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Bis(1,3-diamino-2-propanol-N,N')platinum(II) Chloride 1/3-Hydrate

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Abstract. $[Pt(C_3H_{10}N_2O)_2]Cl_2.1/3H_2O$, $M_r = 452 \cdot 25$, trigonal, $R\bar{3}$, hexagonal axes, $a = 20 \cdot 168$ (6), $c = 8 \cdot 201$ (2) Å, $V = 2889$ (1) Å^3, $Z = 9$, $D_m = 2 \cdot 31$ (4), $D_x = 2 \cdot 34$ g cm^{-3}, graphite-monochromated Mo $K\alpha$ radiation, $\lambda = 0 \cdot 71069$ Å, $F(000) = 1938$, $\mu = 119 \cdot 0$ cm^{-1}, $T = 297$ K, $R = 0 \cdot 0417$ for 1492 unique reflections $(I > 0)$ and 66 parameters. Platinum binds through the two N atoms of each diaminopropanol molecule to give a square-planar environment. The cation has Pt occupying the common vertex of two six-membered rings. The two chloride ions are involved in hydrogen bonding to the O and N atoms of the cation. The water molecule is disordered and at best only weakly hydrogen-bonded to the hydroxyl group. Bond lengths and angles are normal.

Introduction. Attempts to synthesize dichloro(1,3-diamino-2-propanol-N,N')platinum(II) by the reaction of K_2PtCl_4 and 1,3-diamino-2-propanol in water gave one minor product as pale orange crystals which were separated by hand picking. X-ray studies have now identified these crystals as the title compound.

Experimental. Crystals suitable for X-ray analysis were obtained by slow evaporation of an aqueous solution. Density measured by flotation in a $CH_2I_2/CHCl_3$ mixture. Crystal $0 \cdot 3 \times 0 \cdot 3 \times 0 \cdot 5$ mm. Space group $R\bar{3}$ chosen over $R\bar{3}m$ because all atoms except Pt and $O(H_2)$ not in special positions. Justified by successful structure solution. Unit-cell parameters refined by least-squares fit of positional angles of 15 strong independent reflections measured on a Nicolet $P3$ diffractometer. 4869 reflections measured for $2 \cdot 3 < 2\theta < 55 \cdot 1°$, monochromated Mo $K\alpha$ radiation. Intensities of h, k, $\pm l$ measured by the ω–2θ scan technique.

Scan rate $6 \cdot 0$ to $29 \cdot 3°$ min^{-1} in 2θ. The ratio of total background time to scan time is 1:1. Two standard reflections monitored every 48 scans showed that no correction for instrument instability or crystal decay was required. Data averaged to give 1500 unique and 1492 observed reflections $(I > 0)$. $R_{int} = 0 \cdot 024$. Lp and absorption corrections were made (absorption correction factors $16 \cdot 0$–$48 \cdot 9$). Structure solved by heavy-atom method. Anisotropic least-squares refinement (isotropic for oxygen) minimizing $\sum w(|F_o| - |F_c|)^2$, $w = (\sigma_F^2 + 0 \cdot 000684 F_o^2)^{-1}$ excluding unobserved $(I < 0)$ reflections. Some H atoms were located in a difference map but attempts to refine their positional parameters and temperature factors were unsuccessful. Their positions were fixed and temperature factors assigned to be $1 \cdot 5$ times U_{eq} of the atom to which they were attached. Final $R = 0 \cdot 0417$ and $wR = 0 \cdot 0485$. Inspection of F_o and F_c values indicated no correction for secondary extinction was necessary. In final refinement cycle $(\Delta/\sigma)_{max} = 0 \cdot 17$. Final difference map revealed no significant regions of electron density with max. $0 \cdot 63$ and min. $-0 \cdot 75$ e Å^{-3}. Scattering factors for non-hydrogen atoms from *International Tables for X-ray Crystallography* (Cromer & Waber, 1974). Corrections for anomalous dispersion were made for Pt and Cl (Cromer & Ibers, 1974). Calculations employed the *SHELX76* (Sheldrick, 1976) system of programs and *ORTEP* (Johnson, 1976).*

Discussion. The final atomic parameters for non-hydrogen atoms are given in Table 1. Distances and angles are given in Table 2. The molecular cation and cell packing are shown in Figs. 1 and 2 respectively. The Pt atom is bound to both N atoms of each ligand to give a square-planar arrangement. The six-membered rings adopt the chair conformation and the hydroxy group is in an equatorial position. Pt—N distances are similar to those observed in other amine complexes (Barnes, Iball & Weakley, 1975; Iball, MacDougall & Scrimgeour, 1975; Lock & Pilon, 1981; Lock & Zvagulis, 1980; Milburn & Truter, 1966) and the C—C and C—N bond distances are also in good agreement with similar structures (Kallel, Fail, Fuess & Daoud, 1980; Lock, Speranzini & Zvagulis, 1980). Three cations are arranged in a layer about the threefold axis like the blades of a propeller; the direction of tilt of the blades alternates in each layer up the c direction. Between each pair of cations in a layer is a chloride ion. The hydroxy groups point towards the threefold axis giving a channel in which the water molecule lies. The water molecule lies at 3·418 (8) Å from any hydroxy group and since one would expect the water molecule to lie about 3·2 Å from a hydroxy group, even if there were only very weak hydrogen bonding, the water molecule is probably disordered. The high temperature
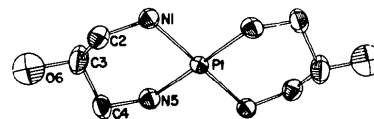

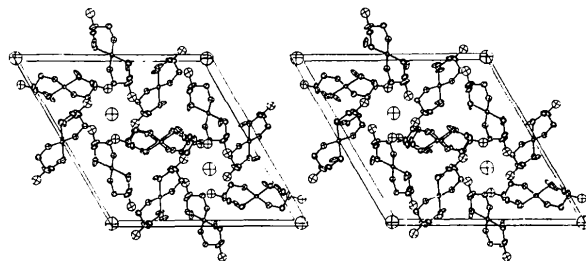Fig. 1. The molecular cation showing the atom numbering.

Fig. 2. The packing within the unit cell. a and b* are parallel to the bottom and sides of the page and the view is down c.

Table 1. *Atomic positions* $(\times 10^4)$ *and thermal parameters* $(Å^2 \times 10^3)$ *for non-hydrogen atoms*

	x	y	z	U_{iso} or U_{eq}
Pt	5000	5000	0	20·3 (2)*
N(1)	4697 (3)	5493 (3)	−1835 (9)	28 (4)*
C(2)	4080 (4)	5679 (4)	−1534 (9)	33 (5)*
C(3)	3347 (5)	4976 (6)	−971 (12)	51 (7)*
C(4)	3408 (5)	4752 (6)	787 (12)	37 (4)*
N(5)	3894 (3)	4390 (3)	854 (7)	31 (4)*
O(6)	2764 (5)	5174 (5)	−990 (9)	80 (2)
Cl	576 (1)	7717 (1)	−1782 (3)	40 (1)
O(7)	0	0	5000	220 (20)

$$* U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33} - U_{12}).$$

Table 2. *Selected interatomic distances* (Å) *and bond angles* (°)

Pt—N(1)	2·058 (7)	C(4)—C(5)	1·49 (1)
C(3)—C(4)	1·54 (1)	C(2)—C(3)	1·52 (1)
C(3)—O(6)	1·42 (2)	Pt—N(5)	2·057 (6)
N(1)—C(2)	1·49 (1)		
N(1)—Pt—N(5)	87·5 (3)	C(3)—C(4)—C(5)	110·4 (8)
C(2)—C(3)—C(4)	112·0 (7)	C(4)—C(3)—N(6)	107·1 (8)
C(2)—C(3)—O(6)	106·9 (9)	N(1)—C(2)—C(3)	111·2 (8)
Pt—N(1)—C(2)	119·2 (4)	C(4)—N(5)—Pt	118·4 (4)
Hydrogen bonds			
N(1)···Cl^i	3·347 (6)	N(5)···Cl^v	3·258 (8)
O(6)···O(7^{iv})	3·418 (8)	O(6)···Cl^{iii}	3·20 (1)
N(1)···Cl^{ii}	3·311 (8)	N(5)···Cl^{vi}	3·306 (7)

Atoms are related to those in Table 1 by the transformations: (i) $\tfrac{1}{3}+x$, $-\tfrac{1}{3}+y$, $-\tfrac{1}{3}+z$; (ii) $\tfrac{1}{3}+(x-y)$, $\tfrac{2}{3}+x$, $-\tfrac{1}{3}-z$; (iii) $-1+y$, $-x+y$, $-z$; (iv) x, $1+y$, z; (v) $-\tfrac{2}{3}+(y-x)$, $\tfrac{2}{3}-x$, $\tfrac{2}{3}+z$; (vi) x, y, $1-z$.

factor is consistent with this model. Refinement of a disordered molecule with partial occupancy did not give a better refinement. That the hydrogen bonding is only weak is confirmed by the infrared spectrum which shows a fairly sharp asymmetric peak at 3428 cm⁻¹. We have observed this behaviour previously (Lock & Pilon, 1981).

The arrangement of the chloride ions brings them fairly close to the axial positions of the square planes, thus maximizing the ionic interactions. However, they are displaced from the axial positions to allow maximum hydrogen bonding to the hydroxy and amine groups of five different surrounding cations.

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The Red–Violet Isomer of Dichlorobis[2-(*m*-tolyl)azopyridine]osmium(II)

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Abstract. $[OsCl_2(C_{12}H_{11}N_3)_2]$, $M_r = 655 \cdot 6$, triclinic, $P\bar{1}$, $a = 8 \cdot 593$ (7), $b = 10 \cdot 78$ (1), $c = 13 \cdot 52$ (1) Å, $\alpha = 79 \cdot 10$ (8), $\beta = 91 \cdot 69$ (7), $\gamma = 78 \cdot 74$ (7)°, $V = 1203$ (2) Å^3, $Z = 2$, $F(000) = 636$, $\lambda(Mo\,K\alpha) = 0 \cdot 7107$ Å, $\mu = 61 \cdot 2$ cm^{-1}, $D_x = 1 \cdot 81$ g cm^{-3}, $R = 0 \cdot 044$ for 2884 observed $[I > 3\sigma(I)]$ reflections. With respect to the pairs of Cl, N(py) and N(azo) atoms coordinating with Os, the isomer has an octahedral *cis–cis–cis* configuration. Relative shortness of Os–N(azo), 1·95 (1), 2·00 (1) Å, compared to Os–N(py), 2·02 (1), 2·05 (1) Å, together with long N=N distances, 1·28 (1), 1·33 (1) Å, indicate considerable π-backbonding power of the azo function.

Introduction. The azoimine chemistry of Os had remained a quite unexplored area until the synthesis, spectra and redox properties of dibromo- and dichloro-bis[2-(*m*-tolyl)azopyridine]osmium(II) were reported by Ghosh, Goswami & Chakravorty (1983). Two isomers of the latter complex, blue–violet and red–violet in solution, have been isolated and characterized by spectral and chemical study. Dihalogenated metal complexes of 2-arylazopyridine may, in principle, occur in five different octahedral configurations. The coordinating pairs of halogen, N(py) and N(azo) atoms may be arranged *trans–trans–trans* (*ttt*), *trans–cis–cis* (*tcc*), *cis–trans–cis* (*ctc*), *cis–cis–trans* (*cct*) or *cis–cis–cis* (*ccc*). A structural study of the blue–violet isomer has already established its configuration to be *ctc* (Ghosh, Mukhopadhyay, Goswami, Ray & Chakravorty, 1984). The results also indicated the presence of strong Os–N(azo) bonding, similar to the Ru–N(azo) bonds in the 2-phenylazopyridine complexes of ruthenium (Seal & Ray, 1984). The present work was undertaken to determine the configuration of the coordination octahedron in the red–violet isomer, as well as to look for evidence, if any, of superior π-backbonding power of the azo function in this complex.

Experimental. Specimen size $0 \cdot 3 \times 0 \cdot 2 \times 0 \cdot 15$ mm. Nicolet Syntex *R*3 diffractometer, graphite-monochromated Mo*K*α radiation. 15 reflections (to $2\theta = 18 \cdot 51°$) for measurement of lattice parameters. D_m not measured since all suitable liquids available were solutions of bromides and iodides with which the crystal reacted; ω–2θ scans, $\theta_{max} = 25°$, h 0 to 10, k −12 to 12, l −15 to 15; 3946 unique reflections measured (no merging of equivalents), 1062 with $I \le 3\sigma(I)$ considered unobserved; 012 and 131 used as standards, intensities showed no decay throughout data collection; no absorption correction; structure solved by Patterson and successive Fourier syntheses. Least-squares refinement on F; atomic scattering factors and f', f'' for Os from *International Tables for X-ray Crystallography* (1974). Block diagonal approximation after the introduction of anisotropic thermal parameters. Towards the end of the refinement, the weighting scheme $[w = 1/\sigma^2(F)]$ was modified so as to reflect the trends in $|\Delta F|$, by adopting the following empirical values of $\sigma(F)$ (Seal & Ray, 1981): for $|F_o| \le 14 \cdot 7$, $\sigma(F) = 0 \cdot 282F_o$; for $14 \cdot 7 < |F_o| \le 16 \cdot 8$, $\sigma(F) = 0 \cdot 221F_o$; for $16 \cdot 8 < |F_o| \le 18 \cdot 6$, $\sigma(F) = 0 \cdot 196F_o$; for $18 \cdot 6 < |F_o| \le 20 \cdot 6$, $\sigma(F) = 0 \cdot 163F_o$; for $20 \cdot 6 < |F_o| \le 22 \cdot 8$, $\sigma(F) = 0 \cdot 133F_o$; for $22 \cdot 8 < |F_o| \le 25 \cdot 8$, $\sigma(F) = 0 \cdot 114F_o$; for $25 \cdot 8 < |F_o| \le 29 \cdot 4$, $\sigma(F) = 0 \cdot 091F_o$; for $29 \cdot 4 < |F_o| \le 34 \cdot 2$, $\sigma(F) = 0 \cdot 077F_o$; for $34 \cdot 2 < |F_o| \le 44 \cdot 3$, $\sigma(F) = 0 \cdot 068F_o$; for $|F_o| > 44 \cdot 3$, $\sigma(F) = 0 \cdot 063F_o$. Sixteen H atoms kept fixed at their calculated positions; those belonging to the two CH_3 groups could not be located. Refinement converged [max. $(\Delta/\sigma) = 0 \cdot 459$] at $R = 0 \cdot 044$, $wR = 0 \cdot 051$, $S = 1 \cdot 004$, for 2884 observed reflections. Final difference map showed max. and min. peaks of $0 \cdot 8$ and $-0 \cdot 8$ e Å^{-3}. All calculations carried out on a Burroughs 6700 computer; *XRAY ARC* program system (*World List of Crystallographic Computer Programs*, 1973) locally adapted for the B6700. Program sequence *NORMAL–EXFFT–SEARCH* from the *MULTAN*78