)	Cl(3)—Mo—Cl(4)	92.20 (3)
Cl(1)—Mo—Cl(4)	92.71 (3)	Cl(3)—Mo—N(1)	87.51 (7)
Cl(1)—Mo—N(1)	85.99 (7)	Cl(3)—Mo—N(2)	83.79 (7)
Cl(1)—Mo—N(2)	90.32 (6)	Cl(4)—Mo—N(1)	95.04 (7)
Cl(2)—Mo—Cl(3)	92.80 (4)	Cl(4)—Mo—N(2)	169.50 (8)
Cl(2)—Mo—Cl(4)	94.63 (3)	N(1)—Mo—N(2)	75.1 (1)
Cl(2)—Mo—N(1)	170.31 (7)		

a difference map was less than $1e \text{ \AA}^{-3}$. Atomic scattering factors and corrections for anomalous dispersion from *International Tables for X-ray Crystallography* (1974). Refinement using *SDP-Plus* (Frenz, 1983).

Discussion. The molecular structure is shown in Fig. 1. Atomic coordinates and some relevant bond distances and angles are listed in Tables 1 and 2 respectively.*

The Mo atom is surrounded by four Cl ions and a bipyridine ligand in a distorted octahedral arrangement. The bipyridine occupies two *cis*-equatorial sites while the Cl ions are found in axial and equatorial positions. The angle between the mean planes of the two pyridine rings is $9.3 (3)^\circ$.

The average Mo—Cl distance is 2.43 Å, which is consistent with values observed in other molybdenum(III) complexes, such as $K_3[MoCl_6]$, $(Mo-Cl)_{av} = 2.45 \text{ \AA}$ (Amilius, Van Laar & Rietveld, 1969); $[MoCl_4(thf)_2]^-$, $(Mo-Cl)_{av} = 2.43 \text{ \AA}$ (Hills, Leigh, Hutchinson & Zubieta, 1985) and $[MoCl_3(C_5H_5N)_3]$, $(Mo-Cl)_{av} = 2.433 (5) \text{ \AA}$ (Brencic, 1974). The axial chlorides are slightly bent towards the bipyridine ligand $[Cl(1)-Mo-Cl(3) = 172.17 (3)^\circ]$.

* Lists of observed and calculated structure factors, anisotropic temperature factors, calculated hydrogen positions and a complete list of bond lengths and angles and a selection of least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44215 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The Mo—N distances 2.156 (3) and 2.169 (2) Å are in the range observed for other molybdenum complexes, such as [Mo(H₂NO)₂(NO)(bpy)], (Mo—N)_{av} = 2.189 Å (Weighardt, Holzback, Weiss, Nuker & Prikner, 1979) and [Mo(OPrⁱ)₂(bpy)₂], (Mo—N)_{av} = 2.118 Å (Chisholm, Huffman, Rothwell, Bradley, Kress & Woodruff, 1981). The bipyridine ligand parameters in [MoCl₄(bpy)]⁻ do not vary significantly from those in the free ligand, which contains *trans*-nitrogen atoms.

The cation is found as a regular tetrahedron with an average P—C(phenyl) of 1.796 (2) Å. In the phenyl rings the average C—C distance is 1.383 (10) Å in a range 1.360–1.395 Å. Two close distances are to be noted in this structure arising from C(8) and C(9) across the centre of symmetry. They are C(8)—C(8) 3.37 and C(8)—C(9) 3.38 Å.

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Structure of a Dipotassium Tetracyanomercurate(II) Salt with Dibenzo-18-crown-6

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Abstract. Bis[(dibenzo[*b,k*][1,4,7,10,13,16]hexaoxacyclooctadeca-2,11-diene)potassium] tetracyanomercurate(II) dihydrate, [K(C₂₀H₂₄O₆)₂][Hg(CN)₄].2H₂O, *M_r* = 1139.7, triclinic, *P* $\bar{1}$, *a* = 14.050 (4), *b* = 14.111 (4), *c* = 14.750 (4) Å, α = 99.49 (2), β = 100.98 (2), γ = 115.87 (2)°, *U* = 2479 (1) Å³, *Z* = 2, *D_m* = 1.50 (3), *D_x* = 1.53 g cm⁻³, λ (Mo *K* α) = 0.7107 Å, μ = 33.27 cm⁻¹, *F*(000) = 1148, room temperature, final *R* = 0.048 for 6479 [*I* > 3 σ (*I*)] independent observed reflections. The structure of the molecule essentially consists of two moieties: one has the tetrahedral tetracyanomercurate(II) anion linked through a cyanide group to a potassium-crown-ether cation [K...N 2.759 (8) Å] while the other is an independent (dibenzo-18-crown-6)potassium complex cation in which the central metal ion is also seven-

coordinate (six O atoms from the macrocycle and the seventh from a water molecule). The average K...O distances are 2.741 and 2.759 Å respectively, excluding the distance to the water molecule for the second fragment which is 2.672 (7) Å.

Introduction. It is well known that the K ion is strongly coordinated to the six oxygen atoms of dibenzo-18-crown-6 and forms the most stable complex amongst Group Ia cations (Izatt, Eatough & Christensen, 1973). Although many compounds containing the [K-DB18C6]⁺ cation have been prepared and characterized there have been relatively few structure reports except for the iodide (Aldoshin, D'yachenko, Tkachev & Atovmyen, 1981; Hilgenfeld & Saenger, 1981), a series of aluminates (Atwood, Hunter, Rogers &