

Disorder in the Structure of Dibromodiammineplatinum (II) Tetrabromodiammineplatinum (IV)

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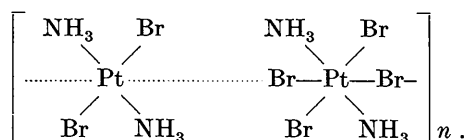
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The chain structure previously reported is confirmed, but disorder in the stacking of the chains has been observed.

Introduction

The compound previously described as $\text{Pt}(\text{NH}_3)_2\text{Br}_3$ has been shown by Brosset (1948) to have a chain structure along which square planar $\text{Pt}(\text{NH}_3)_2\text{Br}_2$ and octahedral $\text{Pt}(\text{NH}_3)_2\text{Br}_4$ groups alternate, thus



From the chemistry and other properties (Cohen & Davidson, 1951) it is rational to suppose that the two groups contain Pt(II) and Pt(IV) respectively, and that it is an addition compound correctly formulated as $\text{Pt}(\text{NH}_3)_2\text{Br}_2 \cdot \text{Pt}(\text{NH}_3)_2\text{Br}_4$. During a recent investigation of the pseudo-trivalent state in platinum we re-examined this compound, and observed a disorder effect not previously reported.

Previous work

Brosset's examination showed the crystals to be orthorhombic with cell dimensions

$$[a] = 16.36, [b] = 15.42, [c] = 11.06 \text{ \AA}$$

space group $Fddd$, and sixteen molecules of $\text{Pt}(\text{NH}_3)_2\text{Br}_3$ per unit cell. On rotation photographs taken about each of the major axes the odd layer lines were very faint; reflexions were observed on the even layer lines only when $h+k+l = 4n$. The structure is thus approximated by a body-centred subcell containing two molecules, which fact enabled the platinum atom sites to be deduced. Intensities were estimated (but not measured), and Fourier syntheses based on the signs of the platinum contributions gave the positions of the bromine and nitrogen atoms. The structure is shown diagrammatically in Fig. 1.

Experimental

The crystals for this examination were prepared by the same method used by Brosset, and were the same

bronze-coloured needles. Rotation photographs obtained were similar to those previously described, the spacing of the strong layer lines corresponding to subcell dimensions identical within the accuracy of measurement ($\pm 0.01 \text{ \AA}$). However, the odd layer lines from a crystal mounted about $[c]$ consisted not of discrete spots but of even, continuous streaks. On a stationary-crystal photograph the streaks were still continuous, but were somewhat uneven, giving a blotchy effect; Weissenberg photographs did not

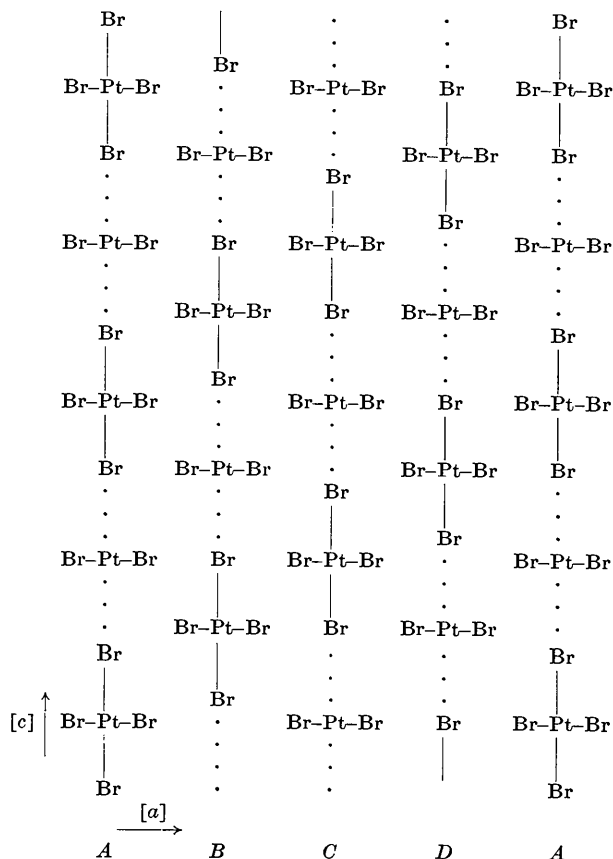


Fig. 1. Diagram of the structure as determined by Brosset. The chains A and B are at different heights along $[b]$. Two ammonia molecules are co-ordinated to every platinum atom, these coinciding with the platinum in this projection.

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resolve the streaks into row lines. Doubling of the $[a]$ and $[b]$ subcell-axes was not observed, even on very long exposures.

With a very small crystal and $\text{Cu } K\alpha$ radiation, zero-level Weissenberg photographs were taken about $[b]$ and $[c]$, using the multiple-film method. Intensities were measured visually, and the Lorentz and polarization corrections, and an approximate absorption correction (Sutor, Calvert & Llewellyn, 1954), were applied.

Discussion

The occurrence of normal even layer lines together with weak continuous odd layer lines shows that the structure is predominantly ordered, but that that component which causes the doubling of $[c]$ is ordered in this direction only. This suggests the existence in the structure of chains parallel to $[c]$, the disorder arising in their stacking, and it may be seen from Fig. 1 that such chains do exist in the structure proposed by Brosset. The principal interactions between the chains occur through the atoms of the co-ordination square normal to $[c]$, and as this is the same for all platinum atoms a stacking fault which arises from the translation of any chain by $\frac{1}{2}c$ will be only slightly less favourable energetically than the ideal structure. It is then reasonable to suppose that such faults will occur frequently, and thus lead to the above state of disorder.

Various ideal structures are possible, corresponding to the ambiguity in space group arising from the present inability to index the weak reflexions; there is no reason from the results of this work alone to assume that the $[a]$ and $[b]$ axes are doubled, as in Fig. 1. The calculation of the (001) Fourier projection is not affected by this ambiguity, i.e. the ordered and disordered structures are identical in this projection, and it is only necessary to assume centrosymmetry to deduce, following Brosset, that all amplitudes probably have positive sign. For the (010) projection a difference does arise. If the space group is $Fddd$ then $h0l$ is absent for h odd, l odd, i.e. the planes $h0l$ are not affected by the disorder, and the resulting projection is of the ordered structure. If, however, such chains as A and C in Fig. 1 are identical the space group is $Pmmn$, the $[a]$ and $[b]$ dimensions now being half those previously referred to. The apparent absence of $h0l$ for l odd is not a space-group requirement but the result of the disorder, and hence any projection based only on the strong reflexions is of the disordered structure. Using the present data, electron-density maps were obtained which were very similar to those published by Brosset,* except in the disordered projection, and the chain structure is thus confirmed. In the disordered projection the bromine atom (Br_1) which links the platinum atoms appeared not localized

* The differences are so small that it is not thought necessary to reproduce the new diagrams.

Table 1. *Observed and calculated amplitudes*

Planes are indexed with respect to the unit cell described by Brosset

Planes $hk0$				Planes $h0l$			
h	k	F_o	F_c	h	l	F_o	F_c
0	4	91	146	10	2	31	30
0	8	94	126	10	6	49	27
0	12	66	84	10	10	35	22
0	16	56	66	10	14	49	17
2	2	49	83	12	0	68	80
2	6	70	69	12	4	63	66
2	10	49	53	12	8	63	64
2	14	42	39	12	12	52	47
2	18	31	28	12	16	28	39
4	0	72	63	14	2	70	70
4	4	38	36	14	6	63	63
4	8	45	45	14	10	59	54
4	12	31	26	14	14	38	43
4	16	35	24	16	0	23	27
6	2	146	130	16	4	21	18
6	6	87	110	16	8	28	21
6	10	70	86	16	12	17	14
6	14	49	65	18	2	24	36
6	18	56	47	18	6	24	33
8	0	96	94	18	10	14	28
8	4	108	76	20	0	43	55
8	8	70	73	20	4	38	45
8	12	49	49				
8	16	59	42				

closer to one than the other, but as an elongated peak, symmetrically placed, its height only half that of the bromine of the coordination square (Br_2). The back-shift procedure (Booth, 1946) was applied to correct for series-termination errors. The coordinates of the atoms distinguishable in projection, with reference to the unit cell described by Brosset, are as follows:

Atom	x	y	z
Pt	0	0	0
Br_1	0	0	0.226
Br_2	0.150	0	0
N	0	0.125	0

Amplitudes were calculated using the atomic scattering factors listed in the *Internationale Tabellen* (1935), mean isotropic temperature factors of 1.7 and 2.2 \AA^2 being applied to the (001) and (010) projections

respectively. The observed and calculated amplitudes are listed in Table 1. Omitting the values for 220, 040 and 004, which were assumed to be affected by extinction, the reliability factors as normally defined are 0.18 for $hk0$ and 0.16 for $h0l$.

The bond lengths within the coordination square are $\text{Pt}-\text{Br}_1$ 2.45 Å, $\text{Pt}-\text{N}$ approximately 1.9 Å. Within the chain the $\text{Pt}-\text{Br}_2$ bonds are of length 2.50 and 3.03 Å, i.e. the bromine atom is attached to the closer platinum by a normal bond, but is also involved in a weak interaction with the more distant platinum atom. It should be noted that on neither projection did the peak corresponding to Br_2 show any elongation in the direction of the $\text{Pt}-\text{Br}$ bond as would be expected if the bonds in the square and octahedral complexes were markedly different in length. No diffuse streaking was detected on the even layer lines and, although this would have been more difficult to see than on the odd lines because of the heavier background, it may be concluded that the disorder is effectively restricted to the atom Br_1 . The non-equivalent coordinates listed in Brosset's paper, which lead to differing bond lengths in the groups, appear to have been chosen arbitrarily.

Numerous attempts were made to obtain more ordered crystals by modifying the crystallization procedure, but these were not successful. Similar disorder effects have been observed in other compounds of the same chemical and structural type, namely $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ (E. W. Hughes, private communication) and Wolfram's red salt, $\text{Pt}(\text{C}_2\text{H}_5\text{NH}_2)_4\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ (B. M. Craven & D. Hall, to be published).

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Crystal Structure of the Low-Temperature Form of Monoethylamine Hydrobromide

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The structure of *l.t.*- $\text{C}_2\text{H}_5\text{NH}_3\text{Br}$ has been determined by the heavy-atom method. The unit-cell dimensions are: $a = 8.361$, $b = 6.261$, $c = 4.630$ Å, $\beta = 93.0^\circ$. The space group is $P2_1/m$ and the two molecules in the unit cell lie in the mirror planes. The x and z parameters and the temperature factors of Br, N and C are refined by a modification of the difference-synthesis method. After application of a semi-empirical correction for secondary extinction, maxima in the electron density are found about the expected H positions. The final reliability index for ($h0l$) reflexions is 2.39%. An empirical scattering curve for Br is determined and found to be in good agreement with recent theoretical values by Thomas & Umeda.

1. Introduction

The complete crystal structures of the lower mono-*n*-alkylammonium halides are known, except for the monoethylammonium halides. $\text{C}_2\text{H}_5\text{NH}_3\text{Br}$ and $\text{C}_2\text{H}_5\text{NH}_3\text{I}$ exist in a low-temperature and a high-temperature modification; the transition temperatures are 92°C . and 55°C . respectively. For $\text{C}_2\text{H}_5\text{NH}_3\text{Cl}$ no transition was found below the melting point (96°C .).

Groth (1906) gives crystallographic data for *l.t.*- $\text{C}_2\text{H}_5\text{NH}_3\text{Br}$ (monoclinic; probably sphenoidic; $a:b:c = 1.3329:1.0:0.7413$; $\beta = 93^\circ 1'$; $D_m = 1.741 \text{ g.cm.}^{-3}$) and the isomorphous *l.t.*- $\text{C}_2\text{H}_5\text{NH}_3\text{I}$ ($a:b:c = 1.3096:1.0:0.7255$; $\beta = 92^\circ 6'$; $D_m = 2.100 \text{ g.cm.}^{-3}$). Hendricks (1928), who investigated these compounds by X-ray diffraction, found the following unit-cell dimensions (after a rearrangement of axes to conform to the usual conventions):

$\text{C}_2\text{H}_5\text{NH}_3\text{Br}$: $a = 8.32$, $b = 6.24$, $c = 4.63 \text{ kX.}$; $\beta = 93^\circ 1'$.
 $\text{C}_2\text{H}_5\text{NH}_3\text{I}$: $a = 8.68$, $b = 6.63$, $c = 4.81 \text{ kX.}$; $\beta = 92^\circ 6'$.

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