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Bis(1,3-diaminopropane)diiodoplatinum(IV) Diiodide Dihydrate

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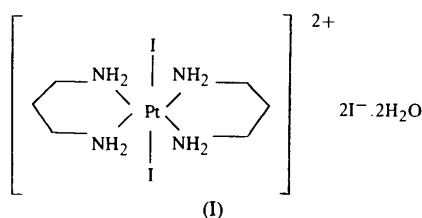
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Abstract

The structure of the title compound, $[\text{PtI}_2(\text{C}_3\text{H}_{10}\text{N}_2)_2] \cdot \text{I}_2 \cdot 2\text{H}_2\text{O}$, consists of six-coordinate monomeric $[\text{Pt}(\text{diamine})_2\text{I}_2]^{2+}$ cations, I^- anions and water molecules. Pt has tetragonal bipyramidal coordination geometry. Linear $\text{I} \cdots \text{I} - \text{Pt} - \text{I} \cdots \text{I}$ units are arranged in the direction of the *b* axis.

Comment

The reaction between K_2PtCl_4 and KI gives rise to several kinds of iodoplatinates in addition to K_2PtI_4 (Beachle, Rotter, Thiele & Clark, 1992). The reaction of K_2PtI_4 , prepared by this path, with amines thus easily yields a mixture of products. The title compound, (I), was obtained during an investigation of the nature of a black contaminant found in the crude product of an earlier synthesis (Oksanen, Kivekäs, Lumme & Laitalainen, 1991). The formation of black by-products has also occasionally been mentioned in the literature for the reactions of K_2PtCl_4 or $\text{K}[\text{PtCl}_3\text{NH}_3]$ with amines or pyridine derivatives (Connors *et al.*, 1972; Kong & Rochon, 1978; Hydes, 1982).



The structure of the title compound consists of six-coordinate monomeric $[\text{Pt}(\text{diamine})_2\text{I}_2]^{2+}$ units, I^- ions and water molecules. Pt has tetragonal-bipyramidal coordination geometry and the complex cation has point symmetry *mm*. The six-membered Pt–diamine ring is in a chair conformation. The puckering of the two bidentate amine ligands, both in the same direction from the coordination plane of the centre atom, differs from that found in *trans*-dichlorobis(1,3-diaminopropane)-platinum(IV) tetrachloroplatinate (Delafontaine, Tofforoli, Khodadad & Rodier, 1988). The present arrangement is relatively rare among 1,3-diaminopropane and 1,3-diamino-2-propanol complexes.

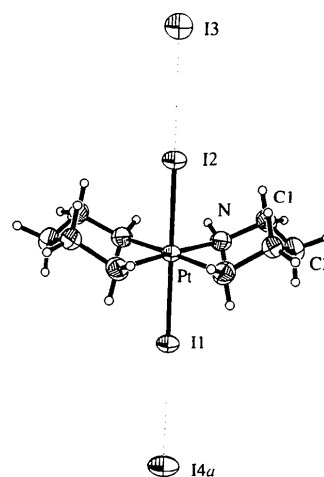


Fig. 1. Structure of the complex showing 50% probability displacement ellipsoids.

The $\text{Pt}^{\text{IV}}-\text{I}$ bond lengths of 2.6925 (11) and 2.7140 (9) Å are almost equal to those of 2.684 (1) Å in bis(1,2-diaminoethane)diiodoplatinum(IV) diiodide dihydrate (Freckmann & Tebbe, 1981) and 2.75 (4) Å in bis(1,3-diaminopropane)platinum(II) bis(1,3-diaminopropane)diiodoplatinum(VI) tetraperchlorate (Cannas, Marongiu, Keller, Müller & Martin, 1984).

The uncoordinated I3 atom displays a short contact [3.593 (1) Å] to the coordinated I2 atom. The $\text{I1} \cdots \text{I4}$ ($-x, -y, 1 - z$) distance is longer [3.834 (1) Å]. The exactly linear $\text{I} \cdots \text{I} - \text{Pt} - \text{I} \cdots \text{I}$ units are arranged in the direction of the *b* axis. A similar almost linear moiety has been found in bis(1,2-diaminoethane)diiodoplatinum(IV) diiodide dihydrate (Freckmann & Tebbe, 1981).

Several $\text{N}-\text{H} \cdots \text{I}$, $\text{N}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{I}$ hydrogen bonds link the anions, cations and water molecules together (Fig. 2, Table 3).

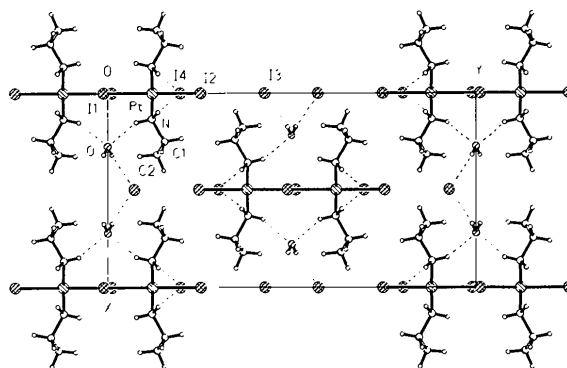


Fig. 2. Packing diagram of the unit cell.

Experimental

A black colloidal solution of K_2PtCl_4 (0.6 mmol, 249.1 mg) and KI (3 mmol, 498.0 mg) in molar ratio 1:4 was warmed moderately and one molecular equivalent of 1,3-diamino-

propane (0.5 ml, 1.2 M solution) was added to the solution under vigorous stirring. A greenish precipitate contaminated with black particles formed rapidly. A similar greenish crude product with black particles was obtained in a previous synthesis with 1,3-diamino-2-propanol (Oksanen *et al.*, 1991). When a second molecular equivalent of the ligand was added to the mixture, the greenish precipitate gradually turned bright yellow and the black contamination disappeared. The mixture was heated with a few drops of concentrated HCl for several hours. During the heating the yellow precipitate slowly turned partly black. From the hot filtrate, lustrous black needles were obtained by slow evaporation. The crystals were of very good quality with well formed crystal faces. The crystals appeared dark red under the light of a microscope.

Crystal data

[PtI ₂ (C ₃ H ₁₀ N ₂) ₂] ₂ ·2H ₂ O	Mo K α radiation
$M_r = 886.98$	$\lambda = 0.71073 \text{ \AA}$
Orthorhombic	Cell parameters from 18 reflections
<i>Cmcm</i>	$\theta = 8-13^\circ$
$a = 10.741 (2) \text{ \AA}$	$\mu = 13.63 \text{ mm}^{-1}$
$b = 20.532 (4) \text{ \AA}$	$T = 293 (2) \text{ K}$
$c = 8.776 (2) \text{ \AA}$	Needle
$V = 1935.4 (7) \text{ \AA}^3$	$0.20 \times 0.15 \times 0.10 \text{ mm}$
$Z = 4$	Black
$D_x = 3.044 \text{ Mg m}^{-3}$	
D_m not measured	

Data collection

Nicolet P3 diffractometer	$\theta_{\max} = 30^\circ$
ω - 2θ scans	$h = 0 \rightarrow 15$
Absorption correction:	$k = 0 \rightarrow 28$
ψ scans (North, Phillips & Mathews, 1968)	$l = 0 \rightarrow 12$
$T_{\min} = 0.845$, $T_{\max} = 1.00$	3 standard reflections monitored every 100 reflections
1575 measured reflections	intensity decay: none
1575 independent reflections	
1101 observed reflections	
$[I > 2\sigma(I)]$	

Refinement

Refinement on F^2	$\Delta\rho_{\max} = 1.013 \text{ e \AA}^{-3}$
$R[F^2 > 2\sigma(F^2)] = 0.0328$	$\Delta\rho_{\min} = -1.306 \text{ e \AA}^{-3}$
$wR(F^2) = 0.0788$	Extinction correction:
$S = 0.923$	<i>SHELXL93</i> (Sheldrick, 1993)
1575 reflections	Extinction coefficient:
55 parameters	0.00022 (3)
H atoms: see below	Atomic scattering factors from <i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
$w = 1/[\sigma^2(F_o^2) + (0.0402P)^2 + 7.0411P]$	
where $P = (F_o^2 + 2F_c^2)/3$	
$(\Delta/\sigma)_{\max} = 0.084$	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

		$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$		
	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Pt	0	0.12125 (2)	1/4	0.03014 (13)
I1	0	-0.01093 (3)	1/4	0.0370 (2)
I2	0	0.25239 (4)	1/4	0.0427 (2)

13	0	0.42738 (5)	1/4	0.0563 (3)
14	0	0.19766 (5)	3/4	0.0561 (3)
O	0.2787 (7)	0	0	0.052 (2)
N	-0.1348 (5)	0.1196 (2)	0.0806 (6)	0.0414 (12)
C1	-0.2543 (6)	0.1546 (3)	0.1053 (10)	0.050 (2)
C2	-0.3222 (10)	0.1336 (5)	1/4	0.055 (3)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Pt—N	2.075 (5)	N—C1	1.487 (8)
Pt—I2	2.6925 (11)	C1—C2	1.527 (9)
Pt—I1	2.7140 (9)		
N'—Pt—N	178.1 (2)	N'—Pt—I1	89.07 (12)
N'—Pt—N''	91.5 (3)	N—C1—C2	113.4 (6)
N'—Pt—I2	90.93 (12)	C1'''—C2—C1	112.5 (8)

Symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (ii) $-x, y, z$; (iii) $x, y, \frac{1}{2} - z$.

Table 3. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	H...A	D...A	D—H...A
N—H1...O'	2.16	2.985 (6)	153
N—H2...I4''	2.72	3.616 (5)	174
O—HO1...I3'''	2.64	3.563 (5)	162

Symmetry codes: (i) $-x, -y, -z$; (ii) $x, y, z - 1$; (iii) $\frac{1}{2} - x, \frac{1}{2} - y, -z$.

The H atoms of the water molecule were located from a difference synthesis; all other H atoms were included in calculated positions (C—H and N—H 0.96 and 0.90 \AA) and refined isotropically ($U = 0.080 \text{ \AA}^2$) using a riding model. The high residual electron density of 1.013 e \AA^{-3} lies *ca* 1.71 \AA from the Pt ion. A similar but much higher maximum has been reported earlier for platinum compounds (Mégnamisi-Bélombé & Endres, 1985; Oksanen *et al.*, 1991).

Data collection: P3 diffractometer software (Nicolet XRD Corporation, 1980). Cell refinement: P3 diffractometer software. Data reduction: P3 diffractometer software. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1105). 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':6',2''-Terpyridine(1-methylimidazole-*N*³)platinum(II) Perchlorate Acetonitrile Solvate

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Abstract

The title compound, $[\text{Pt}(\text{C}_{15}\text{H}_{11}\text{N}_3)(\text{C}_4\text{H}_6\text{N}_2)](\text{ClO}_4)_2 \cdot \text{C}_2\text{H}_3\text{N}$, is formed by reaction of chloro-2,2':6',2''-terpyridineplatinum(II) chloride dihydrate with 1-methylimidazole in the presence of excess amounts of NaClO_4 . The platinum center is approximately square-planar N_4 -coordinated to the tridentate terpyridine and monodentate 1-methylimidazole with Pt–N 1.943 (7)–2.026 (7) Å. The imidazole ring forms a dihedral angle of $66.5(2)^\circ$ with the planar Pt–terpyridine ring system. The crystal packing is dominated by π – π stacking interactions with the absence of any short metal···metal interactions.

Comment

A primary interest in Pt^{II} complexes derives from the finding that a number of its amine complexes possess antitumor properties, accounting for the large number of investigations into its coordination properties with biological molecules such as DNA (*e.g.* Pasini & Zunino, 1987, and references therein).

Complexes of the type $[\text{Pt}(\text{tpy})\text{X}]^{n+}$ ($\text{tpy} = 2,2':6',2''$ -terpyridine) belong to the class of compounds referred to as metallo-intercalators (Lippard, 1978). Intercalation of a Pt–tpy moiety into DNA occurs between two Watson–Crick base pairs, unwinding the DNA helix and puckering the deoxyribose rings (Wang, Nathans, van der Marel, van Boom & Rich, 1978). However, other modes of interaction with DNA by Pt-based drugs also involve direct covalent binding (Pasini & Zunino, 1987).

As part of an investigation into metal-ion–biomolecule interactions (Buncel, Joly & Jones, 1986; Buncel, Joly & Yee, 1989; Buncel, Clement & Onyido, 1994; Buncel & Clement, 1995; Clement, Roszak & Buncel, 1996) we have studied the complex formed between $[\text{Pt}(\text{tpy})\text{Cl}]\text{Cl}$ and 1-methylimidazole (MeIm) as a model for the interaction of Pt^{II} complexes with DNA. In this case the nitrogen base (MeIm) displaces chlorine and binds covalently to the terpyridineplatinum(II) cation. We report here the crystal and molecular structure of the acetonitrile solvate of the resulting complex, $[\text{Pt}(\text{tpy})(\text{MeIm})](\text{ClO}_4)_2 \cdot \text{MeCN}$, (I).

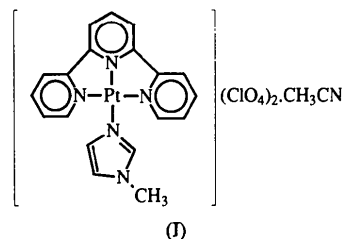


Fig. 1 shows the cation of (I) viewed perpendicularly to the PtN_4 coordination plane. The dihedral angle between the least-squares Pt–terpyridine plane and the plane of the imidazole ring is $66.5(2)^\circ$, which is probably a result of steric interactions between the C16 and C18 H atoms of imidazole and the C1 and C15 H atoms of terpyridine. The restricted bite angle of the tridentate terpyridine ligand has caused a small distortion at the Pt atom from square-planar geometry. The *cis* N1–Pt–N2 and N2–Pt–N3 angles are less than 90° [$80.5(3)$ and $81.3(3)^\circ$, respectively], as is commonly observed in terpyridine complexes (*e.g.* Bailey, Catalano & Gray, 1993; Yip, Cheng, Cheung & Che, 1993; Jennette, Gill, Sadownik & Lippard, 1976; Aldridge, Stacy & McMillin, 1994). The

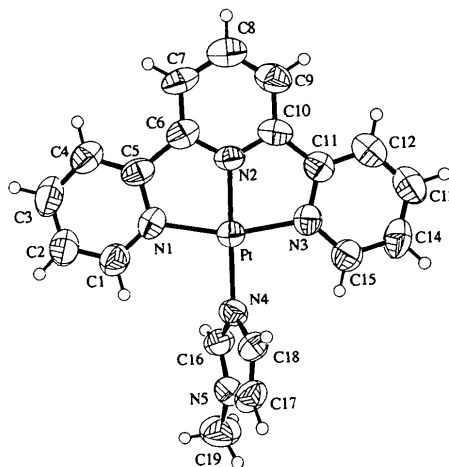


Fig. 1. Molecular structure of the title cation with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as unlabeled spheres of arbitrary size.