

carboxylato ligands and the bridging aqua ligands. The arrangement of the bridging ligands is also similar to that in the hemerythrin model complexes [$\{\text{Fe}(\text{pz}_3\text{-BH})\}_2(\mu\text{-X})(\mu\text{-O}_2\text{CR})_2\}^n$ [pz = pyrazolyl, X = O, R = H or CH₃, n = 0; Armstrong, Spool, Papefthymiou, Frankel & Lippard (1984)] where the Fe^{III} centres are bridged by an oxo and two carboxylato ligands and a protonated analogue (X = OH, R = CH₃, n = 1+; Armstrong & Lippard, 1984), which has a bridging hydroxo ligand.

The substitution of the two cyclooctadiene ligands in (II) by four PMe₂Ph ligands to give (I) results, as expected, in a marked increase in the Ru–ligand bond lengths *trans* to these phosphine ligands. In (II), the bridging trifluoroacetato ligands are slightly asymmetric with an average Ru–O bond *trans* to a π olefin of 2.128 (5) Å and *trans* to a unidentate trifluoroacetato ligand of 2.088 (5) Å, whereas in (I) the asymmetry is much greater with an average Ru–O bond *trans* to a phosphine ligand of 2.205 (7) Å and *trans* to a unidentate trifluoroacetato ligand of 2.090 (6) Å. The Ru–O(aqua) bond lengths (also *trans* to phosphine ligands) are also longer in complex (I) [average 2.234 (5) Å] compared with (II) [average 2.146 (5) Å]; the aqua bridges are, however, symmetrical within experimental error in both complexes. Commensurate with the increase in some of the bridging Ru–O bond lengths, the non-bonded Ru...Ru distance increases from 3.733 (1) in (II) to 3.881 (1) Å in (I). It is interesting to note here that, despite the lengthening of the Ru–(bridging ligand) bonds in (I),

(II) is significantly more susceptible to breakdown of the $\{\text{Ru}_2(\text{O}_2\text{C}_2\text{F}_3)_2(\mu\text{-O}_2\text{C}_2\text{F}_3)_2(\mu\text{-OH}_2)\}$ core with attack by nucleophiles (*e.g.* phosphines, amines and isonitriles) than is (I). It can be speculated that this difference in reactivity may be attributable to a more strained ligand arrangement in the core of (II) than in (I). The distortion from ideal octahedral geometry for the core ligands in (I) is slightly less than in (II) with a mean absolute deviation from ideal geometry (90 or 180°) for the O–Ru–O angles of 3.4 in (I) and 5.9° in (II).

Intensity data were collected at the National Institute for Materials Research, CSIR, Pretoria.

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Acta Cryst. (1986). **C42**, 49–51

Structure of (2,2'-Bipyridyl)tetrachloroplatinum(IV)

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(Received 4 June 1985; accepted 17 September 1985)

Abstract. $[\text{PtCl}_4(\text{C}_{10}\text{H}_8\text{N}_2)]$, $M_r = 493.1$, monoclinic, Pn , $a = 8.117$ (1), $b = 6.734$ (4), $c = 12.294$ (3) Å, $\beta = 104.15$ (2)°, $V = 651.6$ Å³, $Z = 2$, $D_x = 2.513$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 116.1$ cm⁻¹, $F(000) = 456$, $T = 294$ K, final $R = 0.048$ for 1933 reflections. The Pt is six-coordinate in essentially octahedral geometry with Pt–Cl 2.306 (3) to

2.320 (3) Å and Pt–N 2.038 (8) and 2.044 (9) Å. The Pt–Cl bond lengths reveal significant *trans* effects, the shorter bonds being *trans* to N.

Introduction. Oxidative addition reactions of planar four-coordinate Pt^{II} complexes have been the subject of considerable interest (Buse, Keller & Pritzkow, 1977; Gray, Gulliver, Levason & Webster, 1983). Generally, these oxidations have been achieved by reaction with molecular halogens and in some cases coordinated

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multihalide anions have resulted. This study reports the first structure of a mononuclear $[\text{Pt}^{\text{IV}}(\text{bpy})(\text{tetrahalide})]$ complex. The structure of the Pd^{IV} analogue has been reported recently (Gray *et al.*, 1983).

Experimental. The title compound was obtained by zinc tetrachloride oxidation of an aqueous solution of $[\text{Pt}^{\text{II}}(\text{diamine})(\text{bpy})]^{2+}$ ($\text{bpy}=2,2'$ -bipyridyl) complex and formed as a precipitate. Single crystals were obtained by vapour diffusion of ethanol into a dimethyl sulfoxide solution of the complex. Data collected using Enraf-Nonius CAD-4 automatic diffractometer, graphite-monochromated $\text{Mo } K\alpha$ radiation; 25 independent reflections with $10^\circ \leq 2\theta \leq 41^\circ$ used for least-squares determination of cell constants. Intensities of three reflections monitored, less than 1% decomposition. Structure solved by heavy-atom methods (Sheldrick, 1976); H atoms included at calculated sites (C—H 0.97 Å). Full-matrix least-squares refinement based on F values converged with shifts $< 0.6\sigma$. Max. excursions in final difference map, $+5.0 \text{ e } \text{Å}^{-3}$, were located close to the Pt atom and the next-largest excursions were $\pm 1.0 \text{ e } \text{Å}^{-3}$. All calculations performed with *SHELX76* (Sheldrick, 1976). Scattering factors (neutral Pt for Pt^{II}) and anomalous-dispersion terms taken from *International Tables for X-ray Crystallography* (1974). Data-collection and refinement parameters are collected in Table 1. Final positional parameters are listed in Table 2.*

Discussion. The structure of $[\text{Pt}(\text{bpy})\text{Cl}_4]$ consists of discrete neutral molecules, packed with no intermolecular contacts significantly shorter than the sum of the relevant van der Waals radii. The structure is isostructural with that of the recently reported equivalent Pd^{IV} complex (Gray *et al.*, 1983). Bond lengths and selected angles are listed in Table 3 and an *ORTEP* plot (Johnson, 1965) of the complex molecule with atom labelling is shown in Fig. 1.

$\text{Pt}^{\text{IV}}\text{—Cl}$ bond lengths *trans* to N are the same as those observed in the structure of $[\text{Pt}^{\text{II}}(\text{bpy})\text{Cl}_2]$ (Osborn & Rogers, 1974) while the Pt—N bond lengths are about 0.04 Å longer than those observed in the same structure. Bond lengths to mutually *trans* Cl atoms are slightly longer than those *trans* to N. Similar *trans* influences have been observed in $[\text{Pd}(\text{bpy})\text{Cl}_4]$ (Gray *et al.*, 1983) and in $[\text{Pt}^{\text{IV}}(\text{bpy})\text{I}_4]\text{I}_2$ (Buse *et al.*, 1977). The Pt—N bond lengths are the same as those observed in $[\text{Pd}(\text{bpy})\text{Cl}_4]$ (Gray *et al.*, 1983). However, the Pt—Cl distances are all 0.01–0.02 Å longer than

* Lists of structure amplitudes, anisotropic thermal parameters of non-hydrogen atoms, positional and thermal parameters of H atoms and details of least-squares-planes' calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42476 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Summary of data-collection and processing parameters

Crystal dimensions	0.10 × 0.10 × 0.10 mm
Data-collection range	$2^\circ < 2\theta < 60^\circ$
Scan width	$(0.80 + 0.35 \tan \theta)^\circ$
Horizontal counter aperture	$(2.00 + 0.50 \tan \theta)$ mm
Scan type	ω -1.33 θ
Absorption correction:	
number of sampling points	1728
max. correction	3.212
min. correction	2.009
Range of hkl	$-11 \rightarrow 10, 0 \rightarrow 9, 0 \rightarrow 17$
Total data collected	2157
Unique data after merging	2097
R_{int}	0.002
Data with $I > 2.5\sigma(I)$	1933
Total variables	155
R	0.048
wR	0.059
Weighting constants	$g = 1.0, k = 0.0057$
	$[w = g/(\sigma^2 F_o + kF_o^2)]$

Table 2. Positional ($\times 10^4$) and equivalent isotropic thermal parameters

$B_{\text{eq}} = (8\pi^2/3)(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta)$				
	x	y	z	$B_{\text{eq}}(\text{Å}^2)$
Pt	7500	6983 (1)	7500	1.62
Cl(1)	5967 (4)	8781 (4)	5977 (3)	2.86
Cl(2)	8959 (4)	5187 (5)	9043 (3)	2.72
Cl(3)	9832 (4)	9017 (5)	7659 (3)	2.57
Cl(4)	8540 (4)	4961 (5)	6308 (3)	2.94
N(1)	6437 (10)	8647 (13)	8534 (7)	1.48
N(2)	5392 (11)	5288 (14)	7447 (8)	2.02
C(1)	7041 (19)	10371 (20)	9000 (12)	2.67
C(2)	6222 (22)	11383 (20)	9701 (12)	3.01
C(3)	4734 (23)	10693 (23)	9861 (12)	3.76
C(4)	4106 (19)	8914 (22)	9373 (13)	3.37
C(5)	4958 (20)	7895 (18)	8700 (13)	2.10
C(6)	4383 (14)	6015 (16)	8104 (10)	2.10
C(7)	2942 (18)	5044 (21)	8172 (16)	3.36
C(8)	2489 (37)	3278 (21)	7488 (38)	3.00
C(9)	3522 (19)	2598 (26)	6931 (15)	2.80
C(10)	4978 (16)	3631 (19)	6874 (11)	2.44

Table 3. Selected bond lengths (Å) and angles ($^\circ$)

Pt—Cl(1)	2.320 (3)	Pt—Cl(2)	2.316 (3)
Pt—Cl(3)	2.306 (3)	Pt—Cl(4)	2.307 (3)
Pt—N(1)	2.038 (8)	Pt—N(2)	2.044 (9)
C(1)—N(1)	1.334 (14)	C(5)—N(1)	1.363 (15)
C(6)—N(2)	1.374 (14)	C(10)—N(2)	1.319 (16)
C(2)—C(1)	1.389 (19)	C(3)—C(2)	1.352 (24)
C(4)—C(3)	1.380 (23)	C(5)—C(4)	1.384 (20)
C(6)—C(5)	1.480 (15)	C(7)—C(6)	1.360 (18)
C(8)—C(7)	1.451 (33)	C(9)—C(8)	1.291 (42)
C(10)—C(9)	1.387 (19)		
Cl(1)—Pt—Cl(2)	178.3 (1)	Cl(3)—Pt—Cl(4)	89.1 (1)
Cl(3)—Pt—Cl(2)	89.8 (1)	Cl(4)—Pt—Cl(1)	90.1 (1)
Cl(4)—Pt—Cl(2)	91.1 (1)	Cl(3)—Pt—Cl(1)	91.5 (1)
Cl(1)—Pt—N(1)	89.5 (3)	Cl(1)—Pt—N(2)	89.2 (3)
Cl(2)—Pt—N(1)	89.2 (3)	Cl(2)—Pt—N(2)	89.5 (3)
N(1)—Pt—N(2)	81.3 (4)	Cl(3)—Pt—N(1)	94.9 (2)
Cl(3)—Pt—N(2)	176.0 (3)	Cl(4)—Pt—N(1)	176.1 (2)
Cl(4)—Pt—N(2)	94.8 (3)	Pt—N(1)—C(1)	125.4 (8)
Pt—N(1)—C(5)	114.3 (7)	Pt—N(2)—C(6)	113.4 (7)
Pt—N(2)—C(10)	126.2 (8)		

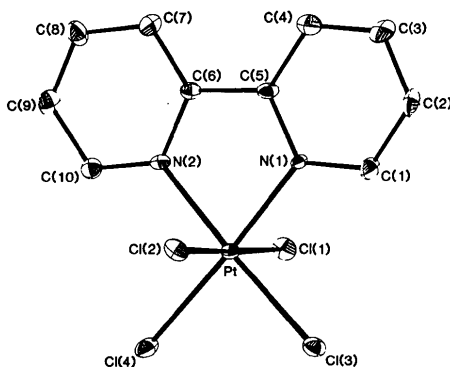


Fig. 1. View of $[\text{Pt}(\text{bpy})\text{Cl}_4]$ with the atom-numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

the equivalent Pd—Cl distances though the same relative *trans* effects on these distances are observed in each structure.

Acta Cryst. (1986), **C42**, 51–53

A 1:1 Complex between 1,4,7,10,13,16-Hexaoxacyclooctadecane (18-Crown-6) and Mercury(II) Iodide

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(Received 1 April 1985; accepted 10 September 1985)

Abstract. $\text{C}_{12}\text{H}_{24}\text{O}_6 \cdot \text{HgI}_2$, $M_r = 718.7$, monoclinic, $C2/m$, $a = 13.049(5)$, $b = 11.241(3)$, $c = 9.285(2)$ Å, $\beta = 134.89(3)^\circ$, $V = 965$ Å³, $Z = 2$, $D_x = 2.47$ g cm⁻³, $\text{Cu K}\alpha$, $\lambda = 1.54178$ Å, $\mu = 410$ cm⁻¹, $F(000) = 660$, room temperature, $R = 0.036$ for 558 unique observed reflections with $|F_o| > 3\sigma(|F_o|)$. The complex has crystallographic $2/m$ symmetry and approximate molecular D_{3d} symmetry. The structure is composed of linear HgI_2 entities inserted normal to the mean plane of the macrocycle with the Hg atom positioned at its centre. The coordination of the Hg atom is hexagonal bipyramidal with axial Hg—I bond distances of 2.622(1) Å and a mean equatorial Hg...O distance of 2.86(2) Å. The accommodation of the large Hg atom within the macrocycle results in a significant

increase in the magnitude of the O—C—C—O torsional angles from the values normally observed in complexes of 18-crown-6 in which the ligands adopt the all-*gauche* conformation with pseudo D_{3d} symmetry.

Introduction. During our recent investigations (Allwood, Crosby, Pears, Stoddart & Williams, 1984) on the complexation of sulfonium cations by 18-crown-6 (18C6), we attempted to isolate a 2:1 crystalline complex between $\text{MeSPh}_2^+\text{HgI}_3^-$ and 18C6 from MeOH. In fact, the first crystals we isolated corresponded to a 1:1 complex between HgI_2 and 18C6, indicating that $\text{MeSPh}_2^+\text{HgI}_3^-$ had disproportionated to $\text{MeSPh}_2^+\text{I}^-$ and HgI_2 under the conditions of the crystal-growing experiment. In view of the

Least-squares-planes' calculations show that the two rings of the bipyridyl group are essentially planar [all deviations less than 0.04 (2) Å], are coplanar, meeting at an angle of 2.2 (7)°, and that no atoms of the ligand deviate by more than 0.08 (2) Å from the plane defined by Pt, Cl(3), Cl(4), N(1) and N(2).

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