Chloro(dimethyl sulfoxide-κS)[(1R,3S)-1,2,2-trimethylcyclopentane-1,3-diamine-κ²N,N′]platinum(II) trichloro(dimethyl sulfoxide-κS)platinum(II)

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The molecule of the title compound, [PtCl($C_8H_{18}N_2$)(C_2H_6OS)][PtCl$_3$(C_2H_6OS)], contains one cation and one anion, each with a square-planar coordination around the Pt^{II} centre. The bond lengths and angles of Pt with N, Cl and S atoms are also typical of diamine dichloroplatinum(II) complexes.

Comment

In the past ten years, some platinum(II) complexes containing intercalating phenanthroline (phen) ligands and chiral diamine ancillary ligands have shown potential as anti-cancer 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), in a fashion similar to the organic intercalator ethidium bromide (Jennette *et al.*, 1974). From ^{1}H NMR spectroscopy, it has been shown that these complexes intercalate DNA from the minor 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 structure and chirality of the ancillary ligand (Fisher, 2005; 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. Using circular dichroism, NMR and viscosity measurements, complexes containing the (*R*,*S*)- and (*S*,*R*)-tcmp (1,3-diamino-1,2,2-trimethylcyclopentane) ligands have been shown to exhibit chiral discrimination *in vitro* and when binding to DNA (Jaramillo *et al.*, 2006). It is therefore important to study the structural features of each platinum complex, as small geometric changes may greatly affect the biological activity of each platinum complex.

(I)
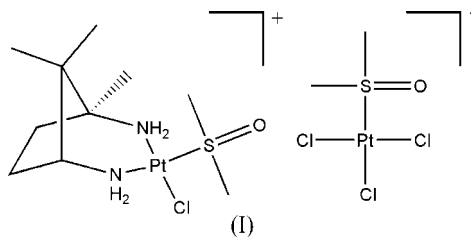
During the synthesis of [Pt(*R*,*S*-tcmp)(phen)]Cl$_2$ by the method of McFadyen *et al.* (1985), the title complex, (I), crystallized as a by-product of the reaction. In the structure of (I) (Fig. 1), the bond lengths and angles (Table 1) are within normal ranges (Allen *et al.*, 1987). It consists of the complex cation [$C_{10}H_{24}ClN_2OPtS$]$^+$ with the counter-anion
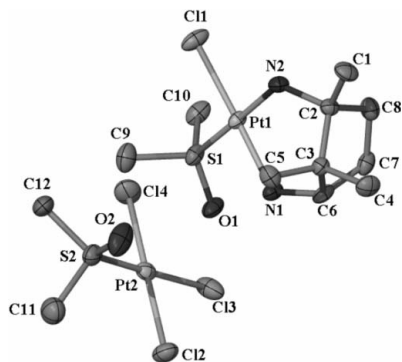
Figure 1
The asymmetric unit of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted.

$[C_2H_6Cl_3OPtS]^-$, and both of them exhibit square-planar coordination around the Pt^{II} centres. The bond lengths and angles of Pt with N, Cl and S atoms (Table 1) are also typical of diamine dichloroplatinum(II) complexes (Brodie *et al.*, 2006). In the complex cation, the bite angle (N—Pt—N) of the tcmp ligand is 92.3 (2)°, and the average of the Pt—N bond lengths is 2.062 (5) Å, while in the complex anion, the average of the Pt—Cl bond lengths is 2.3064 (18) Å. The internuclear separation between Pt1 and Pt2 is 5.562 (6) Å. The shape of the complex may well affect its ability to intercalate within DNA and, through that, its cytotoxicity.

In the crystal structure, the intra- and intermolecular N—H···O and N—H···Cl hydrogen bonds (Table 2) linking the ions may be effective in the stabilization of the crystal structure.

Experimental

(R,S)-tcmp (0.14 g, 1.0 mmol) dissolved in water (50 ml) was slowly added to a mixture of *cis*-[Pt(DMSO)$_2$Cl$_2$] (0.42 g, 1.0 mmol) in water (50 ml) and the suspension was stirred at room temperature for 24 h. The solvent was removed under reduced pressure and the residue dissolved in warm water (40 ml) containing excess lithium chloride (0.50 g). Crystals of the title complex were obtained after heating the solution on a steam bath until the volume was reduced to approximately 10 ml.

Crystal data

$[PtCl(C_8H_{18}N_2)(C_2H_6OS)]$-
  $[PtCl_3(C_2H_6OS)]$
$M_r = 830.48$
Orthorhombic, $P2_12_12_1$
$a = 11.5381$ (12) Å
$b = 11.9979$ (13) Å
$c = 16.5192$ (18) Å
$V = 2286.8$ (4) Å^3

$Z = 4$
$D_x = 2.412$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 12.88$ mm^{-1}
$T = 296$ (2) K
Block, yellow
$0.20 \times 0.20 \times 0.15$ mm

Data collection

Bruker SMART 1000 CCD
  diffractometer
ω scans
Absorption correction: multi-scan
  (*SADABS*; Sheldrick, 1996)
  $T_{min} = 0.097$, $T_{max} = 0.149$

14847 measured reflections
5213 independent reflections
4947 reflections with $I > 2\sigma(I)$
$R_{int} = 0.054$
$\theta_{max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.063$
$S = 1.02$
5213 reflections
224 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0344P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.90$ e Å^{-3}
$\Delta\rho_{min} = -1.39$ e Å^{-3}
Absolute structure: Flack (1983),
  with 2253 Friedel pairs
Flack parameter: −0.002 (7)

Table 1
Selected geometric parameters (Å, °).

Pt1—N1	2.049 (5)	Pt2—S2	2.2000 (17)
Pt1—N2	2.074 (5)	Pt2—Cl2	2.2982 (18)
Pt1—S1	2.2159 (16)	Pt2—Cl4	2.3010 (19)
Pt1—Cl1	2.3044 (16)	Pt2—Cl3	2.3201 (18)
N1—Pt1—N2	92.3 (2)	S2—Pt2—Cl2	89.30 (6)
N1—Pt1—S1	89.32 (15)	S2—Pt2—Cl4	93.50 (7)
N2—Pt1—S1	177.37 (14)	Cl2—Pt2—Cl4	176.88 (7)
N1—Pt1—Cl1	176.41 (15)	S2—Pt2—Cl3	173.61 (8)
N2—Pt1—Cl1	86.08 (15)	Cl2—Pt2—Cl3	87.89 (7)
S1—Pt1—Cl1	92.44 (6)	Cl4—Pt2—Cl3	89.46 (8)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1NA···Cl3	0.92	2.35	3.223 (6)	160
N1—H1NB···O1	0.92	2.35	2.928 (7)	121
N1—H1NB···Cl1^i	0.92	2.82	3.599 (7)	144
N2—H2NB···O1^{ii}	0.92	2.16	2.982 (6)	147

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

H atoms were positioned geometrically, with N—H = 0.92 Å (for NH$_2$) and C—H = 1.00, 0.99 and 0.98 Å for methine, methylene and methyl H, respectively, and constrained to ride on their parent atoms, with U_{iso}(H) = xU_{eq}(C,N), where $x = 1.5$ for methyl H and $x = 1.2$ for all other H atoms. The maximum and minimum residual electron density are at distances of 0.95 and 0.75 Å, respectively, from atom Pt1.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 2001) and *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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