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Key indicators

Single-crystal X-ray study T = 294 KMean $\sigma(\text{C}-\text{C}) = 0.005 \text{ Å}$ Disorder in main residue R factor = 0.015 wR factor = 0.034 Data-to-parameter ratio = 16.0

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(Cyclobutane-1,1-dicarboxylato)(2-morpholinoethylamine)platinum(II) trihydrate

The reaction of 2-morpholinoethylamine and cyclobutane-1,1dicarboxylic acid with potassium tetrachloroplatinate(II) produced the monomeric title complex, $[Pt(C_6H_6O_4)(C_6H_{14}-N_2O)]$ ·3H₂O. The Pt^{II} ion is tetracoordinated and situated in a square-planar environment. Received 4 September 2006 Accepted 3 December 2006

Comment

cis-Diamminedichloroplatinum(II) (cisplatin) is one of the most effective anti-cancer drugs currently available for the treatment of testicular, lung, bladder and other carcinomas. However, the clinical usefulness of this drug has frequently been limited by serious nephroto- and gastrointestinal toxicity and the development of acquired resistance (Wong & Giandomenico, 1999). In an attempt to overcome these drawbacks of cisplatin, numerous analogues have been prepared and evaluated in a search for alternative active agents. Among these compounds, cis-diammine(cyclobutane-1,1-dicarboxylato)platinum(II) (carboplatin) is the only second-generation platinum complex commercially available worldwide at present (Jakuper et al., 2003). It has been reported that platinum complexes with different amine carriers, such as 1,2diminocyclohexane, could overcome some cross-resistance of cisplatin or carboplatin (Ho et al., 2003). The title compound, (I), is a new soluble carboplatin analogue containing an asymmetric chelating diamine, 2-morpholinoethylamine, as its carrier, and anticancer tests are presently being carried out.



The title complex consists of discrete monomeric molecules. The Pt^{II} ion has the expected square-planar geometry exhibiting the usual structure parameters. The basal square plane

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Figure 1

The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.



Figure 2

A packing view of (I), nearly perpendicular to the *ac* plane. Dashed lines represent hydrogen bonds. H atoms not involved in hydrogen bonding have been omitted.

is composed of the 2-morpholinoethylamine molecule, which acts as a bidentate ligand through its 2-morpholinoethylamine N atoms, and the cyclobutane-1,1-dicarboxylate O atoms. The cyclobutane-1,1-dicarboxylate ligand displays similar features to those described in the literature (Tu *et al.*, 2004; Zhang *et al.*, 2002; Ali *et al.*, 2002). The five-membered chelate rings which the ligand 2-morpholinoethylamine and the other sixmembered chelate rings which the ligand 1,1-cyclobutanedi-

carboxylate formed with the Pt^{II} atom adopt the boat conformation, and the cyclobutane ring is nearly perpendicular to the Pt^{II} coordination plane.

The compound forms a hydrogen-bonded structure (Fig. 2) in which one of the amino H atoms serves as a donor to the O atom of the morpholinyl ring of an adjacent molecule. The other H atom of the amino group engages in interactions with the water molecules, and these hydrogen-bond interactions (Table 2) give rise to a three-dimensional network. The 2-morpholinoethylamine ligand has earlier been shown to chelate with nickel(II) isothiocyanate (Laskar *et al.*, 2001), nickel(II) dicyanamide (Konar *et al.*, 2005) and dicopper(II) diperchlorate oxalate (Mukherjee *et al.*, 2001) complexes.

Experimental

Potassium tetrachloroplatinate(II) (2.5 g, 0.006 mmol) was dissolved in water (50 ml) and treated with KI (6 g, 0.036 mmol). After standing in the dark for 30 min at room temperature, a solution of 2morpholinoethylamine (0.78 g, 0.006 mmol) in water (20 ml) was added dropwise. The mixture was stirred for 4 h and the yellow precipitate which formed was filtered off. To a suspension of MPEA– PtI₂ (MPEA is 2-morpholinoethylamine) (2.5 g, 0.044 mmol) in water (100 ml) was added disilver cyclobutane-1,1-dicarboxylate (1.54 g, 0.043 mmol), and the reaction mixture was stirred at 313 K for 36 h. The AgI which had formed was filtered off and the filtrate was concentrated at 313 K under reduced pressure to 5 ml, whereupon a white crystalline product precipitated. The title compound was recrystallized from water to obtain crystals of (I) suitable for X-ray crystallography.

Z = 4

 $D_x = 2.002 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

Block, colourless

0.24 \times 0.19 \times 0.13 mm

8167 measured reflections

3786 independent reflections 3509 reflections with $I > 2\sigma(I)$

 $\mu = 8.15 \text{ mm}^{-1}$

T = 294 (2) K

 $\begin{aligned} R_{\rm int} &= 0.019\\ \theta_{\rm max} &= 28.3^\circ \end{aligned}$

Crystal data

 $[Pt(C_6H_6O_4)(C_6H_{14}N_2O)]\cdot 3H_2O$ $M_r = 521.44$ Monoclinic, Cc a = 15.8575 (9) Å b = 12.3884 (7) Å c = 9.0359 (5) Å $\beta = 102.8890$ (10)° V = 1730.37 (17) Å³

Data collection

Bruker APEXII CCD area-detector diffractometer φ and ω scans Absorption correction: multi-scan (Sheldrick, 2002) $T_{\min} = 0.203, T_{\max} = 0.346$

Refinement

Refinement on F^2 $(\Delta/\sigma)_{\rm max} = 0.003$ $\Delta \rho_{\rm max} = 0.59 \ {\rm e} \ {\rm \AA}^{-3}$ $R[F^2 > 2\sigma(F^2)] = 0.015$ $wR(F^2) = 0.034$ $\Delta \rho_{\rm min} = -0.72 \text{ e } \text{\AA}^{-3}$ S = 0.87Extinction correction: SHELXL97 3786 reflections (Sheldrick, 1997) Extinction coefficient: 0.00297 (8) 237 parameters H atoms treated by a mixture of Absolute structure: Flack (1983), with 1632 Friedel pairs independent and constrained refinement Flack parameter: 0.016 (7) $w = 1/[\sigma^2(F_0^2)]$ where $P = (F_o^2 + 2F_c^2)/3$

metal-organic papers

 Table 1

 Selected geometric parameters (Å, $^{\circ}$).

2.019 (4)	N2-C12	1.491 (6)
2.023 (6)	N2-C9	1.500 (6)
2.023 (5)	N2-C8	1.527 (9)
2.045 (7)	O5-C10	1.418 (5)
1.295 (5)	O5-C11	1.420 (6)
1.233 (4)	C9-C10	1.511 (5)
1.476 (6)		
87.4 (2)	O3-Pt1-N2	178.24 (14)
177.92 (18)	N1-Pt1-N2	85.9 (3)
93.4 (2)	C1-O1-Pt1	120.0 (3)
93.3 (2)	C6-O3-Pt1	120.7 (4)
	2.019 (4) 2.023 (6) 2.023 (5) 2.045 (7) 1.295 (5) 1.233 (4) 1.476 (6) 87.4 (2) 177.92 (18) 93.4 (2) 93.3 (2)	$\begin{array}{cccc} 2.019 & (4) & N2-C12 \\ 2.023 & (6) & N2-C9 \\ 2.023 & (5) & N2-C8 \\ 2.045 & (7) & O5-C10 \\ 1.295 & (5) & O5-C11 \\ 1.233 & (4) & C9-C10 \\ 1.476 & (6) \\ \hline \\ 87.4 & (2) & O3-Pt1-N2 \\ 177.92 & (18) & N1-Pt1-N2 \\ 93.4 & (2) & C1-O1-Pt1 \\ 93.3 & (2) & C6-O3-Pt1 \\ \hline \end{array}$

Table 2

Hydrogen-bond geometry (Å, °).

$D - H \cdot \cdot \cdot A$	D-H	$H \cdot \cdot \cdot A$	$D \cdots A$	$D - \mathbf{H} \cdot \cdot \cdot A$
$O8-H8D\cdots O2^{i}$	0.86 (3)	2.07 (3)	2.864 (4)	153 (6)
O8−H8C···O6 ⁱⁱ	0.90 (3)	1.79 (3)	2.697 (5)	177 (6)
$O7 - H7D \cdot \cdot \cdot O2$	0.82(3)	2.07 (3)	2.859 (5)	161 (6)
$O7-H7C \cdot \cdot \cdot O4^{iii}$	0.85(3)	2.10 (4)	2.885 (4)	154 (6)
$O6-H6B\cdotsO8^{iv}$	0.88(2)	1.82 (3)	2.698 (5)	176 (5)
$O6-H6A\cdots O4^{v}$	0.83 (3)	1.91 (3)	2.713 (4)	163 (6)
$N1-H1A\cdots O6^{vi}$	0.90	2.00	2.891 (5)	173
$N1-H1A\cdots O6^{vi}$	0.90	2.00	2.891 (5)	173
		•> 1 1	(***) . 1	. 1 . 1

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

All H atoms were initially located in a difference Fourier map. They were then placed in calculated positions, with C-H = 0.96-0.97 Å and N-H = 0.90 Å, and they were included in the refinement in the riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}(C,N)$.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine

structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2000); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2000) and *DIAMOND* (Bergerhoff, 1996).

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