

## THE CRYSTAL STRUCTURE OF TETRAMERIC TRIMETHYLPLATINUM(IV) HYDROXIDE

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### SUMMARY

The crystal structure of tetrameric trimethylplatinum(IV) hydroxide,  $[(\text{CH}_3)_3\text{PtOH}]_4$ , has been determined using three dimensional neutron data. The compound crystallises out in a cubic unit cell, space group selected  $I_{\bar{4}3m}$ ; cell dimensions,  $a = 10.14(1)$  Å. The four platinum atoms of the tetramer are at the corners of a regular tetrahedron and are linked to one another by bridging hydroxyl oxygens. Three methyl groups complete the octahedral coordination around each platinum. Interatomic distances are Pt-O 2.20(4), Pt-C 2.02(3), Pt-Pt 3.41(4), O-H 0.93(8), C-H 1.12(5), 1.06(4) Å.

### INTRODUCTION

Using X-ray diffraction, Rundle and Sturdivant<sup>1</sup> determined the crystal structures of tetrameric trimethylplatinum(IV) chloride and tetramethylplatinum. Although only the heavy platinum atoms were located with any degree of certainty, these compounds represented the first examples of cubane type arrangements, and until recently have been textbook examples. While the structure of trimethylplatinum(IV) chloride has not been questioned, doubt has been expressed about the existence of tetramethylplatinum<sup>2</sup>. The original compound examined was possibly trimethylplatinum(IV) hydroxide, which has been found to be isomorphous with the reported tetramethylplatinum. The present neutron diffraction analysis was carried out in order to locate all the atoms in the structure, and to provide structural data for a spectroscopic investigation.

### EXPERIMENTAL

Tetrameric trimethylplatinum(IV) hydroxide was obtained from an aqueous solution of trimethylplatinum sulphate by precipitation with a base. A white approximately prismatic crystal  $[1.1 \times 1.2 \times 1.8$  mm, elongated along the (110) axis] was grown from chloroform over a period of three months.

#### *Crystal data*

$\text{C}_{12}\text{H}_{40}\text{O}_4\text{Pt}_4$ ; mol. wt., 1028.8; cubic;  $a = 10.14(1)$  Å; (tetramethylplatinum<sup>1</sup>,  $a = 10.145$  Å);  $U = 1043$  Å<sup>3</sup>;  $Z = 2$ ;  $D_c = 3.28$  g·cm<sup>-3</sup>; space group, either  $I_{\bar{4}3m}$  ( $T_d^3$ ).

$I_{432}(O^5)$ , or  $I_{m3m}(O_h^2)$ ; neutron radiation,  $\lambda = 1.189 \text{ \AA}$ ;  $\mu$  (for neutrons)  $= 3.0 \text{ cm}^{-1}$ ;  $\mu$  (for X-radiation,  $\text{CuK}_\alpha$ )  $= 521 \text{ cm}^{-1}$ ;

The crystal was mounted on the A.I.N.S.E. four circle neutron diffractometer, installed on the A.A.E.C. reactor HIFAR at Lucas, Heights, New South Wales. A total of 199 reflections were collected using a  $\theta/2\theta$  step scan technique; of these 127 were below minimum observable intensity. The spectrometer was monitor controlled, and the monochromatic beam intensity at the specimen was approximately  $10^5 \text{ n} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$ . The data were corrected for Lorentz factors, while no correction was made for absorption or extinction. Of the possible space groups, the non-centric  $I_{43m}$  was chosen on the basis of statistical tests. For the calculation of structure factors, the following scattering lengths were used<sup>3</sup>:  $b_{\text{Pt}} = 0.95 \times 10^{-12} \text{ cm}$ ,  $b_{\text{C}} = 0.661 \times 10^{-12} \text{ cm}$ ,  $b_{\text{O}} = 0.577 \times 10^{-12} \text{ cm}$  and  $b_{\text{H}} = -0.375 \times 10^{-12} \text{ cm}$ .

The observed structure factors were initially converted to absolute values by applying a scale factor,  $K$ , obtained from the intensity of the (2 0 0) reflection of a standard potassium bromide crystal. The final scaling of these observed structure factors was determined by least squares.

A standard deviation was assigned to each integrated intensity according to the expression:

$$\sigma^2(Q_j) = Q_j + 2 B_j + (\alpha + \beta \cdot Q_j)^2$$

where  $Q_j$  = integrated intensity;  $B_j$  = background count;  $\alpha = Q_{\text{min}}$ , the minimum observed intensity; and  $\beta$  is the standard deviation of the standard reflection. The structure was refined using Dr. G. Cox's version of ORFLS (IBM 360/50).

#### STRUCTURE REFINEMENT

Symmetry restrictions allow two sets of methyl hydrogen positions, and refinement of both sets was attempted with the basic X-ray parameters of Rundle and

TABLE 1

ATOMIC CO-ORDINATES AND ISOTROPIC THERMAL PARAMETERS ( $\text{\AA}^2$ )

Atom	$x/a$	$y/a$	$z/a$	$B$
<i>Trimethylplatinum(IV) hydroxide</i> <sup>a</sup>				
Pt(c) <sup>b</sup>	0.381(2) <sup>c</sup>	0.619	0.619	2.2(1)
O(c)	0.596(3)	0.596	0.596	2.2(3)
C(g)	0.377(2)	0.623	0.818(1)	4.1(2)
H(1)(g)	0.303(4)	0.697	0.854(4)	9.3(9)
H(2)(h)	0.359(2)	0.530(1)	0.862(2)	6.2(3)
H(3)(c)	0.649(7)	0.649	0.649	4.3(7)
<i>Tetramethylplatinum</i> <sup>1</sup>				
Pt(c)	0.380(2)	0.620	0.620	
C(c)	0.610	0.610	0.610	
C(g)	0.375	0.625	0.820	

<sup>a</sup> This work. <sup>b</sup> Type of special position. <sup>c</sup> Standard deviations are given in brackets.

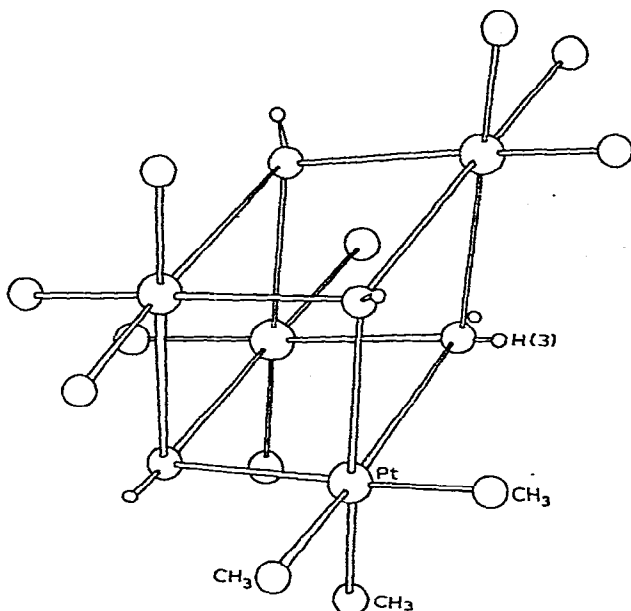


Fig. 1. Tetrameric trimethylplatinum(IV) hydroxide.

Sturdivant<sup>1</sup>. Using seven cycles of full matrix least squares, the model incorporating one set refined to a conventional *R* factor (observed reflections) of 0.08. The second set failed to refine. A difference synthesis based on the final atomic coordinates yielded no spurious peaks. Table 1 compares refined atomic parameters with those found by Rundle and Sturdivant<sup>1</sup>.

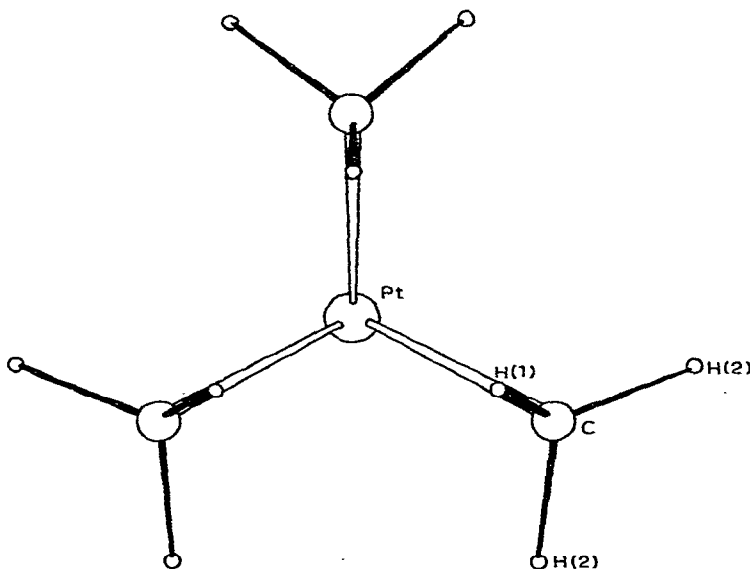


Fig. 2. Environment of methyl hydrogen atoms.

## DISCUSSION

With crystallographically imposed  $T_d$  point symmetry, the tetrameric trimethylplatinum hydroxide has four platinum atoms at the vertices of a regular tetrahedron (Fig. 1). These are bridged by hydroxyl oxygens which lie on a smaller interpenetrating tetrahedron, with the resultant combination approximating a cube. Three methyl groups complete the octahedral coordination about each platinum.

TABLE 2

## MOLECULAR GEOMETRY

<i>Interatomic distances (Å)<sup>a</sup></i>			
Pt-O	2.20(4)	C-H(2)	1.06(4)
Pt-C	2.02(3)	C-C <sup>11</sup>	2.80(4)
Pt-Pt <sup>1</sup>	3.41(5)	H(2)-H(2) <sup>111</sup>	1.59(4)
O-O <sup>1</sup>	2.75(6)	H(1)-H(2)	1.79(5)
O-H(3)	0.93(8)	H(1)-H(1) <sup>11</sup>	2.25(8)
C-H(1)	1.12(5)		
<i>Intramolecular angles (°)<sup>a</sup></i>			
Pt-O-Pt	102(2)	C-Pt-O	97(2)
O-Pt-O	78(2)	H(1)-C-H(2)	110(3)
C-Pt-C	88(1)	H(2)-C-H(2) <sup>111</sup>	97(3)

<sup>a</sup> X = x, y, z; X<sup>1</sup> = x,  $\bar{x}$ ,  $\bar{x}$ ; X<sup>11</sup> = x, z, y; X<sup>111</sup> =  $\bar{y}$ ,  $\bar{x}$ , z.

TABLE 3

## INTERATOMIC DISTANCES IN TRIMETHYLPLATINUM COMPOUNDS

Pt-C(Å)	Pt-O(Å)
<i>Tetrameric Trimethylplatinum(IV) hydroxide<sup>a</sup></i>	
2.02(3)	2.20(4)
<i>Trimethyl(8-quinolinolato)platinum(IV)<sup>3</sup></i>	
2.00(4), 2.01(6)	2.22(3), 2.22(4)
2.03(3), 2.07(6)	2.23(3), 2.29(4)
2.12(4), 2.17(9)	
<i>Ethylenediaminebis[trimethyl(acetylacetonato)platinum(IV)]<sup>4</sup></i>	
2.03(7), 2.12(8)	2.16(4), 2.18(4)
2.17(8)	
<i>Trimethyl(4,6-nonanedionato)platinum(IV)<sup>5</sup></i>	
2.00(3), 2.02(4)	2.14(2), 2.16(2)
2.04(3)	
<i>Trimethyl(ethyl acetoacetato)platinum(IV)<sup>6</sup></i>	
1.96(7), 2.14(9)	2.18(5), 2.19(5)
2.17(10)	

<sup>a</sup> This work.

Interatomic distances and angles are shown in Table 2. Fig. 2 shows the environment of the methyl hydrogen atoms.

Table 3 compares some interatomic distances with X-ray determinations of similar trimethylplatinum compounds. The closest hydrogen atoms in adjacent methyl groups are 2.3 Å apart. The body-centered cell is made up of two tetramers. The shortest intermolecular distance is 2.2 Å [from H(methyl) to H(hydroxyl)]. Table 4 lists observed and calculated structure amplitudes.

Recently, a number of structures, having a tetrahedral arrangement of metal atoms as a molecular chassis, have been reported. The adjacent metal atoms may be linked directly<sup>8</sup>, partially bridged<sup>9,10</sup>, or have all metal atoms linked by bridging groups. The latter may be classified according to whether the donor group links two<sup>11,12</sup> or three metal atoms<sup>13</sup>. Tetrameric trimethylplatinum hydroxide and tetrameric methylzinc methoxide<sup>13</sup> are examples of compounds having single bonded oxygens capable of spanning three metal atoms. The small differences between these structures may be caused by the substitution of six-coordinate octahedral platinum for four-coordinate tetrahedral zinc.

TABLE 4

OBSERVED<sup>a</sup> AND CALCULATED STRUCTURE AMPLITUDESEach line consists of indices  $k, l, 7(F_o)$ , and  $7(F_c)$ .

$h=0$	$h=1$		$h=2$		$h=3$		$h=4$		$h=6$			
1	1	60 61	1	2 48 48	0	0 16 12	3	4 49 48	4	8 22 29	0	0 74 75
	3	34 30		4 14 11	2	2 18 22	3	6 15 15	0	0 79 77	6	6 36 39
	5	78 76	1	6 91 88		8 25 33		8 22 24	4	4 92 89		10 35 34
	7	29 17		10 46 40		10 38 35		10 23 23	5	5 63 60		
	9	43 47	2	3 13 8	3	3 22 16	4	5 32 25		7 15 16		$h=7$
2	4	14 23		5 35 36		5 20 21		9 28 21		9 40 41	7	7 17 5
	5	44 44	3	4 25 25		7 21 20	5	6 35 31	6	6 18 30		
	9	26 27		6 40 38	4	4 24 33		8 24 15		10 16 15		$h=8$
4	4	97 96		10 32 29		6 24 35				10 9 12	0	0 28 35
	6	21 26	4	5 55 50	5	5 29 25						
	8	26 33		9 40 34	6	6 22 23						
	10	31 36	5	6 60 60		10 33 32						
									$h=5$			$h=10$
									5	6 40 43	0	0 64 60
5	5	86 83		8 20 21	7	7 18 17				8 17 28		
	9	53 55		10 21 28	10	10 8 22				10 13 26		$h=12$
9	9	26 33	7	10 16 17							0	0 16 19
												$h=14$
											0	0 19 26

<sup>a</sup> Unobserved reflections have been omitted from this Table. For reflection (4 9 9)  $F_c(26)$  exceeded background by two standard deviations.

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