

Fig. 1. The crystal structure of $\text{Hg}_3\text{S}_2\text{Cl}_2$.

Isometric: $a = 8.949 \pm 0.002 \text{ \AA}$, $U = 716.7 \text{ \AA}^3$, $D_m = 6.895 \pm 0.086 \text{ g.cm}^{-3}$. $Z = 4$, $D_x = 6.827 \text{ g.cm}^{-3}$.
Space group $I2_13$ (no. 199).

Atomic positions

12 Hg in 12(b); $x, 0, \frac{1}{2}$; with $x = 0.3029 \pm 0.0005$
8 S in 8(a); x, x, x ; with $x = 0.2709 \pm 0.0029$
8 Cl in 8(a); x, x, x ; with $x = 0.0107 \pm 0.0028$

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Trimethylplatinum(IV) iodide and its misrepresentation as hexamethyldiplatinum*. By GABRIELLE DONNAY, *Geophysical Laboratory, Carnegie Institution of Washington, Washington, D.C., U.S.A.*, LAWRENCE B. COLEMAN, NILDE G. KRIEGHOFF, and D. O. COWAN, *The Johns Hopkins University, Baltimore, Md., U.S.A.*

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Transparent, tan-colored trimethylplatinum(IV) iodide crystals have cell dimensions $17.77_{\pm 5}$, $19.39_{\pm 6}$, $17.12_{\pm 5} \text{ \AA}$, $\beta = 115^\circ 41' \pm 5'$, space group $P2_1/a$, and 32 molecules per cell. These data duplicate the ones erroneously ascribed to hexamethylplatinum by Illuminati & Rundle [*J. Amer. Chem. Soc.* (1949) **71**, 3575], whose published (010) Patterson projection enables eight tetramers of the molecule to be located in the crystal structure. This tetramer has a configuration similar to that reported for the tetramer of trimethylplatinum(IV) chloride.

Trimethylplatinum(IV) iodide has been assumed (Kite, Smith & Wilkins, 1966) to be cubic and isostructural with trimethylplatinum(IV) chloride (Rundle & Sturdivant, 1947), although Burovaya (1949) studied its morphology, pointed out that it is monoclinic, point group $2/m$, and observed forms 001, 110, 100, 011, leading to axial elements $a:b:c = 1.778:1.1826$; $\beta = 116^\circ 02'$. Our own data follow.

On recrystallizing $\text{Pt}(\text{CH}_3)_3\text{I}$, two distinct phases are obtained. One phase, recrystallized from benzene, is solvated; the other, recrystallized from toluene, is not. The solvated phase loses its benzene molecules within minutes when exposed to air. The change in crystal phase is readily observed because, although the crystal faces are perfectly preserved, the tan-colored transparent crystals turn yellow and opaque. Such a yellow pseudomorph gives a spotty

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In the structure (Fig. 1) the Hg is octahedrally (*trans*) coordinated to:

2 S at $2.45 \pm 0.02 \text{ \AA}$
2 Cl at 2.87 ± 0.01
2 Cl at 3.38 ± 0.04

The bond angles within the octahedra are:

S-Hg-S $166 \pm 1^\circ$
Cl-Hg-Cl $78.7 \pm 0.1^\circ$
(2) Cl-Hg-Cl $86.2 \pm 0.6^\circ$
Cl-Hg-Cl $109 \pm 1^\circ$

Each octahedron shares a face with an adjoining octahedron, the Hg-S-Hg angle between octahedra being $92 \pm 1^\circ$. This results in the nearest Hg-Hg distance being $3.546 \pm 0.004 \text{ \AA}$.

The structure was refined by least-squares using isotropic temperature coefficients and correcting for anomalous scattering, until the R value for 255 hkl reflections was 0.08 (weighted, $R = 0.077$). The resulting isotropic temperature factors are $B_{\text{Hg}} = 2.74 \pm 0.03$; $B_{\text{S}} = 1.5 \pm 0.3$ and $B_{\text{Cl}} = 1.8 \pm 0.2$. The F calculated are compared with F observed in Table 1.

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X-ray powder pattern, showing a grain size of at least 1000 \AA and little preferred orientation. This powder pattern is identical with that of the $\text{Pt}(\text{CH}_3)_3\text{I}$ recrystallized from toluene, thus showing that no toluene molecules are captured in the phase obtained from toluene. A combustion analysis, performed by J. Walter, gave C 9.83, H 2.65%; calculated for $\text{Pt}(\text{CH}_3)_3\text{I}$: C 9.8; H 2.5%.

The unsolvated crystals are brittle, 2 to 3 mm in largest dimension, transparent, tan-colored, thick-tabular (100) with point-group symmetry $2/m$. Optical extinction is sharp parallel to an edge which is chosen as the b axis. The observed forms, measured with excellent signals on the optical goniometer, are indexed 100, 021, 001, and 120. The cell to which these indices refer has dimensions: $a = 17.77 \pm 5$, $b = 19.39 \pm 6$, $c = 17.12 \pm 5 \text{ \AA}$ and $\beta = 115^\circ 41' \pm 5'$, cell volume = 5316 \AA^3 (precession films, Cu $K\alpha$, $\lambda = 1.5418 \text{ \AA}$), and axial ratios $a:b:c = 0.9165:1:0.8829$, requiring a transformation matrix 001/020/100 to be applied to Burovaya's morphological cell. The observed forms thus indicate a

morphological halving of b , which will be shown to have structural significance.

The density, determined rapidly in toluene on the Berman balance, is $3.58 \pm 20 \text{ g.cm}^{-3}$, leading to 31.2 molecules per cell. For 32 molecules (8 tetramers?) the calculated density is 3.67 g.cm^{-3} , well within the experimental accuracy of our density determination. Rotation, Weissenberg, and powder photographs were taken. The observed systematic extinctions are $0k0$ with k odd and $h0l$ with h odd, leading to space group $P2_1/a$. In addition, reflections $h0l$ with l odd are mostly unobserved: even on a 23-hour exposure of the $(010)_0^*$ net, only 403, 603, $60\bar{1}$ and $80\bar{3}$ appear, and they are very faint. We conclude that the heavy atoms, platinum and iodine, when projected onto (010) , outline a mesh ($a'c'$), with $a'=a/2$, $c'=c/2$. A rotation pattern about the b axis shows odd layers to be faint, indicating a structural pseudo-halving of b .

A search in *Crystal Data* (Donnay, Donnay, Cox, Kennard & King, 1963) for compounds with similar cell dimensions leads to 'hexamethyldiplatinum' (Illuminati & Rundle, 1949; Gilman & Lichtenwalter, 1938) with the following data: $a=17.35$, $b=18.99$, $c=17.79 \text{ kX}$, $\beta=116^\circ$, $P2_1/c$, measured density 3.65 g.cm^{-3} . After interchanging a and c and converting kX to \AA , these cell dimensions agree to 0.3, 1.5 and 1.3% respectively with our own data; the space group is the same and the observed density of Illuminati & Rundle is closer to our calculated value of 3.67 g.cm^{-3} than is our own observation. Structurally

absent reflections $h0l$ with h odd are mentioned by Illuminati & Rundle too. The difference in b dimension appears excessive, but their b may have been obtained from a rotation pattern and then it could be that far off. The last doubt concerning the true identity of these authors' 'hexamethyldiplatinum' disappeared when we studied their published Patterson projection $P(xz)$. According to their own interpretation, this projection shows 16 heavy atomic centers falling on two pseudo-eightfold positions:

$$x, z; \bar{x}, \bar{z}; \frac{1}{2}-x, \bar{z}; \frac{1}{2}+x, z;$$

$$x, \frac{1}{2}+z; \bar{x}, \frac{1}{2}-z; \frac{1}{2}-x, \frac{1}{2}-z; \frac{1}{2}+x, \frac{1}{2}+z$$

with $x_I=0.313$, $z_I=0.125$ and $x_{II}=0.138$, $z_{II}=0.008$. (The y coordinates of the first four sites are independent of those of the second four sites and should be labelled y and y' .) These coordinates led to satisfactory agreement between observed and calculated intensities for $h0l$ reflections, but the two authors state that 'the complete structure has not yet been determined' and in the 20 years that have elapsed since their article appeared nothing more has been published about it. Using their coordinates with our cell dimensions and our cell content of 32 $\text{Pt}(\text{CH}_3)_3\text{I}$, we obtain (Fig. 1) a reasonable projection of the structure onto (010) . Each atomic position represents the superposition of two Pt-I pairs from two tetramers directly below each other at a distance of $b/2$ along the b axis. This is an unusual packing indicating a possible association between tetramers along b . One would normally expect the layers of tetramers to

Table 1. Proposed fractional coordinates of $[\text{Pt}(\text{CH}_3)_3\text{I}]_4$ in space group $P2_1/a$

$a=17.77$, $b=19.39$, $c=17.12 \text{ \AA}$, $\beta=115^\circ 41'$. All atoms are in general fourfold position: $xy z; \bar{x}\bar{y}\bar{z}; \frac{1}{2}-x, \frac{1}{2}+y, \bar{z}; \frac{1}{2}+x, \frac{1}{2}-y, z$.

	x	y	z		x	y	z
Pt _I	0.313	y	0.625	I _I	0.313	$y+0.146$	0.625
Pt _{II}	0.138	$(y+0.146)$	0.508	I _{II}	0.138	y	0.508
Pt _{III}	0.187	y	0.375	I _{III}	0.187	$y+0.146$	0.375
Pt _{IV}	0.362	$(y+0.146)$	0.492	I _{IV}	0.362	y	0.492
Pt _{I'}	0.313	y'	0.625	I _{I'}	0.313	$y'+0.146$	0.625
Pt _{II'}	0.138	$(y'+0.146)$	0.508	I _{II'}	0.138	y'	0.508
Pt _{III'}	0.187	y'	0.375	I _{III'}	0.187	$y'+0.146$	0.375
Pt _{IV'}	0.362	$(y'+0.146)$	0.492	I _{IV'}	0.362	y'	0.492

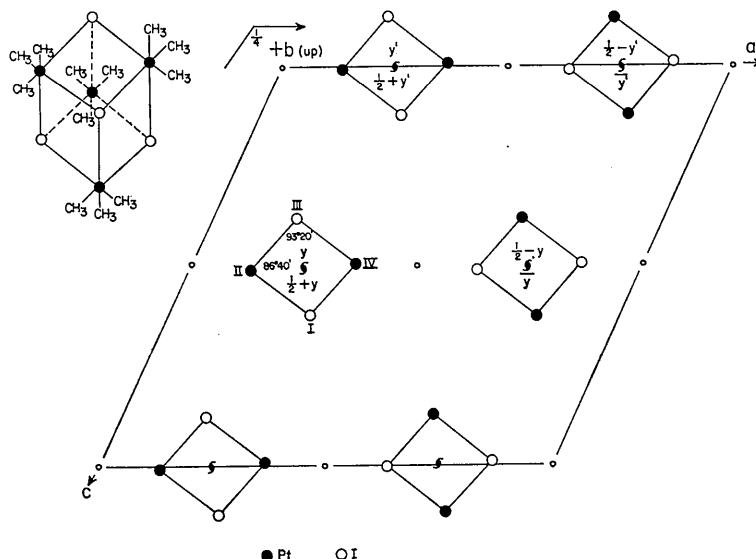


Fig. 1. The crystal structure of trimethylplatinum(IV) iodide projected onto (010) . A perspective drawing of one tetramer, $[\text{Pt}(\text{CH}_3)_3\text{I}]_4$, is shown in the upper left corner.

imbricate so as to approximate the efficient hexagonal close-packing, which is here roughly indicated by the cell dimensions in (010), $a \sim c$, $\beta \sim 120^\circ$. The hexagonal c/a ratio of 1.63, of the ideal hexagonal close-packing, is however replaced by a ratio of 2.33, which is far from the required value.

The only information given by Illuminati & Rundle about their $P(XY)$ projection is that 2.83 Å (2.82 kX) constitutes an important interatomic distance, parallel to b . If we assume it to be the Pt-I distance in the tetramer, a reasonable trial structure can be obtained (Table 1), with acceptable interatomic distances and angles (Table 2). The distance between adjacent Pt-I layers of neighboring tetramers along b is 6.86 Å, which is reasonable considering the fact that the $\text{Pt}(\text{CH}_3)_3$ group has a radius of about 4.0 Å and the I^- radius is 2.2 Å. How the columns of tetramers separated by $c/2$ are displaced relative to each other cannot be ascertained from Illuminati & Rundle's data. The minimum distance between tetramers in the (010) projection is 5.7 Å, less than the predicted minimum distance, so that y' and y must differ.

Table 2. Interatomic distances and interbond angles in the proposed tetramer $[\text{Pt}(\text{CH}_3)_3\text{I}]_4$ with number of occurrences

$\text{Pt}_I - \text{I}_{II}$	2.88 Å	4x	$\text{Pt}_I - \text{I}_{II} - \text{Pt}_{III}$	$86^\circ 40'$	4x
$\text{Pt}_{II} - \text{Pt}_{III}$	2.77	4x	$\text{I}_{II} - \text{Pt}_{III} - \text{I}_{IV}$	$93^\circ 20'$	4x
$\text{Pt}_I - \text{I}_I$	2.83	4x	$\text{Pt}_I - \text{I}_{II} - \text{Pt}_{II}$	$90^\circ 0'$	16x
Average Pt-I 2.83					

A comparison of $\text{Pt}(\text{CH}_3)_3\text{Cl}$ (Rundle & Sturdivant, 1947) and $\text{Pt}(\text{CH}_3)_3\text{I}$ shows a strong similarity of individual

tetramers. The point-group symmetry of the chloride tetramer is $\bar{4}3m$; that of the iodide is 2 with pseudosymmetry $\bar{4}3m$. The Pt-Cl distance is 2.48 Å, as compared with an average of 2.83 Å for the iodide. The difference of 0.35 Å is a normal one between M-Cl and M-I values in the literature (*International Tables for X-ray Crystallography*, 1962). The angle Pt-Cl-Pt is 99° and thus differs more from 90° than the four nonright angles in the iodide tetramer. The difference in the packing of the tetramers which is responsible for the difference in their crystal systems remains baffling. No further work on this compound is contemplated by us.

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Notes and News

Announcements and other items of crystallographic interest will be published under this heading at the discretion of the Editorial Board. The notes (in duplicate) should be sent to the General Secretary of the International Union of Crystallography (G. Boom, Department of Metallurgy, University of Oxford, Parks Road, Oxford, England). Publication of an item in a particular issue cannot be guaranteed unless the draft is received 8 weeks before the date of publication.

International Union of Crystallography Inter-Congress Meeting, 1968

The Commission on Crystallographic Apparatus of the International Union of Crystallography is organizing a meeting on *Accurate Determination of X-ray Intensities and Structure Factors*, to take place in Churchill College, Cambridge, England, from 24 to 28 June 1968.

The meeting will provide a forum for the assessment of measurement of X-ray structure-factor (F) values derived from small and large single crystals and powders by conventional procedures, and from perfect crystals by the Pendellösung technique. The various sources of error in the different procedures, and their correction or elimination will be considered. Comparison of experimental values with those based on theoretical calculations should provide a valuable commentary on the current state of solid-state studies, particularly in relation to features of structure studies dependent on the absolute accuracy of experimentally determined structure factors.

As the meeting is organized as one of specialists, with restricted attendance, participation is by invitation only. Any crystallographer who could contribute to the discus-

sion and wishes to be considered by the Organizing Committee should apply to the Chairman, Dr A. McL. Mathieson, Division of Chemical Physics, C.S.I.R.O., P.O. Box 160, CLAYTON, Victoria 3168, Australia.

As a record of the meeting for future reference, it is proposed to publish the (invited) lectures plus discussion in an issue of *Acta Crystallographica* Section A.

International Union of Crystallography Eighth General Assembly and International Congress of Crystallography

The Eighth General Assembly and International Congress of Crystallography of the International Union of Crystallography will be held in the United States of America in August 1969. The provisional time table is as follows.

From August 7 to 11 inclusive, a Topical Meeting on *The Crystallography of Biologically Important Substances* will be held at the Center for Crystallographic Research, Roswell Park Memorial Institute, Buffalo, New York. From August 13 to 21 inclusive, the General Assembly and International Congress, comprising the principal scientific sessions and the work of the Union's Commissions, will take