199. *The Stereochemistry of Sesquiethylenediaminetrimethylplatinic Iodide.*

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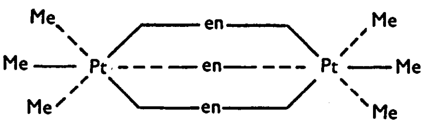
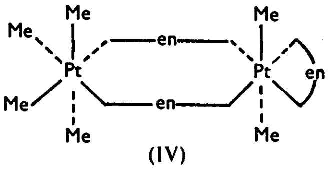
Sesquiethylenediaminetrimethylplatinic iodide has been shown by *X*-ray crystal-structure analysis to contain the cation $[\text{en}\ (CH_3)_3Pt\ \text{en}\ Pt(CH_3)_3\ \text{en}]^{2+}$. The two halves of the ion are related by a 2-fold axis perpendicular to the C–C bond of the bridging ethylenediamine molecule. Each platinum atom is surrounded octahedrally by three nitrogen and three carbon atoms in the *cis*-configuration of the type PtA_3X_3.

Sesquiethylenediaminetrimethylplatinic iodide, empirical formula $Pt(CH_3)_3I,1\frac{1}{2}\text{en}$ (en = ethylenediamine), was first prepared by Lile and Menzies.[1] The molecule must clearly contain at least two platinum atoms, and, as Lile and Menzies suggested,[2] its most likely formation is as a complex salt (I), in the positive ion of which the platinum atoms would be held together by one or more ethylenediamine groups and each have an octahedral configuration. The formation of polynuclear structures by means of halogen or methyl bridges such as occur in trimethylplatinic chloride and tetramethylplatinum [3] is extremely unlikely, but the structure (II), cannot be entirely be excluded. The *X*-ray investigation reported in this paper was undertaken to discriminate between this structure (II) and the various stereochemical forms of structure (I).

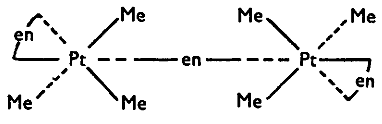
(I) $[Pt_2Me_6\ \text{en}_3]I_2$ $[PtMe_6][Pt\ \text{en}_3]I_2$ (II)



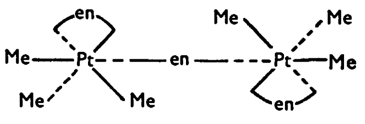
(III)



(IV)



(V)



(VI)

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[1] Lile and Menzies, *J.*, 1949, 1168; W. J. Lile, Thesis, Bristol, 1937.

[2] Cf. Foss and Gibson, *J.*, 1951, 299.

[3] Rundle and Sturdivant, *J. Amer. Chem. Soc.*, 1947, **69**, 1561.

Not counting enantiomers there are eight possible isomers of structure (I)—one with three en bridges, two with two bridges, and five with one bridge; of these, however, only (III), (IV), (V), and (VI), together with (II), satisfy the requirement which emerged from the preliminary X-ray examination, that the molecule must have at least a two-fold axis of symmetry. While further discrimination could be effected by finding the positions of the platinum atoms, a detailed analysis has been necessary to determine the structure finally; notwithstanding the large scattering power of platinum and iodine it has been possible to locate all the carbon and nitrogen atoms unequivocally and thereby to show that the structure is (VI).

EXPERIMENTAL

The sample was prepared and analysed by Messrs. Johnson Matthey and Co. [Found: Pt, 42·6. Calc. for $Pt_2en_3(CH_3)_6I_2$: Pt, 42·7%]. The acicular crystals were set up about the needle axis [001], and rotation and Weissenberg photographs were taken with Cu-K_α radiation. The unit cell dimensions are $a = 16{\cdot}54 \pm 0{\cdot}01$, $b = 12{\cdot}10 \pm 0{\cdot}01$, $c = 12{\cdot}92 \pm 0{\cdot}05$ Å; the value for c was obtained by measurement of a rotation photograph, and the other two by Straumanis's method (approximate values having been obtained from Weissenberg photographs). The measured volume, 2586 Å^3, with 4 molecules (M, 914) per unit cell gives a calculated density of 2·38. It was not possible to measure the density of the iodide because the small crystals dissolved in both aqueous and organic liquids; however the density of the nitrate, $Pt_2\,en_3\,Me_6(NO_3)_2$, determined by flotation in cadmium borotungstate solution, was 2·12, so that 2·38 is a reasonable value for the iodide.

The following classes of reflections were found to be systematically absent: hkl when $h + k + l = 2n + 1$; $0kl$ when $k = 2n + 1$ $(l = 2n + 1)$; $h0l$ when $h = 2n + 1$ $(l = 2n + 1)$. Hence the space group is either (i) $Iba - C_{2v}^{21}$ or (ii) $Ibam - D_{2h}^{26}$, the molecular symmetry required being (i) 2 or (ii) 222 or $2/m$.

Weissenberg photographs of the $(hk0)$ zone were taken by a multiple-film technique. Of a possible 128 reflections, 100 were observed and their intensities estimated visually by comparison with a calibration slip; Lorentz and polarisation corrections were applied, giving a set of relative values of F^2. Approximately absolute values and temperature factors were determined by Wilson's method. The intensities were redetermined by a different observer and the agreement $\sum|\Delta F|/\sum F$ between the two sets was 0·073.

No absorption correction was made. The crystal approximated to a cylinder 0·01 mm. in diameter and 1·0 mm. long; the linear absorption coefficient is 425 cm.$^{-1}$.

STRUCTURE DETERMINATION.

In either possible space group the molecules (or constituent ions) of sesquiethylenediaminetrimethylplatinic iodide must occupy special positions, in *Ibam* with symmetry 222 (three two-fold axes) or $2/m$ (two-fold axis and plane) and in *Iba* with symmetry 2 (two-fold axis). In form (IV) the two-fold symmetry axis must pass through both platinum atoms, whereas in (III), (V), and (VI) it must be perpendicular to the line joining them; form (IV) can therefore be rejected because it is impossible to accommodate two molecules end-to-end along the Pt–Pt direction in a c-axis of only 13 Å, as would be required by the symmetry. The possible symmetries, positions of the platinum atoms, and corresponding Patterson peaks in an $hk0$ projection for the other stereochemical forms are as follows:

	Symmetry		Pt co-ordinates		Patterson Pt peaks
Form.	*Ibam*	*Iba*	*Ibam*	*Iba*	in projection
(II)	222	2	$0, 0, \frac{1}{4}$, etc. and $\frac{1}{2}, 0, \frac{1}{4}$, etc.	$00z$, etc. and $0, \frac{1}{2}, z'$, etc.	$0, \frac{1}{2}$; $\frac{1}{2}, 0$
(III)	—	2	—	xyz, etc.	$2x, 2y$; $2x, 0$; $0, 2y$
(V)	$2/m$	2	$x, y, 0$, etc.	xyz, etc.	$2x, 2y$; $2x, 0$; $0, 2y$
(VI)	—	2	—	xyz, etc.	$2x, 2y$; $2x, 0$; $0, 2y$

The Table shows that the location of the platinum peaks in an $(hk0)$ Patterson projection will discriminate between form (II) on the one hand and (III), (V), and (VI) on the other, but that further information will be necessary to distinguish between the last three.

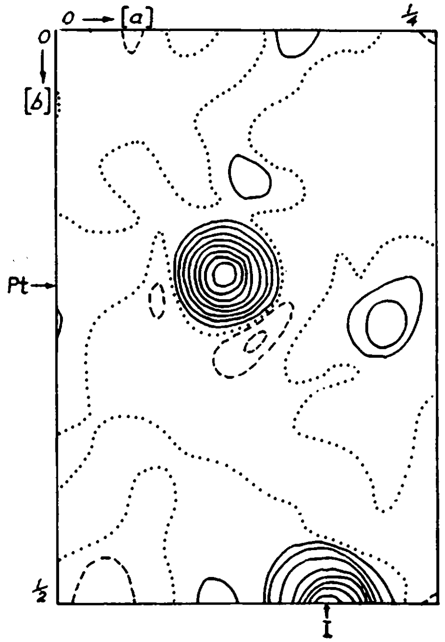

FIG. 1. *Electron density projection along [001], the contours are at 10e/Å² intervals, the zero contour is dotted.*

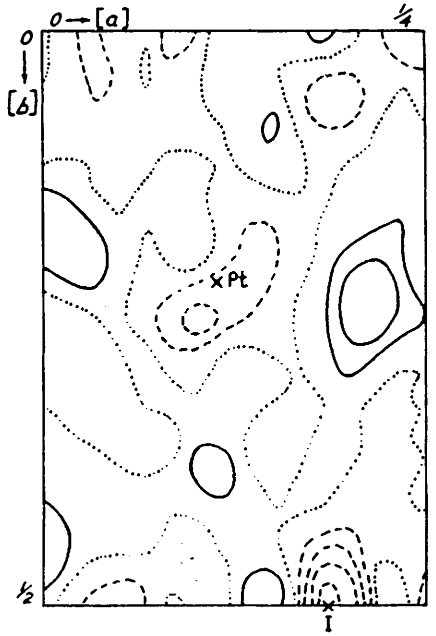

FIG. 2. *Electron density difference ($\rho_0 - \rho_c$) projected along [001], contours at 4e/Å², negative contours dashed, zero dotted.*

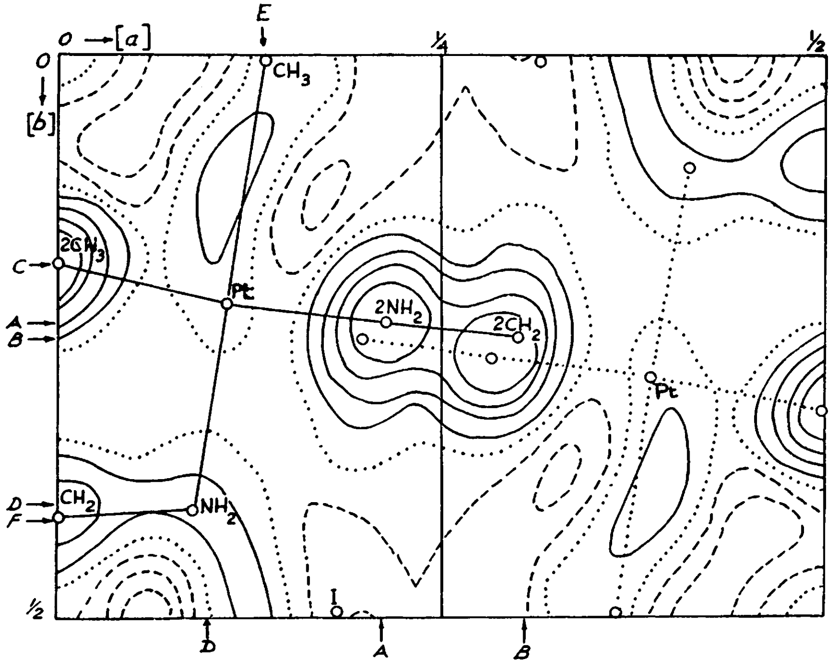

FIG. 3. *Electron density difference ($\rho_0 - \rho_c$) projected along [001] calculated from reflections with sin θ <0·5. Positive contours full lines, zero dotted lines, negative contours dashed lines, at arbitrary equal intervals.*

An $(hk0)$ Patterson projection was computed and gave a consistent set of Pt–Pt peaks at $0,2y$, $2x,0$, and $2x,2y$, with $x = 0{\cdot}110$, $y = 0{\cdot}215$, and Pt–I and I–I peaks corresponding to iodine atoms at $x = 0{\cdot}18$ and $y = 0{\cdot}50$. There are no peaks at $0,\frac{1}{2}$, so that the structure (II) can be eliminated. Discrimination between the other possibilities would be effected only by finding the carbon and nitrogen atoms and since it was hardly to be expected that these could be located from a Patterson synthesis, it was now necessary to compute Fourier syntheses, in the first instance on the assumption that the signs of all the terms were determined by the contributions of the platinum and the iodine atoms. Some structure factors were calculated from the co-ordinates given above, with the scattering factors for platinum and iodine from the International Tables multiplied by a temperature factor $\exp -B(\sin^2\theta)/\lambda^2$ with $B = 2{\cdot}0 \times 10^{-16}$ cm.^{2}; this value of B was obtained by Wilson's method.[4] Reasonable agreement with the observed structure factors was obtained, so the signs of all F's were calculated from the Patterson co-ordinates and used with the observed amplitudes to carry out a Fourier synthesis. The resulting projection of the electron density is shown in Fig. 1; the positions of the maxima are Pt at 0·112, 0·218, and I at 0·184, 0·500, the latter peak being due to the overlapping of two iodide ions at x,y,z and $x,y,\frac{1}{2} + z$, with y nearly $\frac{1}{2}$. The low density in the regions near 0,0 and $0,\frac{1}{2}$ indicates that a triple ethylenediamine bridge is unlikely while the high density at about $\frac{1}{4},\frac{1}{4}$ is consistent with a non-bridging chelate ethylenediamine so that although individual light atoms are not yet clearly shown this preliminary glimpse suggests configuration (V) or (VI).

In the hope of resolving the light atoms a difference synthesis (in which the coefficients were observed structure amplitudes minus amplitudes calculated for platinum and iodine only) was calculated, the signs being determined by the Pt and I co-ordinates from the Fourier map except that y_{I} was arbitrarily taken to be 0·490. The most important feature in the resulting $(\rho_0 - \rho_c)$ map (Fig. 2) is the negative region $(\rho_0 < \rho_c)$ round the iodine position; there is no trace of the positive peak to be expected if further removal from $y = \frac{1}{2}$ is required, and the explanation must be that the temperature factor of the iodine is too low; examination of Fig. 1 also shows an electron density for the superimposed iodide ions lower than that to be expected from a comparison with the platinum peak. Accordingly, for the subsequent calculations, the B factor for iodine was assumed to be 3·0; values of $B = 2{\cdot}0$ and $B = 3{\cdot}0$ for platinum and iodine respectively correspond to r.m.s. displacements of 0·16 and 0·195 Å, which are almost exactly in the ratio, 0·81, to be expected from the atomic masses.

Fig. 2, although still not showing the light atoms very clearly, indicates the need for small shifts of the platinum and iodine atoms, and the co-ordinates finally adopted were: Pt, $x = 0{\cdot}111$, $y = 0{\cdot}216$; I, $x = 0{\cdot}181$, $y = 0{\cdot}495$; the last co-ordinate was chosen after calculations by trial and error with the $(0k0)$ planes. The agreement index $R = \sum|F_0 - F_c|/\sum|F_0|$ at this stage was 0·20.

Although the value of R calculated for all planes was 0·20, that for planes with $\sin\theta < 0{\cdot}5$ was 0·25 and that for planes with $\sin\theta > 0{\cdot}5$ was 0·16, in complete contrast to the normal increase of R with $\sin\theta$. This was clearly due to the fact that the light atoms, not yet allowed for in the calculated F's, make a much larger contribution to the low-order than to high-order planes. Accordingly, an $(hk0)$ difference synthesis was calculated with F's for planes having $\sin\theta < 0{\cdot}5$ only, with the result (Fig. 3) that light atom peaks appeared clearly.

The large peaks A, B, and C evidently each represent more than one atom and it was assumed that A and B were due to non-bridging ethylenediamine molecules viewed edge-on in the projection as shown. In addition, after preliminary trials of other possibilities which gave less good agreement, C was taken to be two methyl groups attached to the same platinum atom, and overlapping in projection. If the platinum valencies were octahedral there should be atoms at approximately D and E, and of these evidently D is the nitrogen of the bridging ethylenediamine and F is the CH_2 of this bridge (the 2-fold axis of the molecule is thus at $0,\frac{1}{2},z$). With these assumptions and some adjustments of the atomic positions in detail the agreement index was reduced to $R = 0{\cdot}118$ for $(hk0)$ planes with

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[4] Wilson, *Acta Cryst.*, 1949, **2**, 318.

Comparison of observed and calculated structure factors.

hkl	$F_{obs.}$	$F_{calc.}$	*hkl*	$F_{obs.}$	$F_{calc.}$	*hkl*	$F_{obs.}$	$F_{calc.}$	*hkl*	$F_{obs.}$	$F_{calc.}$
000	—	(1624)	060	87	− 79	110	105	− 85	170	359	−381
200	196	−170	260	150	−125	310	266	270	370	394	420
400	496	−434	460	81	51	510	355	−368	570	167	144
600	55	83	660	251	274	710	62	76	970	239	−193
800	184	114	860	255	−203	910	234	257	11,7,0	147	−170
10,0,0	469	478	10,6,0	81	− 54	11,1,0	200	−218	13,7,0	299	298
12,0,0	159	− 88	12,6,0	134	132				15,7,0	134	124
14,0,0	302	−342				130	416	−454	17,7,0	159	−193
18,0,0	204	202	080	164	160	330	402	415			
			280	214	−227	530	80	− 69	190	164	170
020	334	−271	680	163	139	730	50	− 27	590	344	−366
220	206	−226	880	207	−223	930	139	−116	790	88	43
420	238	279				11,3,0	182	265	990	299	336
620	463	463	0,10,0	310	293	13,3,0	210	233	11,9,0	83	− 94
820	430	−504	4,10,0	182	−181	15,3,0	123	80	13,9,0	139	−124
10,2,0	230	−251	10,10,0	134	110	17,3,0	128	−201	15,9,0	74	− 55
12,2,0	283	282	14,10,0	155	−166				17,9,0	43	45
14,2,0	146	58				150	285	282			
18,2,0	178	−197	0,12,0	98	− 43	350	125	80	1,11,0	195	−180
			2,12,0	131	−109	550	498	−585	3,11,0	215	240
040	620	772	4,12,0	144	160	750	67	94	5,11,0	101	74
240	262	−259	6,12,0	155	170	950	420	498	9,11,0	115	− 82
440	293	−312	8,12,0	200	−212	11,5,0	81	− 94	13,11,0	130	165
640	125	104	10,12,0	94	− 62	13,5,0	166	−101			
10,4,0	259	276	12,12,0	92	92	15,5,0	101	− 47	5,13,0	150	−127
12,4,0	119	− 85				17,5,0	105	50	9,13,0	101	107
14,4,0	200	−251	0,14,0	250	233						
18,4,0	121	111	4,14,0	179	−185						

$\sin\theta < 0{\cdot}5$ and $R = 0{\cdot}143$ for all (*hk*0) planes. A table of observed and calculated structure) factors is given.) This very substantial improvement in R leaves no doubt as to the correctness of the assigned structure which is (VI), *i.e.*, one in which each platinum atom has *cis*-configuration of the attached C_3N_3. The final fractional co-ordinates are :

	Pt	I	2N (peak A)	2C (peak B)	2Me (peak C)	Me (peak E)	N (bridge)	C (bridge)
x	0·111	0·181	0·213	0·298	0·000	0·135	0·088	0·000
y	0·216	0·495	0·231	0·252	0·184	0·015	0·408	0·436

Owing to overlap in the projection the Pt–C and Pt–N distances cannot be considered to be very accurate, but their average value is 2·45 Å which is in agreement with accepted values. The Pt–Pt distance is 7·79 Å.

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