

The angles of the coordination sphere have almost regular values, the largest deviation being found for the Sb—Rh—Cl angle [84.1(1)°]. The Cl—Rh—C—C torsion angle is 34.3° so that the steric hindrance between the Ph and the Cl ligand should not be high. The Cl—Rh—Cl' angle is 175.7(1)°.

The Sb atom has an approximate tetrahedral geometry with Sb—C distances averaging 2.128(2) Å. This value is in agreement with the mean values of 2.145 and 2.188 Å previously found for other compounds (Lamprecht *et al.*, 1984; Mague, 1970). The C—Sb—C angles average 100.5(3)° while previously reported mean values are 101.0° (Lamprecht *et al.*, 1984) and 102.3° (Mague, 1970). The Rh—Sb—C bond angles range from 111.8(2) to 121.7(2)°.

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## (1,3-Diamino-2-propanol-*N,N'*)diiodoplatinum(II) and (1,3-Diamino-2-propanol-*N,N'*)dichloroplatinum(II)

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**Abstract.** (1) [PtI<sub>2</sub>(C<sub>3</sub>H<sub>10</sub>N<sub>2</sub>O)], *M<sub>r</sub>* = 539.0, monoclinic, *P*<sub>2</sub>/*n*, *a* = 10.756(2), *b* = 7.211(1), *c* = 12.113(1) Å, β = 90.20(1)°, *V* = 939.3(3) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 3.81 g cm<sup>-3</sup>, graphite-monochromated Mo *K*α radiation, λ = 0.71069 Å, μ = 223 cm<sup>-1</sup>, *F*(000) = 936, *T* = 298 K, *R* = 0.046 for 1080 unique reflections with *I* > 3σ(*I*). (2) [PtCl<sub>2</sub>(C<sub>3</sub>H<sub>10</sub>N<sub>2</sub>O)], *M<sub>r</sub>* =

356.1, monoclinic, *P*<sub>2</sub>/*n*, *a* = 8.497(3), *b* = 8.784(2), *c* = 10.735(5) Å, β = 105.79(3)°, *V* = 771.0(5) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 3.07 g cm<sup>-3</sup>, graphite-monochromated Mo *K*α radiation, λ = 0.71069 Å, μ = 198 cm<sup>-1</sup>, *F*(000) = 648, *T* = 298 K, *R* = 0.054 for 1456 unique reflections with *I* > 3σ(*I*). In both compounds the amine ligand coordinates to the central metal ion

through both N atoms forming six-membered rings in chair conformation with axially oriented hydroxyl groups. The four ligand atoms coordinate to the metal ion in an essentially *cis*-planar arrangement. The packing of the molecules differs significantly in the two compounds.

**Introduction.** The title compounds were prepared for our studies on oligomerization reactions of platinum (Laitalainen, Okuno & Tomohiro, 1987; Shimura, Tomohiro, Laitalainen, Moriyama, Uemura & Okuno, 1988; Oksanen, Kivekäs, Lumme, Valkonen & Laitalainen, 1989). Earlier attempts to synthesize (1,3-diamino-2-propanol-*N,N'*)dichloroplatinum(II) for crystal structure determination by the reaction of K<sub>2</sub>PtCl<sub>4</sub> with 1,3-diamino-2-propanol in water have given one minor product as pale orange crystals, which has been analysed as bis(1,3-diamino-2-propanol-*N,N'*)platinum(II) chloride  $\frac{1}{3}$ -hydrate (Brown & Lock, 1987). Usually the reaction has resulted in a precipitate consisting predominantly of pink bis(1,3-diamino-2-propanol-*N,N'*)platinum(II)-tetrachloroplatinum (Appleton & Hall, 1972). We have now prepared and determined the structures of (1,3-diamino-2-propanol-*N,N'*)dichloroplatinum(II) and (1,3-diamino-2-propanol-*N,N'*)diiodoplatinum(II). The reactions of K<sub>2</sub>PtI<sub>4</sub> and K<sub>2</sub>PtCl<sub>4</sub> with 1,3-diamino-2-propanol in water are different in that the iodine compound gives greenish-yellow (1,3-diamino-2-propanol-*N,N'*)diiodoplatinum(II) and not a bis-amine as with the chlorine compound. The white (1,3-diamino-2-propanol-*N,N'*)dichloroplatinum(II) can then be prepared by replacing the I atoms with Cl atoms.

**Experimental.** Compound (1) was prepared by the reaction of K<sub>2</sub>PtCl<sub>4</sub>, KI and 1,3-diamino-2-propanol in molar ratio 1:4:1 in warm aqueous media (313 K). The greenish crude product was contaminated with black particles. The product was dissolved in boiling methanol, filtrated while hot and diluted with warm water of five times the volume. Small crystals were obtained after 4 weeks of slow evaporation at room temperature. Compound (2) was prepared by removing the I atoms from compound (1) with Ag<sub>2</sub>SO<sub>4</sub>. KCl was added to the filtrate and small crystals slowly formed in the dilute water solution. A small rod-shaped crystal of size 0.06 × 0.06 × 0.12 mm (1) and a small transparent plate-like crystal of size 0.03 × 0.08 × 0.09 mm (2) were measured with a Nicolet P3F diffractometer. The unit-cell parameters were determined on the basis of 22 (1) and 25 (2) well centred reflections in the angular range 20 < 2θ < 30°. The intensity data were collected in the ω-scan mode with scan speed 1.0–15.0° min<sup>-1</sup> in the range 5 < 2θ < 50° (*hkl*: *h* 0→13, *k* 0→9, *l* -15→15) for (1) and 1.5–20.0° min<sup>-1</sup> in the range 3 < 2θ < 55° (*hkl*:

*h* 0→12, *k* 0→12, *l* -14→14) for (2). Intensities were collected up to (sin θ)/λ = 0.5947 Å<sup>-1</sup> (1) and (sin θ)/λ = 0.6497 Å<sup>-1</sup> (2). The intensities of 3 standard reflections were measured after every 57 reflections and they showed no significant variation. 1806 (1) and 1875 (2) unique reflections were measured, of which 1080 (1) and 1456 (2) were observed according to the criterion *I* > 3σ(*I*). The structures were solved by SHELXS86 (Sheldrick, 1986). Full-matrix least-squares refinements were performed using XTAL2.2 (Hall & Stewart, 1987), which minimizes the function ∑w(|F<sub>o</sub>| - |F<sub>c</sub>|)<sup>2</sup>, where w = 1/σ<sup>2</sup>(F<sub>o</sub>). All the non-H atoms were refined anisotropically. The O—H H atom was excluded from the calculations but all the other H atoms were fixed at calculated positions. The final cycle of least-squares refinement with 83 parameters gave R = 0.046, wR = 0.044, S = 2.50, (Δ/σ)<sub>max</sub> = 0.10, Δρ<sub>max</sub> = 2.96, Δρ<sub>min</sub> = -2.61 e Å<sup>-3</sup> for (1) and R = 0.054, wR = 0.062, S = 5.09, (Δ/σ)<sub>max</sub> = 0.09, Δρ<sub>max</sub> = 6.43, Δρ<sub>min</sub> = -3.10 e Å<sup>-3</sup> for (2). The exceptionally high residual electron density in compound (2) lies at about 1 Å from the Pt ion. Nearly as high a maximum (5.6 e Å<sup>-3</sup>) in a platinum compound has been mentioned previously (Mégnamisi-Bélombé & Endres, 1985). Attempts to find a reason for our high maximum were unsuccessful (details are given in supplementary material). A minor crack, that might have been produced while fixing the crystal on top of the glass fibre, could be responsible. Empirical

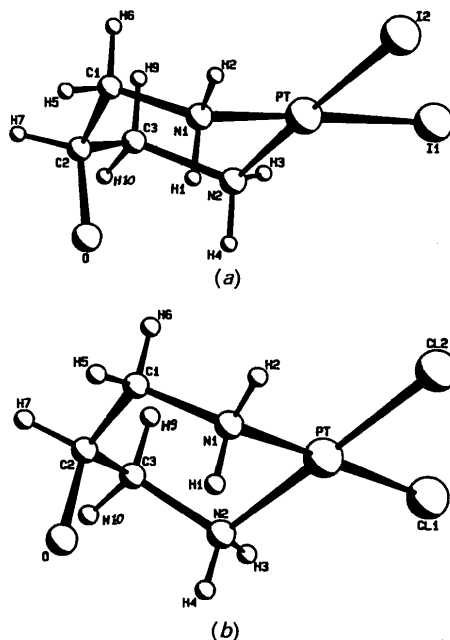


Fig. 1. The molecular structures of (a) [Pt(NH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>CHOH<sub>2</sub>I<sub>2</sub>] and (b) [Pt(NH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>CHOHCl<sub>2</sub>] showing the atom numbering. The OH H atoms have been omitted.

Table 1. Positional and equivalent isotropic thermal parameters ( $\text{\AA}^2$ ) for compounds (1) and (2)
$$U_{eq} = (1/3)[U_{22} + 1/\sin^2\beta(U_{11} + U_{33} + 2U_{13}\cos\beta)].$$

Compound (1)	x	y	z	$U_{eq}$
Pt	0.38376 (9)	0.1542 (2)	0.15893 (5)	0.0302 (5)
I(1)	0.4798 (2)	0.0143 (3)	0.3385 (1)	0.044 (1)
I(2)	0.4921 (2)	0.4723 (3)	0.1913 (1)	0.043 (1)
N(1)	0.299 (2)	0.260 (3)	0.017 (1)	0.05 (1)
N(2)	0.300 (2)	-0.097 (3)	0.139 (2)	0.04 (1)
O	0.116 (1)	0.000 (3)	-0.024 (1)	0.06 (2)
C(1)	0.301 (2)	0.143 (4)	-0.085 (2)	0.05 (2)
C(2)	0.235 (2)	-0.042 (4)	-0.065 (2)	0.04 (2)
C(3)	0.301 (2)	-0.169 (4)	0.015 (2)	0.05 (2)

Compound (2)	x	y	z	$U_{eq}$
Pt	0.12184 (7)	0.07928 (7)	0.34606 (6)	0.0230 (3)
Cl(1)	0.3183 (5)	0.0666 (5)	0.5420 (4)	0.033 (2)
Cl(2)	0.0811 (6)	0.3351 (5)	0.3725 (5)	0.035 (2)
N(1)	-0.054 (2)	0.087 (2)	0.173 (1)	0.028 (6)
N(2)	0.155 (2)	-0.148 (2)	0.317 (1)	0.032 (7)
O	-0.053 (1)	-0.198 (1)	0.053 (1)	0.035 (6)
C(1)	-0.185 (2)	-0.031 (2)	0.163 (2)	0.033 (8)
C(2)	-0.117 (2)	-0.189 (2)	0.164 (2)	0.024 (8)
C(3)	0.003 (2)	-0.239 (2)	0.282 (2)	0.036 (9)

absorption correction was made by  $\psi$  scanning for 6 reflections. The relative intensities varied from 1.00 to 0.22. The refining cycles were run with and without the correction for absorption, but the changes in the maximum and thermal parameters were negligible. In (1) the  $\psi$  scans of several strong reflections showed no considerable absorption and the correction was not made. Neutral-atom scattering factors were those included in the program systems and the anomalous dispersions for all the atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).\*

**Discussion.** In both compounds the amine ligand coordinates to the central metal ion through both N atoms forming six-membered rings in a chair conformation with axially oriented hydroxyl groups. The coordination of the four ligand atoms to the central metal is essentially *cis*-planar. In (1) the Pt ion shows a weak tendency to rise above the plane formed by the four ligand atoms. The deviation of the Pt ion from the plane is 0.026 (9)  $\text{\AA}$  for (1) and 0.003 (6)  $\text{\AA}$  for (2). The configurations of the molecules and the numbering systems are shown in Figs. 1(a) and 1(b), respectively. The positional and equivalent isotropic thermal parameters are given in Table 1 and the selected bond lengths and angles in Table 2.

The Pt—N distances of 2.07 (2) and 2.03 (2)  $\text{\AA}$  and the Pt—I distances of 2.592 (2) and 2.599 (2)  $\text{\AA}$  for

\* Lists of structure factors, anisotropic thermal parameters, H-atom positions, hydrogen bond distances and least-squares-plane data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53564 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

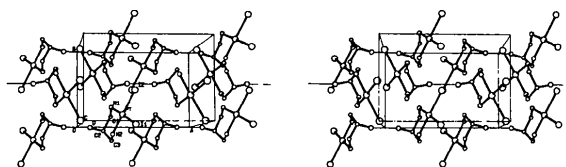
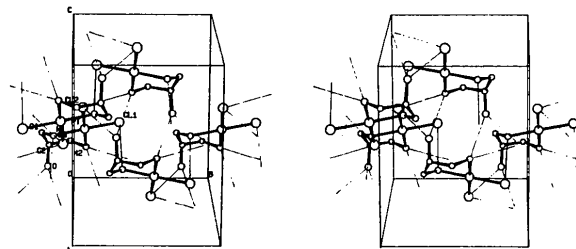
Table 2. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for compounds (1) and (2); X denotes halogen atom

	(1)	(2)	(1)	(2)
Pt—X(1)	2.592 (2)	2.305 (4)	X(1)—Pt—X(2)	92.72 (6) 91.7 (2)
Pt—X(2)	2.599 (2)	2.303 (4)	X(1)—Pt—N(2)	85.5 (6) 89.7 (4)
Pt—N(1)	2.07 (2)	2.05 (1)	X(1)—Pt—N(1)	177.3 (5) 179.1 (4)
Pt—N(2)	2.03 (2)	2.05 (2)	X(2)—Pt—N(2)	178.1 (5) 178.5 (4)
N(1)—C(1)	1.50 (3)	1.51 (2)	X(2)—Pt—N(1)	89.2 (6) 88.9 (4)
N(2)—C(3)	1.59 (3)	1.48 (2)	N(1)—Pt—N(2)	92.6 (8) 89.7 (5)
C(1)—C(2)	1.45 (4)	1.50 (2)	Pt—N(1)—C(1)	118 (2) 113 (1)
C(2)—C(3)	1.51 (4)	1.47 (2)	Pt—N(2)—C(3)	113 (1) 115 (1)
C(2)—O	1.41 (3)	1.44 (2)	N(1)—C(1)—C(2)	110 (2) 111 (1)
			N(2)—C(3)—C(2)	113 (2) 115 (2)
			C(1)—C(2)—C(3)	114 (2) 117 (2)
			C(1)—C(2)—O	108 (2) 106 (1)
			C(3)—C(2)—O	109 (2) 112 (2)

Hydrogen bond contacts ( $\text{\AA}$ )

	(1)	(2)
O...O <sup>i</sup>	2.58 (2)	
N(1)...O <sup>i</sup>		2.97 (2)
N(1)...Cl(1 <sup>iii</sup> )		3.40 (1)
N(2)...Cl(2 <sup>iii</sup> )		3.42 (2)
O...Cl(1 <sup>iii</sup> )		3.22 (1)

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

Fig. 2. The packing of the  $[\text{Pt}(\text{NH}_2\text{CH}_2)_2\text{CHOH}]_2$  molecules viewed down the *c* axis.Fig. 3. The packing of the  $[\text{Pt}(\text{NH}_2\text{CH}_2)_2\text{CHOHCl}]_2$  molecules viewed down the *a* axis.

(1) are normal (Raudaschl-Sieber, Lippert, Britten & Beauchamp, 1986; Oksanen *et al.*, 1989) as are the Pt—N distances of 2.05 (1) and 2.05 (2)  $\text{\AA}$  and Pt—Cl distances of 2.305 (4) and 2.303 (4)  $\text{\AA}$  for (2) (Iball, MacDougall & Scrimgeour, 1975; Mahal, Van Eldick, Roodt & Leipoldt, 1987). However, there are some significant differences in the bond angles around platinum between the compounds. The puckering of the rings is different, which appears in the deviations of the C(2) and O atoms from the plane through Pt, N(1) and N(2), which are 0.70 (5) and 0.66 (5)  $\text{\AA}$ , respectively, for (1) and 0.94 (3) and 0.32 (3)  $\text{\AA}$  for (2).

The packings of the molecules are shown in Figs. 2 and 3. The differences in the packings of the molecules appear in the shortest intermolecular Pt...Pt distances [4.569 (2) Å for (1) and 5.139 (2) Å for (2)] and the hydrogen bond contacts. Although the positions of the H atoms in the hydroxyl groups have not been determined, the short intermolecular O...O distance of 2.58 (2) Å in (1) indicates a strong hydrogen bond between the atoms, resulting in hydrogen bonded pairs of molecules. Owing to the centre of inversion between the O atoms, the O—H H atoms are most probably disordered. There are no other short interatomic contact distances in (1) and the pairs are held in the lattice with weak van der Waals interactions. In (2) the intermolecular O...O distance of 3.84 (2) Å is evidently too great for hydrogen bonding but hydrogen bonding does play an important role in stabilizing the crystal through a network involving N(1)...O [2.97 (2) Å], N(1)...Cl(1) [3.40 (1) Å], N(2)...Cl(2) [3.42 (2) Å] and O...Cl(1) [3.22 (1) Å].

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## Synthesis and Structure of (CH<sub>3</sub>)<sub>2</sub>AsC(CF<sub>3</sub>)=C(CF<sub>3</sub>)As(CH<sub>3</sub>)<sub>2</sub>W(CO)<sub>2</sub>Br<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>

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**Abstract.** Dibromodicarbonyl[2,5-dimethyl-3,4-bis(trifluoromethyl)-2,5-diarsahexa-3-ene-As,As']-(triphenylphosphine)tungsten, (L-L)W(CO)<sub>2</sub>Br<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> [L-L = (CH<sub>3</sub>)<sub>2</sub>AsC(CF<sub>3</sub>)=C(CF<sub>3</sub>)As(CH<sub>3</sub>)<sub>2</sub>], C<sub>28</sub>H<sub>27</sub>As<sub>2</sub>Br<sub>2</sub>F<sub>6</sub>O<sub>2</sub>PW, *M<sub>r</sub>* = 1033.99, triclinic, *P* $\bar{1}$ , *a* = 9.381 (3), *b* = 12.662 (2), *c* = 14.276 (3) Å,  $\alpha$  = 79.17 (2),  $\beta$  = 82.38 (2),  $\gamma$  = 83.57 (2)°, *V* = 1644 (1) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 2.088 (1) Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha)$  = 0.71069 Å,  $\mu$  = 85.50 cm<sup>-1</sup>, *F*(000) = 980, *T* = 223 (2) K. *R* value of 0.063 using 5206 independent reflections in range 3° ≤ 2θ ≤ 50° with *I*/σ(*I*) ≥ 2.0. The crystal structure shows the W atom to be seven-coordinate with a geometry most closely approximated by a capped trigonal prism with the capping group being a Br atom [(W—Br) = 2.648 (1) Å]. The capped face consists of one Br atom [(W—Br) = 2.675 (1) Å], an arsenic atom

[(W—As) = 2.609 (2) Å], a P atom [(W—P) = 2.548 (1) Å] and a carbonyl carbon atom [(W—C) = 1.95 (1) Å].

**Introduction.** There are few reported examples of stereochemically rigid seven-coordinate structures. As part of a series of studies of a seven-coordinate system involving tungsten and molybdenum and the ligand (L-L) where L-L = (CH<sub>3</sub>)<sub>2</sub>AsC(CF<sub>3</sub>)=C(CF<sub>3</sub>)As(CH<sub>3</sub>)<sub>2</sub> using X-ray crystallography and variable temperature NMR studies, we report here the synthesis, structure and the fluxional behaviour of the complex (L-L)W(CO)<sub>2</sub>Br<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>. Earlier work on a variety of seven-coordinate complexes of metal carbonyls has shown that they can be described by either a monocapped octahedral (MCO) geometry (Cotton, Falvello & Meadows, 1985; Mercer & Trotter, 1974) or a monocapped trigonal prismatic (MCTP) geometry (Drew & Wilkins, 1973;

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