

**cis-Amminedichloroisopropylamine-  
platinum(II) by X-ray powder  
diffraction analysis**

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Received 16 March 2006

Accepted 13 April 2006

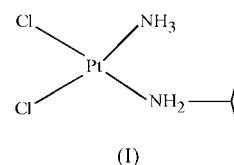
Online 24 May 2006

The title compound,  $[\text{PtCl}_2(\text{C}_3\text{H}_9\text{N})(\text{NH}_3)]$ , was obtained from potassium tetrachloroplatinate(II) by a two-step route. *Ab initio* crystal structure determination was carried out using X-ray powder diffraction techniques. Patterson and Fourier syntheses were used for the atom locations and the Rietveld technique for the final structure refinement. The Pt coordination is close to planar, with Cl atoms in a *cis* orientation. Molecules are combined into groups of two molecules, with antiparallel  $\text{PtN}_2\text{Cl}_2$  planes and a shortest  $\text{Pt}\cdots\text{Pt}$  distance of 3.42 Å. The molecule groups are packed in a parquet motif into corrugated layers parallel to *ab*. The molecules in the layers are linked by  $\text{H}-\text{N}\cdots\text{Cl}$  hydrogen bonds.

**Comment**

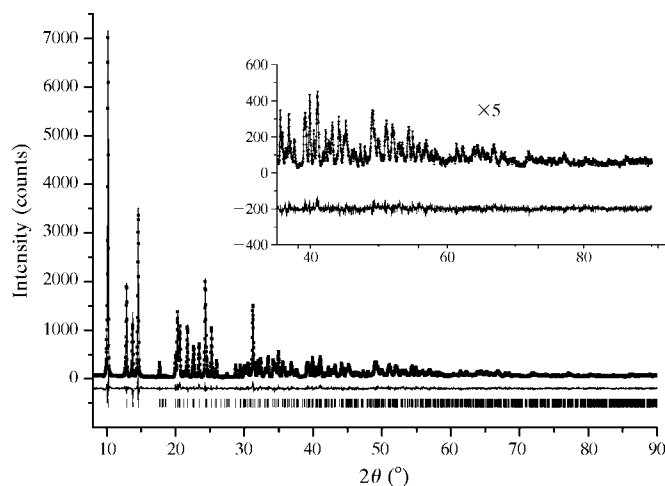
Asymmetric diamminedichloroplatinum(II) complexes exhibit high anticancer activity. Such activity is also observed in *cis*-amminedichloroisopropylamineplatinum(II) (Bradner *et al.*, 1980; Hydes, 1981). The first evidence of asymmetric complex formation with amines was presented by Grinberg & Smolenskay (1961). The synthesis of *cis*-amminedichloroisopropylamineplatinum(II) has been described by several workers (Hydes, 1981; Zhelegovskay & Fat'kin, 1986; Zhelegovskay *et al.*, 1991). It consists of the chemical reaction of potassium tetrachloroplatinate(II) with isopropylamine, followed by the refinement of the target product. The main synthetic difficulty stems from a requirement for a low level of impurities. High purity is important for medical applications, as well as for the measurement of the various physico-chemical properties of the substance. Successful investigation of the compound is strongly dependent upon reliable methods of identification; the purity of *cis*-amminedichloroisopropylamineplatinum(II) has been estimated by elemental chemical analysis, IR spectroscopy, chromatography and conductometry and, since these are not direct methods of identification, errors are possible. An attempt to use X-ray diffraction for the determination of *cis*-amminedichloroisopropylamine-

platinum(II) was described by Zhelegovskay *et al.* (1991). However, the X-ray reference diffraction data they obtained were of low reliability because of the absence of crystallographic data. With regard to the problem of crystallographic investigation of ammine halogen platinates, it is pertinent to mention that the structure of *trans*-dichlorodiammineplatinum was defined by Porai-Koshits (1954) and redefined by Milburn & Truter (1966). These last authors also determined the structure of  $\alpha$ -*cis*-dichlorodiammineplatinum (Milburn & Truter, 1966). However,  $\beta$ -*cis*-dichlorodiammineplatinum, the well known pharmaceutical preparation cisplatin, has not been structurally described to date (ICSD, 2005). In the present paper, the results of a crystal structure determination of *cis*-amminedichloroisopropylamineplatinum(II), (I), performed using the X-ray powder diffraction method, are presented.

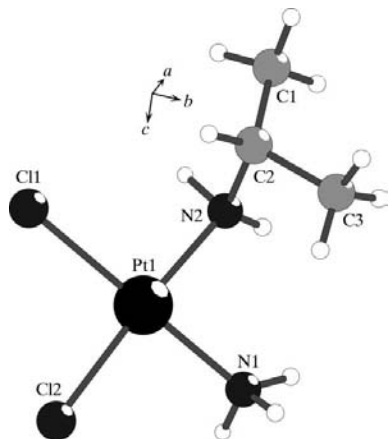


The powder pattern of (I) is presented in Fig. 1. The crystal structure of (I) is of the molecular type. The geometry of the molecule is presented in Fig. 2. Atoms N1, N2, Cl1, Cl2 and Pt1 form a slightly distorted plane. The distances Pt–N and Pt–Cl (Table 2) agree with known values from the literature (Wells, 1984; Allen, 2002; ICSD, 2005). The isopropylamine ligand induces a more distorted square-planar Pt coordination than ammine (Milburn & Truter, 1966). Isopropylamine does not connect to other molecules by hydrogen bonds. Thus, the distortion is a result of the difference in volume of ammine and isopropylamine.

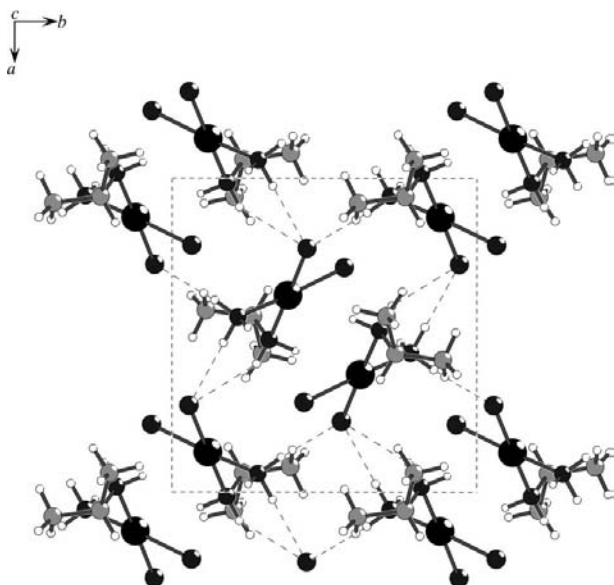
Molecules of (I) are combined into groups of two with antiparallel  $\text{PtN}_2\text{Cl}_2$  planes. The shortest  $\text{Pt}\cdots\text{Pt}$  distance in the group is 3.42 Å (Fig. 3), which is very close to the value observed in *cis*-dichlorodiammineplatinum (3.41 Å; Milburn & Truter, 1966). However, the overall molecular arrangements



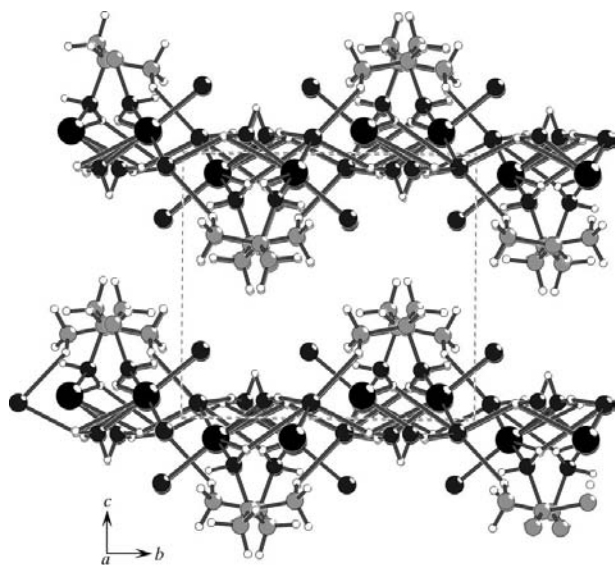
**Figure 1**  
Observed (dots), calculated (superimposed solid line) and difference profiles for (I) after the Rietveld refinement. The reflection positions are marked underneath.



**Figure 2**  
Ball-and-stick drawing of the molecular complex of (I). The H-atom positions were generated using molecular graphics software *XP* (Siemens, 1989).



**Figure 3**  
The arrangement of the complex molecules in the layer.



**Figure 4**  
The arrangement of the layers in the crystal structure.

in these structures are different. In contrast with the columnar packed structure observed in the flat *cis*-diamminedichloro-platinum(II) complex, in the structure of (I), the groups of two molecules are packed in a parquet motif into a corrugated layer parallel to *ab* (Fig. 3).

The molecules of (I) are linked into layers by hydrogen bonds of the N—H···Cl type. The probable candidates for hydrogen bonds, with Cl···N distances of 3.13 and 3.53 Å, are shown in Fig. 3. The arrangement of the layers in the structure is shown in Fig. 4. Bulky isopropylamine ligands project above and below each layer. There are no hydrogen bonds between layers.

### Experimental

The synthesis of *cis*-amminedichloroisopropylamineplatinum(II) involves the reaction of potassium tetrachloroplatinate(II) (3 g) with ammonium oxalate (0.77 g) dissolved in water (24 ml) and heating at 333 K for 30 min. After cooling, isopropylamine (0.8 g) was added and the resulting mixture left for 2 h. Hydrochloric acid (40 ml) was then added (Kazbanov *et al.*, 1997). The yellow substance which precipitated was refined according to the method of Kazbanov *et al.* (2002), then filtered off, washed and dried in air.

#### Crystal data

[PtCl<sub>2</sub>(C<sub>3</sub>H<sub>7</sub>N)(NH<sub>3</sub>)]  
*M<sub>r</sub>* = 342.14  
 Monoclinic, *P*2<sub>1</sub>/*a*  
*a* = 10.3661 (2) Å  
*b* = 9.5622 (2) Å  
*c* = 9.1261 (2) Å  
 $\beta$  = 108.386 (1)°  
*V* = 858.43 (3) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 2.647 Mg m<sup>-3</sup>  
 Cu *K*α radiation  
*T* = 293 K  
 Specimen shape: flat sheet  
 20.0 × 20.0 × 0.5 mm  
 Specimen prepared at 101 kPa  
 Specimen prepared at 293 K  
 Particle morphology: thin powder,  
 yellow

#### Data collection

DRON-4 powder diffractometer  
 Specimen mounting: packed powder  
 pellet  
 Specimen mounted in reflection  
 mode

Scan method: step  
 2θ<sub>min</sub> = 6.0, 2θ<sub>max</sub> = 110.0°  
 Increment in 2θ = 0.0°

#### Refinement

Refinement on *F*<sup>2</sup>  
*R<sub>p</sub>* = 0.083  
*R<sub>wp</sub>* = 0.111  
*R<sub>exp</sub>* = 0.086  
*R<sub>B</sub>* = 0.051  
*S* = 1.29  
 Wavelength of incident radiation:  
 1.54056 Å  
 Excluded region(s): none

Profile function: Pearson VII  
 692 reflections  
 58 parameters  
 H-atom parameters constrained  
 Weighting scheme based on  
 measured s.u.'s  
 (Δ/σ)<sub>max</sub> = 0.1  
 Preferred orientation correction:  
 March-Dollase correction

**Table 1**

Selected geometric parameters (Å, °).

Pt1—N2	2.051 (7)	C1—C2	1.537 (9)
Pt1—N1	2.021 (3)	C2—C3	1.539 (7)
Pt1—Cl1	2.341 (3)	C2—N2	1.560 (7)
Pt1—Cl2	2.333 (3)	Pt1···Pt1 <sup>i</sup>	3.418 (3)
Cl1—Pt1—Cl2	88.18 (9)	Cl2—Pt1—N1	91.0 (1)
N1—Pt1—N2	84.8 (1)	C1—C2—C3	115.3 (5)
Cl1—Pt1—N2	96.1 (1)		

Symmetry code: (i)  $-x + 2, -y, -z + 2$ .

X-ray powder diffraction data have been deposited in the JCPDS-ICDD PDF2 database (ICDD, 2003). Cell parameters were obtained from *d* spacings by indexing and refining using programs described in Visser (1969) and Kirik *et al.* (1979). The space group was determined from the analysis of systematic absences. The structural investigations were carried out using a full-profile structure analysis package based on a modified version of the Rietveld refinement program *DBWS-9006PC* (Wiles & Young, 1981). The intensities of 80 reflections were estimated from the powder pattern by means of the full-profile fitting procedure (Le Bail *et al.*, 1988) and used in the Patterson synthesis. Pt and Cl atoms were located directly from the Patterson map. The positions of light atoms N and C were defined from a Fourier synthesis. H atoms were not located, but they were included in the refined structure models and rigidly connected to their C and N atoms. The final refinement was carried out using the Rietveld method (Rietveld, 1969).

Data collection: DRON-4 software; cell refinement: *POWDER* (Kirik *et al.*, 1979); data reduction: DRON-4 software; program(s) used to solve structure: modified *DBWS-9006PC* (Wiles & Young, 1981); program(s) used to refine structure: modified *DBWS-9006PC*; molecular graphics: *XP* (Siemens, 1989).

The preparation of the X-ray powder diffraction data was supported by the ICDD (Grant-in-Aid No. 9310).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3009). Services for accessing these data are described at the back of the journal.

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