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The Crystal Structure of Tetraethylammonium Tetrabromo-$\mu\mu'$-Dibromoplatinum(II)

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The crystal structure of tetraethylammonium tetrabromo-$\mu\mu'$-dibromoplatinum(II)

$$[N(C_2H_5)_4]Pt_2Br_6$$

has been determined from three-dimensional data. The refinement by full-matrix least-squares computations has shown the halogen-bridged anion to be practically planar and structurally consistent with the use of $5d_{(x^2-y^2)}6s6p^2$ bonding orbitals by the platinum atom. The difference in terminal and bridged platinum–bromine bond lengths can be explained in terms of the ionic packing.

Introduction

In a previous communication (Harris, Livingstone & Stephenson, 1958), the alleged trivalent platinum ion $PtBr_3^-$ was shown to exist in solution and in the solid state as the halogen bridged anion $Pt_2Br_6^{2-}$. Interest lies in the relative lengths of the terminal and bridged platinum–bromine bonds, and the results are now reported of a three-dimensional crystal structure analysis of tetraethylammonium tetrabromo-$\mu\mu'$-dibromoplatinum(II), $[N(C_2H_5)_4]_2Pt_2Br_6$.

Crystal data

The crystals were small dark brown prisms obtained from nitrobenzene solution. The cell parameters were measured from Weissenberg photographs taken with Cu $K\alpha$ radiation and zero layer precession photographs taken with Mo $K\alpha$ radiation. The crystal density was measured by flotation in a mixture of methylene iodide and benzene.

$[N(C_2H_5)_4]_2Pt_2Br_6$, M.W. = 1129·7

Triclinic,

$$a=7{\cdot}60,\ b=8{\cdot}38,\ c=12{\cdot}34\ \text{Å}\,.$$
$$\alpha=105{\cdot}6^\circ,\ \beta=84{\cdot}0^\circ,\ \gamma=112{\cdot}8^\circ.$$
$$U=697{\cdot}6\ \text{Å}^3,\ D_m=2{\cdot}60,\ D_x=2{\cdot}66\ \text{g.cm}^{-3}\,.$$

$Z=1$, Space group $P\bar{1}$.

Experimental

The intensity data were recorded on multiple film equi-inclination Weissenberg photographs (Cu $K\alpha$), taken by rotation around [100], ($h=0, \ldots, 3$). The intensities of the reflections, which were estimated by eye, were correlated by means of $h0l$ data collected from zero level precession photographs taken with Mo $K\alpha$ radiation. No absorption corrections were made to the 1199 observed reflections.

The structure determination and refinement

The positions of the platinum and bromine atoms were obtained from $h0l$ and $0kl$ Patterson projections. These atomic coordinates were then refined by successive difference-Fourier electron density projections on the (100) and (010) planes. A three-dimensional difference Fourier synthesis was then computed with all observed reflections by assigning the phase angles of the platinum and bromine atom contributions and subtracting these structure factor contributions from the scaled data before summation. The resulting electron distribution revealed the approximate positions of the atoms in the tetraethylammonium ion.

A series of three cycles of differential syntheses and structure factors was computed, in which the carbon and nitrogen parameters were held constant and only the positional and isotropic thermal parameters of the heavy atoms were allowed to change. The atomic scattering factors used in the structure factor calculations were those of Thomas & Umeda (1957) for platinum and Thomas & Fermi (1935) for bromine, carbon and nitrogen. The dispersion corrections of Dauben & Templeton (1955) were applied to the atomic form factor for platinum. The reliability index was reduced from an initial $R=0{\cdot}24$ to 0·19.

At this stage, a refinement of the positional and isotropic thermal parameters of the lighter atoms was attempted with cycles of differential syntheses. This refinement was not successful because of the omission of off-diagonal terms, which are apparently quite appreciable. Very low values were obtained for the electron density curvatures of the light atoms (Table 1), and gave quite unreasonable atomic shifts of the order of 0·7 Å. This was particularly true for $A(HH)$ because data had been truncated along the a axis.

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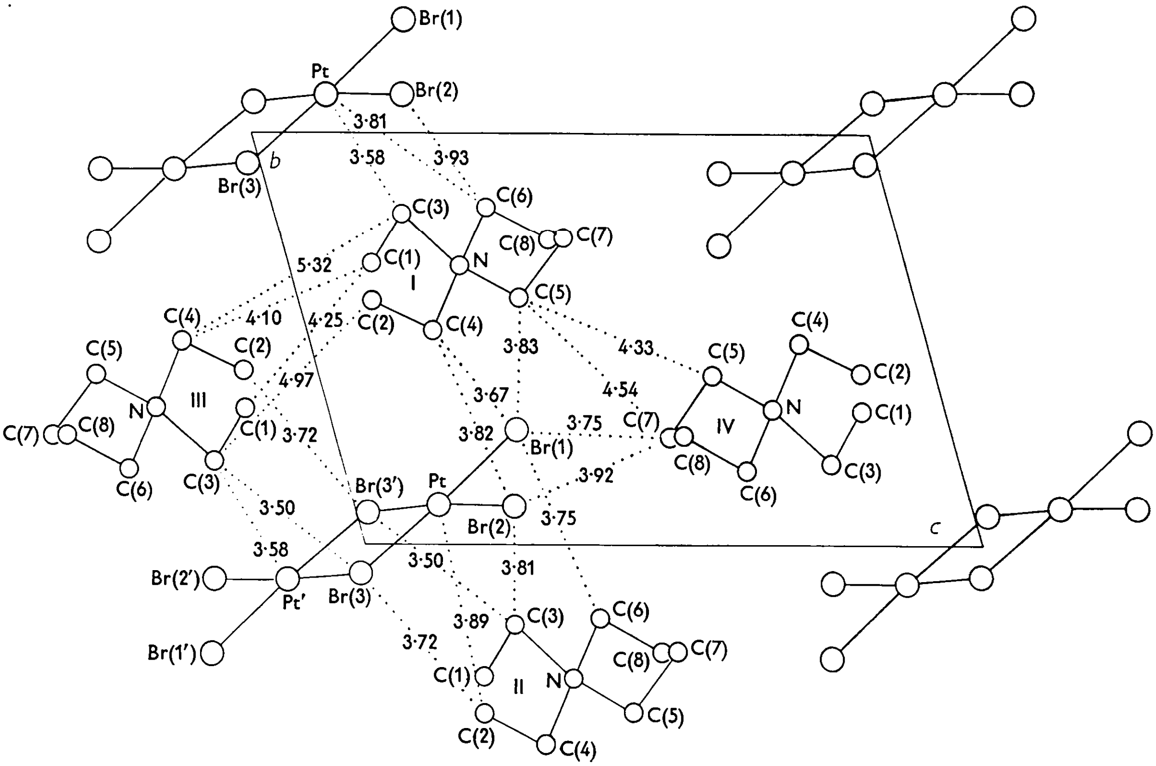

Fig. 1. Ionic packing in the crystal of tetraethylammonium tetrabromo-$\mu\mu'$-dibromoplatinum(II). Projection along the *a* axis showing interionic approach distances.

Molecule (I) x, y, z; (II) $-1+x, -1+y, z$; (III) $1-x, 1-y, -z$; (IV) $-x, 1-y, 1-z$

Table 1. *Atomic peak heights* (eÅ^{-3}) *and curvatures* (eÅ^{-5})

Atom		ϱ	$-A(HH)$	$-A(KK)$	$-A(LL)$	$A(HK)$	$A(KL)$	$A(HL)$
Pt	obs.	102·0	337	1046	1103	120	407	−29
	calc.	114·7	382	1107	1217	139	384	− 8
Br(1)	obs.	30·9	97	287	308	39	89	− 2
	calc.	36·9	124	333	378	42	110	− 3
Br(2)	obs.	30·7	111	283	303	40	89	−34
	calc.	34·5	128	291	348	45	98	−17
Br(3)	obs.	27·6	98	241	322	40	96	−25
	calc.	31·3	118	282	323	36	98	−15
N(1)	obs.	5·0	12	48	53	5	15	− 6
	calc.	4·5	14	47	37	7	15	2
C(1)	obs.	2·3	12	8	9	2	−5	−17
	calc.	1·6	2	13	1	2	−1	− 4
C(2)	obs.	3·8	13	17	37	4	12	1
	calc.	3·5	10	23	38	4	18	6
C(3)	obs.	1·5	4	23	12	7	1	4
	calc.	3·8	14	43	21	7	18	− 1
C(4)	obs.	3·6	4	31	30	7	20	7
	calc.	4·9	9	26	54	8	17	2
C(5)	obs.	3·8	4	36	19	7	18	16
	calc.	5·8	15	44	54	11	21	5
C(6)	obs.	2·9	11	31	2	3	14	7
	calc.	3·9	17	31	24	6	17	3
C(7)	obs.	4·1	1	22	30	6	7	3
	calc.	3·9	1	22	19	4	8	3
C(8)	obs.	3·0	6	5	15	3	7	5
	calc.	3·3	4	2	35	1	10	6

Table 2. *Atomic parameters and standard deviations*

Atom	x/a	y/b	z/c	B	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(B)$
Pt	0·0676	0·0977	0·1435	2·95 Å^2	0·0018 Å	0·0011 Å	0·0010 Å	0·06 Å^2
Br(1)	0·9454	0·2746	0·2976	4·15	0·006	0·004	0·004	0·09
Br(2)	0·3072	0·0946	0·2599	4·61	0·007	0·005	0·004	0·09
Br(3)	0·1775	0·9261	0·9809	4·86	0·008	0·005	0·005	0·10
N	0·5980	0·6730	0·2769	3·06	0·04	0·03	0·03	0·47
C(1)	0·4138	0·6750	0·1333	4·69	0·05	0·03	0·03	0·55
C(2)	0·8283	0·5859	0·1191	7·77	0·07	0·06	0·05	1·18
C(3)	0·6025	0·8023	0·2040	3·22	0·05	0·03	0·03	0·54
C(4)	0·7014	0·5167	0·2045	3·11	0·05	0·03	0·03	0·59
C(5)	0·4652	0·5920	0·3585	4·51	0·06	0·04	0·03	0·64
C(6)	0·7886	0·8164	0·3465	5·82	0·06	0·05	0·04	0·86
C(7)	0·3904	0·7428	0·4568	5·82	0·07	0·06	0·05	1·17
C(8)	0·8478	0·7349	0·4316	5·93	0·07	0·05	0·05	1·07

The trial structure did converge to the correct solution when a full-matrix least-squares treatment of data was used. Positional and isotropic thermal parameters for each atom were allowed to vary, and after two cycles the reliability index had been reduced to $R=0{\cdot}14$. The weighting scheme $w^2=(1+I^2.10^5)^{-1}$ was used.

A further cycle indicated only small adjustments in the parameters of the heavy atoms (about 0·3 σ) and shifts to the light atom parameters were generally less than the respective standard deviations. The final atomic parameters and standard deviations are listed in Table 2. Individual atomic scaling factors were kept constant during the least-squares refinement, and consequently the thermal parameters calculated for the bromine atoms are slightly high owing to the omission of a dispersion correction term to the atomic form factor for bromine. Table 3 lists some short intermolecular non-bonding approach distances: Table 4 contains an analysis of the planarity of platinum and bromine atoms within the anion: the distances and angles between atoms in the anion $Pt_2Br_6^{2-}$ are listed in Table 5 and illustrated in Fig. 2. Table 6 contains a comparison between bond lengths in the $Pt_2Br_6^{2-}$

Table 3. *Some short intermolecular non-bonding approaches*

Only those intermolecular approaches are listed which were less than the sums of the van der Waals radii as given by Pauling (1960); *i.e.* carbon (methyl group) 2·0 Å, bromine 1·95 Å, platinum 2·07 Å

	d	$\sigma(d)$
Pt(I)–C(2)(II)	3·89 Å	0·06 Å
–C(3)(II)	3·58	0·04
–C(6)(II)	3·81	0·05
Br(1)(I)–C(5)(I)	3·83	0·05
–C(7)(IV)	3·75	0·06
–C(6)(II)	3·75	0·05
Br(2)(I)–C(4)(I)	3·82	0·04
–C(5)(I)	3·74	0·05
–C(7)(IV)	3·92	0·06
–C(6)(II)	3·93	0·05
–C(3)(II)	3·81	0·04
–C(1)(II)	3·80	0·04
Br(3)(I)–C(2)(II)	3·72	0·06
–C(3)(III)	3·50	0·04

Molecule	
(I)	x, y, z
(II)	$-1+x, -1+y, z$
(III)	$1-x, 1-y, -z$
(IV)	$-x, 1-y, 1-z$

Table 4. *Analysis af the planarity of the* [*Pt*$_2$Br$_6$]$^{2-}$ *anion*

Deviations, Δ, from least-squares planes $AX+BY+CY=D$ referred to crystallographic axes

Best plane through		PtBr(1)Br(2)Br(3) Pt′Br(1′)Br(2′)Br(3′)†		PtBr(1)Br(2)Br(3) Br(3′)		Br(1)Br(2)Br(3) Br(3′)	
A		0·3054		0·2975		0·2975	
B		0·7222		0·7281		0·7281	
C		−0·4114		−0·4105		−0·4105	
D		0·000		0·0042		−0·0001	
Atom	$\sigma_\perp{}^* \times 10^3$	$\Delta \times 10^3$	$\Delta/\sigma_\perp$	$\Delta \times 10^3$	$\Delta/\sigma_\perp$	$\Delta \times 10^3$	$\Delta/\sigma_\perp$
Pt	1 Å	20 Å	20·0	18 Å	18·0	22 Å	
Br(1)	4	24	6·0	40	10·0	−44	−11·0
Br(2)	5	−34	− 6·8	−49	− 9·8	45	− 9·0
Br(3)	5	62	12·4	43	8·6	47	− 9·6
Pt′	1	−20	−20	−26		−22	
Br(1′)	4	−24	− 6·0	−48		−44	
Br(2′)	5	34	6·8	41		45	
Br(3′)	5	−62	−12·4	−52	−10·4	−47	− 9·4
$\Sigma(\Delta/\sigma_\perp)^2$			1272		702		383
X (99%)			20·1		15·1		13·3

* $\sigma_\perp=[A^2\sigma^2(X)+B^2\sigma^2(Y)+C^2\sigma^2(Z)]^{\frac{1}{2}}$.

† Related to unprimed atoms by centre of symmetry.

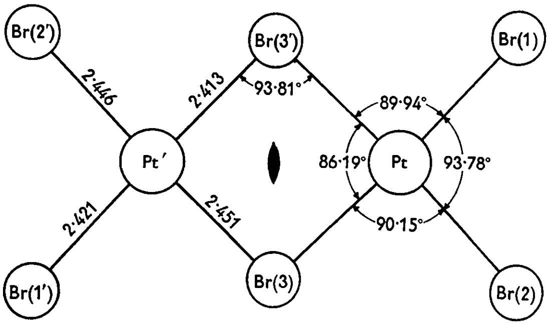

Fig. 2. Bond lengths and angles in the $Pt_2Br_6{}^{2-}$ anion.

Table 5. *Interatomic distances and angles in the anion* $Pt_2Br_6^{2-}$ *with standard deviations*

	a	$\sigma(d)$
Pt–Br(1)	$2{\cdot}42_1$ Å	0·005 Å
Pt–Br(2)	$2{\cdot}44_6$	0·006
Pt–Br(3)	$2{\cdot}41_3$	0·007
Pt–Br(3')	$2{\cdot}45_1$	0·007
Br(1) · · · Br(2)	$3{\cdot}55_4$	0·008
Br(2) · · · Br(3)	$3{\cdot}44_1$	0·008
Br(3) · · · Br(3')	$3{\cdot}32_3$	0·012
Br(3') · · · Br(1)	$3{\cdot}44_4$	0·008
Pt · · · Pt'	$3{\cdot}55_2$	0·002
	β	$\sigma(\beta)$
Br(1)–Pt–Br(2)	93·78°	0·19°
Br(2)–Pt–Br(3)	90·15	0·20
Br(3)–Pt–Br(3')	86·19	0·21
Br(1')–Pt–Br(3')	86·94	0·19
Pt–Br(3')–Pt'	93·81	0·09

Table 6. *A comparison between bond lengths in the* $Pt_2Br_6^{2-}$ *anion*

Bonds for comparison	Difference in bond lengths d	Standard deviation (σ) in d	d/σ
Br(1)–Pt, Pt–Br(2)	0·025 Å	0·010 Å	2·50
Br(1)–Pt, Pt–Br(3')	0·030	0·010	3·00
Pt–Br(2), Pt–Br(3)	0·033	0·011	3·00
Pt–Br(3), Pt–Br(3')	0·038	0·012	3·17

t (99%) 2·58

anion and Table 7[*] lists the final observed and calculated structure factors for comparison.

Discussion

The halogen-bridged anion is practically planar. The best least-squares planes through various atoms in the anion (Table 4) have been calculated following Schomaker, Waser, Marsh & Bergman (1959) with a diagonal weight matrix. The statistical analysis, χ^2 test (Weatherburn, 1947), of the significance of the distances from the planes, Δ, shows that they are highly significant for the calculated mean planes. These departures from planarity are probably due to different environmental factors affecting each bromine atom.

Although there is no significant difference between the angles Br(1)–Pt–Br(3') and Br(2)–Pt–Br(3) ($\Delta/\sigma = 0{\cdot}7$), the angle Br(1)–Pt–Br(2) involving the terminal bromine atoms is significantly greater than 90° ($\Delta/\sigma = 19$) and the angle subtended at the platinum atom by the two bridged bromine atoms is less than 90° ($\Delta/\sigma = 19$). This can be understood in terms of the repulsive forces operating between the negatively charged bromine atoms. The charge on the bridged bromine atoms will be slightly smaller than that on the terminal bromine atoms due to an increase in coordination. Increasing the coordination about the bridging bromine atoms is equivalent to a withdrawal of electrons from these atoms and hence an increased effective electronegativity. At the same time the net charge on the bromine atoms will become lower. The repulsive force between Br(1) and Br(2) (non-bonding approach 3·55 Å) is therefore greater than between Br(2) and Br(3) (non-bonding approach 3·44 Å) which in turn is greater than that between Br(3) and Br(3') (non-bonding approach 3·23 Å). This arrangement of angles between bonds to the transition metal agrees well with data obtained for the $Cu_2Cl_6^{2-}$ anion (Rundle, 1962). The disposition of the bromine atoms around platinum is consistent with the use of $5d_{(x^2-y^2)}6s6p^2$ bonding orbitals by the platinum atom.

Although there has been an increase in the effective electronegativities of the bridging halogen atoms there is the opposite effect with the transition metal. Electrons are transferred to platinum, and this decreases the positive charge as well as the effective electronegativity. The difference between the electronegativities of the transition metal and the halogen in the bridge is increased and an increase in bond length should occur. This is observed in the $Cu_2Cl_6^{2-}$ anion ($\Delta \simeq 0{\cdot}04$ Å) and also in Al_2Cl_6 ($\Delta = 0{\cdot}15$ Å), but is not found to be the case in the $Pt_2Br_6^{2-}$ anion. Each platinum–bromine bond in the bridge is equal in length to the *trans*-oriented terminal platinum–bromine bond and one such set of bond lengths is longer than the other.

Table 6 compares sets of Pt–Br bond lengths. The estimated standard deviation (σ) of the difference in bond lengths (d) was calculated with the use of the maximum value of the standard deviation in atomic coordinate ($\sigma(x)$) as an estimate of the standard deviation in positional coordinate of an atom. The situations in which two bonds were formed to one atom or where atoms in different bonds were related by a centre of symmetry, or a combination of both cases, were taken into account in the calculation of the

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[*] Table 7 has been deposited as Document number 7633 with the A.D.I. Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C., U.S.A. A copy may be secured by citing the Document number and by remitting \$6·25 for photoprints, or \$2·50 for 35 mm microfilm. Advance payment is required. Make cheques or money orders payable to: Chief, Photoduplication Service, Library of Congress.

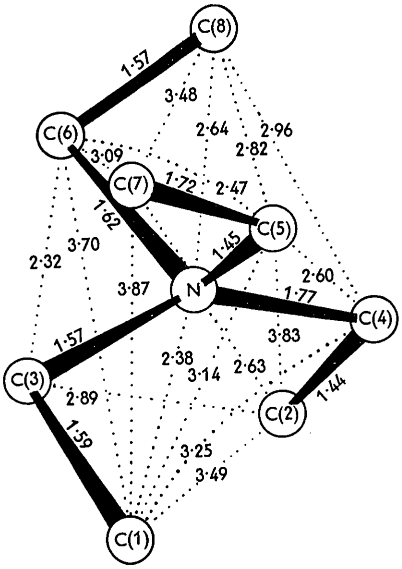

Fig. 3. Schematic depiction of the tetraethylammonium cation. The mean standard deviation in the distances shown is 0·08 Å.

standard deviation in *d*. The off-diagonal terms in the correlation matrix were neglected.

A possible explanation for the lengthening of the Pt–Br(3′) and Pt–Br(2) bonds is the close approach of the tetraethylammonium cation to the Pt–Br(3′) bond at atom C(3). Normal interionic approach distances of the order of 3·8 Å are observed (Table 3), except for this methylene group which approaches to 3·58 Å from the platinum atom and 3·50 Å from the bromine in the Pt–Br(3′) bond. The subsequent lengthening of this bond may result in a slight lengthening of the Pt–Br(2) bond distance since the $5d_{(x^2-y^2)}$ orbital which is directed toward the four bonded bromine atoms has a centre of symmetry.

The tetraethylammonium ion packs into a parallelepiped which is approximately 384 Å^3 in volume. It is bounded on one side by the plane whose equation with respect to the crystallographic axes is $0{\cdot}76x+0{\cdot}63y+0{\cdot}08z=4{\cdot}99$. The atomic coordinates (x, y, z) in this equation are actual values in Å. Atoms C(1), C(4), C(5) and C(7) lie practically in this plane whilst the atom in the cation which is furthermost from the plane is C(6), at a distance of 1·99 Å. Adding twice the van der Waals radius of a methyl group to this figure of 1·99 Å we obtain an estimate of 6 Å for the depth of the parallelepiped, whilst in each of the remaining two directions the cation extends approximately 8 Å. The distances between bonded and non-bonded atoms are shown in Fig. 3.

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