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(4,7-Dimethyl-1,10-phenanthroline)(ethylenediamine)platinum(II) dichloride tris(deuterium oxide) solvate

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In the molecule of the title compound, $[Pt(C_{14}H_{12}N_2)(C_2H_4D_4N_2)]Cl_2\cdot 3D_2O$, the complex dication has square-planar coordination to the Pt^{II} atom from *N*-donor atoms. A small tilt of 4.34 (6)° is observed between the plane of the phenanthroline (phen) ligand and the coordination plane. The phen ligands are assembled along [010], with π–π stacking interactions between phen ligands of interleaved complexes. The structure also reveals hydrogen-bond interactions between the complex ion, its counter-ions and the solvent molecules. The introduction of methyl residues onto the phen ligand at positions 4 and 7 does not appear to alter the geometry of the complex significantly.

Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.004 Å
R factor = 0.018
wR factor = 0.038
Data-to-parameter ratio = 17.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

In the last five years some platinum(II) complexes containing derivatized 1,10-phenanthroline (phen) ligands have shown potential as anticancer drugs (Brodie *et al.*, 2004). These complexes are able to intercalate within the base-stack of DNA (Lippard *et al.*, 1976; Cusumano *et al.*, 1999; Wang *et al.*, 1978), similar to the organic intercalator ethidium bromide (Jennette *et al.*, 1974). From ^{1}H NMR spectra, it has been shown that these complexes intercalate DNA from the minor

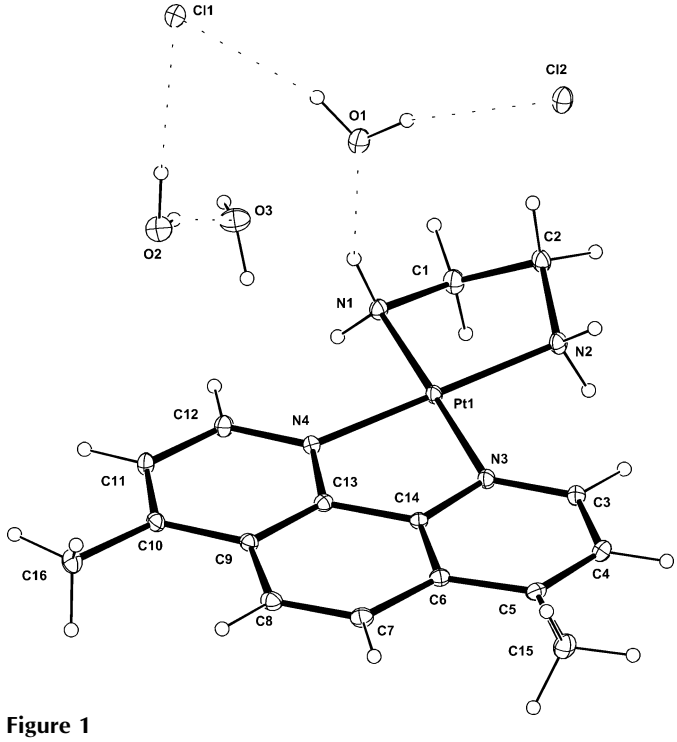
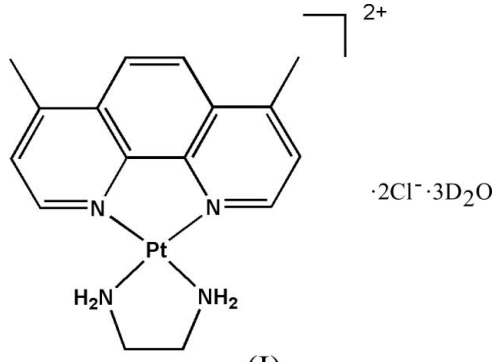


Figure 1
A view of the title compound, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines.

groove between cytosine and guanosine base pairs (Collins *et al.*, 2000). Recently, our group has shown that the cytotoxicity of platinum intercalators can be modulated by changing the number and location of methyl groups on the phen ligand and changing the ancillary ligand (Brodie *et al.*, 2004; Jaramillo *et al.*, 2006). These complexes are also able to overcome cisplatin resistance in selected cancer cell lines, although the mechanism by which they do this is not known. Circular dichroism, NMR and viscosity measurements do not display significantly different DNA binding modes. It is therefore important to study the structural features of each platinum complex, as small structural changes may greatly affect the ability of each platinum complex to bind DNA. We present here the crystal structure of the title platinum complex, (I).



(I)

The asymmetric unit of (I) contains the complex molecule, three deutero-water solvent molecules and two Cl^- counterions (Fig. 1). The substituted phen ligand is essentially planar, with the largest deviation from the least-squares plane being 0.030 (3) Å for atom C5. The four N atoms defining the coordination geometry are coplanar and the metal ion is displaced by only 0.009 (1) Å from that plane. The least-squares coordination plane is slightly inclined with respect to the phen plane, with a dihedral angle of 4.34 (6)°. Similarly, a deviation of 2.34 (1)° is observed in the unsubstituted analogue ethylenediamine-*N*,*N*′-(1,10-phenanthroline-*N*,*N*′)-platinum(II) dichloride dihydrate (Kato & Takahashi, 1999). Larger tilts are observed in other methyl-substituted phenanthrolines with bulky ligands opposite the phen ligand (Romeo *et al.*, 2005).

The coordination sphere bonds are as might be expected (Kato & Takahashi, 1999) and the square-planar coordination 'bite' angles are likewise unremarkable. Thus, the methyl subsituents at positions 4 and 7 of the phen ligand evidently have minimal impact on the geometry of the complex. In contrast, the nature of the ligand opposing the phen ligand can significantly perturb the geometry and shape of the complex (Romeo *et al.*, 2005). The shape of the complex may well effect its ability to intercalate within DNA and, through that, its cytotoxicity. Our results suggest subtle changes may be sufficient to alter significantly the binding of a complex to DNA.

The phen ligands of complex (I) are assembled along [010], with offset π–π stacking interactions between adjacent phen ligands. Hydrogen-bond interactions link the complex ion, counterions and solvent molecules together (Fig. 1), to form tube-like networks of hydrogen bonds along the $(\frac{1}{2}, y, \frac{1}{4})$ and $(\frac{1}{2}, y, \frac{3}{4})$ screw axes.

Experimental

The synthesis of the title complex was as described previously by Brodie *et al.* (2004). Briefly, 4,7-Dimethyl-1,10-phenanthroline (0.283 g, 1.36 mmol) was reacted with an equimolar amount of K_2PtCl_4 (0.56 g, 1.36 mmol) in water (4 ml) and dimethyl sulfoxide (12 ml). The resultant yellow precipitate was then refluxed with ethylenediamine (0.40 g, 6.66 mmol) to yield a clear yellow solution. The product was purified by precipitation with $NaClO_4$ (5 ml) and washed with HCl (1 *M*), water, acetone, ethanol and ether, then converted back to the chloride salt using Amberlite ion-exchange resin. Crystals of the title complex formed in a sealed NMR tube from a solution in D_2O.

Crystal data

$[Pt(C_{14}H_{12}N_2)(C_2H_4D_4N_2)]Cl_2\cdot 3D_2O$
M_r = 598.41
Monoclinic, $P2_1/c$
a = 11.3986 (16) Å
b = 7.1092 (10) Å
c = 24.761 (4) Å
β = 101.623 (2)°
V = 1965.4 (5) Å^3
Z = 4
D_x = 2.022 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 7.44 mm^{-1}
T = 150 (2) K
Acicular, pale yellow
0.44 × 0.06 × 0.05 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
ω scans
Absorption correction: Gaussian [*GAUSSIAN* (Coppens *et al.*, 1965) and *XPREP* (Siemens, 1995)]
T_{min} = 0.212, T_{max} = 0.720
19380 measured reflections
4717 independent reflections
4126 reflections with $I > 2\sigma(I)$
R_{int} = 0.034
θ_{max} = 28.3°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.018
$wR(F^2)$ = 0.038
S = 1.01
4717 reflections
277 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.02P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.007
$\Delta\rho_{max}$ = 1.63 e Å^{-3}
$\Delta\rho_{min}$ = −0.46 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pt1—N3	2.019 (2)	Pt1—N1	2.034 (2)
Pt1—N4	2.027 (2)	Pt1—N2	2.044 (2)
N3—Pt1—N4	80.97 (8)	N3—Pt1—N2	98.33 (9)
N3—Pt1—N1	178.93 (8)	N4—Pt1—N2	179.05 (9)
N4—Pt1—N1	98.02 (9)	N1—Pt1—N2	82.67 (9)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—D1OA···Cl2	0.86 (2)	2.41 (2)	3.257 (2)	166 (3)
O1—D1OB···Cl1	0.87 (2)	2.32 (2)	3.160 (2)	162 (3)
O2—D2OA···Cl1	0.88 (2)	2.40 (2)	3.284 (2)	175 (3)
O2—D2OB···O3	0.86 (2)	1.95 (2)	2.788 (3)	168 (4)
O3—D3OA···Cl1^{i}	0.86 (2)	2.35 (2)	3.177 (2)	164 (3)
O3—D3OB···Cl2^{ii}	0.86 (2)	2.32 (2)	3.181 (2)	174 (3)
N1—D1NA···Cl1^{i}	0.84 (3)	2.43 (3)	3.226 (3)	159 (3)
N1—D1NB···O1	0.93 (3)	1.97 (3)	2.836 (3)	155 (3)
N2—D2NA···Cl2^{i}	0.96 (3)	2.27 (3)	3.216 (3)	166 (2)
N2—D2NB···Cl2^{iii}	0.82 (3)	2.61 (3)	3.336 (2)	149 (3)

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

The water and amine D atoms were located in a difference synthesis and refined isotropically [O—D = 0.856 (18)–0.881 (18) Å and U_{iso}(H) = 0.025 (8)–0.066 (13) Å^2; N—D = 0.82 (3)–0.96 (3) Å and U_{iso}(H) = 0.030 (8)–0.040 (9) Å^2]. The remaining H atoms were positioned geometrically, with C—H = 0.95, 0.99 and 0.98 Å for aromatic, methylene and methyl H, respectively, and constrained to ride on their parent atoms, with U_{iso}(H) = xU_{eq}(C), where x = 1.5 for methyl H, and x = 1.2 for all other H atoms. The largest residual electron-density peak is 1.634 e Å^{-3} at 0.9 Å from the Pt site.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT* and *XPREP* (Siemens, 1995); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Xtal3.6* (Hall *et al.*, 1999), *ORTEPII* (Johnson, 1976) and *WinGX* (Farrugia, 1999); software used to prepare material for publication: *SHELXL97*.

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