The Structure of Platinic Acid

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Abstract. $H_2Pt(OH)_6$, monoclinic, $C2/c$, $a = 8.459$ (5), $b = 7.184$ (5), $c = 7.429$ (4) Å, $\beta = 93.71$ (2)° at 297 K, $Z = 4$, $D_m = 4.17$, $D_c = 4.408$ Mg m^{-3}. The structure is a slight distortion of the K_2PtCl_6 type, with nearly regular $Pt(OH)_6$ octahedra forming an approximately face-centred cubic array. Short $O \cdots O$ distances between octahedra suggest strong hydrogen bonding.

Introduction. This study was undertaken to establish the structural formula of platinic acid, which has been written variously as $PtO_2.4H_2O$, $Pt(OH)_4.2H_2O$ and, most commonly, $H_2Pt(OH)_6$ (Mellor, 1937; Hartley, 1973). While the crystal structures of its Li, Na and K salts have been determined (Trömel & Lupprich, 1975; Björling, 1941), previous X-ray data on the parent acid appear to be limited to an incomplete description of its unindexed powder pattern (Keenan, Giesemann & Smith, 1954).

The compound was prepared as a pale-yellow powder from Na_2PtCl_6 by Bellucci's method (Sidgwick, 1950), except that a more crystalline product was obtained by performing the precipitation with acetic acid from a hot solution. The X-ray powder pattern was indexed, and lattice parameters were determined by least squares from Guinier photographs taken with Cu $K\alpha_1$ radiation, with ThO_2 ($a = 5.5972$ Å) as an internal standard. The large e.s.d.'s in the parameters reflect differences between samples; for a single sample the accuracy is about five times better. The source of the variation is not known, but impurities, including water, or disorder are possibilities. When part of the sample used for the structure determination was decomposed at 1073 K to yield Pt metal, the weight loss was within 1% of the theoretical value, which suggests reasonable purity.

All reflexions with $h + k \neq 2n$, and $h0l$ reflexions with $l \neq 2n$ were absent, so that the space group is Cc or $C2/c$. However, all reflexions with $k + l \neq 2n$ were very weak; indeed only 7 of the 72 accessible reflexions of this class were actually observed, which suggests an F-centred array of Pt atoms and implies that the space group is $C2/c$. Intensities were obtained from Guinier photographs with a recording micro-

densitometer and measurement of the peak areas with a planimeter. The region of reciprocal space scanned, $2\theta < 86°$, contains 95 unique reflexions with $k + l = 2n$, but overlap reduces the number of distinct peaks to 70, of which one was not observed. The much weaker reflexions with $k + l \neq 2n$ were not included in the refinement.

During the refinement it became clear that there was a dependence of intensity on Bragg angle which was not well accounted for by the Guinier Lorentz–polarization factor with absorption corrections (Sas & de Wolff, 1966) unless unrealistic values for the specimen absorption and temperature factor were assumed. Diffractometer intensities were therefore collected with Ni-filtered Cu $K\alpha$ radiation from a pure sample, and also from samples diluted with flour and with PVA emulsion: agreement between the three sets was good, indicating the absence of preferred orientation. The final data set was a composite of the diffractometer and Guinier data, with the Guinier data adjusted for the difference in Lp factors for the two techniques.

A set of relative scattering amplitudes was derived from the Guinier intensity data, assuming all the reflexions in an unresolved group to have the same value of F, and used to construct a Patterson map which indicated that the O atoms formed an almost regular octahedron about Pt. O atom coordinates estimated from the Patterson map, together with scale and an overall isotropic temperature factor, were refined with *POWDER* (Rossell & Scott, 1975) and the refinement converged rapidly. Scattering factors for

Table 1. *Fractional atomic coordinates*

E.s.d.'s of the last digit are in parentheses. Overall isotropic temperature factor $B = 1.65$ (11) Å^2.

	x	y	z
Pt	0.25	0.25	0.0
O(1)	0.469 (5)	0.352 (5)	0.088 (5)
O(2)	0.151 (4)	0.514 (6)	−0.005 (6)
O(3)	0.185 (3)	0.218 (8)	0.267 (4)

neutral atoms with corrections for anomalous dispersion (*International Tables for X-ray Crystallography*, 1974) were used. $R_w = \{[\sum w(I_o - I_c)^2/\sum wI_o^2]^{-1/2} = 0.037$ with the composite data set. The weights were $w = (I_o + I_{min})^{-1}$, where I_{min} is approximately equal to the weakest measured reflexion: the factor $\frac{1}{2}$ provides numerical comparability with residuals based on F. The parameters obtained are listed in Table 1;* no structural significance should be given to the temperature factor.

At this stage, as a check on the correctness of the structure, the intensities of the accessible reflexions with $k + l \neq 2n$ were calculated. Of the 72 possible reflexions only eight had intensities exceeding 1σ; seven of these eight reflexions were in fact observed and semi-quantitative estimates of their intensities agreed quite well with the calculated values. It was felt, however, that to include the whole of this class of reflexions in the refinement, most with arbitrary small intensities, would artificially increase the number of observations.

Discussion. The structure of platinic acid can be described as a face-centred cubic array of $Pt(OH)_6$ octahedra, distorted by strong hydrogen bonds between adjacent octahedra. Bond lengths and angles within the octahedron are given in Table 2. The octahedron is regular within the limits of experimental error, and the mean Pt—O distance of 2·08 Å is in fair agreement with the values of 2·11, 2·05 and 1·96 Å found for the Li, Na and K salts respectively (Trömel & Lupprich, 1975; Björling, 1941). Fig. 1 illustrates the packing of the octahedra, and indicates an asymmetric set of five short O···O distances between adjacent octahedra: all

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* A list of diffractometer powder intensity data has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34724 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths (Å) and angles (°) within the octahedron*

E.s.d.'s of the last digits are in parentheses.

Pt—O(1)	2·06 (4)	O(1)—O(2)	2·97 (6)
Pt—O(2)	2·07 (4)	O(1)—O(2^i)	2·88 (6)
Pt—O(3)	2·11 (3)	O(2)—O(3)	2·94 (6)
O(1)—Pt—O(2)	91·9 (16)	O(2)—O(3^i)	2·97 (6)
O(2)—Pt—O(3)	89·4 (16)	O(3)—O(1)	2·98 (6)
O(3)—Pt—O(1)	91·4 (16)	O(3)—O(1^i)	2·91 (6)

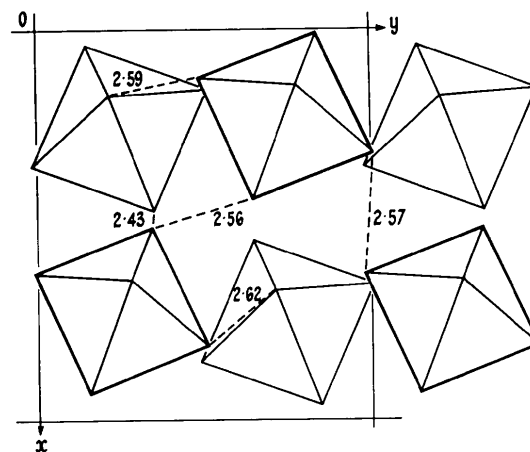Symmetry transformation

(i) $\frac{1}{2} - x, \frac{1}{2} - y, -z$

Fig. 1. Packing of $Pt(OH)_6$ octahedra projected on to the *ab* plane. Full lines denote octahedra centred at $z = \frac{1}{4}$. Broken lines indicate an asymmetric set of short O···O distances; the lengths (Å) have e.s.d.'s of about 0·06 Å.

the remaining distances between octahedra are >2·98 Å. These short distances suggest that the $Pt(OH)_6$ groups are linked by a framework of fairly strong hydrogen bonds. The distance of 2·43 Å is exceptionally short for a hydrogen bond in an inorganic crystal, though shorter distances have been reported for organic crystals (see *e.g.* Gonschorek & Küppers, 1975): this could repay further study if single crystals become available.

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