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Crystal Structure of Tetramethylammonium Hexachloroplatinate(IV)

ROLF W. BERG and INGER SØTOFTE

Chemistry Department A and B, The Technical University of Denmark, DK-2800 Lyngby, Denmark

The room-temperature structure of $\{(CH_3)_4N\}_2[PtCl_6]$ has been reinvestigated using single crystal X-ray diffraction methods. Within reasonable approximation, the structure could be described in the cubic system, space group $Fm3m$, $a = 12.720 \pm 0.004$ Å. Weighted full matrix least squares anisotropic minimization for 113 independent averaged reflections resulted in a final $R_w = 0.026$ and a flat difference Fourier map. All atoms except hydrogen were found. Some indications of a yet unknown noncubic super-structure in the crystal at room temperature are presented and discussed.

An increasing number of crystalline systems exhibiting structural phase transitions have been studied over the past few years. Thus, it has been shown[1-3] that compounds of the type $\{(CH_3)_4N\}_2[MCl_6]$ with M = Sn, U, Zr, Te, exhibit phase transitions at lower temperatures. The origin of these transitions is not clear and the structural behaviour during the transformations is not understood. Recently, the phase transformation was detected at *ca.* 175 K in $\{(CH_3)_4N\}_2PtCl_6$ as well,[4] using variable low temperature far infrared and Raman spectroscopy. Although the room temperature structure of this compound has been studied[5] by single crystal methods in 1926, we found it of interest to undertake an accurate determination. A number of authors[6-10] have concluded from optical examination of crystals or from powder X-ray diffraction experiments that the compound $\{(CH_3)_4N\}_2PtCl_6$ crystallizes with cubic symmetry, whereas Adams and Morris[11] reported the presence of weak forbidden lines of high *hkl* indices in their powder X-ray photographs. Therefore, as a first step towards an understanding of what happens during the low temperature phase transition, the present work was undertaken, so that at least an accurate determination of the room temperature structure was available.

EXPERIMENTAL

Orange red tetramethylammonium hexachloroplatinate(IV) was prepared by mixing equivalent amounts of $(CH_3)_4NCl$ and H_2PtCl_6 dissolved in dilute hydrochloric acid. A crystal of convenient size *ca.* $0.25 \times 0.12 \times 0.12$ mm, showing octahedral faces was obtained by slowly cooling a solution saturated at *ca.* 80 °C. With this crystal mounted on a CAD4F ENRAF-NONIUS automatic four circle diffractometer and using graphite monochromated Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å), two data sets having reflections within a maximum value of $\sin\theta/\lambda = 0.571$ were measured ($0 \leq h,k,l \leq 14$). Three standard reflections, {006}, were repeatedly recorded to check that long term stability remained. 473 and 624 reflections resulted with intensity I larger than $2\sigma(I)$, where $\sigma(I)$ was determined from the counting statistics. The intensities were Lp corrected, but no correction was made for absorption or anomalous dispersion. The data set with 624 reflections is described below. The lattice parameters obtained from the first data set were $a = 12.725(2)$ Å, $b = 12.716(2)$ Å, $c = 12.719(3)$ Å, $\alpha = 89.99(2)°$, $\beta = 90.02(1)°$, $\gamma = 90.01(1)°$. Assuming cubic symmetry, the reflections could be averaged into a set consisting of 113 independent reflections. The internal agreement factor over the set of reflections $R_{int}(F_{obs}^2) = \sum|F_{obs}^2 - \langle F_{obs}^2\rangle|/\sum F_{obs}^2$ was then 0.034. The subsequent crystallographic calculations were done using the X-ray system,[12] and ORTEP.[13] Atomic scattering factors for Pt, Cl, N and C were those of Cromer and Mann.[14] Hydrogen atoms were included near the end of refinement but were finally neglected. A list of the observed and calculated structure factors is obtainable from the authors.

Table 1. Positional and thermal parameters (U_{ij} in units of 10^{-4} Å^2) with estimated standard deviations for independent ones. The temperature factor expression is exp $[-2\pi^2\sum_{ij}h_ih_ja_i^*a_j^*U_{ij}]$.

Atom	X/a	Y/b	Z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	0.0	0.0	0.0	447(5)	447	447	0	0	0
Cl	0.1803(3)	0.0	0.0	436(20)	1585(28)	1585	0	0	0
N	0.25	0.25	0.25	493(38)	493	493	0	0	0
C	0.3174(8)	0.3174	0.3174	1927(95)	1927	1927	−667(71)	−667	−667

CRYSTAL DATA

$\{(CH_3)_4N\}_2PtCl_6$. M = 556.1 g/mol. Cubic-(pseudo): $a = 12.720(4)$ Å at 21 °C. $V = 2058.03$ Å^3. $Z = 4$. $D_c = 1.79$. $D_o = 1.81$ g/cm^3 at 16 °C[7] and 1.802(1) g/cm^3.[9] $F(000) = 1064$; $\mu(MoK\alpha) = 79.3$ cm^{-1}. Systematic absences according to space group $Fm3m$ (No. 225, O_h^5): hkl when $h+k$, $k+l$ and $l+h$ are odd. However, weak super lattice reflexes were observed, corresponding to a doubling of the lattice constant in at least two directions.

RESULTS AND DISCUSSION

The cubic lattice parameter obtained above is in reasonable accord with previous results (10.65 Å,[5] 10.66 Å,[11] and 10.72 Å for a crystal with 5 % Ir substitution[10]). Therefore, the space group $O_h^5 = Fm3m$ suggested in the literature[5] was tested against the intensity data, using full matrix least squares minimization and anisotropic temperature factors. Indeed a reasonable structure resulted, see Table 1. The function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights used were estimated by Nielsen's method:[15] $w = xy$, with $x = 1$ for $\sin\theta/\lambda \geq a$; $x = ([\sin\theta/\lambda]/a)^2$ for $\sin\theta/\lambda < a = 0.3294$ and $y = b/F_o$ or F_o/b for $F_o \geq b$ or $F_o < b$, respectively, with $b = 84.10$. For all unobserved reflections $w = 0$. In a normal probability plot, a correlation coefficient $\rho = 0.994$ was obtained,[15] indicating an almost normal distribution of the weighted residuals. The final R-values were: $R = \sum||F_o| - |F_c||/\sum F_o = 0.027$ and $R_w = (\sum w(F_o - F_c)^2/\sum wF_o^2)^{\frac{1}{2}} = 0.026$, and no pronounced peak was seen in the difference Fourier map.

In the final structure these atoms were localized: 4 Pt occupy Wyckoff position a(0,0,0); 24 Cl $e(x,0,0)$; 8 N c(1/4,1/4,1/4) and 32 C $f(x,x,x)$. The chlorine parameter ≈ 0.185 which can be calculated from Huggins' results[5] compares very well with our value of 0.1803 ± 0.0003. The carbon parameter has not been determined previously.

As discussed in detail by Ohe,[2] there are for carbon two possible values of x which would satisfy *both* the C – N bond length *and* the symmetry of the space group: (*i*) all methyl groups point towards platinum ($x \approx 0.18$) and (*ii*) all methyl groups point towards the empty $b(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ position of the cell ($x \approx 0.32$). The value determined here was 0.3174(8) which shows the second case as the one realised. It is of interest to note that this configuration was also found for $\{(CH_3)_4N\}_2SnCl_6$,[16] $\{(CH_3)_4N\}_2CeCl_6$,[17] and $\{(CH_3)_4N\}_2PtF_6$[18] and is probably the most favourable one in all crystals of this kind. Furthermore, the bond lengths and angles obtained were indeed very close to commonly accepted values (Table 2). A stereoscopic view of the structure is shown in Fig. 1.

The anisotropic parameters (Table 1) show quite large values for U_{22}^{Cl} and U_{33}^{Cl}, and for carbon. Although absorption and anomalous dispersion may partly be responsible for this, the obtained values hint to either quite intensive oscillations of the rigid ions or an unresolved superposition of different orientations of octahedra and tetrahedra, or (less probably) to distortions of these highly symmetric ions.

Table 2. Interatomic distances (Å) of the structure, compared with values of the literature.

	This work		Other works
Pt – Cl	2.293(4)		2.323(1)[a]
Pt – C	5.205(8)		
Pt – N	5.508(1)		
Cl – Cl	3.243(4),	5.751(4)	3.285(2)[a]
Cl – C	3.719(5),	4.658(1)	3.75(4)[b], 3.78[d]
Cl – N	4.584(1)		>4.0[b]
C – N	1.484(6),	5.635(10)	1.48(1)[c]
C – C	2.423(10),	4.647(15)	2.44(3)[b]

[a] In K_2PtCl_6.[19] [b] In $(CH_3)_3NHCl$, average value.[20] [c] In $\{(CH_3)_4N\}_2B_6H_6$.[21] [d] In $(CH_3)_4NCl$.[22]

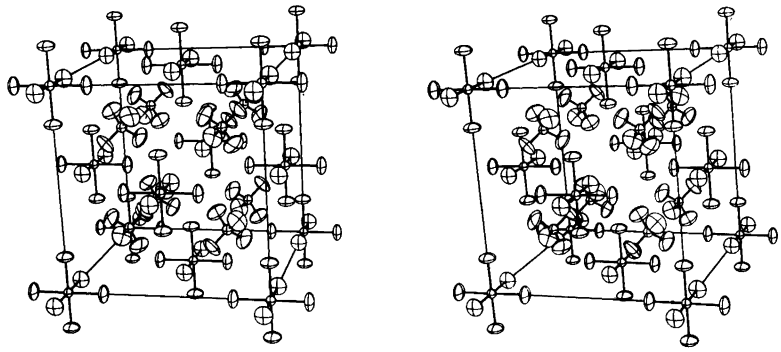

Fig. 1: Stereoscopic view of the structure of tetramethylammonium hexachloroplatinate(IV), in the cubic approximation. Thermal ellipsoids of 40 % charge density are shown. The hydrogen atoms are not shown.

Disordered models were tried with isotropic thermal parameters, but were not significantly better than the anisotropic simple model of Table 1.

EVIDENCE FOR A NONCUBIC SUPER-LATTICE STRUCTURE

As noted, Adams and Morris[11] found noncubic features in their X-ray powder photographs. We found the following noncubic features, each of which taken alone is not convincing; but taken as a whole they indicate that the crystal structure as described above is not strictly adequate:

(*i*) With the *Fm3m* extinction conditions relaxed, we remeasured the complete octant $0 \leq h,k,l \leq 14$ in order to see if the structure could be solved in a less symmetric cell. In this way we got the second data set, with 151 extra integer *hkl* reflections not being *Fm3m* permitted but satisfying the $I > 2\sigma(I)$ criterion. Of these, 58, 29 and 12 reflections were above the 3, 4, or 5 $\sigma(I)$ level, respectively. Very prominent ($I \gtrapprox 5\sigma(I)$) were all permutations within the sets {550}, {552}, {330} and {863}; observed were also all of {772} and {634}. On the other hand, none of these reflections have $|F_o|$ greater than 6 % of the greatest observed values of {004} and {111}. No obvious symmetry governed the intensities of the reflections. *E.g.* (869) was at the 3.6 $\sigma(I)$ level, while (896) *etc.* all were very weak. The length of the axes obtained from the reflections in the second data set were $a = 12.719(2)$ Å, $b = 12.713(2)$ Å, $c = 12.714(2)$ Å, which also tend to indicate a noncubic cell (*cf.* the values of the first data set, which gave the same trend).

(*ii*) Using photographic single crystal X-ray techniques (Cu$K\alpha$ radiation, oscillation and Weissenberg mode) we were able to record additional reflections from this and another crystal in positions corresponding to doubling of two or three of the 12.72 Å axes of the basic unit cell. We did not determine accurate intensities of these "superlattice" reflections, because the crystal seemed to be twinned with respect to the superstructure and because of the problems caused by the short wavelength (Mo$K\alpha$) available at the diffractometer.

(*iii*) A finely powdered sample was tested by neutron scattering. Preliminary results could not be interpreted using the 12.72 Å cubic *Fm3m* cell. Either a lower symmetry or another set of axes was necessary to explain the full structure, including hydrogen atoms.

(*iv*) The optical isotropy was examined in a petrographic microscope and a weak but nonvanishing double refraction was found in all crystallites examined.

(*v*) The angles between the external faces of a several millimeter large single crystal was measured using a two-circle precision reflection goniometer. Deviations were found from the theoretical angles of a cuboctahedron but they were just within the estimated standard deviation of the measurement (0.1°), so that no safe evidence against the cubic description was obtained in this way.

Taken together all these experiments, and especially (*i*) to (*iii*), point to a noncubic symmetry. We have tried to use the reflections from the second diffractometer data set for an estimation of the structure. However, the attempt was not particularly successful. It was possible to get convergence

($R = 0.13$) in a $P4/m$ cell of the same 12.72 Å size but with 42 parameters. In a similar cell with triclinic symmetry and 133 parameters, an R-value of 0.093 could be obtained. Taking into account the increased number of parameters, we do not consider such models as more appropriate.[23] On the other hand, it was gratifying that the refinements of these data produced values for the parameters, very similar to those derived from the first data set.

This situation is not unique. As an example we can compare our results with those obtained on $Cs_2LiCr(CN)_6$, having a quite analogous structure with Li in the center of the cell.[24] Although the structure was shown[24] by other means *not* to be cubic, it was possible to refine its X-ray structure in space group $Fm3m$ down to $R = 0.025$. This was taken as evidence for only a slight distortion from the highly symmetric structure. Other similar examples found in the fluorides of type A_2MF_6 have been discussed in Ref. 25 and papers cited there.

Therefore, also for our compound it must be concluded that the strong scattering power of Pt, combined with other features such as absorption and a probable multiple twinned superstructure make a complete structure determination difficult, especially when the distortion is small. The cell found here by X-ray diffraction is probably the basic fragment of a noncubic cell with larger dimensions, which hopefully can be more accurately determined in the future with the help of neutron diffraction on the perdeuterated compound.

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