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Structure of 2-Adamantylammonium Trichloro(ethylamine)platinate(II)

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Abstract. 2-Adamantylammonium trichloro(ethylamine)platinate(II), $[C_{10}H_{18}N][PtCl_3(C_2H_7N)]$, $M_r = 498.79$, monoclinic, $P2_1/n$, with $a = 12.401$ (10), $b = 6.859$ (15), $c = 20.199$ (15) Å, $\beta = 100.72$ (6)°, $V = 1688$ (2) Å^3, $Z = 4$, $D_x = 1.962$ Mg m^{-3}, $\lambda(Mo\ K\alpha) = 0.71069$ Å, $\mu = 8.86$ mm^{-1}, $F(000) = 960$, $T = 295$ K, $R = 0.060$ for 1801 unique observed reflections. Pt has square-planar coordination with bond distances Pt—Cl = 2.281 (4), 2.278 (4), 2.301 (4) Å and Pt—N = 2.03 (1) Å. The $[Pt(C_2H_5NH_2)Cl_3]^-$ anion is normal but the C atoms in the adamantane ring show very high thermal motion. The crystal structure is stabilized by hydrogen bonding between the amine groups and the chloro ligands. The N···Cl distances range from 3.12 (2) to 3.34 (1) Å.

Introduction. The cage molecule 1-adamantanamine $(C_{10}H_{15}NH_2)$ has been the subject of some attention lately, chiefly because of its antiviral (Hay, Wolstenholme, Shehel & Smith, 1985; Widell, Hansson, Oeberg & Nordenfelt, 1986; Fletcher, Hirschfield & Forbes, 1965) and antitumor activity (Ho, Hakala & Zakrsewski, 1972). Moreover, platinum(II) complexes containing the related 1,2-adamantanediamine ligand (Shionogi & Co. Ltd, 1983) apparently possess antitumor activity comparable to that of the commercially licensed drug cisplatin, *cis*-Pt(NH$_3$)$_2$Cl$_2$ (Rosenberg, van Camp, Trosko & Mansour, 1969). A convenient synthetic route to mixed-amine platinum(II) complexes of the type *cis*-Pt(L)(L')Cl$_2$ (L,L' = methylamine, ethylamine, cyclobutylamine, cyclopentylamine *etc.*) has been developed recently and we felt that it would be worthwhile attempting to synthesize similar complexes containing various adamantanamine ligands. It is our ultimate hope that such synthetic combina-

tions might result in compounds with enhanced antitumor activity and reduced toxicity.

Reaction of K[Pt(EtNH$_2$)Cl$_3$] with 2-adamantanamine (2-adam) does apparently yield the mixed-amine complex [Pt(EtNH$_2$)(2-adam)Cl$_2$] but, upon treatment with dilute HCl during the work-up of the product, yellow crystals of the [2-adamH]$^+$.-[Pt(EtNH$_2$)Cl$_3$]$^-$ salt are also produced. This complex is probably the result of displacement of the coordinated adamantanamine ligand by Cl$^-$ and subsequent quarternization of the amine group. We have now characterized the ionic compound by X-ray diffraction and report the results here.

The crystal structure was also of interest to us in view of our ongoing work on order–disorder phase transitions in organic molecular crystals, including substituted adamantane derivatives (Bélanger-Gariépy, Brisse, Harvey, Butler & Gilson, 1987, 1990; Harvey, Gilson & Butler, 1987). The room-temperature phases in such 'plastic crystalline' materials are usually disordered and the phase transitions take place at low temperatures or under high external pressures. The transitions are exothermic and consequently the materials are beginning to be exploited in various passive heat-storage systems. In the case of our complex, we anticipated that the adamantylammonium ion might be disordered at room temperature.

Experimental. 1 mmol of K[Pt(EtNH$_2$)Cl$_3$], synthesized by the method already reported (Rochon, Melanson & Doyon, 1987) and 1.1 mmol of 2-adamantanamine were stirred together in a minimum quantity of water for 90 min. Then 0.1M HCl (10 ml) was added to the solution and the mixture was stirred for a further 10 min. The resulting yellow

Table 1. *Atomic coordinates with their e.s.d.'s and thermal parameters* ($\times 10^4$ *for* Pt, Cl *and* $\times 10^3$ *for* C, N)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{eq}(\text{Å}^2)$
Pt	1103·9 (4)	2265·4 (8)	1753·5 (3)	440
Cl(1)	1847 (3)	−362 (5)	1311 (2)	678
Cl(2)	417 (3)	4878 (6)	2235 (2)	708
Cl(3)	354 (3)	3385 (6)	694 (2)	746
N(1)	551 (1)	275 (2)	416 (1)	82
N(2)	171 (1)	128 (2)	270 (1)	54
C(1)	758 (2)	322 (5)	467 (1)	129
C(2)	673 (6)	413 (12)	431 (2)	503
C(3)	667 (2)	473 (5)	357 (2)	206
C(4)	754 (3)	624 (3)	380 (2)	137
C(5)	867 (3)	552 (5)	408 (3)	219
C(6)	834 (3)	454 (8)	479 (2)	289
C(7)	810 (6)	211 (6)	433 (2)	407
C(8)	820 (2)	234 (5)	360 (2)	222
C(9)	717 (2)	319 (6)	330 (1)	189
C(10)	903 (2)	394 (6)	384 (1)	141
C(11)	97 (1)	13 (2)	303 (1)	82
C(12)	135 (1)	−33 (3)	376 (1)	85

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Pt—Cl(1)	2·281 (4)	C(4)—C95)	1·49 (5)
Pt—Cl(2)	2·278 (4)	C(5)—C(6)	1·72 (6)
Pt—Cl(3)	2·301 (4)	C(5)—C(10)	1·29 (5)
Pt—N(2)	2·03 (1)	C(7)—C(8)	1·51 (5)
C(1)—C(2)	1·32 (7)	C(8)—C(9)	1·44 (4)
C(1)—C(6)	1·30 (5)	C(8)—C(10)	1·52 (4)
C(1)—C(7)	1·28 (6)	C(11)—C(12)	1·49 (2)
C(2)—C(3)	1·54 (6)	N(1)—C(2)	1·75 (8)
C(3)—C(4)	1·50 (4)	N(2)—C(11)	1·47 (2)
C(3)—C(9)	1·38 (5)		

Cl(1)—Pt—Cl(2)	177·6 (1)	C(2)—C(1)—C(7)	115 (4)
Cl(1)—Pt—N(2)	89·9 (3)	C(2)—C(3)—C(4)	89 (3)
Cl(1)—Pt—Cl(3)	91·3 (1)	C(2)—C(3)—C(9)	104 (4)
Cl(2)—Pt—N(2)	87·9 (3)	C(3)—C(4)—C(5)	117 (3)
Cl(2)—Pt—Cl(3)	90·9 (1)	C(3)—C(9)—C(8)	124 (3)
Cl(3)—Pt—N(2)	178·1 (3)	C(4)—C(3)—C(9)	108 (3)
Pt—N(2)—C(11)	116·9 (9)	C(4)—C(5)—C(6)	95 (3)
N(1)—C(2)—C(1)	114 (5)	C(4)—C(5)—C(10)	120 (3)
N(1)—C(2)—C(3)	95 (4)	C(5)—C(10)—C(8)	118 (3)
N(2)—C(11)—C(12)	117 (1)	C(6)—C(1)—C(7)	95 (3)
C(1)—C(2)—C(3)	123 (5)	C(6)—C(5)—C(10)	98 (3)
C(1)—C(6)—C(5)	113 (3)	C(7)—C(8)—C(9)	104 (3)
C(1)—C(7)—C(8)	127 (4)	C(7)—C(8)—C(10)	87 (3)
C(2)—C(1)—C(6)	104 (4)	C(9)—C(8)—C(10)	110 (3)

precipitate was filtered off and the filtrate was evaporated to dryness. The yellow residue was dissolved in acetone and filtered to remove KCl and unreacted K$_2$PtCl$_4$. The filtrate was again evaporated to dryness. The crystals used for the crystallographic work were recrystallized by slow evaporation of an acetone solution.

Yellow crystal; faces and dimensions (mm): 10$\bar{1}$–$\bar{1}$01 (0·120), 103–$\bar{1}$03 (0·100), 101–$\bar{1}$0$\bar{1}$ (0·192), 1$\bar{1}$1–$\bar{1}$1$\bar{1}$ (0·366) and 111–$\bar{1}$1$\bar{1}$ (0·366); Syntex P$\bar{1}$ diffractometer; graphite-monochromatized Mo $K\alpha$ radiation; space group determined from a set of precession photographs; cell parameters from refined angles of 15 centered reflections; 4236 independent

reflections measured up to $2\theta < 55°$ by a 2θ–θ scan technique; range of *hkl*: $h = 0 \rightarrow 16$, $k = 0 \rightarrow 8$, $l = -26 \rightarrow 25$; standard reflections 51$\bar{1}$, 131, 006, variations $\sim 2\cdot 0\%$; 1801 unique observed reflections [($I_{net} < 2\cdot 5\sigma(I)$)] were used to solve the structure; $\sigma(I)$ and scan rate as in Melanson, Hubert & Rochon (1975); absorption correction based on equations of crystal faces (transmission factors from 0·242 to 0·465); data corrected for Lorentz and polarization effects.

Position of Pt atom determined by three-dimensional Patterson map; other non-H atoms located by structure-factor and Fourier-map calculations; H atoms fixed at calculated positions (C—H = 0·95 and N—H = 0·85 Å) with isotropic $B = 6\cdot 0$ Å^2, except for —CH$_3$ (H could not be located), one H atom in the —NH$_3^+$ group was located and the other two H-atom positions were calculated; refinement by full-matrix least-squares calculations minimizing $\Sigma w(F_o - F_c)^2$; ratio max. least-squares shift to e.s.d. in final refinement cycle < 0·9 for C(2) and < 0·5 for other atoms; isotropic secondary-extinction corrections: extinction coefficient = 1·7 × 10^2 (Coppens & Hamilton, 1970); scattering curves of Cromer & Waber (1965) for Pt, Cl, N, C and of Stewart, Davidson & Simpson (1965) for H; anomalous-dispersion terms of Pt and Cl from Cromer (1965) included in the calculations, which were performed on a Cyber 830 with programs of Melanson, Hubert & Rochon (1975); individual weights $w = 1/\sigma^2$ (*F*); $\Delta\rho_{max} = 1\cdot 0$ e Å^{-3} (close to Pt) in final Fourier synthesis; goodness of fit 1·36; $R = 0·060$ and $wR = 0·049$.

Discussion. The refined atomic parameters are given in Table 1.* A labeled diagram of the complex

* Lists of anistropic thermal factors, weighted least-squares planes, calculated H-atom coordinates, torsion angles for the adamantanammonium ion and observed and calculated structure factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52428 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
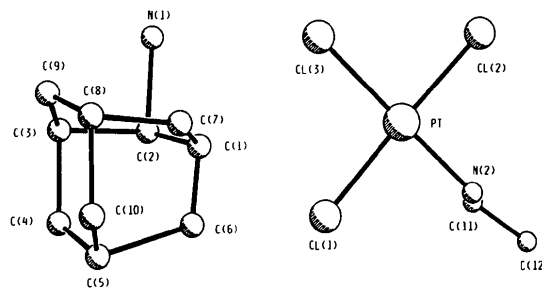

Fig. 1. Labeled diagram of the compound [2-C$_{10}$H$_{15}$NH$_3$]-[Pt(C$_2$H$_5$NH$_2$)Cl$_3$].

$[2\text{-}C_{10}H_{15}NH_3]$ $[Pt(EtNH_2)Cl_3]$ is shown in Fig. 1. As expected, the platinum complexed ion has square-planar geometry and the angles around the Pt atom are close to 90 and 180°. The weighted best coordination plane was calculated through the five atoms. The deviations are: Pt, -0.0005 (5); Cl(1), 0.018 (4); Cl(2), 0.021 (4); Cl(3), -0.005 (4); and N(2), -0.05 (11) Å. The bond lengths and angles are listed in Table 2. The Pt—Cl are 2.281 (4), 2.278 (4) Å for the *cis* bonds, and 2.301 (4) Å for the *trans* bond. The two Pt—Cl bonds *cis* to the amine ligand seem slightly shorter than the *trans* bond. The values found in $[Pt(isopropylamine)Cl_3]^-$ are 2.296 (4) and 2.299 (3) Å for the *cis* bonds and 2.320 (3) Å for the *trans* bond (Rochon, Melanson & Doyon, 1987). In $K[Pt(cyclopentylamine)Cl_3]$ the corresponding values are 2.311 (4), 2.302 (4) and 2.315 (4) Å (Dion, Beauchamp, Rochon & Melanson, 1989). In the three compounds the *trans* bond seems slightly longer but at the moment we do not believe that the difference is significant. The Pt—N bond is 2.03 (1) Å and agrees well with the published values found in aminechloroplatinum(II) complexes (Lock & Zvagulis, 1981; Rochon, Melanson & Doyon, 1987; Dion, Beauchamp, Rochon & Melanson 1989; Melanson & Rochon 1984, 1985). The organic ligand is normal with bond distances $N(2)\text{—}C(11) = 1.47$ (2) and $C(11)\text{—}C(12) = 1.49$ (2) Å and angles $Pt\text{—}N(2)\text{—}C(11) = 116.9$ (9) and $N(2)\text{—}C(11)\text{—}C(12) = 117$ (1)°.

Most C atoms in the 2-adamantylammonium cage are disordered as evidenced by the high thermal factors especially those of C(2) and C(7), resulting in very high e.s.d.'s in the bond distances and angles. The C—C bond distances vary from 1.28 (6) to 1.72 (6) Å with an average value of 1.44 Å. The C—C—C angles range from 89 (3) to 127 (4)° (average = 108°). From the previous work on adamantane derivatives, disorder of the adamantane ring system was expected at room temperature. Our
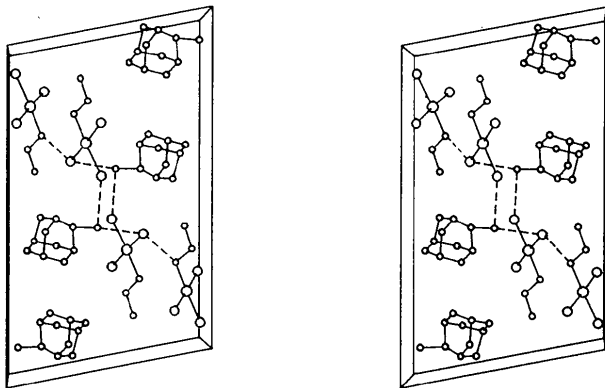

Fig. 2. Stereoscopic view of the packing in the unit cell (*c* axis vertical, down *b* axis; dashed lines correspond to H bonds).

Table 3. *Distances* (Å) *and angles* (°) *between atoms involved in hydrogen bonds with e.s.d.'s in parentheses*

N(1)···Cl(1^i)	3.18 (1)	C(2)—N(1)···Cl(1)	123 (2)
N(1)···Cl(3^{ii})	3.23 (2)	C(2)—N(1)···Cl(3)	99 (2)
N(1)···Cl(3^i)	3.12 (2)	C(2)—N(1)···Cl(3)	141 (2)
N(2)···Cl(1^i)	3.34 (1)	Pt—N(2)···Cl(1)	113.5 (4)

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

values can be compared to those obtained for the disordered room-temperature phase of adamantanecarboxylic acid where the C—C bonds range from 1.453 (16) to 1.602 (16) Å and C—C—C angles from 103.1 (9) to 116.0 (11)°. The corresponding values for the ordered low-temperature phase of the acid are 1.527 (4) to 1.548 (3) Å and 108.4 (2) to 111.3 (2)° (Bélanger-Gariépy, Brisse, Harvey, Gilson & Butler, 1990).

Adamantane $(C_{10}H_{16})$ itself and many of its derivatives are well known to undergo order–disorder phase transitions (Donohue & Goodman, 1967) over a wide temperature range and with a large variation in entropy of the transition. With the exception of 1-adamantanol, $C_{10}H_{15}OH$ (Harvey, Gilson & Butler, 1987), the phase transitions occur below room temperature and the room-temperature phases are usually disordered (Wahl, Greene & Bordner, 1973; Chacko & Zand, 1973; Bélanger-Gariépy *et al.*, 1987, 1990).

The torsion angles have been calculated and the list is part of the deposited material. Fig. 2 shows the packing of the molecules in the unit cell. It consists of layers of anions and cations parallel to the diagonal plane (101). The hydrophilic moiety of $2\text{-}C_{10}H_{15}NH_3^+$ is oriented towards the chloride ligands of the Pt complexed anions. The crystal structure is stabilized by hydrogen bonding. All the H atoms in the $-NH_3^+$ group are involved in hydrogen bonds with the chloride ligands. Two of these are shown in Fig. 2, the third is down the *b* axis. The distances and angles between atoms involved in hydrogen bonds are shown in Table 3. One of the H atoms of the ethylamine ligand is also involved in hydrogen bonding with Cl(1). The N···Cl distances vary from 3.12 (2) to 3.34 (1) Å.

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Coordination Complex of Na$^+$ and α-D-Glucose

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Abstract. The structure of α-D-glucose–NaCl is presented. $C_6H_{12}O_6.1/2(NaCl).0\cdot39(H_2O)$, $M_r = 216\cdot40$, trigonal, $P3_121$, $a = b = 9\cdot721$ (3), $c = 17\cdot06$ (1) Å, $V = 1396$ (1) Å^3, $D_m = 1\cdot54$ (1), $D_x = 1\cdot54$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71073$ Å, $\mu = 2\cdot859$ cm^{-1}, $F(000) = 683\cdot4$, $T = 293$ K, final $R = 0\cdot044$ for 744 reflections with $I \geq 3\sigma(I)$. The Na$^+$ residues on a crystallographic twofold axis and is coordinated by six hydroxyls orginating from four separate glucose molecules. The chloride ion is not involved in direct ionic interactions with the sodium ion.

Introduction. In the course of developing chemically modified carbohydrates of potential value to industry, Dr John Robyt and co-workers (Department of Biochemistry and Biophysics, Iowa State University) reacted succinyl dichloride with sucrose. The initial product was an intramolecularly crosslinked form of sucrose, whose covalent structure could not be deduced by spectroscopic analysis. Upon standing for several months, the purified product, a syrup, yielded crystals. The crystal structure revealed only a glucose molecule interacting with Na$^+$ and Cl$^-$. The presence of Na$^+$ and Cl$^-$ was unexpected. As the small amount of crystalline sample precluded chemical analysis, new crystals were grown from an aqueous solution of glucose and NaCl. The new structure, identical to the original, appears below. Results of limited chemical analysis of the new crys-

tals agree with the model from X-ray refinement. The crystal structure represents the only example in the literature where hydroxyls from carbohydrates occupy the entire coordination shell of an Na$^+$. Furthermore, the interaction of Na$^+$ and glucose observed here may be relevant to the mechanism of action of the α-D-glucose:Na$^+$ cotransporter in biological systems (Wright, Seckler & Overath, 1986).

Experimental. All chemicals used were of reagent grade. Crystals were grown by slow evaporation of water from a solution of D-glucose:NaCl in a 2:1 molar ratio. Dr John Robyt kindly provided crystals used in the original analysis, as mentioned above. The crystal used for the structure reported here measured approximately $0\cdot5 \times 0\cdot4 \times 0\cdot65$ mm. All data were collected on a Syntex $P2_1$ diffractometer using a graphite monochromator and Mo $K\alpha$ radiation ($\lambda = 0\cdot71073$ Å). Unit-cell parameters resulted from a least-squares analysis of 15 reflections ($22 \leq 2\theta \leq 25°$). Data were collected to $2\theta = 50°$ [(sinθ/$\lambda)_{max} = 0\cdot595$ Å^{-1}] over two asymmetric units of reciprocal space ($0 \leq h \leq 11$, $-10 \leq k \leq 0$, $0 \leq l \leq 20$) using variable-speed ω scans. A single standard reflection showed no decrease in intensity throughout data collection. Intensities were corrected for Lp effects and an empirical absorption correction (transmission factors varied from $0\cdot82$–$0\cdot87$) was applied. Systematic absences occurring at $l \neq 3n$ for