

Fig. 4. Cation-dipole interaction model; ionic and van der Waals radii: Na⁺ 0.97, K⁺ 1.33 (*Handbook of Chemistry and Physics*, 1977), O 1.40, N 1.50 Å (Bondi, 1964); expected distances: Na⁺-O 2.37, Na⁺-N 2.47, K⁺-O 2.73, K⁺-N 2.83 Å.

4CN-NA and 4NO₂-NA. In 4NO₂-NA, Na⁺ makes contact directly with the bidentate ligand, whereas in 4CN-NA this interaction is, in part, indirect through a water molecule (Fig. 1).

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trans-Bis(2-aminoethanol)diodoplatinum(II)

BY F. D. ROCHON AND R. MELANSON

Département de Chimie, Université du Québec à Montréal, CP 8888, Montréal, Canada H3C 3P8

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Abstract

trans-[Pt(NH₂-CH₂-CH₂-OH)₂I₂], C₄H₁₄I₂N₂O₂Pt, *M_r* = 571.07, was synthesized from the isomerization of the *cis* compound in water. It crystallizes in the monoclinic space group *P*2₁/*c* with *a* = 9.838 (5), *b* = 14.919 (6), *c* = 8.351 (3) Å, β = 96.76 (4)°, *V* = 1217 (1) Å³, *Z* = 4, *D_x* = 3.116, *D_m* = 3.12 (1) Mg m⁻³ (floatation) and μ(Mo Kα) = 16.637 mm⁻¹. The parameters were refined by full-matrix least-squares calculations to a conventional *R* of 0.057 and *R_w* = 0.056 for 1590 observed reflections. The coordination

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around the Pt atom is square-planar. The Pt-I bond distances are 2.604 (1) and 2.602 (1) Å, while the Pt-N bonds are 2.047 (15) and 2.082 (13) Å. The crystal is stabilized by intermolecular hydrogen bonds between the hydroxyl groups.

Introduction

Since the discovery of the antitumor activity of some Pt compounds, the importance of Pt chemistry has markedly increased. We have been involved, for many

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years, in a program of synthesizing new Pt complexes and of studying their reactions and structures in solution and in the solid state. We have been studying mostly the interactions between Pt and nitrogen bases (*L*). Many compounds, *cis*-[PtL₂X₂] (*X* = halogen), isomerize to the *trans* isomers under certain conditions (Kong & Rochon, 1979; Rochon, Kong & Melanson, 1980, 1981; Lock & Zvagulis, 1981; and Lippert, Lock & Speranzini, 1981). Since *trans*-[PtL₂X₂] compounds have no antitumor activity, the study of these isomerization reactions is important.

The biochemical mechanism of action of the Pt drug is not known. A few years ago, Macquet & Theophanides (1976), Goodgame, Jeeves, Phillips & Skapski (1975) and Dehand & Jordanov (1976) all suggested the possibility of forming a closed-ring chelate between the Pt species in the *cis* configuration and N(7) and O(6) of the guanosine residue of DNA. In an attempt to synthesize a Pt compound containing a similar chelate, we have studied, in different conditions, the reactions of Pt with many model molecules, one of which was 2-aminoethanol. As expected, since this molecule is not a particularly good model, after many attempts, we were unable to prepare a Pt complex where 2-aminoethanol would be a bidentate ligand.

We have synthesized *cis*- and *trans*-[Pt(NH₂-CH₂-CH₂-OH)₂I₂], but only the *trans* isomer gave suitable crystals.

K₂PtCl₄ was purchased from Johnson Matthey Inc. and recrystallized from water. 2-Aminoethanol was obtained from Eastman and purified with charcoal.

trans-[Pt(2-aminoethanol)₂I₂] was prepared by the following method. A K₂PtI₄ solution was first obtained by mixing K₂PtCl₄ (0.415 g in 5 ml H₂O) and KI (0.67 g in 5 ml H₂O) for 5 min. Two mmol of 2-aminoethanol was then added to the K₂PtI₄ solution and a precipitate appeared immediately. After 30 min, the precipitate {*cis*-[Pt(2-aminoethanol)₂I₂]} was filtered off and washed with water. The isolated compound was suspended in water and a few drops of 2-aminoethanol were added. The mixture was stirred till the solution became clear, then it was evaporated to dryness. The residue, *trans*-[Pt(2-aminoethanol)₂I₂], was washed a few times with cold water, then dissolved in hot water and recrystallized.

Precession photographs showed systematic absences indicating the monoclinic space group *P*2₁/*c*. The cell parameters were obtained by least-squares refinement from the setting angles of 15 automatically centered reflections on a Syntex *P*1 diffractometer using graphite-monochromatized Mo *K*α radiation, λ(Mo *K*α) = 0.71069 Å.

The intensity data were collected from a plate measuring 0.208 × 0.199 × 0.113 mm. A total of 3570 independent reflections were measured in the region of 2θ < 60° by the θ-2θ scan technique using

Mo *K*α radiation. The scan rate was 1° (2θ) min⁻¹ for most reflections, but rates as high as 24° min⁻¹ were selected for strong reflections by the auto-collection program. A 2θ scan range of 1° below *K*α₁ and 1° above *K*α₂ was selected. The background time to scan time ratio was 0.40. Three standard reflections measured after every 47 reflections showed variations less than 2% from their respective means. Reflections with *I*_{net} < 3.0σ(*I*) were considered as unobserved, where σ(*I*) was calculated as already described (Melanson & Rochon, 1975). An absorption correction based on the equations of the crystal faces was applied to all reflections. The transmission factors varied from 0.067 to 0.239. The data were then corrected for Lorentz and polarization effects. This set of 1590 observed reflections was used for the structure determination.

The atomic scattering factors of Cromer & Waber (1965) were used for Pt, I, O, N and C atoms, and those of Stewart, Davidson & Simpson (1965) were used for H. The anomalous-dispersion terms (Cromer, 1965) of Pt and I were included in the calculations.

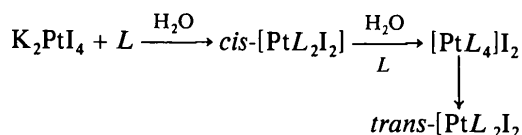
The structure was solved by the heavy-atom method. The positions of Pt and the two I atoms were located from a Patterson map. The positions of all the other atoms, except the H atoms, were obtained from a Fourier map. Refinement was by full-matrix least squares minimizing ∑ w(|*F*_o| - |*F*_c|)² where w = 1/σ²(*F*). The H atoms, except the hydroxyl H atoms, were fixed at their calculated positions (C-H = 0.95, N-H = 0.85 Å) and assigned isotropic temperature factors *B* = 6.0 Å². An isotropic secondary-extinction coefficient (Coppens & Hamilton, 1970) was also refined. The refinement converged to *R* = ∑ ||*F*_o| - |*F*_c|| / ∑ |*F*_o| = 0.057 and *R*_w = [∑ w(|*F*_o| - |*F*_c|)² / ∑ w|*F*_o|²]^{1/2} = 0.056. The final difference Fourier map showed a few peaks up to 1.5 e Å⁻³ close to the Pt atom and some weaker peaks around the I atoms. Attempts to locate the H atoms of the hydroxyl groups were not successful. The calculations were carried out with a Cyber 171 computer and the programs used have already been described (Melanson & Rochon, 1975).*

Discussion

We have synthesized *cis*- and *trans*-[Pt(NH₂-CH₂-CH₂-OH)₂I₂]. The *cis* compound was isolated from the reaction of K₂PtI₄ and 2-aminoethanol (1:2) in water, while the *trans* isomer was obtained by isomerization of the *cis* isomer in water in the presence

* Lists of structure factors, anisotropic thermal parameters and calculated H-atom positions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36466 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

of the free ligand. The reaction scheme was as follows ($L = \text{NH}_2\text{-CH}_2\text{-CH}_2\text{-OH}$):



The crystal structure has confirmed that the product is the *trans* isomer. The refined atomic parameters of the compound are listed in Table 1. A labelled diagram of the molecule is shown in Fig. 1. The bond lengths and angles are given in Table 2.

The coordination around Pt is square-planar. The weighted mean plane through the five atoms and the deviations from this plane are shown in Table 3. The angles around Pt are close to the expected values of 90° and 180° .

Table 1. Positional parameters and temperature factors (all $\times 10^4$) with *e.s.d.*'s in parentheses

	x	y	z	U_{eq}^* (\AA^2)
Pt	1324.7 (7)	2325.5 (4)	1681.6 (7)	374 (3)
I(1)	2726 (1)	844 (1)	1707 (2)	568 (8)
I(2)	-35 (1)	3816 (1)	1778 (1)	560 (8)
O(1)	5768 (12)	2972 (8)	553 (15)	563 (80)
O(2)	-3165 (12)	1761 (8)	2804 (15)	621 (86)
N(1)	2945 (13)	2998 (9)	822 (16)	450 (84)
N(2)	-273 (15)	1662 (9)	2515 (16)	536 (95)
C(1)	3947 (19)	3403 (11)	2065 (21)	559 (114)
C(2)	5212 (21)	3679 (13)	1190 (25)	688 (139)
C(3)	-1348 (18)	1294 (12)	1180 (26)	656 (135)
C(4)	-2609 (20)	1004 (12)	2060 (22)	614 (123)

$$* U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13} \cos \beta).$$

Table 2. Bond distances (\AA) and angles ($^\circ$)

Pt—I(1)	2.604 (1)	I(1)—Pt—I(2)	177.7 (1)
Pt—I(2)	2.602 (1)	I(1)—Pt—N(1)	89.2 (4)
Pt—N(1)	2.082 (13)	I(1)—Pt—N(2)	90.8 (4)
Pt—N(2)	2.047 (15)	I(2)—Pt—N(1)	90.9 (4)
N(1)—C(1)	1.47 (2)	I(2)—Pt—N(2)	89.1 (4)
N(2)—C(3)	1.54 (2)	N(1)—Pt—N(2)	179.7 (5)
C(1)—C(2)	1.57 (3)	Pt—N(1)—C(1)	115 (1)
C(3)—C(4)	1.57 (3)	Pt—N(2)—C(3)	114 (1)
C(2)—O(1)	1.33 (2)	N(1)—C(1)—C(2)	106 (1)
C(4)—O(2)	1.43 (2)	N(2)—C(3)—C(4)	106 (1)
		C(1)—C(2)—O(1)	111 (2)
		C(3)—C(4)—O(2)	110 (1)

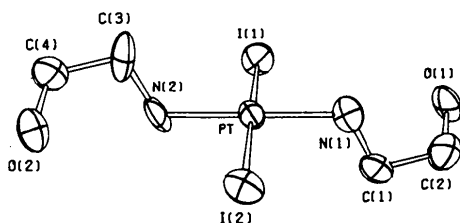


Fig. 1. Labelled diagram of the molecule.

Table 3. Deviations (\AA) of atoms from the platinum plane

*Pt	0.0187 (6)	C(1)	-1.312 (18)
*I(1)	-0.0340 (12)	C(2)	-1.097 (20)
*I(2)	-0.0337 (12)	O(1)	-0.603 (12)
*N(1)	0.017 (13)	C(3)	1.441 (21)
*N(2)	0.031 (14)	C(4)	1.225 (19)
		O(2)	0.637 (13)

* Atoms defining the plane. The equation of the weighted mean plane is $-0.2981x - 0.1706y - 0.9392z + 2.2595 = 0$.

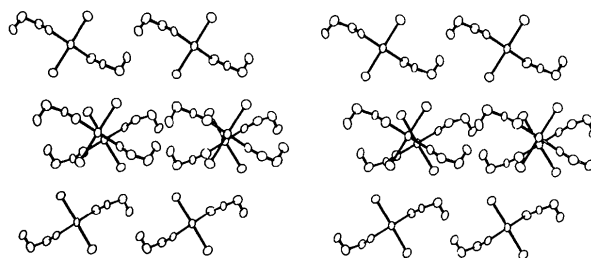


Fig. 2. Stereoscopic diagram of the packing in the *trans*-[Pt($\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-OH}$) $_2\text{I}_2$] crystal (*a* axis horizontal and *b* axis vertical).

The Pt—I lengths are normal [2.604 (1) and 2.602 (1) \AA]. Values of 2.60 and 2.61 \AA have been reported for *trans*-diiodoplatinum compounds (Hitchcock, Jacobson & Pidcock, 1977; Alcock & Leviston, 1974; Thiele & Wagner, 1978).

The Pt—N distances [2.047 (15) and 2.082 (13) \AA] agree well with the values published for *trans*-diamine compounds (Zanotti, Del Pra, Bombieri & Tamburro, 1978; Rochon & Melanson, 1980). The two 2-aminoethanol ligands are arranged so that one ligand is above the Pt plane and the second below it. The whole molecule has an approximate center of symmetry (Figs. 1 and 2).

The packing of the molecules is shown in Fig. 2. The crystal consists of layers of molecules parallel to the *ac* plane. The layers are held together in the *b* direction by van der Waals forces. Inside the layers, the structure is stabilized by intermolecular hydrogen bonding involving the hydroxyl groups. The O(1)···O(2) distances are 2.66 and 2.73 \AA and the angles are close to the tetrahedral values (Table 4), therefore favoring strong hydrogen bonds. The N atoms do not seem to participate in the hydrogen-bonding system. There are two short intermolecular contacts [N(1)···O(1) = 2.79 and N(2)···O(2) = 2.86 \AA], but the C—N···O and C—O···N angles (59°) are not favorable for hydrogen bonding. There are no hydrogen bonds involving the I atoms.

The square planes lie over each other inside the layers. The Pt—Pt distance is $\sim 4.2 \text{\AA}$. This arrangement is common in *cis* amine structures (Srivastava,

Table 4. Possible hydrogen bonds involving the two non-equivalent H atoms

	Transformation (on last atom)	O...O (Å)	∠C—O...O (°)
C(2)—O(1)—H...O(2)	$x + 1, y, z$	2.73 (2)	113 (1)
C(2)—O(1)—H...O(2)	$x + 1, \frac{1}{2} - y, z - \frac{1}{2}$	2.66 (2)	117 (1)
C(4)—O(2)—H...O(1)	$x - 1, y, z$	2.73 (2)	111 (1)
C(4)—O(2)—H...O(1)	$x - 1, \frac{1}{2} - y, z + \frac{1}{2}$	2.66 (3)	134 (1)

Froehlich & Eichhorn, 1978) where hydrogen bonding between the amine and X groups in adjacent molecules gives rise to a Pt—Pt separation of 3.4 Å. Such short distances are usually not observed in *trans* compounds. In this structure, the shortest Pt—Pt distance is mainly determined by I—I contacts, the sum of the van der Waals radii being 4.3 Å.

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The Structure of the Monobarium Salt of Glucose 6-Phosphate Heptahydrate

BY S. K. KATTI, T. P. SESHADRI AND M. A. VISWAMITRA

Department of Physics and ICMR Centre on Genetics and Cell Biology, Indian Institute of Science, Bangalore – 560 012, India

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Abstract

$C_6H_{11}O_9P^{2-} \cdot Ba^{2+} \cdot 7H_2O$, $M_r = 521.5$, is monoclinic, space group $P2_1$, $a = 11.881$ (4), $b = 8.616$ (5), $c = 8.350$ (4) Å, $\beta = 102.95$ (3)°, $Z = 2$, $U = 833.0$ Å³, $d_m = 2.09$, $d_c = 2.08$ Mg m⁻³, $F(000) = 516$. Mo $K\alpha$ ($\mu = 0.034$ mm⁻¹) intensity data. R is 0.068 for 1603 reflections. Of the two endocyclic C—O bonds in the glucose ring, C(5)—O(5) [1.463 (23)] is longer than C(1)—O(5) [1.395 (23) Å]. The pyranose sugar ring takes a ⁴C₁ chair conformation. The Cremer—Pople

puckering parameters are, $\theta = 6.69^\circ$, $Q = 0.619$ Å and $\varphi = 263.7^\circ$. The conformation about the exocyclic C(5)—C(6) bond is *gauche-gauche*, in contrast to *gauche-trans* observed in the structure of glucose 1-phosphate. The phosphate ester bond, P—O(6), is 1.61 (1) Å. It is similar in length to the 'high-energy' P~O bond in phosphoenolpyruvate. The Ba²⁺ ion is surrounded by nine O atoms within a distance of 2.95 Å, of which seven are from water molecules. There is an intramolecular hydrogen bond between the sugar hydroxyl O(4) and phosphate oxygen O(12).

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