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Bis[tris(2-hydroxyethyl)ammonium] Hexachloroplatinate(IV)

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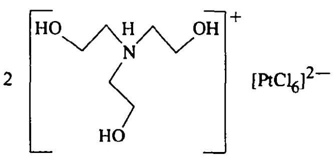
Abstract

The title compound, $[HN(C_2H_4OH)_3]_2[PtCl_6]$, comprises $[HN(C_2H_4OH)_3]^+$ and $[PtCl_6]^{2-}$ ions. In the cation, the ammonium H atom forms an intramolecular bifurcated hydrogen bond with two O atoms. The anions and cations are joined in polymeric chains through hydrogen bonds involving the hydroxyl H atom and the coordinated Cl atoms. The crystal structure is of the antifluorite type.

Comment

During the course of studies on the coordination compounds of tris(2-hydroxyethyl)amine, the hexachloroplatinate(IV) salt, (I), was synthesized. Only eight hexachloroplatinate(IV) structures among 38 entries found in the Cambridge Structural Database (Allen *et al.*, 1991) contain substituted ammonium ions as the cation.



(I)

The structure of (I) consists of tris(2-hydroxyethyl)ammonium cations, $[HN(C_2H_4OH)_3]^+$, and hexachloroplatinate(IV) anions, $[PtCl_6]^{2-}$. An antifluorite-type structure is adopted in which each of the $[PtCl_6]^{2-}$ ions is surrounded by a cubic array of eight $[HN(C_2H_4OH)_3]^+$ cations, while each cation is tetrahedrally surrounded by four anions. The lattice thus shows 4+8 coordination.

The anion is centrosymmetric with an almost regular octahedral shape. The average Pt—Cl bond length is 2.318 (3) Å, which is comparable to those found in other hexachloroplatinate(IV) structures [2.323 (1) (Williams, Dillin & Milligan, 1973), 2.312 (5) (Bisi-Castellani, Manotti-Lanfredi, Tiripicchio, Maresca & Natile, 1984), 2.321 (3) (Toffoli, Venumiere, Khodadad, Rodier & Julien, 1985), 2.326 (4) (Elyoubi, Ghozlen, Mlik & Daoud, 1986), 2.311 (1) (Delafontaine, Toffoli, Khodadad, Rodier & Julien, 1987) and 2.318 (1) Å (Clark & Hall, 1989)], but significantly longer than that of tetramethylammonium hexachloroplatinate(IV) [2.293 (4) Å (Berg & Søtofte, 1978)].

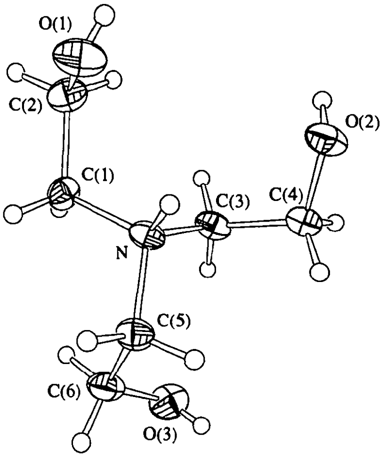


Fig. 1. A view of the tris(2-hydroxyethyl)ammonium cation with the non-H-atom displacement ellipsoids at the 40% probability level. H atoms are drawn as spheres of arbitrary radii.

The average C—N bond length in the cation is 1.51 (2) Å, which is similar to the values found in other ammonium hexachloroplatinate(IV) compounds, *e.g.* 1.48 (2) (Toffoli, Venumiere, Khodadad, Rodier & Julien, 1987), 1.484 (6) (Berg & Søtofte, 1978), 1.505 (3) (Bisi-Castellani, Manotti-Lanfredi, Tiripicchio, Maresca & Natile, 1984), 1.51 (1) (Clark & Hall, 1989) and 1.54 (3) Å (Elyoubi, Ghozlen, Mlik & Daoud, 1986). The bond lengths and angles (see Table 1) indicate that the geometry of the cation is very similar to that previously reported for the chloride and hydrogen sulfide salts (Mootz, Brodalla & Wiebcke, 1990), and the bromide salt (Yılmaz, İçbudak, Ölmez & Howie, 1996). Changing the anion in the structure does not seem to alter significantly the geometry of the cation.

The ammonium H atom forms intramolecular bifurcated hydrogen bonds with the O(1) and O(2) atoms (Table 2), and forms an intermolecular hydrogen bond with the O(2) atom of the adjacent cation. The hydroxy H atoms also take part in hydrogen bonding between the cations [$O(2)\cdots O(3)(\frac{1}{2}+x, \frac{3}{2}-y, \frac{1}{2}+z)$ 2.892 (7) Å]. The cations in the structure of (I) are thus linked by hydrogen bonds involving the ammonium H atom and some of the hydroxy groups. The $[HN(C_2H_4OH)_3]^+$ cations and $[PtCl_6]^{2-}$ anions are held together by an extensive system of hydrogen bonds of the $O—H\cdots Cl$ type (Table 2). The ammonium H atom does not participate in the hydrogen bonding between anions and cations. The hydroxy H atoms of the cation and the

Cl atoms of the anion form some strong hydrogen bonds [O(3)···Cl(1)($\frac{1}{2}+x$, $\frac{1}{2}-y$, $z-\frac{1}{2}$) 3.363 (6) Å], while others are remarkably weaker [O(2)···Cl(2)($\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$) 3.615 (5) Å].

Experimental

The title compound, bis[tris(2-hydroxyethyl)ammonium] hexachloroplatinate(IV), was prepared by the reaction of tris(2-hydroxyethyl)amine with hexachloroplatinic acid in ethanol and recrystallized from water to obtain suitable single crystals for X-ray analysis.

Crystal data

$(C_6H_{16}NO_3)_2[PtCl_6]$
$M_r = 708.21$
Monoclinic
$P2_1/n$
$a = 7.570$ (3) Å
$b = 13.670$ (6) Å
$c = 11.560$ (5) Å
$\beta = 102.90$ (4)°
$V = 1166.0$ (9) Å^3
$Z = 2$
$D_x = 2.017$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 14 reflections
$\theta = 10$–12°
$\mu = 6.803$ mm^{-1}
$T = 298$ K
Tabular
0.40 × 0.30 × 0.14 mm
Yellow–orange

Data collection

Nicolet *P*3 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.137$, $T_{\max} = 0.226$
2319 measured reflections
1861 independent reflections
1493 reflections with $F > 4\sigma(F)$

$R_{\rm int} = 0.020$
$\theta_{\max} = 25°$
$h = -9 \rightarrow 8$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 13$
2 standard reflections frequency: 50 min intensity decay: 2.2 and 2.8%

Refinement

Refinement on *F*
$R = 0.029$
$wR = 0.024$
$S = 2.02$
1493 reflections
139 parameters
H atoms: see below
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\max} = 0.05$, but as high as 0.49 for U_{11} of O(1) and 0.86 for *x* of H(O1)
$\Delta\rho_{\max} = 0.8$ e Å^{-3}
$\Delta\rho_{\min} = -1.1$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Cl(1)—Pt	2.314 (2)	Cl(2)—Pt	2.318 (2)
Cl(3)—Pt	2.321 (2)	C(2)—O(1)	1.416 (8)
C(4)—O(2)	1.425 (7)	C(6)—O(3)	1.424 (8)
C(1)—N	1.510 (8)	C(3)—N	1.511 (8)
C(5)—N	1.514 (7)	C(2)—C(1)	1.506 (8)
C(4)—C(3)	1.497 (7)	C(6)—C(5)	1.496 (8)
Cl(2)—Pt—Cl(1)	89.46 (7)	Cl(3)—Pt—Cl(2)	90.84 (7)
Cl(3$^{\rm i}$)—Pt—Cl(1)	89.91 (7)	Cl(3$^{\rm i}$)—Pt—Cl(2)	89.16 (7)
C(5)—N—C(1)	112.7 (5)	C(3)—N—C(1)	112.2 (5)
C(2)—C(1)—N	110.6 (5)	C(5)—N—C(3)	113.3 (5)
C(4)—C(3)—N	111.7 (5)	C(1)—C(2)—O(1)	107.3 (5)
C(6)—C(5)—N	115.1 (5)	C(3)—C(4)—O(2)	111.2 (5)
Cl(3)—Pt—Cl(1)	90.09 (7)	C(5)—C(6)—O(3)	114.7 (6)
Cl(2$^{\rm i}$)—Pt—Cl(1)	90.54 (7)		

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

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
N—H(N)···O(1)	2.35 (7)	2.794 (8)	110 (5)
N—H(N)···O(2)	2.52 (7)	2.976 (8)	112 (5)
N—H(N)···O(2$^{\rm i}$)	2.19 (7)	2.976 (7)	145 (6)
O(1)—H(O1)···Cl(1$^{\rm ii}$)	2.93 (7)	3.417 (5)	133 (7)
O(1)—H(O1)···Cl(2$^{\rm ii}$)	2.91 (7)	3.523 (6)	156 (8)
O(1)—H(O1)···Cl(3$^{\rm iii}$)	3.08 (7)	3.536 (5)	130 (7)
O(2)—H(O2)···Cl(2$^{\rm ii}$)	3.06 (7)	3.615 (5)	126 (6)
O(2)—H(O2)···O(3$^{\rm iv}$)	2.14 (7)	2.892 (7)	150 (7)
O(3)—H(O3)···Cl(1$^{\rm v}$)	2.71 (8)	3.363 (6)	153 (8)
O(3)—H(O3)···Cl(3$^{\rm v}$)	2.87 (8)	3.408 (6)	134 (7)

Symmetry codes: (i) $1-x, 1-y, -z$; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (iv) $\frac{1}{2}+x, \frac{3}{2}-y, \frac{1}{2}+z$; (v) $\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$.

Methylene H atoms were placed in calculated positions with a C—H distance of 0.95 Å and refined riding upon their parent C atoms with a common group $U_{\rm iso}$. The hydroxy and amino H atoms were found in $\Delta\rho$ maps and refined isotropically in the usual manner, except that a group $U_{\rm iso}$ was used for the hydroxyl H and the O(1)—H(O1) bond distance was constrained.

Data collection: *P*3 *Software* (Nicolet Instrument Corporation, 1970). Cell refinement: *P*3 *Software*. Data reduction: *RDNIC* (Howie, 1980). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEX* (McArdle, 1994).

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: AB1374). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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trans-Diaquabis(pyridine-2-carboxamide-N^1,O)copper(II) Dichloride and Dibromide

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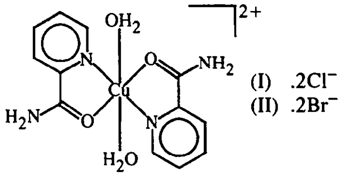
Abstract

Crystals of the title compounds, $[Cu(C_6H_6N_2O)_2(H_2O)_2]Cl_2$, (I), and $[Cu(C_6H_6N_2O)_2(H_2O)_2]Br_2$, (II), are isomorphic. The structures consist of centrosymmetric complex cations and separate chloride or bromide ions linked by hydrogen bonding. The pyridine-2-carboxamide molecules ($C_6H_6N_2O$) are coordinated by the ring N and amide O atoms, forming the base of an elongated octahedron. Bond lengths in (I) and (II), respectively: short Cu—N of 1.960 (1) and 1.965 (2), Cu—O of 1.981 (1) and 1.981 (2), and axial Cu—H_2O of 2.418 (2) and 2.417 (3) Å.

Comment

The structures of pyridine-2-carboxamide complexes have not been intensively investigated. The Cambridge Structural Database (Version 5.11) (Allen & Kennard, 1993) gives information about only one Cd^{II} and two Cu^{II} structures with $R < 0.06$ (Castro *et al.*, 1990; Cantarero, Amigó, Faus, Julve & Debaerdemaeker, 1988; Batsanov *et al.*, 1986). This work presents a redetermination of the structure of *trans*-diaquabis(pyridine-2-carboxamide-N^1,O)copper(II) dichloride, (I), which was originally investigated by X-ray photographic methods and refined to $R = 0.13$ (Brown, MacSween, Mercer & Sharp, 1971), and the structure determination of the corresponding bromide, (II).



(I) $.2Cl^-$
(II) $.2Br^-$

The structures of compounds (I) and (II) are shown in Figs. 1(*a*) and 1(*b*), respectively. The cations display inversion symmetry. Crystals of (I) and (II) are isostructural. Our investigation of (I) is not consistent with the earlier investigation, giving not only distinctly different bond lengths, but also different (but similar) unit-cell constants and unit-cell volume. The Cu atom is in an elongated octahedral environment, with four short and two long bonds. The short bonds [Cu—N 1.960 (1) in (I) and 1.965 (2) in (II); Cu—O 1.981 (1) in (I) and 1.981 (2) Å in (II)] are formed by the chelating ligand bonding through the amide O and ring N atoms. In the less symmetrical $[Cu(pyridine\text{-}2\text{-}carboxamide)_2(H_2O)(NO_3)]^+$ cation (Castro *et al.*, 1990), where pyridine-2-carboxamide in a very similar coordination mode also forms short Cu—O and Cu—N bonds, the Cu—O bonds [average 1.955 (2) Å] are distinctly shorter than the Cu—N bonds [average 1.976 (3) Å]. In the mononuclear [Cu(pyridine-2-carboxamide){bis(2-pyridylcarbonyl)amido}]$^+$ cation (Cantarero *et al.*, 1988), where the Cu atom is also in an elongated octahedral environment, the pyridine-2-carboxamide ligand is coordinated *via* the N atom of the pyridine ring and the O atom of the amide group with bond distances of 2.001 (4) and 2.316 (3) Å, respectively. The short Cu—N bond here is distinctly longer than in the investigated structures (I) and (II).

In compounds (I) and (II), the water molecules occupy the axial positions of the octahedron forming two long bonds of 2.418 (2) in (I) and 2.417 (3) Å in (II), typical for long Cu—H_2O bonds (Orpen *et al.*, 1989). The chelate rings are not ideally planar. The deviations of the Cu and N2 atoms from the ideal plane formed by atoms N1, C2, C1 and O2 are respectively −0.135 (3) and 0.028 (3) Å for (I), and −0.141 (4) and 0.012 (5) Å for (II). The carboxamide group and Cu atom are not coplanar with the pyridine ring. The observed deviations of the C1, O2, N2 and Cu atoms from the least-squares plane of this ring are respectively 0.052 (3), 0.060 (3), 0.098 (3) and −0.112 (2) Å for (I) and 0.054 (4), 0.085 (5), 0.086 (5) and −0.093 (4) Å for (II).

We can conclude that in the 3σ range the geometrical shape of the $[Cu(pyridine\text{-}2\text{-}carboxamide)_2(H_2O)_2]^{2+}$ complex cation is identical in the chloride and bromide salts and that the mode of (pyridine-2-carboxamide)–Cu^{II} coordination may be different in the less symmetrical Cu^{II} complexes (Castro *et al.*, 1990; Cantarero *et al.*, 1988).