

Structures of $\text{K}[\text{Pt}(\text{Cl})_3(\text{C}_4\text{H}_{11}\text{N})]\cdot 0.5\text{H}_2\text{O}$ and $[\text{Pt}(\text{NH}_3)_4][\text{Pt}(\text{Cl})_3(\text{C}_3\text{H}_9\text{N})]_2$

BY FERNANDE D. ROCHON AND ROBERT MELANSON

Département de chimie, Université du Québec à Montréal, CP 8888, Succ. A, Montréal, Canada H3C 3P8

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Abstract. Potassium *tert*-butylaminetrichloroplatinate(II) hemihydrate, $\text{K}^+\cdot\text{C}_4\text{H}_{11}\text{Cl}_3\text{NPt}^-\cdot 0.5\text{H}_2\text{O}$, $M_r = 422.70$, monoclinic, $C2/c$, $a = 29.640$ (13), $b = 6.008$ (2), $c = 12.471$ (6) Å, $\beta = 93.41$ (4)°, $V = 2217$ (2) Å³, $Z = 8$, $D_x = 2.538$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 13.84$ mm⁻¹, $F(000) = 1560$, $T = 295$ K, $R = 0.029$ for 1743 unique observed reflections. Pt has square-planar coordination with Pt—Cl = 2.313 (4), 2.309 (4), 2.304 (4) and Pt—N = 2.03 (1) Å. The compound crystallizes with a molecule of water located on a twofold axis. The water molecule is exceptionally close to the K^+ ion [$\text{O}\cdots\text{K}^+ = 2.771$ (6) Å]. Packing energy around the K^+ seems an important stabilizing factor. The amino group is hydrogen bonded to one chloro ligand. Tetraammineplatinum bis[trichloro(isopropylamine)platinate(II)], $\text{H}_{12}\text{N}_4\text{Pt}^{2+}\cdot 2\text{C}_3\text{H}_9\text{Cl}_3\text{NPt}^-$, $M_r = 984.33$, monoclinic, $P2_1/c$, $a = 9.291$ (4), $b = 8.120$ (4), $c = 15.140$ (5) Å, $\beta = 90.91$ °, $V = 1142.0$ (8) Å³, $Z = 2$, $D_x = 2.861$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 19.36$ mm⁻¹, $F(000) = 888$, $T = 295$ K, $R = 0.052$ for 2129 unique observed reflections. The Pt atom of the cation is located on an inversion centre with bond distances Pt—N = 2.044 (11) and 2.066 (9) Å. In the anion, the *cis* Pt—Cl = 2.301 (3) and 2.300 (4) Å while the *trans* bond is 2.321 (4) Å. Pt—N = 2.023 (10) Å. The structure seems stabilized by extensive hydrogen bonding involving the ammine ligands and the amino group with the chloro ligands.

Introduction. Although the syntheses of $\text{K}[\text{Pt}(\text{NH}_3)\text{Cl}_3]$ and $\text{K}[\text{Pt}(\text{pyridine})\text{Cl}_3]$ have been known for many years, the methods for the synthesis of monoamine platinum(II) complexes have been reported just recently (Rochon & Fleurent 1988; Rochon, Melanson & Doyon, 1987). These compounds are very important starting materials for the synthesis of mixed-ligand complexes of the type $\text{Pt}(\text{am})(L)\text{Cl}_2$. The reaction of $[\text{Pt}(\text{am})\text{Cl}_3]^-$ with L in water will produce the *cis* isomer (unless the amine is very bulky) since the *trans* effect of Cl is larger than that of amines. *cis* mixed-ligand complexes are important molecules in view of the potent antitumor activity of such compounds. If compounds with two different neutral ligands could be systematically synthesized, the screening range of platinum complexes

would be largely extended and antitumor activity, toxicity and solubility could be significantly modified.

One of the reported methods for the synthesis of primary monoamine Pt^{II} compounds is restricted to bulky amines like *tert*-butylamine (Rochon & Fleurent, 1988) while the second is more general and should be applicable to almost any amine ligand (Rochon, Melanson & Doyon, 1987). We have already reported the crystal structure of the isopropylamine (Rochon, Melanson & Doyon, 1987) and cyclopentylamine (Dion, Beauchamp, Rochon & Melanson, 1989) compounds and we have found that the potassium salts crystallize with water of hydration which could also be clearly observed by infrared spectroscopy. The molecules of water are believed to play an important stabilizing role in these crystal structures. The O atom is very close to the K^+ ion with $\text{O}\cdots\text{K}^+$ distances of 2.756 (9) – 2.778 (8) Å. Hydrogen bonds were observed between the amino groups and the chloro ligands. In order to continue the study, especially on the role of the cation and the water molecules in these structures, we have replaced the K^+ ion by a much larger cation $[\text{Pt}(\text{NH}_3)_4]^{2+}$. We now report the crystal structure of $[\text{Pt}(\text{NH}_3)_4][\text{Pt}(\text{isopropylamine})\text{Cl}_3]_2$. These results are compared with those obtained on $\text{K}[\text{Pt}(\text{isopropylamine})\text{Cl}_3]\cdot\frac{1}{2}\text{H}_2\text{O}$ described earlier. We report also the crystal structure of the Pt^{II} complex with a more bulky ligand, $\text{K}[\text{Pt}(\text{tert-butylamine})\text{Cl}_3]\cdot\frac{1}{2}\text{H}_2\text{O}$, which again crystallizes with water of hydration.

Experimental. The compounds $\text{K}[\text{Pt}(\text{isopropylamine})\text{Cl}_3]\cdot\frac{1}{2}\text{H}_2\text{O}$ and $\text{K}[\text{Pt}(\text{tert-butylamine})\text{Cl}_3]\cdot\frac{1}{2}\text{H}_2\text{O}$ (I) were synthesized as already reported (Rochon & Fleurent, 1988). Compound (I) was recrystallized from water. The complex salt $[\text{Pt}(\text{NH}_3)_4][\text{Pt}(\text{isopropylamine})\text{Cl}_3]_2$ (II) was synthesized from the reaction of $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ with $\text{K}[\text{Pt}(\text{isopropylamine})\text{Cl}_3]\cdot\frac{1}{2}\text{H}_2\text{O}$ in 1:2 proportion in water. Compound (II) was recrystallized from water.

The experimental details of the two crystal structure determinations are shown in Table 1. Syntex $P1$; graphite-monochromatized $\text{Mo } K\alpha$ radiation; cell parameters from refined angles of 15 centered reflections (range 11–25°); $\sigma(I)$ calculated as in Melanson

Table 1. *Experimental details of the two crystal structures* $K[Pt(tert\text{-butylamine})Cl_3] \cdot \frac{1}{2}H_2O$ (I) and $Pt(NH_3)_4[Pt(isopropylamine)Cl_3]_2$ (II)

	(I)	(II)
Max. 2θ ($^\circ$)	52	60
Quadrants	$h, k, \pm l$	$h, k, \pm l$
Scan technique	$2\theta/\theta$	$2\theta/\theta$
Scan speed ($^\circ \text{ min}^{-1}$)	1.5–24.0	1.0–24.0
Standard reflections, variations (%)	622; 10.4, 2; 333	040; 400; 008
No. of independent reflections	2196	3355
Observed reflections	1743 ($I_{net} > 2.5\sigma$)	2129 ($I_{net} > 2.5\sigma$)
h, k, l	0→36, 0→7, -15→15	0→13, 0→11, -21→21
Crystal faces and dimensions (mm)	(001)–(001)(0.125) (100)–(100)(0.019) (010)–(011), (011)(0.332)	(102)–(102)(0.053) (103)–(103)(0.096) (101)–(101)(0.096) (110)–(110)(0.231) (121)–(121)(0.260)
Transmission factors	0.048–0.590	0.045–0.157
Max. shift/e.s.d.	0.04	0.03
$\Delta\rho_{max}$ ($e \text{ \AA}^{-3}$)	0.71 (close to Pt)	1.6 (close to Pt)
R	0.029	0.052
wR	0.030	0.049
Weighting scheme	$1/\sigma^2(F)$	$1/\sigma^2(F)$
Standard deviation (unit weight)	1.47	1.56

& Rochon (1975); absorption correction based on equations of crystal faces; data corrected for Lorentz and polarization effects; atomic scattering factors of Cromer & Mann (1968) for Pt, Cl, K, O, N, C and of Stewart, Davidson & Simpson (1965) for H; anomalous-dispersion terms of Pt, Cl and K from Cromer (1965).

Patterson maps showed positions of Pt; other non-H atoms located by structure factor and Fourier map calculations. A residual peak in (I) located on the twofold axis was assigned to a molecule of water. Refinement for both structures using full-matrix least-squares calculations minimizing $\sum w(F_o - F_c)^2$; isotropic secondary-extinction correction (Coppens & Hamilton, 1970); several H atoms located from a difference Fourier map, others were calculated with C—H = 0.95 and N—H = 0.85 Å, all fixed with isotropic $B = 6.0 \text{ \AA}^2$; H atoms of water molecule not located; calculations on a Cyber 860 with programs of Melanson & Rochon (1975).*

Discussion. The refined atomic parameters are listed in Table 2*. Labeled diagrams of the two structures are shown in Figs. 1 and 2. The bond distances and angles are listed in Table 3. The coordination around the Pt atoms in both crystals is square planar and the angles around the Pt atom are close to the expected values of 90 and 180°. For each crystal the weighted best coordination plane was calculated through the

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54254 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Refined coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^4$)*

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
(I)				
Pt	990.5 (1)	7119.0 (5)	6533.6 (2)	279
K	399 (1)	13408 (3)	3988 (1)	434
Cl(1)	540 (1)	3968 (4)	6550 (2)	401
Cl(2)	584 (1)	8352 (3)	5007 (2)	425
Cl(3)	1371 (1)	5990 (4)	8101 (2)	502
N	1369 (2)	9985 (11)	6539 (5)	336
C(1)	1814 (3)	10104 (14)	6027 (6)	365
C(2)	1931 (4)	12574 (14)	5952 (8)	530
C(3)	1775 (4)	9074 (18)	4911 (7)	574
C(4)	2169 (3)	8941 (18)	6731 (8)	563
O	0	9523 (14)	7500	476
(II)				
Pt(1)	2838.9 (5)	5418.6 (6)	7320.1 (3)	338
Pt(2)	0	0	0.5	342
Cl(1)	2798 (4)	2967 (4)	8082 (2)	510
Cl(2)	830 (4)	4594 (4)	6504 (2)	540
Cl(3)	3018 (4)	7822 (4)	6525 (2)	522
N(1)	4542 (10)	6120 (12)	8079 (6)	395
N(2)	486 (14)	2374 (13)	6670 (7)	591
N(3)	359 (12)	448 (13)	6329 (6)	482
C(1)	4247 (15)	6789 (18)	8993 (8)	514
C(2)	5627 (17)	7087 (20)	9499 (10)	678
C(3)	3384 (18)	8444 (20)	8896 (9)	699

Table 3. *Bond distances (Å) and angles ($^\circ$)*

(I)			
Pt—Cl(1)	2.317 (2)	N—C(1)	1.50 (1)
Pt—Cl(2)	2.314 (2)	C(1)—C(2)	1.53 (1)
Pt—Cl(3)	2.299 (2)	C(1)—C(3)	1.52 (1)
Pt—N	2.055 (7)	C(1)—C(4)	1.50 (1)
Cl(1)—Pt—Cl(2)	89.79 (7)	N—C(1)—C(2)	106.3 (7)
Cl(1)—Pt—Cl(3)	90.27 (8)	N—C(1)—C(3)	110.4 (7)
Cl(1)—Pt—N	177.8 (2)	N—C(1)—C(4)	109.4 (7)
Cl(2)—Pt—Cl(3)	177.15 (8)	C(2)—C(1)—C(3)	110.1 (7)
Cl(2)—Pt—N	89.6 (2)	C(2)—C(1)—C(4)	109.5 (7)
Cl(3)—Pt—N	90.3 (2)	C(3)—C(1)—C(4)	111.0 (7)
Pt—N—C(1)	122.1 (5)		
(II)			
Pt(1)—Cl(1)	2.301 (3)	Pt(2)—N(2)	2.044 (11)
Pt(1)—Cl(2)	2.321 (4)	Pt(2)—N(3)	2.066 (9)
Pt(1)—Cl(3)	2.300 (4)	C(1)—C(2)	1.50 (2)
Pt(1)—N(1)	2.023 (10)	C(1)—C(3)	1.57 (2)
N(1)—C(1)	1.52 (2)		
Cl(1)—Pt(1)—Cl(2)	89.9 (1)	N(2)—Pt(2)—N(3)	92.3 (4)
Cl(1)—Pt(1)—Cl(3)	176.4 (1)	N(2)—Pt(2)—N(3)'	87.8 (4)
Cl(1)—Pt(1)—N(1)	88.7 (3)	Pt(1)—N(1)—C(1)	117.9 (8)
Cl(2)—Pt(1)—Cl(3)	91.7 (1)	N(1)—C(1)—C(2)	111 (1)
Cl(2)—Pt(1)—N(1)	177.6 (3)	N(1)—C(1)—C(3)	109 (1)
Cl(3)—Pt(1)—N(1)	89.8 (3)	C(2)—C(1)—C(3)	110 (1)

five atoms. The deviations are for (I): Pt, 0.0023 (3); Cl(1), -0.006 (2); Cl(2), 0.049 (2); Cl(3), -0.061 (2); N, -0.067 (6) Å and for (II): Pt(1), -0.0021 (5); Cl(1), 0.062 (3); Cl(2), -0.006 (3); Cl(3), 0.063 (3); N(1), -0.068 (9) Å. In $[Pt(NH_3)_4][Pt(isopropylamine)Cl_3]_2$ (II), the Pt atom of the cation is located on an inversion center, as expected for space group $P2_1/c$. The structure of $K[Pt(tert\text{-butylamine})Cl_3] \cdot \frac{1}{2}H_2O$ (I) is very similar to the analogues reported for isopropylamine (Rochon, Melanson &

Doyon, 1987) and cyclopentylamine (Dion, Beauchamp, Rochon & Melanson, 1989). All these compounds crystallize with half a molecule of water per Pt atom. When the K ion is replaced by a larger ion capable of forming hydrogen bonds such as $[Pt(NH_3)_4]^{2+}$, the compound crystallizes without water of hydration. The enhanced lattice energy and the presence of hydrogen bonds between the different

Table 4. Distances (Å) and angles (°) between atoms involved in hydrogen bonds

N...Cl(1 ⁱ)	3.430 (7)	O...Cl(1 ⁱⁱ)	3.366 (7)
O...Cl(1 ⁱ)	3.366 (7)	C(1)—N...Cl(1)	128.0 (5)
		Pt—N...Cl(1)	101.2 (2)
(II)			
N(1)...Cl(1 ⁱⁱⁱ)	3.40 (1)	N(2)...Cl(2 ^v)	3.26 (1)
N(2)...Cl(1 ^{iv})	3.26 (1)	N(3)...Cl(2)	3.41 (1)
N(2)...Cl(2)	3.32 (1)	N(3)...Cl(3 ^{vi})	3.27 (1)
Pt(1)—N(1)...Cl(1)	113.5 (4)	Pt(2)—N(2)...Cl(2)	139.5 (5)
C(1)—N(1)...Cl(1)	117.2 (7)	Pt(2)—N(3)...Cl(2)	105.6 (4)
Pt(2)—N(2)...Cl(1)	104.5 (4)	Pt(2)—N(3)...Cl(3)	94.8 (4)
Pt(2)—N(2)...Cl(2)	109.0 (4)		

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

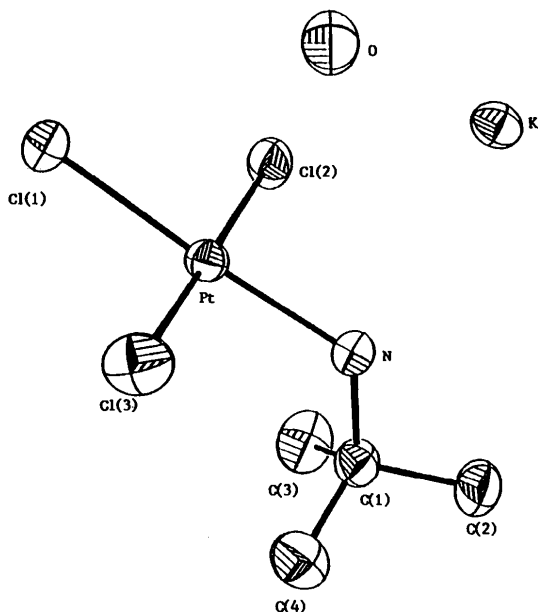


Fig. 1. Labeled diagram of (I).

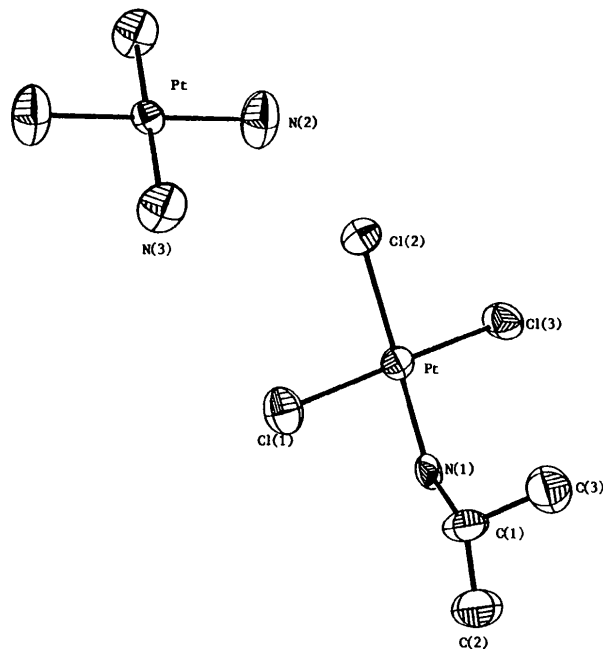


Fig. 2. Labeled diagram of the two ions $[Pt(NH_3)_4]$ and $[Pt(isopropylamine)Cl_3]_2$ (II).

ions are sufficient to stabilize the crystal. This is confirmed also in the crystal structure of 2-adamantylammonium $[Pt(ethylamine)Cl_3]$ which crystallizes without water of hydration (Rochon, Melanson, Doyon & Butler, 1990). This structure is stabilized by hydrogen bonds between the large cation and the chloro ligands.

The *cis* Pt—Cl bond distances are 2.314 (2) and 2.299 (2) Å for (I) and 2.300 (4) and 2.301 (3) Å for (II), while the bonds *trans* to the amine ligand seem slightly longer 2.317 (2) (I) and 2.321 (4) Å (II). These values agree well with the published values found in other monoaminotrichloroplatinum(II) compounds (Dion, Beauchamp, Rochon & Melanson, 1989; Rochon, Melanson & Doyon, 1987) with *cis* bonds between 2.296 (4) and 2.311 (4) Å and *trans* bonds which vary from 2.315 (4) to 2.320 (3) Å. For 2-adamantylammonium $[Pt(ethylamine)Cl_3]$ (Rochon, Melanson, Doyon & Butler, 1990) the *trans* bond is longer [2.301 (4) Å] than the *cis* bonds [2.278 (4) and 2.281 (4) Å]. In $[Pt(NH_3)_4][Pt(2,6-lutidine)Cl_3]_2$ the three Pt—Cl bonds are identical [*cis*: 2.302 (2), 2.303 (2); *trans*: 2.309 (2) Å] (Rochon & Melanson, 1980). Therefore the *trans* influence of amines might be slightly larger than that of pyridine derivatives. But other factors, like the presence of π bonds which probably exist in Pt—pyridine complexes and the presence of hydrogen bonding can influence bond lengths.

The Pt—N (amine) bond distances are 2.055 (7) (I) and 2.023 (10) Å (II), similar to the values of 2.024 (5) – 2.040 (13) Å found in the structures described above. The Pt—N bonds in $[Pt(NH_3)_4]^{2+}$ (II) are 2.044 (11) and 2.066 (9) Å, close to the values [2.052 (7) and 2.057 (5) Å] found in $[Pt(NH_3)_4]^{2+}[Pt(2,6-lutidine)Cl_3]_2$ (Rochon & Melanson, 1980) and those reported in Pt—ammine complexes (Milburn & Truter, 1966; Melanson & Rochon, 1978; Faggiani, Lippert, Lock & Rosenberg, 1978; Lippert, Lock, Rosenberg & Zvagulis, 1978). These values are slightly longer than the values found for Pt—amine or pyridine compounds. Ammine ligands usually form

more extensive hydrogen bonds than primary or secondary amines, which could account for the slight lengthening of the Pt-NH₃ bonds. The organic ligands isopropylamine and *tert*-butylamine have normal bond lengths and angles.

The packing of the molecules in the crystal K[Pt(*tert*-butylamine)Cl₃] $\cdot\frac{1}{2}$ H₂O (I) is shown in Fig. 3. The O atom of the water molecule is located on a twofold axis, exceptionally close to two K⁺ ions, with distance O \cdots K⁺ = 2.771 (6) Å, and forms hydrogen bonds with two Cl(1) ligands with distance O \cdots Cl(1) = 3.366 (7) Å (Table 4). The K⁺ ion is also surrounded by five Cl atoms at distances 3.167 (3) – 3.326 (3) Å, suggesting that packing energy around the K⁺ ion is an important stabilizing factor in the crystal. There is one N \cdots Cl(1) contact [3.430 (7) Å] within the accepted range for hydrogen bonding (Stout & Jensen, 1968), suggesting that the amino group might be involved in hydrogen bonding with one *trans* chloro ligand. The packing of the molecules consists of layers of complexed anions separated by layers of K⁺ and water molecules parallel to the *bc* plane. Fig. 3 shows clearly that the hydrophilic parts of the molecules are located around *x* = 0 and 0.5 where the K⁺ ions, the water molecules

and the chloro ligands are found, while the hydrophobic *tert*-butyl groups are orientated towards each other around *x* = 0.25 and 0.75.

The intramolecular structure of the ion [Pt(isopropylamine)Cl₃]⁻ is identical for the two ions K⁺ and [Pt(NH₃)₄]²⁺. The differences are in their intermolecular interactions. In the potassium salt, the packing energy around the K⁺ ion seems a very important stabilizing factor, with a short K⁺ \cdots O contact of 2.778 (8) Å and six chlorine atoms at distances of 3.199 (4) – 3.316 (4) Å from the K⁺ ion. There may also be one weak hydrogen bond [distance N \cdots Cl = 3.42 (1) Å] between the —NH₂ group and the *trans* Cl ligand, but this interaction does not seem an important stabilizing factor. In the [Pt(NH₃)₄]²⁺ complex salt, the hydrogen bonding involving the NH₃ ligands is extensive and is a very important factor for stabilizing the crystal. A list of the possible hydrogen bonds is shown in Table 4. There is also a weak intermolecular hydrogen bond between the amine and one of the Cl ligands. A stereoscopic view of the unit cell is shown in Fig. 4. The packing consists of layers of cations located at *x* = 0 and parallel to the *bc* plane, separated by layers of complexed anions with the hydrophilic chloro ligands oriented towards the [Pt(NH₃)₄]²⁺ layers and the hydrophobic isopropyl groups located inside at *x* = $\frac{1}{2}$.

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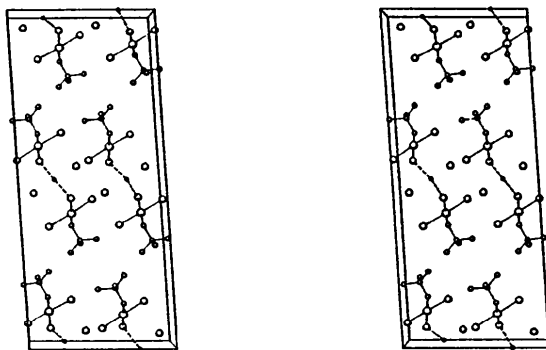


Fig. 3. Stereoscopic view of the packing in (I). Dark circles correspond to the water O atoms. The *a* axis is vertical and the *c* axis is horizontal.

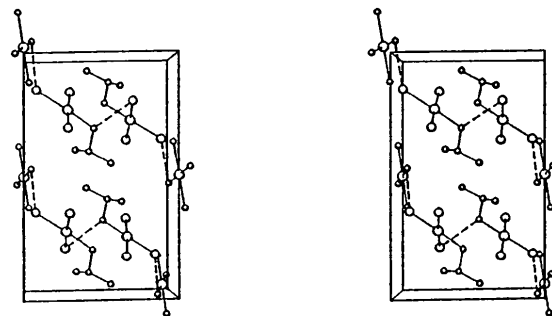


Fig. 4. Packing of the ions in (II). The *a* axis is horizontal and the *c* axis is vertical.