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Channel Inclusion of Potassium and Tetrachloroplatinate Ions in a Complex Formed between 1,3-diamino-2-propanone and K_2PtCl_4 in an Acidic Medium

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Abstract. The crystalline complex dipotassium 1,3-diammonio-2-propanone tetrachloroplatinate trihydrate, formulated as $K_2[(NH_3CH_2C)_2O][PtCl_4]_2 \cdot 3H_2O$, has been prepared while synthesizing complexes analogous to *cis*-dichlorodiamine Pt(II). Its structure is orthorhombic, space group *Pnma*, $M_r = 896.1$, $F(000) = 1640$, $a = 8.428(4)$, $b = 20.360(10)$, $c = 12.141(7)$ Å, $V = 2083.3$ Å^3, $Z = 4$, $D_x = 2.860$ g cm^{-3}, $\mu(\text{Mo}K_\alpha) = 196$ cm^{-1}, final $R = 0.083$ for 1379 unique reflections. The structure consists of a very extended hydrogen bonded network which involves half of the $PtCl_4^{2-}$ ions, the organic molecules and the water molecules of hydration, leaving large oval channels which accommodate potassium cations and tetrachloroplatinate anions. Within the channel the potassium and tetrachloroplatinate ions pack in columns extending along the *a* axis. The dense packing is rather reminiscent of that found in the neat salt where each potassium ion is surrounded by six chlorine atoms which describe a polyhedron of a distorted trigonal prism with $K^+ \cdots Cl$ distances ranging between 3.163–3.187 Å. There is some indirect evidence for the formation of 1,3-diammonio-2-propanone dications which counterbalance the charges of half of the $PtCl_4^{2-}$ ions by protonation of each of the amino nitrogens. The carbonyl oxygens, however, are involved only in a very weak $O \cdots C{=}O$ interactions along the *a* axis.

Key words. Diaminopropanone, potassium tetrachloroplatinate, channel inclusion, crystal structure.

Supplementary Data relating to this article have been deposited with the British Library at Boston Spa, Wetherby, West Yorkshire, U.K., as supplementary publication No. SUP82101 (8 pages).

1. Introduction

In the course of our studies on the synthesis of derivatives analogous to the antitumor drug *cis*-dichlorodiamine Pt(II) [1], we have reacted several trifunctional amino derivatives with K_2PtCl_4 under various experimental conditions [2]. The reaction of 1,3-diamino-2-propanone (DAP) with K_2PtCl_4 produced a crystalline complex whose IR spectrum indicated that neither the amino groups nor the carbonyl group were bonded to the metal atom. Thus, it was deemed worthwhile to undertake a complete structure analysis of this unexpected new complex.

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2. Experimental

2.1. PREPARATION OF THE COMPLEX

Equimolecular solutions of 1,3-diamino-2-propanone hydrochloride and K_2PtCl_4 in water, were cooled in an ice bath under an atmosphere of nitrogen. After two days, a brown precipitate was obtained which could not be recrystallized. This precipitate was removed and the filtrate was allowed to evaporate slowly, until a large dark red shapeless crystal was obtained. Chemical analysis was in accord with the empirical formula: $DAP \cdot H_2PtCl_4 \cdot K_2PtCl_4 \cdot 3H_2O$, calculated (%): C 4.02, H 1.80, N 3.13, Cl 31.64; found (%): C 4.04, H 1.71, N 3.14, Cl 31.55; analysis of potassium by flame photometry was in accord with the suggested formula.

2.2. INTENSITY MEASUREMENTS AND STRUCTURE SOLUTION

A single shapeless crystalline fragment of about 0.3 mm in diameter was cut from a large crystal and mounted on the Philips PW 1100/20 four circle diffractometer.

Table I. Crystal data and details of structure refinement

Formula	$C_3H_{10}ON_2 \cdot K_2Pt_2Cl_8 \cdot 3H_2O$
Formula weight	896.1
F(000)	1640
a(Å)	8.428(4)
b(Å)	20.360(10)
c(Å)	12.141(7)
V(Å^3)	2083.3
Z	4
Space group	*Pnma*
D_m	2.84
D_c(g cm^{-3})	2.86
μ(MoK_α, cm^{-1})	196
Scan mode	$\omega/2\Theta$
Scan speed ($\omega°$ min^{-1})	3
Scan width ($\omega°$)	1.1
Angular range (2Θ°)	5–50
Background at each side of the peak (sec.)	10
Monitor reflections	1 0 1; 4 0 0; 0 12 0
No. of unique reflections	1752
No. of reflections at the final refinement stage	1379
Criterion for omitting reflections	$F_o \leqslant 3\sigma(F_o)$
No. of refined parameters	79
R^a	0.083
R_w^b	0.097
Weighting scheme (w)	$1.798/(\sigma^2(F_o) + 0.004\,F_o^2)$

$$^aR = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|}$$

$$^bR_w = \frac{\Sigma\sqrt{w}||F_o| - |F_c||}{\Sigma\sqrt{w}|F_o|}$$

Table II. Final fractional coordinates and equivalent temperature factors[a]. Coordinates are $\times 10^4$ and $U_{eq} \times 10^4$ Å^2. E.s.d.s are in parentheses.

Atom	x	y	z	U^{a}_{eq}/U_{iso}
Pt(1)	0	0	0	211(4)
Pt(2)	138(1)	2500	2504(1)	231(3)
Cl(1)	2722(7)	−38(2)	−43(4)	339(13)
Cl(2)	−100(5)	256(3)	−1847(4)	286(11)
Cl(3)	65(5)	1698(3)	1170(4)	295(12)
Cl(4)	198(6)	1696(3)	3843(4)	353(12)
K	−2374(5)	849(3)	2546(4)	380(12)
N(1)	1771(21)	1286(8)	6565(14)	381(12)
C(1)	2624(20)	1886(10)	6140(15)	261(45)
C(2)	1842(28)	2500	6586(19)	202(53)
O(1)	781(24)	2500	7179(13)	293(44)
OW(1)	3307(17)	1339(7)	8626(11)	396(36)
OW(2)	2584(18)	2500	9660(14)	182(44)

$^{a}U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$

Accurate cell parameters were obtained from 25 centered reflections. Crystal density was measured by suspension in a mixture of *s*-tetrabromoethane and toluene. The correct space group was established after some effort due to pseudosymmetry and absorption effects introduced by the platinum atoms. Other pertinent data are presented in Table I.

Intensities were collected with graphite monochromatized MoKα radiation under the conditions described in Table I. Three reflections were measured periodically for monitoring crystal and apparatus stabilities, but no significant variations were found. Intensities were corrected for L_p but not for absorption due to difficulties in defining crystal shape.

The positions of the two independent Pt atoms were found by the Patterson method, and the remaining nonhydrogen atoms were located by difference Fourier maps. Calculations were carried out by the SHELX 77 program package [3]. The Pt, Cl and K atoms were refined anisotropically and the DAP and water molecules isotropically. Hydrogens were not introduced in the structure factor calculations as their contribution was found to be negligible. Unit weights were used throughout the initial stages and statistical weights throughout the final stages of the refinement. Final difference Fourier maps revealed electron density excursions of 5 e Å^{-3} around the Pt atom which were ascribed to absorption effects.

The final fractional coordinates are shown in Table II and anisotropic temperature factors in Table IV. A list of observed vs. calculated structure factors, has been deposited with the British Library.

3. Structure Description and Discussion

An ORTEP [4] stereoscopic diagram of the structure and a perspective drawing of a single channel both viewed approximately along *a* are shown in Figures 1 and 2

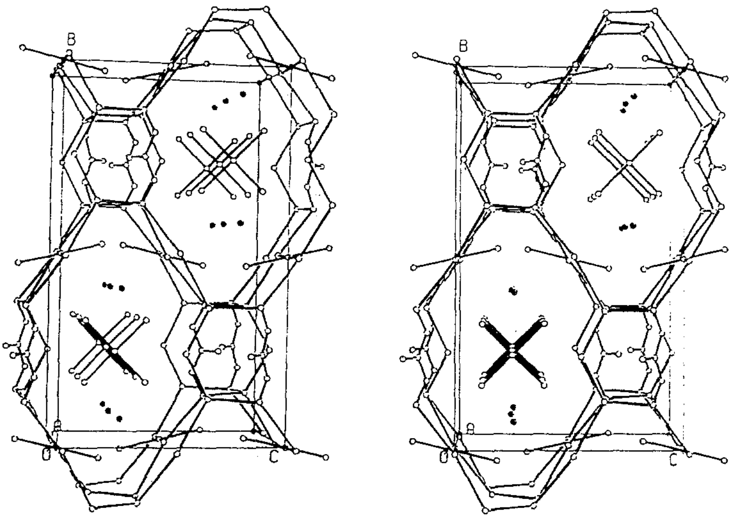

Fig. 1. ORTEP [4] stereoscopic diagram of the crystal structure viewed along *a*. Hydrogen bonds are shown by two thin lines.

respectively. Selected hydrogen bonded and non bonded distances are listed in Table III.

The structure consists of a very extended hydrogen bonded network leaving large oval channels which accommodate salt ions of K^+ and $PtCl_4^{2-}$. In general, all predicted hydrogen bonds shown in Table III, were inferred indirectly from geometrical and chemical considerations.

The walls of the octagonal single channel are formed by hydrogen bond interactions between DAP molecules, half of the $PtCl_4^{2-}$ ions and the water molecules of

Table III. Selected interatomic distances (Å) and angles (deg). E.s.d.s are in parentheses

(a) Bonded		(b) Predicted hydrogen bonded and non bonded.	
Pt(1)—Cl(1)	2.296(6)	N(1)···OW(1)(55501)[a]	2.82
Pt(1)—Cl(2)	2.304(5)	N(1)···OW(1)(45608)	2.93
Pt(2)—Cl(3)	2.301(6)	N(1)···Cl(1)(55507)	3.23
Pt(2)—Cl(4)	2.308(5)	OW(1)···OW(2)(55501)	2.74
C(1)—N(1)	1.51(3)	OW(1)···Cl(1)(55601)	3.27
C(1)—C(2)	1.51(2)	OW(2)···Cl(3)(55601)	3.25
C(2)—O(1)	1.15(3)	OW(2)···Cl(4)(55603)	3.29
Cl(1)—Pt(1)—Cl(2)	91.2(2)	Pt(2)···Pt(2)(55503)	4.214
Cl(3)—Pt(2)—Cl(4)	89.6(2)	$K^+ \cdots K^+$(55508)	4.215
N(1)—C(1)—C(2)	110(1)		
C(1)—C(2)—O(1)	124(1)		

[a] Symmetry equivalent positions are denoted by ORTEP [4] codes as follows:
01 x, y, z; 02 $-x, -y, -z$; 03 $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$; 04 $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$;
05 $-x, \frac{1}{2}+y, -z$; 06 $x, \frac{1}{2}-y, z$; 07 $\frac{1}{2}-x, -y, \frac{1}{2}+z$; 08 $\frac{1}{2}+x, y, \frac{1}{2}-z$.

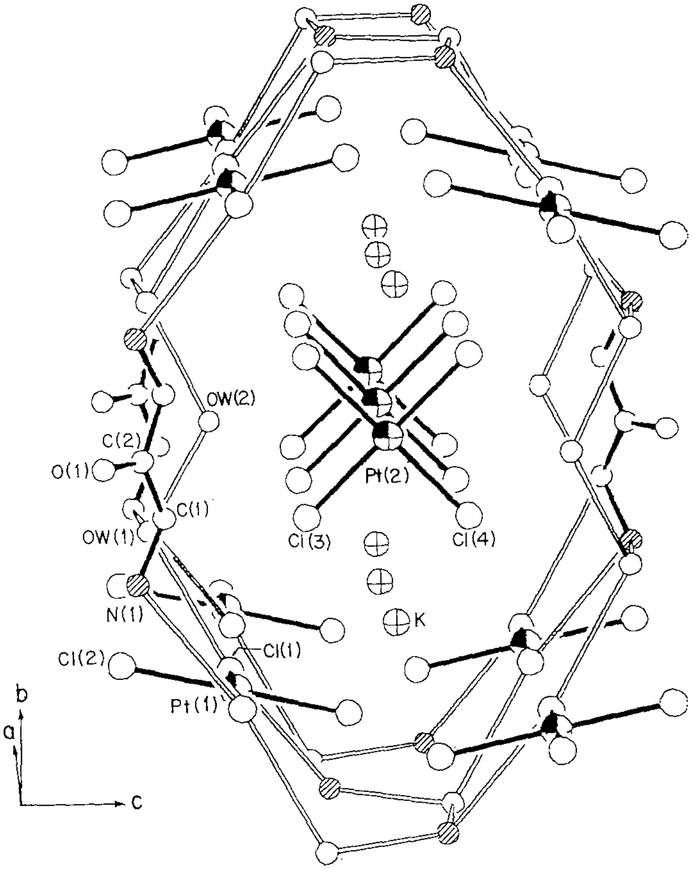

Fig. 2. Perspective diagram of a single channel viewed approximately along *a*. The labels of the tetrachloroplatinate ions and water molecules are displayed for the units at x, y, z, for the DAP molecule at $-1/2+x$, $1/2-y$, $-1/2-z$ and for the potassium ion at $1/2-x$, $-y$, $1/2+z$. The nitrogen atoms and water molecules are shown by hatched and open circles, respectively.

hydration (see Figure 2). The remaining crystallographically independent tetrachloroplatinate anions and the potassium cations as counterions, fill the space defined by the hydrogen bonded network.

Four sides are occupied by $PtCl_4^{2-}$ ions located on inversion centers at (0, 0, 0), (1/2, 0, 1/2), (0, 1/2, 0) and (1/2, 1/2, 1/2) plus ions translated along *a*. Here, the anions having a shape of a square plate, pack with their Pt—Cl diagonal vectors aligned along the *a* axis. Each ion makes normal contacts of 3.832 Å with neighbouring anions via the Cl(1) atoms related by an inversion center at (1/2, 0, 0). Also, there are some weak interactions along *c* between Cl atoms related by the *a* glide plane and the screw axis along *c*. In the *bc* plane, the Cl(1) atoms are involved in hydrogen bonds with atom N(1) of a DAP molecule and one molecule of water, whereas the Cl(2) atoms interact with the potassium ions inside the channel as discussed later.

Table IV. Final anisotropic temperature factors $U_{ij} \times 10^4$ Å^2. E.s.d.s are in parentheses

Atom	U11	U22	U33	U23	U13	U12
Pt(1)	262(8)	91(10)	280(8)	19(4)	−3(4)	6(4)
Pt(2)	237(7)	203(9)	254(7)	0	−12(5)	0
Cl(1)	281(27)	301(32)	437(32)	67(25)	−23(21)	41(20)
Cl(2)	337(26)	232(31)	290(24)	54(23)	−18(18)	5(18)
Cl(3)	367(29)	192(28)	328(26)	−60(22)	2(19)	−21(20)
Cl(4)	446(30)	345(32)	269(25)	36(23)	17(21)	33(23)
K	316(26)	310(29)	514(30)	38(25)	91(22)	0(16)

The right and left sides of the channel are bounded by DAP molecules and trimeric units of water molecules held together by hydrogen bonds. The crystallographic mirror plane at $y = 1/4$, bisects the DAP molecule through the carbonyl bond C(2)—O(1) and also the water molecule OW(2). This water molecule makes two hydrogen bonds with two molecules OW(1) related by the same plane, thus forming a trimeric V-shaped unit. This unit is further hydrogen bonded to the DAP nitrogens N(1) through the terminal molecules OW(1).

Finally, the top and bottom sides of the channel are confined by two DAP nitrogens bonded to two water molecules OW(1) plus the atoms translated along *a*.

A general conclusion can be made that the two neighbouring sides of the channel are connected to each other by N—H···Cl and O—H···Cl bonds.

Inside the channel, the square plates of $PtCl_4^{2-}$ ions and the K^+ cations pack in columns generated and extended by the glide plane and screw axis operating along *a*. Each plate is bisected by the mirror plane at $y = 1/4$ parallel to one of the square edges. Furthermore, the plates align parallel to each other and almost normal to the *a* axis. The anions are separated by a non contact distance of 4.21 Å due to a certain penetration of potassium ions and water molecules OW(2) between the plate planes. The K^+ ions penetrate from the upper and lower sides of the column, whereas one water molecule penetrates from the right or left side, leaving always one side between the plates unoccupied. This packing mode is reminiscent of that found in the structure of the neat K_2PtCl_4 salt [5]. Here, two adjacent tetrachloroplatinate plates are separated by four potassium ions penetrating from all four sides, the distance between plates being 4.13 Å.

Ions of opposite charge are densely packed by electrostatic interactions. A K^+ ion makes rather short and almost equal contact with six chlorines – two atoms from each of the two anions inside the channel and two from one anion of the enclosing network (distance range 3.16–3.19 Å). Thus, the coordination polyhedron around each potassium ion as described in Figure 3 is of a distorted trigonal prism. A rather similar coordination polyhedron has been described in the structure of Zeisse's salt $KPtCl_3—C_2H_4 \cdot H_2O$ [6] where five $K^+\cdots Cl$ distances (range 3.20–3.40 Å) were found to be normal and the sixth remarkably longer (3.76 Å).

Examination of the regions between the channels along *b* and *c*, reveals cyclic units of DAP · $3H_2O$ extending in columns along the *a* axis (see Figure 1). Within

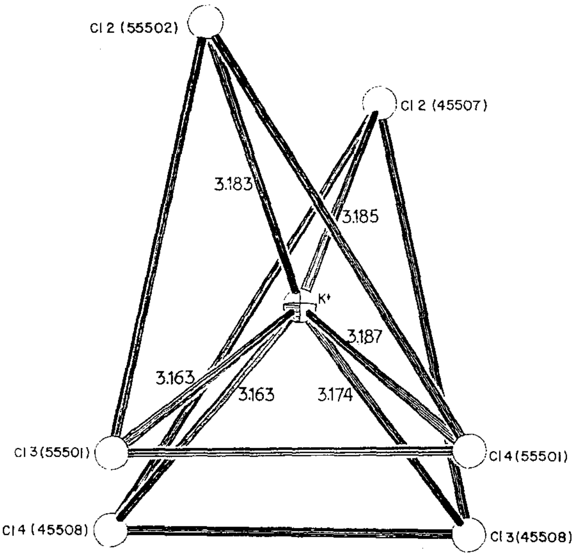

Fig. 3. Coordination polyhedron around the potassium ion. The six chlorines defining the trigonal prism are denoted by ORTEP [4] codes and symmetry positions are given in Table III.

this column, one pair of DAP nitrogens makes bonds to two trimeric units of water molecules along *a* and *c* and also to nearby chlorines Cl(1) of the enclosing network. This arrangement reveals three hydrogen bonds involving each of the nitrogens N(1). Assuming that the DAP molecule is double protonated to counterbalance the charge of half of the $PtCl_4^{2-}$ ions, then each nitrogen can be at most a donor of three bonds. A similar dication has been described in the structure of bis(diethylenetriammonium)tetrachloroplatinate(II) tetrachloride [7]. Protonation on two different molecules was found in 9-ethylguanidinium tetrachloroplatinum(II) dihydrate [8] and also in bis(theophyllium)(tetrachloroplatinum)(II) [9].

Regarding the non-bonded carbonyl oxygens, there is an unusual alignment of the carbonyl groups related by the screw axis along *a* at $y = 1/4$, $z = 3/4$. Every C=O bond is directed towards a nearby carbonyl carbon C(2), perhaps due to weak O···C=O interactions, the O···C distance being 3.64 Å and the O···C=O angle 114°. This type of interaction has been discussed very extensively by Dunitz [10], although he refers to approach distances ranging between 2.8–3.2 Å.

The geometries of the double protonated DAP molecule and the $PtCl_4^{2-}$ ion are quite normal (see Table III).

The DAP molecule assumes an exact crystallographic mirror plane as described before, with the ammonio groups directed *syn* to the carbonyl group, and obviously lacks the proper geometry for binding to the metal.

The two independent square planar $PtCl_4^{2-}$ ions have an average Pt—Cl bond lengths of 2.300(6) Å for the centrosymmetric ion and 2.305 Å for the C_s ion (see Table III). These values do not differ much from other values found in the literature [7, 8]. The centrosymmetric ion however, deviates slightly from an ideal configuration as shown by the Cl(1)—Pt(1)—Cl(2) angle opening of 1.2°, perhaps due to hydrogen bonding effect. Smaller angular deviations of 0.6° were found in the C_s ion.

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