

## The Structure of Deuterated Tetramethylammonium Hexachloroplatinate Investigated by Neutron Powder Diffraction

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### Abstract

Neutron powder diffraction patterns of  $[\text{N}(\text{CD}_3)_4]_2\text{[PtCl}_6\text{]}$  have been measured at room temperature and 90 K and the data have been analysed using the constrained-refinement program *EDINP*. The room-temperature pattern is consistent with an *Fd3c* structure with a unit-cell parameter doubled with respect to that found in earlier single-crystal studies in which the space group was assumed to be *Fm3m*. An improvement in the quality of the fit was obtained when one of the two tetramethylammonium ions in the asymmetric unit was allowed to be disordered over two orientations. The significance of this result is discussed and is thought to be high. The low-temperature structure has not yet been fully determined but the relative weakness of the superlattice reflections indicates that the distortion from *Fm3m* symmetry may be less than at room temperature.

### Introduction

The crystal structure of tetramethylammonium hexachloroplatinate,  $[\text{N}(\text{CH}_3)_4]_2\text{[PtCl}_6\text{]}$ , at room temperature has been studied by Huggins (1926) using single-crystal Laue methods, by others using X-ray powder methods (Vorländer, 1931; Jørgensen, 1963; Adams & Morris, 1967) and, more recently, by Berg & Søtofte (1978) using modern single-crystal X-ray diffractometry. These studies indicate that, to a high degree of accuracy, the compound crystallizes in the  $\text{K}_2\text{[PtCl}_6\text{]}$ -type face-centred cubic antiferroite structure with space group *Fm3m* ( $O_h^h$ ), with  $Z = 4$  and  $a = 12.72 \text{ \AA}$ . However, the presence of several weak

reflections not allowed by the *Fm3m* symmetry (Adams & Morris, 1967; Berg & Søtofte, 1978) indicates that there is a slight deviation from strict antiferroite symmetry. A number of these 'forbidden' reflections were recorded by Berg & Søtofte (1978) and an attempt was made to determine the distorted structure, using these together with the measured *Fm3m* reflections. No significant improvement in the fit was obtained using a unit cell of the same size but with lower symmetry. The extra reflexions were, however, found to be consistent with a unit cell of *Fd3c* symmetry, with a lattice parameter twice that of the *Fm3m* cell (Berg & Nielsen, 1979), similar to that of  $[\text{N}(\text{CH}_3)_4]_2\text{[TeBr}_6\text{]}$ . However, because of a multiple twinned superstructure and the strong X-ray scattering power of Pt, they did not succeed in making a complete structure determination.

In an attempt to overcome these problems we have studied the compound by neutron powder diffraction, with analysis by profile refinement. Preliminary scans of the hydrogenous compound showed that the intensity is dominated by incoherent scattering from the large amount of H in the sample. This contributes a very high background to the diffraction making analysis of weak features such as superlattice reflections virtually impossible. For this reason we have used the deuterated form, which was assumed to be isostructural with the hydrogenous compound. The structure of the deuterated material is, in itself, of interest since it has been the subject of spectroscopic studies aimed at increasing the understanding of the phase transitions in the series of tetramethylammonium hexachlorometallates,  $[\text{N}(\text{CH}_3)_4]_2\text{[MCl}_6\text{]}$  ( $M = \text{Pt, Te, Sn}$ ) (Berg, 1978).

### Experimental

A fine powder of 99% deuterated material was contained in a thin-walled vanadium cylinder of diameter 7 mm and height 50 mm. For the low-temperature measurements the sample was mounted in a Thorflow cryostat and the temperature controlled at 90 K to within 1 K. The neutron powder diffraction patterns were measured on the TAS4 triple-axis spectrometer at Risø operating in the elastic mode with pyrolytic-graphite monochromator, analyser and higher-order filter. The neutron wavelength used was 2.44 Å. The diffraction patterns were recorded from  $2\theta = 16$  to  $100^\circ$  in steps of  $0.1^\circ$ , counting for about 8 min and 4 min per scan point for the room-temperature and low-temperature measurements respectively.

### Constraints

Because of the limited amount of structural information available from neutron powder diffraction data it is often necessary to introduce constraints to reduce the number of free parameters in the least-squares refinement of a complex structure. In the present example the data are insufficient to support a significant variation from ideal molecular shape. We therefore assume throughout the refinements that the  $\text{PtCl}_6$  ions and  $\text{NC}_4$  skeletons retain full octahedral and tetrahedral symmetry respectively, and that the methyl groups retain threefold symmetry with the angle between N–C and C–D bonds equal to the tetrahedral value of  $109.47^\circ$ .

With these assumptions the constrained parameter set consists of the three bond lengths, Pt–Cl, N–C and C–D, and the four orientation angles consistent with the  $Fd3c$  space-group symmetry.

In the  $Fm3m$  structure all the  $\text{PtCl}_6$  ions are related by translation and the  $\text{N}(\text{CD}_3)_4$  (TMA) ions are all identical, with N atoms occupying sites of  $\bar{4}3m$  symmetry. In  $Fd3c$  there is a doubling of the repeat distance relative to the  $Fm3m$  structure. The only rotation of  $\text{PtCl}_6$  allowed by symmetry is about the [111] direction. The TMA ions are divided into two sets: one quarter with N atoms on sites of  $23$  symmetry (TMA1) and three quarters with N atoms at a  $\bar{4}$  point (TMA2). The rotational coordinates consistent with  $Fd3c$  symmetry are:

- $\theta$  (111) rotation of  $\text{PtCl}_6$ ;
- $\psi$  (111) rotation of methyl in TMA1;
- $\varphi$  rotation of methyl in TMA2 about the N–C bond;
- $\chi$  (100) rotation of TMA2 about  $\bar{4}$ .

Expressions for the atomic coordinates in terms of these parameters and the bond lengths are given in Table 1.

For certain values of the angles  $\theta$ ,  $\psi$ ,  $\varphi$  and  $\chi$  the structure becomes equivalent to  $Fm3m$ . The values of the angles were defined so that  $Fm3m$  structures were obtained for the values:

	$Fm3m$ (i)	$Fm3m$ (ii)
$\theta$	0	0
$\psi$	0	$\pi/3$
$\varphi$	0	$\pi/3$
$\chi$	$\pi/2$	$\pi/2$

Table 1. Expressions for the atomic coordinates (in ångströms) based on the system of constraints outlined in the text

		Number of positions, Wyckoff notation and point symmetry	x	y	z
	Pt	32(c) $\bar{3}$	0	0	0
	Cl	192(h) 1	$\rho(1 + 2 \cos \theta)$	$\rho(1 - \cos \theta + \sqrt{3} \sin \theta)$	$\rho(1 - \cos \theta - \sqrt{3} \sin \theta)$
TMA1	N(1)	16(a) 23	$\frac{1}{3}a$	$\frac{1}{3}a$	$\frac{1}{3}a$
	C(1)	64(e) 3	$\frac{1}{3}a + \alpha$	$\frac{1}{3}a + \alpha$	$\frac{1}{3}a + \alpha$
	D(1)	192(h) 1	$\frac{1}{3}a + \alpha + \beta\psi_1$	$\frac{1}{3}a + \alpha + \beta\psi_2$	$\frac{1}{3}a + \alpha + \beta\psi_3$
TMA2	N(2)	48(d) $\bar{4}$	$\frac{1}{3}a$	$\frac{1}{3}a$	$\frac{1}{3}a$
	C(2)	192(h) 1	$\frac{1}{3}a + \alpha$	$\frac{1}{3}a + \alpha(\cos \chi + \sin \chi)$	$\frac{1}{3}a + \alpha(\cos \chi - \sin \chi)$
	D(2')	192(h) 1	$x_{C2} + \beta\Phi_1$	$y_{C2} + \beta(\Phi_2 \cos \chi + \Phi_3 \sin \chi)$	$z_{C2} + \beta(\Phi_3 \cos \chi - \Phi_2 \sin \chi)$
	D(2'')	192(h) 1	$x_{C2} + \beta\Phi_2$	$y_{C2} + \beta(\Phi_1 \cos \chi + \Phi_2 \sin \chi)$	$z_{C2} + \beta(\Phi_2 \cos \chi - \Phi_1 \sin \chi)$
	D(2''')	192(h) 1	$x_{C2} + \beta\Phi_3$	$y_{C2} + \beta(\Phi_3 \cos \chi + \Phi_1 \sin \chi)$	$z_{C2} + \beta(\Phi_1 \cos \chi - \Phi_3 \sin \chi)$
	$3\rho = \text{Pt-C bond length}$		$\psi_1 = \frac{1 - 4 \cos \psi}{3}$		$\Phi_1 = \frac{1 - 4 \cos \varphi}{3}$
	$\sqrt{3}\alpha = \text{N-C bond length}$		$\psi_2 = \frac{1 + 2 \cos \psi - 2\sqrt{3} \sin \psi}{3}$		$\Phi_2 = \frac{1 + 2 \cos \varphi - 2\sqrt{3} \sin \varphi}{3}$
	$\sqrt{3}\beta = \text{C-D bond length}$		$\psi_3 = \frac{1 + 2 \cos \psi - 2\sqrt{3} \sin \psi}{3}$		$\Phi_3 = \frac{1 + 2 \cos \varphi + 2\sqrt{3} \sin \varphi}{3}$

In both these structures the N—C bond points towards the empty  $b(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  position of the  $Fm3m$  unit cell. A further two structures, (iii) and (iv), may be obtained by reversing the sense of the N—C and C—D bonds. The N—C bond then points towards the Pt atom. The X-ray study of Berg & S tofte (1978) argued that structures (i) and (ii) are favoured. These structures differ only in the positions of the H atoms and it was impossible to distinguish between them in the X-ray study.

The expressions for the atomic coordinates given in Table 1 were included explicitly in the constraint subroutine of the refinement program and the derivatives of the atomic coordinates with respect to the constrained parameters  $\theta$ ,  $\psi$ ,  $\phi$ ,  $\chi$ ,  $\rho$ ,  $\alpha$  and  $\beta$  were calculated numerically to double precision.

### Disordered models

With the system of constraints described in the previous section it was possible to allow for disorder in the structure with the addition of only a small number of extra parameters. Each of the angles  $\theta$ ,  $\psi$ ,  $\phi$  and  $\chi$  was allowed to take two different values with occupation probabilities for each orientation defined by  $(1 - p_i)$  and  $p_i$  for each pair of angles,  $i = \theta, \psi, \phi$  and  $\chi$ . The  $\text{PtCl}_6$  ion was allowed to take two orientations defined by  $\theta$  and  $-\theta$ . Similarly, the methyl groups on TMA1 and TMA2 were each allowed two orientations defined by  $\psi$  and  $\psi + \pi/3$ , and  $\phi$  and  $\phi + \pi/3$  respectively. Two models for disorder in the TMA2 ion were used. In the first model the two orientations  $\chi_1$  and  $\chi_2$  were independent. When it was found that the final values of  $\chi_1$  and  $\chi_2$  differed by equal and opposite amounts from  $\pi/2$ , the value corresponding to the  $Fm3m$  structure, a constraint  $\chi_2 = \pi - \chi_1$  was introduced. It was assumed that the temperature factors of the equivalent atoms in disordered pairs were equal. The introduction of disorder therefore required one extra parameter,  $p_i$ , for each of the four angles except for the case with independently oriented TMA2 ions in which two extra parameters were required.

No restriction on the values of  $p_i$  was made. This means that unphysical values outside the range  $0 \leq p_i \leq 1$  were possible in the refinement. The fact that a value of  $p_x$  well within this range was obtained for the room-temperature structure supports the validity of the model.

### Structure refinement

The data were analysed using the profile-refinement program *EDINP* (Pawley, Mackenzie & Dietrich, 1977). In all refinements isotropic temperature factors were used, the data being insufficient to justify the refinement of anisotropic temperature factors. The

profile  $R$  factor which indicates the quality of fit is defined in the usual way by  $R = 100 \sum [(y^{\text{obs}} - y^{\text{calc}})/y^{\text{obs}}]\%$ , where  $y^{\text{obs}}$  and  $y^{\text{calc}}$  are the observed and calculated profile intensities respectively, including the background contribution. The summation is over all points in the scan.

### Room-temperature structure

The room-temperature diffraction pattern was fitted using each of the four possible  $Fm3m$  structures in turn. These gave the  $R$  factors: (i)  $R = 19.2$ , (ii)  $R = 21.5$ , (iii)  $R = 22.6$ , (iv)  $R = 24.5\%$ , with the same number of variable parameters in each case.

A plot of observed and calculated profiles for the 19.2% fit is shown in Fig. 1. The fit to the stronger observed peaks is generally quite good but there are several weak peaks which have no corresponding calculated peak. These latter peaks can be indexed using the  $Fd3c$  cell with the lattice parameter doubled with respect to the  $Fm3m$  cell.

The parameters  $\theta$ ,  $\psi$ ,  $\phi$  and  $\chi$  were then allowed to vary in the refinement process so that the model structure could distort from  $Fm3m$  to  $Fd3c$ . The starting point for the  $Fd3c$  refinement was the best  $Fm3m$  structure, (i). The introduction of these additional degrees of freedom led to a significant improvement in the fit from  $R = 19.2\%$  to  $R = 8.4\%$ . The final parameter values for this refinement are listed in Table 2.

Although the quality of the fit to the measured profile is relatively good the values of some of the isotropic temperature factors indicate that there may be some error in the calculated structure. In particular, the temperature factors of the N and C atoms in TMA2,  $B(\text{N}2)$  and  $B(\text{C}2)$ , are much larger than those of the D atoms,  $B(\text{D}2)$ , in the same group, a result which is clearly unphysical. It may be argued (see later) that the

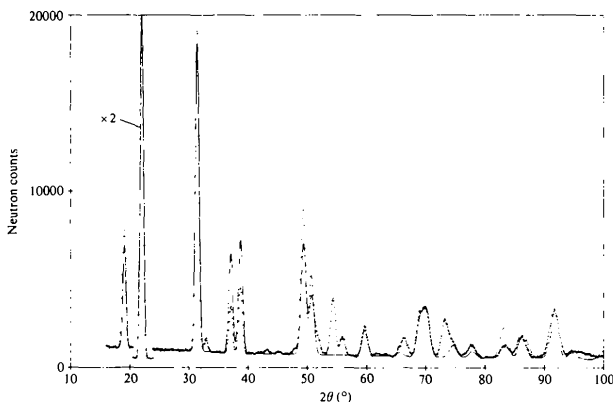


Fig. 1. Measured (points) and calculated (solid line) diffraction patterns at room temperature. The calculated profile corresponds to the 19.2% fit with model structure  $Fm3m$  (i).

Table 2. *The final parameters of the ordered and disordered refinements of the room-temperature structure*

The C–D bond length was kept fixed in all refinements because of its high correlation with the temperature factors  $B(D1)$  and  $B(D2)$ .

	Individual temperature factors		Overall temperature factors	
	Ordered	Disordered	Ordered	Disordered
Neutron wavelength (Å)	2.4436	2.4436	2.4436	2.4436
$2\theta$ range (°)	16 to 100	16 to 100	16 to 100	16 to 100
$2\theta$ step (°)	0.1	0.1	0.1	0.1
Scale factor	0.0367 (3)	0.0359 (3)	0.0357 (4)	0.0354 (3)
Zero of scan (°)	0.044 (3)	0.029 (3)	0.041 (4)	0.29 (3)
Peak shape parameters (deg <sup>2</sup> )				
<u>u</u>	3.9 (3)	4.1 (2)	3.5 (4)	3.5 (3)
<u>v</u>	-1.5 (2)	-1.6 (2)	-1.1 (2)	-1.5 (2)
<u>w</u>	0.57 (3)	0.59 (2)	0.50 (3)	0.57 (3)
Unit-cell parameter <i>a</i> (Å)	25.473 (3)	25.490 (2)	25.476 (4)	25.490 (3)
Bond lengths (Å)				
Pt–C	2.307 (3)	2.301 (3)	2.99 (5)	2.296 (3)
N–C	1.465 (4)	1.479 (4)	1.466 (3)	1.488 (3)
C–D	1.055	1.055	1.055	1.055
Orientation angles (rad)				
$\theta$	0.215 (5)	0.201 (5)	0.232 (7)	0.206 (5)
$\phi$	0.30 (3)	-0.36 (2)	0.02 (3)	-0.31 (2)
$\psi$	2.25 (1)	2.42 (1)	2.19 (2)	2.45 (1)
$\chi$	2.009 (5)	2.050 (6)	1.991 (6)	2.072 (6)
Isotropic temperature factors (standard units)				
<i>B</i> (Pt)	1.0 (4)	1.5 (3)		
<i>B</i> (Cl)	7.0 (3)	4.0 (3)		
<i>B</i> (N1)	-3.3 (9)	0.2 (13)	Overall	Overall
<i>B</i> (C1)	4.4 (11)	12.0 (18)	<i>B</i> = 6.6 (2)	<i>B</i> = 4.3 (1)
<i>B</i> (D1)	11.9 (9)	6.9 (8)		
<i>B</i> (N2)	14.5 (11)	8.6 (9)		
<i>B</i> (C2)	14.7 (10)	6.6 (10)		
<i>B</i> (D2)	4.9 (3)	3.5 (4)		
Occupation probability $p_x$	–	0.199 (8)	–	0.218 (7)
Number of variable parameters	20	21	13	14
<i>R</i> factor (%)	8.4	6.9	9.2	7.4

standard deviations of the parameters calculated by the program are underestimated by a factor of about 3, but even if this is taken into account  $B(N2)$  and  $B(C2)$  are spuriously large compared with  $B(D2)$ . It is well known that the effect of neglecting disorder when it is present is to make the temperature factors spuriously large. We therefore carried out refinements in which the TMA2 ion and the methyl groups were allowed to disorder. Disordering of TMA2 led to an improvement of the fit to  $R = 7.0\%$  but no further improvement was obtained by allowing disorder in the methyl groups or in the  $PtCl_6$  ion.

The TMA2 ion was at first allowed to take two independent orientations  $\chi_1$  and  $\chi_2$  with corresponding occupation probabilities of  $(1 - p_x)$  and  $p_x$ . The final value of  $p_x$  was  $0.18 \pm 0.01$ , which is well within the physically acceptable range of  $0 \leq p_x \leq 1$ . The two values obtained for the orientation of the TMA2 ion were  $\chi_1 = 117.5(3)^\circ$  (82% occupation) and  $\chi_2 = 70(2)^\circ$  (18% occupation). These values correspond to deviations of about  $28^\circ$  and  $-20^\circ$  from the  $90^\circ$

orientation in the  $Fm\bar{3}m$  structure. The uncertainties in these angles may be as much as  $1^\circ$  and  $7^\circ$  respectively if we assume that the standard deviations produced by the program are underestimated by a factor of 3, so that within the uncertainties the two orientations differ by equal and opposite angles from the high-symmetry orientation. This conclusion was tested by constraining the angles  $\chi_1$  and  $\chi_2$  by the relationship  $\chi_2 = \pi - \chi_1$  and repeating the refinement. This refinement gave an  $R$  factor of 6.9% with parameters  $\chi_1 = 117.5(3)^\circ$  and  $p_x = 0.20(1)$ . The slight improvement in the  $R$  factor illustrates the fact that a reasonable constraint can sometimes lead to a better fit than is obtained without the constraint. Although it must always be possible in principle to obtain an equally good fit with the unconstrained parameter set, the constraint in this case has the effect of removing correlation which can impede the refinement from reaching an absolute minimum.

The final parameter values for the 6.9% fit are listed in Table 2 along with the results of the fit using the ordered structure. As in the ordered structure refinement the values of some of the temperature factors are unreasonable. In order to test the significance of the individual thermal parameters we repeated the ordered and disordered refinements using only an overall temperature factor. These refinements gave  $R$  factors of 9.2 and 7.4% for the ordered and disordered structures respectively. The fact that there is only a slight worsening of the fit from 6.9% to 7.4% when the number of parameters is reduced from 21 to 14 is an indication of the insignificance of the individual thermal parameters used in the first two refinements. The final parameters from the two refinements using an overall temperature factor are listed in Table 2 where they may be compared with the earlier results. It can be seen that the values of the structural parameters for the disordered structure are not significantly affected by the change in the thermal-parameter set. The same may be said for most of the parameters in the ordered structure, except for  $\phi$  which is changed by 9 standard deviations.

The significance of the improvement in the fit with the disordered model should ideally be tested by

Table 3. *Points of the  $\mathcal{R}$  distribution (from Hamilton, 1965)*

$n$  = number of observations; the numbers of parameters were  $m = 14$  (disordered) and  $(m - b) = 13$  (ordered).

$(n - m)$	Probability levels						
	50%	25%	10%	5%	2.5%	1.0%	0.5%
28	1.008	1.024	1.050	1.072	1.096	1.128	1.154
24	1.010	1.029	1.059	1.085	1.113	1.152	1.182
20	1.012	1.034	1.072	1.103	1.137	1.185	1.224
16	1.015	1.044	1.091	1.132	1.176	1.238	1.289
12	1.020	1.059	1.125	1.181	1.243	1.333	1.407

applying Hamilton's (1965) test to the  $R$  factors for the ordered and the disordered refinements. This test, however, requires the number of degrees of freedom, a quantity which cannot be found at present for powder data. Here we follow Pawley (1978) in assuming that the number of observations,  $n$ , is given by the number of scan points divided by the average number of scan points in a peak, giving  $n = 900/26 = 34$ . Hamilton (1965) shows that

$$\mathcal{R} = \frac{R(\text{ordered})}{R(\text{disordered})}$$

is distributed as

$$\left[ \frac{b}{(n-m)} F + 1 \right]^{1/2},$$

where  $b$  = number of disorder parameters,  $n$  = number of observations,  $m$  = number of parameters in disordered refinement ( $m - b$  = number of parameters in ordered refinement), and  $F$  is  $F$ -distributed with  $b$  and  $n - m$  degrees of freedom.

The value of  $\mathcal{R}$  must be compared with  $9.2/7.4 = 1.234$  from the refinements. Calculated values of  $\mathcal{R}$  for different probability levels are given in Table 3 with several values of  $n - m$  for comparison. The values for the suggested  $n$  of 34 indicate that the results we have obtained could be accidental with a chance of less than 1 in 200.

A comparison of the refinements with individual and overall thermal parameters can also be done. For the disordered refinements the  $R$ -factor ratio is

$$\frac{R(\text{overall})}{R(\text{individual})} = \frac{7.4}{6.9} = 1.0725,$$

which with  $n = 21$  and  $b = 7$  corresponds to a probability level of less than 50%. In other words, the chance of obtaining an accidental improvement from

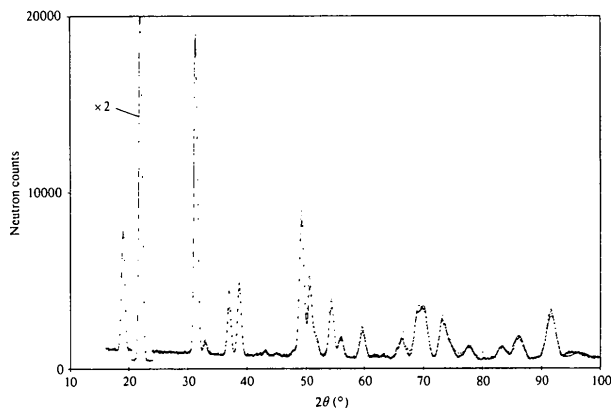


Fig. 2. Measured (points) and calculated (solid line) diffraction patterns at room temperature. The calculated profile corresponds to the final 6.9% fit with  $\chi$ -disordered TMA2.

7.4 to 6.9% by extending the thermal-parameter set is greater than 1 in 2. We conclude therefore that the individual thermal parameters are insignificant.

Together with the result that the occupation probability factor lies within the range of physical reality the statistical significance of 99.5% leads us to conclude that the disordering of the TMA2 group is a real effect. The observed and calculated profiles corresponding to the  $R = 6.9\%$  fit are shown in Fig. 2. The calculated profile obtained with the 7.4% fit is virtually indistinguishable from that shown in Fig. 2 and is therefore not included.

### Low-temperature structure

As with the room-temperature data, the diffraction pattern measured at 100 K was fitted using each of the four possible  $Fm3m$  structures. The  $R$  factors obtained were (i)  $R = 17.4$ , (ii)  $R = 19.1$ , (iii)  $R = 21.2$ , (iv)  $R = 21.1\%$ , with the same variable parameters in each case. The observed and calculated profiles corresponding to the  $R = 17.4\%$  fit are shown in Fig. 3. It is interesting to note the almost complete absence of the superlattice reflections which occurred in the room-temperature pattern shown in Fig. 1. The lowest-order reflection which requires the doubled lattice parameter is the reflection 139 which occurs at a  $2\theta$  value of about  $55^\circ$ . Since the superlattice reflections are very weak it would be expected that the  $Fm3m$  structure would give a good fit to the remainder of the pattern but it is clear from inspection of Fig. 3 that this is not the case. Attempts were made to improve the fit by introducing the extra degrees of freedom allowed by  $Fd3c$ , but the  $R$  factor could not be reduced below 16%. Since we were unable to obtain a satisfactory fit to the low-temperature pattern the final parameter values are not presented here. We plan to collect more powder diffraction data at intermediate and lower temperatures. Since the

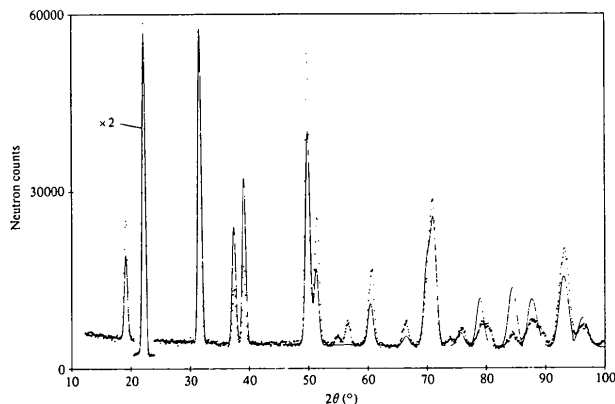


Fig. 3. Measured (points) and calculated (solid line) diffraction patterns at 90 K. The calculated profile corresponds to the 17.4% fit with model structure  $Fm3m$  (i).

primary interest in this and similar materials is in investigating the nature of the structural phase transitions at low temperatures it is important to determine the low-temperature structure. It is hoped that by fitting the diffraction patterns measured at temperatures spaced more closely than in the present work we will be more able to determine any structural changes that occur.

### Standard deviations

It was suggested by Pawley (1978) that the effective number of observations,  $n$ , should be used in the calculation of the standard deviations instead of using the total number of reflections contributing to the scan. In the room-temperature scan the number of contributing reflections is 161, while  $n$  is about 34. The standard deviations should therefore be increased by a factor of

$$\left( \frac{N_{hkl} - m}{n - m} \right)^{1/2},$$

where  $N_{hkl}$  is the number of reflections contributing to the scan and  $m$  is the number of variable parameters.

The standard deviations included in Table 2 were calculated using the total number of reflections contributing to the scan. For a more realistic estimation of the standard deviation of a structural parameter the number in Table 2 should be multiplied by 3 or 7 for the 21- and 14-parameter models respectively. This suggestion is supported by the result that when  $\chi_1$  and  $\chi_2$  were constrained a fit was obtained which was equally as good as in the unconstrained refinement, even though the constrained and unconstrained value of  $\chi_2$  differed by about three calculated standard deviations.

### Conclusions

We have analysed the neutron powder diffraction data measured at room temperature and shown that the structure does not belong to the space group  $Fm\bar{3}m$ . A good fit to the measured pattern was obtained when the structure was allowed to distort within the space group  $Fd\bar{3}c$  which involved a doubling of the lattice parameter. Further improvement was obtained when one of the tetramethylammonium ions was allowed to be disordered over two different orientations, the ratio of occupation probabilities being 4 to 1. The statistical significance of this result is discussed and estimated to be about 99.5%. Further support for the disordered

model comes from the fact that the occupation probability parameter was not restricted to physically possible values yet it reached a value well within the range of acceptability. It is therefore concluded that the structure of  $[N(CD_3)_4]_2[PtCl_6]$  at room temperature belongs to the space group  $Fd\bar{3}c$  and that one of the tetramethylammonium ions is disordered over two orientations which are rotated by equal and opposite angles from the orientation in the space group  $Fm\bar{3}m$ .

The powder diffraction pattern was also measured at low temperature but we have been unable to obtain a satisfactory fit using either  $Fm\bar{3}m$  or  $Fd\bar{3}c$  structures. Although the superlattice reflections are much weaker than at room temperature, implying less distortion from  $Fm\bar{3}m$ , there are large discrepancies between observed intensities and those calculated assuming an  $Fm\bar{3}m$  structure. More low-temperature measurements are planned for the near future.

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*Additional note:* The structure of the hydrogenous compound at room temperature has recently been refined within the  $Fd\bar{3}c$  space group using X-ray measurements (Kurt Nielsen, 1979, private communication). The refinement was unconstrained and the structure was assumed to be ordered. A total of 192 reflections were used in the refinement which reached an  $R$  value of  $R = \sum |F_o - F_c| / \sum |F_o| = 0.045$ , where  $F_o$  and  $F_c$  are the observed and calculated structure factors respectively. The unit-cell parameter was assumed to be  $a = 25.425(4) \text{ \AA}$ .

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