740. *The Preparation and Structure of Halogen-bridged Anionic Complexes of Bivalent Palladium and Platinum.*

By C. M. HARRIS, S. E. LIVINGSTONE, and N. C. STEPHENSON.

The halogen-bridged ions $[Pd_2X_6]^{2-}$ (X = Cl, Br, I) and $[Pt_2X_6]^{2-}$ (X = Br, I) have been isolated from solutions of corresponding tetrahalogeno-ions $[MX_4]^{2-}$ (M = Pd, Pt) as their quaternary ammonium or arsonium salts. *X*-Ray crystal analysis of the compound $[NEt_4]_2[Pt_2Br_6]$ has confirmed the existence of a discrete planar bromo-bridged anion $[Pt_2Br_6]^{2-}$. Cryoscopic ionic-weight measurements on $[NEt_4]_2[Pd_2Br_6]$ and $[AsPh_3Me]_2[Pd_2Cl_6]$ in nitrobenzene, and ebullioscopic measurements on the former in acetone, confirm the existence of the dimeric anions in solution.

NUMEROUS compounds containing $[MX]_4^{2-}$ ions (M = Pd, Pt; X = Cl, Br, I) have been reported.[1] Potassium chloropalladate(II) and chloroplatinate(II) have been shown to be isomorphous and to possess a square planar configuration of chlorine atoms about the metal atom.[2] Gutbier and Fellner,[3] as long ago as 1916, isolated a series of complex palladium(II) chlorides and bromides of organic bases, $[BH][PdX_3]$ (B = tri-*n*-propylamine, tri*iso*butylamine, guanidine, etc.; X = Cl, Br). Nothing has been reported about the structure of these compounds and they have been classed by Sidgwick[4] as examples

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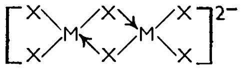
[1] Sidgwick, " The Chemical Elements and their Compounds," Clarendon Press, Oxford, 1950, pp. 1568, 1605.

[2] Dickinson, *J. Amer. Chem. Soc.*, 1922, **44**, 2404.

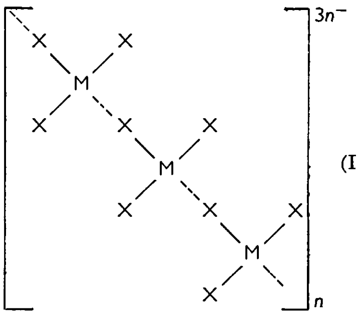
[3] Gutbier and Fellner, *Z. anorg. Chem.*, 1916, **95**, 169.

[4] Sidgwick, *op. cit.*, p. 1561.

of three-covalent palladium. Sundaram and Sandell [5] have recently examined spectrophotometrically the chloro-complexes of palladium present in solutions of palladium(II) perchlorate in M-perchloric acid, containing varying amounts of chloride. They have identified species containing palladium and chlorine atoms in the ratios 1 : 1; 1 : 2; 1 : 3; 1 : 4. The dissociation constants of the alleged species, $[PdCl]^+$, $PdCl_2$, $[PdCl_3]^-$, and $[PdCl_4]^{2-}$, have been recently determined [6] in dilute perchloric acid solution. Sundaram and Sandell observed a lowering of the extinction coefficient of the $[PdCl_4]^{2-}$ ion in perchloric acid on the addition of excess of chloride. Although they postulated the existence of higher complexes, $[PdCl_5]^{3-}$ and $[PdCl_6]^{4-}$, they did not succeed in establishing the composition of these higher complexes. Harris, Livingstone, and Reece [7] recently proved spectrophotometrically the existence of $[PdBr_6]^{4-}$ ions in nitrobenzene solutions of $[PdBr_4]^{2-}$ ions in the presence of an excess of bromide ions. The existence of other ionic species is possible but only one was identified.



(I) (M = Pd, Pt; X = Cl, Br, I)



(II)

The $[PdCl_3]^-$ ion, reported by Sundaram and Sandell to occur in solution, was earlier suggested by Gutbier and Fellner [3] as present in the chloro-compounds prepared by them. Although a tetragonal-distorted octahedral arrangement for palladium(II) has been described,[8] there are no cases in which the palladium(II) atom has been shown to have a co-ordination number less than four. Consequently, we investigated complexes containing the alleged $[PdX_3]^-$ ion and attempted to prepare the corresponding platinum compounds. If these compounds should be four-covalent there are at least two possibilities: a discrete dimeric halogen-bridged anion (I), and a polymeric chain-ion structure (II). The compound $CsCuCl_3$ has been shown by Wells [9] to contain structure (II), where the chains are arranged so as to give the copper atoms a distorted octahedral arrangement.

We have isolated the following new compounds: NMe_4PtI_3; NEt_4MX_3, where M = Pd, X = I, and M = Pt, X = Br, I; $NPhMe_3MI_3$, where M = Pd, Pt; $AsPh_3MePdCl_3$. The chloro- and the bromo-complexes were obtained by metathesis from aqueous solution of $[MX_4]^{2-}$ ions and the substituted ammonium or arsonium halide. The iodo-compounds were prepared by treating aqueous-alcoholic solutions of palladium(II) or platinum(II) iodide containing excess of sodium iodide with the appropriate substituted ammonium iodide.

A two dimensional *X*-ray structural determination has been carried out on a single crystal of the tetraethylammonium compound, NEt_4PtBr_3. The results show that there is no discrete $[PtBr_3]^-$ group in the solid state but the binuclear halogen-bridged anion, $[Pt_2Br_6]^{2-}$, with the dimensions listed on p. 3702. Within experimental error a distinction between a slightly distorted bridge and a completely symmetrical one is not possible. The average Pt–Br bond distances are $2{\cdot}43 \pm 0{\cdot}05$ Å. A refinement using three-dimensional data is in progress to ascertain any small real difference between terminal and

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[5] Sundaram and Sandell, *J. Amer. Chem. Soc.*, 1955, **77**, 855.

[6] Droll, Block, and Fernelius, Pennsylvania State Univ., 1956, Contract No. AT(3)—1—907.

[7] Harris, Livingstone, and Reece, *Austral. J. Chem.*, 1957, **10**, 282.

[8] Harris, Nyholm, and Stephenson, *Nature*, 1956, **177**, 1127.

[9] Wells, *J.*, 1947, 1662.

bridged bond lengths. The average Pt–Br bond distance, 2·43 Å, for all Pt–Br bonds in the molecule agrees, within experimental error, with the sum of the covalent radii (1·31 + 1·14 = 2·45 Å) of these elements.[10] This result is similar to that of Mann and Wells [11] for the bromo-bridged complex of palladium with trimethylarsine, $[Me_3AsPdBr_2]_2$. In this compound all the Pd–Br bond lengths were equivalent at 2·45 Å.

TABLE 1. *Molecular conductivities in nitrobenzene.*

Compound	Colour	Mol. conductance of 10^{-3}M-solutions at 25° (mho cm.$^{-2}$)
$[AsPh_3Me]_2[Pd_2Cl_6]$	Brownish-pink	53·7
$[NEt_4]_2[Pd_2Br_6]$	Brown	60·5
$[NEt_4]_2[Pd_2I_6]$	Black	60·6
$[NPhMe_3]_2[Pd_2I_6]$	Black	60·6
$[NEt_4]_2[Pt_2Br_6]$	Yellowish-brown	55·0
$[NMe_4]_2[Pt_2I_6]$	Yellowish-brown	63·5
$[NPhMe_3]_2[Pt_2I_6]$	Yellowish-brown	56·7
$[NEt_4]_2[Pt_2I_6]$	Yellowish-brown	58·6
$[AsPh_3Me]_2[PdCl_4]$	Pink	51·0
$[NEt_4]_2[PdBr_4]$	Pinkish-brown	60·5
$[AsPh_3Me]_2[PtCl_4]$	Pale pink	Insol.

Single crystals of the analogous palladium compound, which were suitable for the measurement of cell dimensions, could not be obtained. However, the powder photograph of this compound is similar to that of the platinum compound. It is reasonable to assume that all these compounds contain the $[M_2X_6]^{2-}$ anion.

Although many binuclear neutral complexes of bivalent palladium and platinum [12,13] and a cationic bridged complex of platinum(II) [13] have been reported, we know of no palladium or platinum complexes which have been previously shown to contain halogen-bridged anions. The compounds which were prepared in this investigation are listed in Table 1, along with their molecular conductivities in nitrobenzene. The iodo-compounds are interesting since few iodo-bridged complexes of these metals have been reported.[14]

The conductivities of these compounds containing the $[M_2X_6]^{2-}$ ion are comparable with those of di-univalent electrolytes in nitrobenzene. Some tetrahalogeno-complexes with the cations, $[AsPh_3Me]^+$ and $[NEt_4]^+$, were prepared for comparison; they are listed at the bottom of Table 1. The conductivities of these compounds are similar to those of the complexes containing the $[M_2X_6]^{2-}$ ion. We were unable to isolate pure triphenylmethylarsonium tetrachloro-$\mu\mu'$-dichloroplatinate(II), the compound being contaminated with the tetrachloroplatinate(II) derivative: since both products are insoluble, it was not possible to separate them.

Ionic-weight measurements were made (see Table 2) on the chloro- and the bromo-bridged compounds, $[AsPh_3Me]_2[Pd_2Cl_6]$ and $[NEt_4]_2[Pd_2Br_6]$, in order to determine whether the dimeric anions persist as such in solution. The determinations by Foss and Gibson [15] for a uni-bivalent gold complex, $[Au\ dipy\ Et_2]_2[Au_2Et_4(SO_4)_2]$ (dipy = 2 : 2′-dipyridyl), over a comparable concentration range are given for comparison. The mean van't Hoff factors obtained for $[AsPh_3Me]_2[Pd_2Cl_6]$ and $[NEt_4]_2[Pd_2Br_6]$ are comparable with those obtained for $[NEt_4]_2[PdBr_4]$ and Foss and Gibson's gold complex, indicating that the bridged ion is present in solution. If it were assumed that the compounds form a solvated $[MX_3]^-$ ion in solution, the van't Hoff factors, calculated on the monomeric formulæ, would be in the range 1·0—1·1. Measurements by Foss and Gibson [15] on some

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[10] Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, 2nd edn., 1945, p. 179.

[11] Mann and Wells, *J.*, 1938, 702.

[12] Jensen, *Z. anorg. Chem.*, 1935, **225**, 97; Mann, *Ann. Reports*, 1938, **35**, 148; Chatt and Mann, *J.*, 1939, 1622; Chatt, *J.*, 1950, 2301; 1951, 652; Chatt and Hart, *J.*, 1953, 2363; Livingstone and Plowman, *J. Proc. Roy. Soc. New South Wales*, 1950, **84**, 188; 1951, **85**, 116; Livingstone, *J.*, 1956, 1988.

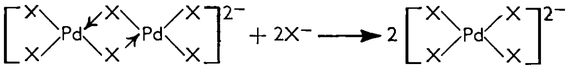
[13] *Idem, ibid.*, p. 1994.

[14] Cf., however, Mann and Purdie, *J.*, 1938, 883.

[15] Foss and Gibson, *J.*, 1949, 3063.

uni-univalent electrolytes in this concentration range give van't Hoff factors of the order of 1·8.

Treatment of $[AsPh_3Me]_2[Pd_2Cl_6]$ and $[NEt_4]_2[Pd_2Br_6]$ in acetone solution with triphenylmethylarsonium chloride and tetraethylammonium bromide, respectively, gives precipitates of the tetrahalogeno-compounds, $[AsPh_3Me]_2[PdCl_4]$ and $[NEt_4]_2[PdBr_4]$. This reaction involves the splitting of the dimeric bridged anions as shown thus:



Attempts were made to convert the bridged platinum complex, $[NEt_4]_2[Pt_2Br_6]$, into the tetrabromo-compound, $[NEt_4]_2[PtBr_4]$, in acetone, but only the original compound was recovered.

It is interesting that most of the bridged compounds were prepared from aqueous solution; this suggests that the bridged ion, $[M_2X_6]^{2-}$, is not decomposed by water.

TABLE 2. *Ionic-weight determinations.*

Compound	Method	Concn. range (%)	Mean obs. ionic wt.	M (theor.)	van't Hoff factor $\frac{M \text{ (theor.)}}{\text{Mean obs. ionic wt.}}$
$[AsPh_3Me]_2[Pd_2Cl_6]$	Cryoscop. in $PhNO_2$	0·13—0·69	490	1069	2·2
$[NEt_4]_2[Pd_2Br_6]$	Cryoscop. in $PhNO_2$	0·17—0·69	465	953	2·0
,,	Ebullioscop. in $COMe_2$	0·69—2·31	425	953	2·2
$[NEt_4]_2[PdBr_4]$	Cryoscop. in $PhNO_2$	0·26	295	686	2·3
$[Au\ dipy\ Et_2]_2[Au_2Et_4(SO_4)_2]$	Cryoscop. in $PhNO_2$	0·6—1·8	758	1524	2·0

EXPERIMENTAL

Triphenylmethylarsonium Tetrachloro-μμ'-dichlorodipalladate(II).—An aqueous solution of potassium tetrachloropalladate(II) (1·28 g.) was added to a solution of triphenylmethylarsonium chloride (2·84 g.) in water (20 ml.). The resulting pink precipitate was filtered off, washed with water, and recrystallised from 80% aqueous acetone (150 ml.) to give brownish-pink crystals of the pure *compound* (Found: C, 42·9; H, 3·4; Cl, 19·8; Pd, 20·0%; *M*, cryoscop. in $PhNO_2$: 0·13% solution, 440; 0·20%, 450; 0·30%, 480; 0·39%, 500; 0·55%, 550; 0·69%, 520 $C_{38}H_{36}As_2Cl_6Pd_2$ requires C, 42·7; H, 3·4; Cl, 19·9; Pd, 20·0%; *M*, 1069).

Tetraethylammonium Tetrabromo-μμ'-dibromodipalladate(II).—Potassium tetrabromopalladate(II) (3·0 g.) dissolved in water (50 ml.) was added to an aqueous solution of tetraethylammonium bromide (1·6 g.). The resulting precipitate was filtered off and recrystallised from 1 : 1 acetone–alcohol (100 ml.) as brown plates (1·8 g.) (Found: C, 20·4; H, 4·4; N, 2·7; Br, 49·5; Pd, 22·4%; *M*, cryoscop. in $PhNO_2$: 0·17% solution, 470; 0·39%, 470; 0·69%, 455; *M*, ebullioscop. in $COMe_2$: 0·69%, 380; 0·86%, 440; 1·35%, 380; 1·71%, 450; 2·31%, 470. Calc. for $C_{16}H_{40}N_2Br_6Pd_2$: C, 20·2; H, 4·2; N, 2·9; Br, 50·2; Pd, 22·4%; *M*, 953).

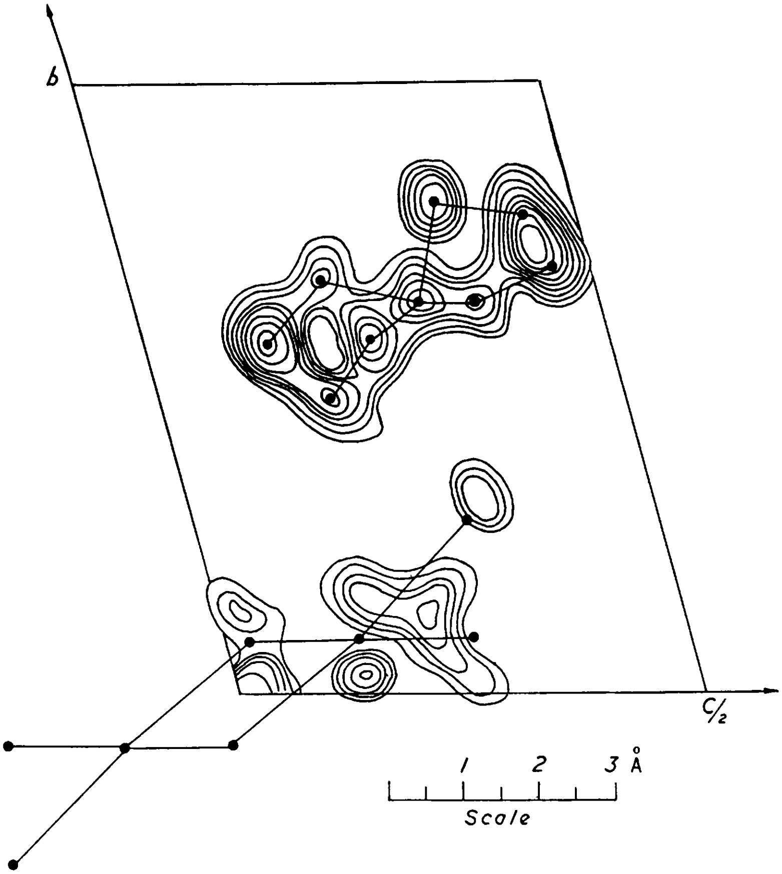
Tetraethylammonium Tetraiodo-μμ'-di-iododipalladate(II).—Palladium(II) iodide (0·40 g.) was dissolved in boiling ethanol (30 ml.) containing sodium iodide (1·5 g.). The filtered solution was added to tetraethylammonium iodide (0·7 g.) in boiling 90% ethanol (10 ml.). There was an immediate precipitate of black crystals of the *compound* which, after a few minutes, was filtered off, and washed with ethanol, followed by ether (yield, 0·64 g.) (Found: C, 15·6; H, 3·4; N, 2·4; Pd, 17·4. $C_{16}H_{40}N_2I_6Pd_2$ requires C, 15·6; H, 3·3; N, 2·3; Pd, 17·3%).

Trimethylphenylammonium Tetraiodo-μμ'-di-iododipalladate(II).—Palladium(II) iodide (1 g.) and sodium iodide (3 g.) were dissolved in hot ethanol (60 ml.) and treated with trimethylphenylammonium iodide (1·45 g.) in 90% ethanol (30 ml.). Crystals began to be deposited from the warm solution. The mixture was placed on the steam-bath for 30 min., cooled, and filtered, and the black crystals (1·35 g.) of the *compound* washed with a little alcohol (Found: N, 2·2; Pd, 17·1. $C_{18}H_{28}N_2I_6Pd_2$ requires N, 2·2; Pd, 17·1%).

Tetraethylammonium Tetrabromo-μμ'-dibromodiplatinate(II).—Potassium tetrachloroplatinate(II) (1 g.) was dissolved in water (20 ml.) containing sodium bromide (1 g.). This solution was added to tetraethylammonium bromide (1 g.) in water (8 ml.). After 3 hr. on the steam-bath, the mixture was filtered and the product (0·84 g.) washed with a little cold water and recrystallised from acetone (50 ml.), to give yellowish-brown plates (0·52 g.) of the *complex* (Found: C, 17·5; H, 3·5; N, 2·5; Br, 41·5; Pt, 35·2. $C_{16}H_{40}N_2Br_6Pt_2$ requires C, 17·0; H, 3·6; N, 2·5; Br, 42·4; Pt, 34·6%). Single crystals for *X*-ray examination were obtained by allowing a nitrobenzene solution to evaporate in air (Found: Pt, 35·1%).

Tetraethylammonium Tetraiodo-μμ′-di-iododiplatinate(II).—Platinum(II) iodide (0·5 g.) was dissolved in a boiling aqueous solution (25 ml.) of potassium iodide (5 g.). The filtered solution was added to tetraethylammonium iodide (1 g.) in water (15 ml.) at the b. p. Buff crystals of the *compound* were immediately precipitated; the product was filtered off and washed with water, followed by ethanol and ether (yield, 0·6 g.) (Found: C, 13·4; H, 2·9; N, 1·8; Pt, 27·9. $C_{16}H_{40}N_2I_6Pt_2$ requires C, 13·6; H, 2·9; N, 2·0; Pt, 27·9%).

First ($F_{obs.}$–$F_{calc.}$) *Fourier synthesis showing resolution of* NEt_4^+ *ion.* $F_{calc.}$ *from* Pt *and* Br *alone.*



(Contours = 1 eÅ^{-2}; *negative regions omitted.*)

Trimethylphenylammonium Tetraiodo-μμ′-di-iododiplatinate(II).—Prepared as for the analogous tetraethylammonium compound by using trimethylphenylammonium iodide (1 g.) (yield 0·8 g.), the *compound* was recrystallised from ethanol (600 ml.) (Found: C, 15·2; H, 2·1; N, 1·8; Pt, 27·4. $C_{18}H_{28}N_2I_6Pt_2$ requires C, 15·2; H, 2·0; N, 2·0; Pt, 27·4%).

Tetramethylammonium Tetraiodo-μμ′-di-iododiplatinate(II).—The yellowish-brown *compound* was prepared as for the analogous tetraethylammonium complex by using tetramethylammonium iodide (1 g.) (yield 0·3 g.) (Found: Pt, 30·0. $C_8H_{24}N_2I_6Pt_2$ requires Pt, 30·0%).

Triphenylmethylarsonium Tetrachloropalladate(II).—Triphenylmethylarsonium tetrachloro-μμ′-dichlorodipalladate(II) (0·52 g.), dissolved in hot acetone (200 ml.), was added to triphenylmethylarsonium chloride (2 g.) in boiling acetone (200 ml.) containing a few ml. of water. Pink crystals of the *complex* (0·84 g.) were slowly deposited (Found: C, 50·0; H, 4·2; Cl, 15·9; Pd, 12·0. $C_{38}H_{36}Cl_4As_2Pd$ requires C, 51·2; H, 4·1; Cl, 15·9; Pd, 12·0%).

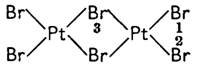
Tetraethylammonium Tetrabromopalladate(II).—This compound was prepared as described by Harris, Livingstone, and Reece [7] (Found: C, 27·8; H, 6·2; N, 3·9; Br, 46·5; Pd, 15·5. Calc. for $C_{16}H_{40}N_2Br_4Pd$: C, 28·0; H, 5·9; N, 4·1; Br, 46·5; Pd, 15·5%).

Triphenylmethylarsonium Tetrachloroplatinate(II).—A solution of potassium chloroplatinate-(II) (0·42 g.) in 2M-hydrochloric acid (30 ml.) was treated at the b. p. with an aqueous solution (20 ml.) of triphenylmethylarsonium chloride (0·75 g.). A pale pink precipitate was filtered off, washed with boiling 2N-hydrochloric acid, then acetone, and dried (yield, 0·9 g.). The *compound* is insoluble in water, acetone, and nitrobenzene (Found: C, 46·6; H, 3·6. $C_{28}H_{36}Cl_4As_2Pt$ requires C, 46·6; H, 3·7%).

Crystallographic Data.—A single crystal of tetraethylammonium tetrabromo-μμ′-dibromodiplatinate(II), obtained by slow evaporation from nitrobenzene, was investigated by *X*-ray diffraction methods. Buerger precession photographs, taken with the use of Mo characteristic radiation, showed the compound to have a triclinic unit cell with dimensions as follows: $a = 7{\cdot}60$, $b = 8{\cdot}38$, $c = 12{\cdot}34$ Å, $\alpha = 105° 35'$, $\beta = 84° 0'$, $\gamma = 112° 50'$ (all $\pm\frac{1}{2}\%$).

The structure analysis has proceeded satisfactorily on the assumption that the space group is $P\bar{1}$ and that the crystal has one unit of $[NEt_4]_2[Pt_2Br_6]$ per unit cell (calculated density = 2·66 g. cm.$^{-3}$; observed density = 2·60 g. cm.$^{-3}$).

The Patterson function, projected on planes 010 and 100, has been calculated. The centric Pt–Pt vector was readily recognised, and by suitable origin shifts the co-ordinates of the bromine atoms were obtained. The signs of all but the weakest of the $h0l$ and $0kl$ structure factors were uniquely determined from these co-ordinates. The refinement has proceeded by successive (F_{obs}–F_{calc}) Fourier synthesis (cf. Figure). Using Hartree atomic scattering factors and an isotropic temperature factor, determined by statistical methods, we have found the reliability indexes to be $R(h0l) = 0{\cdot}14$, $R(0kl) = 0{\cdot}13$.



The refinement of the structure has not yet been carried beyond the stage where bond lengths and angles involving the heavier atoms are established with standard deviations of about 0·03 Å and 2·5°. The following points concerning the stereochemistry of the anion are, however, well established: in the compound, $[NEt_4]_2[Pt_2Br_6]$, there exist discrete $[Pt_2Br_6]^{2-}$ anions which are separated from adjacent anions by distances not less than 6 Å. The $[Pt_2Br_6]^{2-}$ ion is planar and with a configuration as annexed.

The calculated bond angles and distances (Å) are:

Pt–Br$_1$	2·40	$\angle$Br$_3$–Pt–Br$_1$	87° 15′
Pt–Br$_2$	2·41	$\angle$Br$_1$–Pt–Br$_2$	95° 13′
Pt–Br$_3$	2·53	$\angle$Br$_2$–Pt–Br$_4$	87° 32′
Pt–Br$_4$	2·38	$\angle$Br$_4$–Pt–Br$_3$	90° 00′

Bromine atoms Br$_3$ and Br$_4$ are related by a centre of symmetry, and in the $0kl$ electron-density projection a small degree of overlap lends uncertainty to the y-parameters of these bridged bromine atoms. For this reason further three-dimensional refinement of the structure is in progress. From the above information, however, it can be seen, that the bridge deviates little, if any, from a regular square, and, within the present limits of experimental error, the terminal and bridged Pt–Br bond distances have a mean of 2·43 ± 0·05 Å.

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