Received 27 August 2006
Accepted 18 October 2006

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In the molecule of the title compound, [Pt(C_{14}H_{12}N_{2})-(C_{2}H_{4}D_{4}N_{2})]Cl_{2}-3D_{2}O, 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.

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 1H 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.
The asymmetric unit of (I) contains the complex molecule, three deuto-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 CS. 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)°.

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 substituents 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 affect 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 (1, y, z) and (1, y, z) 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\(_2\)PtCl\(_4\) (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 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\(_2\)O.

**Crystal data**

\[\text{[Pt(C}_{14}\text{H}_{12}\text{N}_{2})(\text{C}_{2}\text{H}_{4}\text{D}_{4}\text{N}_{2})]\text{Cl}_{2} \cdot 2\text{D}_{2}\text{O}\]

\[V = 1965.4 (5) \text{ Å}^3\]

\[Z = 4\]

\[D_\text{m} = 2.022 \text{ Mg m}^{-3}\]

\[\mu = 7.44 \text{ mm}^{-1}\]

\[T = 150 (2) \text{ K}\]

\[\text{Acicular, pale yellow}\]

\[0.44 \times 0.06 \times 0.05 \text{ mm}\]

**Data collection**

Bruker SMART 1000 CCD area-detector diffractometer

4380 measured reflections

4126 reflections with \(I > 2\sigma(I)\)

\(\theta_{\text{max}} = 28.3^\circ\)

**Refinement**

Refinement on \(F^2\)

\(R(F^2) = 0.018\)

\(wR(F^2) = 0.038\)

\(S = 1.01\)

4717 reflections

277 parameters

H atoms treated by a mixture of independent and constrained refinement

\[w = 1/\sigma^2(F_\text{o}) + (0.02P)^2\]

where \(P = (F_\text{o}^2 + 2F_\text{c}^2)/3\)

\(\Delta\rho_{\text{max}} = 1.63 \text{ e Å}^{-3}\)

\(\Delta\rho_{\text{min}} = -0.46 \text{ e Å}^{-3}\)

**Table 1**

Selected geometric parameters (Å, °).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Bond</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt1—N3</td>
<td>2.019 (2)</td>
<td>Pt1—N1</td>
<td>2.034 (2)</td>
</tr>
<tr>
<td>Pt1—N4</td>
<td>2.027 (2)</td>
<td>Pt1—N2</td>
<td>2.044 (2)</td>
</tr>
<tr>
<td>N3—Pt1—N4</td>
<td>80.97 (8)</td>
<td>N3—Pt1—N2</td>
<td>98.33 (9)</td>
</tr>
<tr>
<td>N3—Pt1—N1</td>
<td>178.93 (8)</td>
<td>N4—Pt1—N2</td>
<td>179.05 (9)</td>
</tr>
<tr>
<td>N4—Pt1—N1</td>
<td>98.02 (9)</td>
<td>N1—Pt1—N2</td>
<td>82.67 (9)</td>
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</tbody>
</table>
### Table 2
Hydrogen-bond geometry (Å, °).

<table>
<thead>
<tr>
<th>D—H—A</th>
<th>D—H</th>
<th>H—A</th>
<th>D—A</th>
<th>D—H—A</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1—D1O—C12</td>
<td>0.86</td>
<td>2.41</td>
<td>3.257</td>
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<tr>
<td>O1—D1O—C11</td>
<td>0.87</td>
<td>2.32</td>
<td>3.160</td>
<td>162</td>
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<tr>
<td>O2—D2O—C1</td>
<td>0.88</td>
<td>2.40</td>
<td>3.284</td>
<td>175</td>
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<tr>
<td>O2—D2O—O3</td>
<td>0.86</td>
<td>1.95</td>
<td>2.788</td>
<td>168</td>
</tr>
<tr>
<td>O3—D3O—C1</td>
<td>0.86</td>
<td>2.35</td>
<td>3.177</td>
<td>164</td>
</tr>
<tr>
<td>O3—D3O—O3</td>
<td>0.86</td>
<td>2.32</td>
<td>3.181</td>
<td>174</td>
</tr>
<tr>
<td>N1—D1N—Cl1i</td>
<td>0.84</td>
<td>2.43</td>
<td>3.226</td>
<td>159</td>
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<tr>
<td>N1—D1N—O1</td>
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<td>1.97</td>
<td>2.836</td>
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</tr>
<tr>
<td>N2—D2N—Cl2i</td>
<td>0.96</td>
<td>2.27</td>
<td>3.161</td>
<td>166</td>
</tr>
<tr>
<td>N2—D2N—O3</td>
<td>0.96</td>
<td>2.27</td>
<td>3.216</td>
<td>163</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) x, y − 1, z; (ii) −x + 1, y, −z + 1/2; (iii) −x, y − 1/2, −z + 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.

### References