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trans-Tetraamminedichloroplatinum(IV) Dinitrate, $[PtCl_2(NH_3)_4](NO_3)_2$

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Abstract. $M_r = 458\cdot13$, triclinic, $P\bar{1}$, $a = 6\cdot635$ (1), $b = 7\cdot114$ (2), $c = 6\cdot548$ (1) Å, $\alpha = 114\cdot41$ (2), $\beta = 95\cdot52$ (2), $\gamma = 100\cdot33$ (2)°, $V = 271\cdot8$ (1) Å^3, $Z = 1$, $D_x = 2\cdot80$, $D_m = 2\cdot79$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 14\cdot09$ mm^{-1}, $F(000) = 214$, $T = 296$ K. Final $R = 2\cdot16\%$ for 2398 unique observed reflexions. The title compound is one of several types of compounds found in an attempt to prepare *trans*-diamminedinitratoplatinum(II) in water (pH = 1·3) and air. The cation, *trans*-$PtCl_2(NH_3)_4^{2+}$, has normal bond lengths and angles. The two crystallographically equivalent nitrate ions show slight distortions which can be explained in terms of the hydrogen-bonding environment.

Introduction. In continuing the study of the 'aqua species' formed by the loss of chloride from *cis*- or *trans*-$PtCl_2(NH_3)_2$ (Lock, 1980, and references therein), a solution of *trans*-$PtCl_2(NH_3)_2$ was treated with two equivalents of $AgNO_3$, and the AgCl removed by filtration. The resulting solution was allowed to evaporate in air for three weeks, yielding several different solids. The title compound was a minor component, found as colourless, rhombohedral, single crystals with well defined faces. The X-ray structure analysis was performed to identify the compound.

Experimental. 0·6003 g *trans*-$PtCl_2(NH_3)_2$, prepared by the method of Kauffman & Cowan (1963), was dissolved in 1 litre water and a solution of 0·6795 g $AgNO_3$ in 5 ml water was added. The solution was stirred for 24 h at room temperature in the dark. After removal of the AgCl precipitate by filtration, the solution was allowed to evaporate in air for four weeks. The pH was checked daily with a Corning model 130 pH meter, and was found to decrease slowly from 2·4 to about 1·3 pH units. The resulting yellow solution (~10 ml) was refiltered to remove a white precipitate, and then allowed to dry in air (~2 d), yielding a white crystalline powder, small colourless crystals, a yellow crystalline powder and larger colourless (or very pale yellow) crystals. It was determined by elemental and X-ray structural analyses, to be described below, that these larger crystals were *trans*-$[PtCl_2(NH_3)_4](NO_3)_2$ (calc.: Cl 15·48, N 18·34, H 2·64%; measured: Cl 15·45, N 18·41, H 2·61% for selected crystals).

It is known (Kauffman & Cowan, 1963) that the method of preparation of *trans*-$PtCl_2(NH_3)_2$ often gives small amounts of Magnus's Green Salt, $[PtCl_4]$-$[Pt(NH_3)_4]$, as an impurity. Furthermore, the intermediate compound $[Pt(NH_3)_4]Cl_2$ may not be converted to the *trans* species. Air oxidation of this $[Pt(NH_3)_4]^{2+}$ cation in the presence of chloride ion (at any stage of the experiment) would yield the cation of the title compound. It was later determined that a significant amount of chloride ion (10% of the solid residues) had come from the calomel electrode of the pH meter.

D_m measured by flotation in CH_2I_2/CCl_4 mixture. Distorted cube, 0·16 mm on side. θ–2θ scan on a Syntex $P2_1$ diffractometer, min. scan rate 3·66° min^{-1}. 15 reflexions ($32\cdot15 < 2\theta < 46\cdot42°$) for cell-parameter determination. No systematic absences. ψ scan on 20 reflections ($6\cdot47 < 2\theta < 67\cdot58°$) gave absorption curves with max. intensity correction factor of 1·927, Bond (1974) spherical absorption correction ($\mu R = 1\cdot29$, $5\cdot00 < A^* < 5\cdot98$). $2\theta_{max} = 70\cdot13°$. Range of

Table 1. *Atomic coordinates and isotropic thermal parameters* (Å^2 × 10^3)

	x	y	z	U_{eq}*/U_{iso}†
Pt	0	0	0	17·80
Cl	255·1 (1)	−60·4 (1)	215·2 (2)	28·6
N(1)	170·1 (4)	−61·2 (4)	−258·3 (5)	25
N(2)	−146·5 (4)	−317·4 (4)	−137·4 (5)	26
N(3)	680·5 (5)	552·5 (4)	284·4 (5)	26
O(1)	598·2 (6)	388·0 (5)	300·7 (8)	41
O(2)	570·2 (5)	659·2 (5)	239·2 (6)	38
O(3)	876·8 (5)	611·4 (6)	309·7 (7)	42
H(1)	88 (10)	−105 (10)	−373 (11)	37
H(2)	243 (10)	−149 (10)	−253 (10)	37
H(3)	223 (10)	55 (10)	−279 (11)	37
H(4)	−156 (10)	−351 (10)	−17 (11)	38
H(5)	−90 (10)	−417 (10)	−275 (11)	38
H(6)	−309 (10)	−371 (10)	−262 (11)	38

* $U_{eq} = \frac{1}{3}[U_{11} + U_{22} + U_{33} + 2(U_{23}\cos\alpha + U_{13}\cos\beta + U_{12}\cos\gamma)]$.

† U_{iso} for H atoms set to approximately 1·5 U_{eq} of bonded atom.

Table 2. *Intramolecular bond distances* (Å) *and angles* (°)

Pt–Cl	2·310 (1)	N(3)–O(1)	1·251 (5)
Pt–N(1)	2·064 (3)	N(3)–O(2)	1·242 (5)
Pt–N(2)	2·054 (2)	N(3)–O(3)	1·266 (4)
Cl–Pt–N(1)	89·90 (9)	O(1)–N(3)–O(2)	120·3 (3)
Cl–Pt–N(2)	88·79 (9)	O(1)–N(3)–O(3)	120·9 (4)
N(1)–Pt–N(2)	90·2 (1)	O(2)–N(3)–O(3)	118·8 (4)

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hkl: −10—10, −11—11, 0—10. Standards (e.s.d.): 3 0 1 (1·27%), 1 3 0 (1·52%), 0 3 1 (1·80%) measured after every 47 reflexions, overall e.s.d. = 1·53%, no systematic variation observed. 4795 reflexions measured, 2398 unique, $R_{\rm int} = 2\cdot31\%$, 2398 observed ($I > 0$). Pt placed at origin because all reflexions observed, remaining atoms (including H's) found from electron density difference synthesis. $\sum w(|F_o| - |F_c|)^2$ minimized in full-matrix least-squares refinement; parameters refined: positional (except Pt), anisotropic temperature factors (except H's), overall scale, secondary extinction. $R = 2\cdot16$, $wR = 2\cdot76\%$; $S = 0\cdot575$, $w = (\sigma_F^2 + 0\cdot00109F^2)^{-1}$. $\Delta/\sigma_{\rm max} = 0\cdot051$, $\Delta/\sigma_{\rm av} = 0\cdot002$. $\Delta\rho = -1\cdot0$–$1\cdot6$ e Å^{-3} near Pt. $g = 0\cdot7 \times 10^{-4}$. Atomic scattering factors from Cromer & Waber (1974), anomalous-dispersion corrections for Pt and Cl from Cromer (1974). Programs used: *TAPER* (Calabrese & Burnett, 1980) for ψ-scan absorption correction, XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) for initial data reduction and Bond absorption correction, *SHELX*76 (Sheldrick, 1976), *ORTEP*II (Johnson, 1976) for diagrams.

Discussion. Final atomic coordinates and isotropic thermal parameters are in Table 1, bond distances and angles in Table 2.*

The molecular ions and their packing are shown in Fig. 1. The cation, which is on the inversion centre, has bond lengths [Pt—Cl 2·310 (1), Pt—N(1) 2·064 (3), Pt—N(2) 2·054 (2) Å] which are within the ranges previously found in Pt$^{\rm IV}$ complexes [Pt—Cl 2·26–2·309 (6), Pt—N 1·97 (4)–2·068 (17) Å] (Bjorling, 1941; Craven & Hall, 1961; Liu & Ibers, 1970; Faggiani, Howard-Lock, Lock, Lippert & Rosenberg, 1982), although they lie at the longer end of the range. The Pt—NH$_3$ distances in the title compound are significantly longer than those found in *ab*-diammine-*df*-dichloro-*ce*-dihydroxoplatinum(IV) [2·00 (1) Å, Faggiani *et al.*, 1982], but not significantly longer than the 'normal' Pt—NH$_3$ distance of 2·03 Å (Shustorovich, Porai-Koshits & Buslaev, 1975).

The nitrate ion was found to have the expected (Britten, Lock & Pratt, 1982) bond lengths and angles, although the N(3)—O(3) bond is $3\cdot7\sigma$ longer than the N(3)—O(2) bond.

The packing of the ions is completely determined by the ammine-nitrate hydrogen bonding. Each ammine is hydrogen-bonded to the three non-equivalent nitrate O atoms in bonds involving all H atoms. The hydrogen bonds are indicated in Fig. 2. The Cl atom is not involved in any significant hydrogen bonding.

In order to check the possibility of ammine/aqua disorder in the cation, a model with 0·5 N-atom and 0·5 O-atom occupancy in each ammine position, and 0·6667 H-atom occupancy was examined. Initially there was a slight increase in R (= 2·25%), but full-parameter refinement (including occupancy refinement) gave an N:O ratio of 9:1, indicating no disorder.

The bond-valence model of Brown (1981) can be used to explain the difference in bond lengths seen in the nitrate ion [$r_{2,\rm obs} = 1\cdot242$ (5) Å for N(3)—O(2) and $r_{3,\rm obs} = 1\cdot266$ (4) Å for N(3)—O(3)]. Fig. 2 shows that O(3) is hydrogen-bonded to three ammines *via* H(5), H(1) and H(4), while O(2) interacts with H(3) and H(6). Using Brown's O—H bond valence (s) *versus* distance (r) curve, and the assumption that the N—H bonds are all 1·1 Å, the calculated Lewis acid strength of the hydrogen-bonding environment of O(3) is 0·39 valence units; for O(2), $s = 0\cdot22$ v.u. This leaves O(3) with a base strength of 1·61 v.u. and O(2) with 1·78 v.u. for bonding to the central N.

Empirically, $r = 1\cdot43s^{-0\cdot25}$ Å for an N—O bond (Brown, 1981). Thus $r_{3,\rm calc} = 1\cdot269$ Å and $r_{2,\rm calc} = 1\cdot240$ Å, in excellent agreement with the measured values. Table 3 shows hydrogen-bonding distances, selected angles, adjusted distances, and individual bond valences.

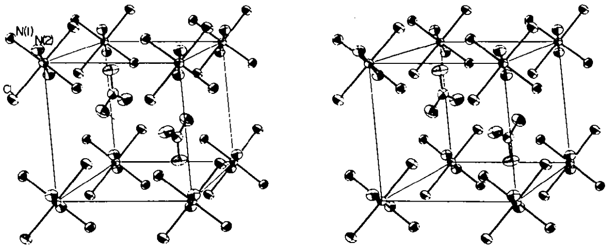

Fig. 1. Stereoview of the packing in the unit cell. **c** and **c** × **b*** are parallel to the bottom and sides of the page and the view is down **b***.

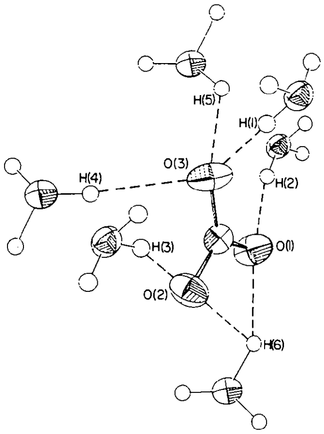

Fig. 2. The hydrogen bonding about the nitrate group shown in the upper left corner of Fig. 1.

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* Lists of anisotropic thermal parameters, bond distances and angles involving H atoms, and observed and calculated structure-factor moduli have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38740 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Hydrogen-bonding distances, angles, and bond valences*

	H···O (Å)	N–H (Å)	N–H···O (°)	N···O (Å)	Adjusted H···O* (Å)	s† (v.u.)
N(1^{i})–H(2^{i})···O(1)	2·09 (7)	0·87 (8)	170 (6)	2·945 (5)	1·86	0·19
N(2^{ii})–H(6^{ii})···O(1)	1·88 (7)	1·19 (6)	149 (5)	2·963 (5)	1·96	0·16
N(1^{iii})–H(3^{iii})···O(2)	2·14 (7)	0·91 (8)	161 (5)	3·010 (5)	1·96	0·16
N(2^{ii})–H(6^{ii})···O(2)	2·50 (7)	1·19 (6)	114 (5)	3·179 (4)	2·54	0·07
N(2^{i})–H(5^{i})···O(3)	2·12 (7)	1·04 (6)	134 (6)	2·939 (5)	2·08	0·13
N(1^{iv})–H(1^{iv})···O(3)	2·31 (5)	0·79 (7)	150 (7)	3·014 (4)	2·05	0·13
N(2^{v})–H(4^{v})···O(3)	2·26 (8)	0·92 (8)	170 (3)	3·165 (6)	2·08	0·13

Symmetry operators to transform from coordinates in Table 1: (i) $1 - x, -y, -z$; (ii) $-x, -y, -z$; (iii) $1 - x, 1 - y, -z$; (iv) $1 + x, 1 + y, 1 + z$; (v) $1 + x, 1 + y, z$.

* O···H distance recalculated with consideration of the angle at H to adjust for a 1·1 Å N–H bond (Brown, 1982).

† For the O···N hydrogen bond, 0·02 v.u. are added to the *s* value from the O–H curve (Brown, 1982).

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The Structure (Neutron) of Phase II Caesium Nitrate at 298 K, $CsNO_3$

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Abstract. $M_r = 194{\cdot}92$, trigonal, $P3_1$ (or its enantiomorph $P3_2$), $a = 10{\cdot}95\ (2)$, $c = 7{\cdot}80\ (2)$ Å, $V = 809{\cdot}94$ Å^3, $Z = 9$, and $D_x = 3{\cdot}597$ Mg m^{-3}, $\lambda = 1{\cdot}249$ Å, $\mu = 0{\cdot}0576$ mm^{-1}. The single-crystal neutron diffraction intensity data were moderately affected by extinction. Inclusion of an isotropic extinction correction was found adequate to allow for this and when combined with anisotropic temperature factors in the least-squares refinement of 859 (non-equivalent-averaged) reflections gave a converged conventional *R* factor of 0·066. The structure has the Cs atoms forming a pseudocubic sublattice with nine pseudocubes per unit cell. The NO_3-groups' configurations within the unit cell are derived from an asymmetric unit of three NO_3 groups. Average N–O distances and O–N–O angles are 1·24 (4) Å and 120 (4)° respectively. Each NO_3 group is essentially parallel to one of the faces of its surrounding Cs-atom pseudocube and one of the N–O bonds is almost parallel to a pseudocube cell edge. The relationship between the crystal structure and previously reported pyroelectricity is discussed. The thermal ellipsoids of the O atoms were found to be markedly anisotropic and are illustrated.

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