An X-Ray Diffraction Study of the Structures of the Hexachloro- and Hexabromoplatinate(IV) Ions in Aqueous Solution

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The structures of the $PtCl_6^{2-}$ and $PtBr_6^{2-}$ complexes in aqueous solution were determined by means of X-ray diffraction measurements of concentrated solutions of hexachloro- and hexabromoplatinic acids. Analysis of X-ray scattering data showed that the $PtCl_6^{2-}$ and $PtBr_6^{2-}$ complexes have a regular octahedral symmetry. The interatomic distances within the complexes are: Pt–Cl, 2.33 Å; *cis*-Cl–Cl, 3.30 Å; *trans*-Cl–Cl, 4.66 Å; Pt–Br, 2.47 Å; *cis*-Br–Br, 3.50 Å; *trans*-Br–Br, 4.94 Å. These distances are in good agreement with those reported in crystals of hexahalogenoplatinate(IV) compounds.

It is well known that platinum(IV) has a coordination number of six and forms stable hexahalogeno complexes with halide ions, which have an octahedral symmetry in the solid state.[1-3] Results from infrared and Raman spectroscopic measurements suggested that hexahalogenoplatinate(IV) complexes have a regular octahedral configuration in aqueous solutions.[4]

Vaughan *et al.*[5] carried out X-ray scattering measurements of solutions of hexachloro- and hexabromoplatinic acids, and they concluded that the observed data are in accord with the octahedral model of these complexes and that the platinum–halogen distances within the complexes are 2.39 Å for Pt–Cl and 2.43 Å for Pt–Br. The former is *ca.* 0.06 Å longer than that in crystals and the latter is shorter by 0.03 Å. Moreover, the peaks which corresponded to the *trans*–halogen–halogen distances were not seen in their radial distribution curves.

In a previous work,[6] we found that the $AuCl_4^-$ and $AuBr_4^-$ complexes have a square planar symmetry and the gold–halogen distances within the complexes are 2.29 Å for Au–Cl and 2.43 Å for Au–Br, which are very similar to those in crystals.

This paper describes X-ray scattering measurements on concentrated solutions of hexachloro- and hexabromoplatinic acids and compares the values of interatomic interactions within these complexes with the results reported by Vaughan *et al.* in aqueous solutions[5] and those in crystals.[1-3]

Experimental

Preparation and Analysis of Sample Solutions. Sample solutions of hexachloro- and hexabromoplatinic acids were prepared by dissolving metallic platinum of 99.99% purity in solutions of hydrochloric and hydrobromic acids, respectively, containing nitric acid and by removing the nitric acid by repeated evaporation with the corresponding hydrohalogenic acids.

The content of platinum in the sample solutions was determined gravimetrically both by reduction of platinum(IV) to metal with formic acid and by ignition of precipitates of ammonium hexahalogenoplatinate(IV) to platinum metal.[7] The results of analysis obtained by the two procedures agreed each other within the error of 0.2%. The chloride- and bromide-ion concentrations were determined gravimetrically as AgCl and AgBr, respectively, after reduction of the platinum(IV) with formic acid. The hydrogen-ion concentrations were calculated from the relation $[H^+]=[X^-]-4[Pt^{4+}]$.

The density of the solutions was determined with a pycnometer.

Table 1. Compositions of the solutions (in g-atom/l)

	Hexachloroplatinic acid solution	Hexabromoplatinic acid solution
Pt	2.882	2.739
Br	—	17.11
Cl	18.57	—
O	36.89	34.75
H	80.81	75.64

The compositions of the sample solutions are given in Table 1.

Measurements and Treatment of X-Ray Diffraction Intensities. X-Ray scattering measurements were carried out with an X-ray diffractometer (JEOL Co., Tokyo) in a room thermostated at 25±1 °C according to procedures described in previous papers.[8,9] Mo$K\alpha$ radiation (λ=0.7107 Å) was used for the irradiation of the sample solutions. The slit-openings were 1/12°, 1/4°, and 1° over the scattering angle ranges of 2° to 12°, 6° to 30°, and 12° to 140°, respectively. The scattered intensities were measured at discrete points between the scattering angle 2θ=2° and 140°. The whole angle range was scanned twice in order to examine the reproducibility of the measured intensities. The intensities measured at the same angle usually agreed within 2%. The measured intensities $I(s)$, which were normalized to a common slit width, and then corrected for polarization in the solution and in the monochromator and scaled to electron units by means of the usual ways,[6,8,9] were used to calculate the reduced intensities $i(s)$ according to the following equation.

$$i(s) = I(s) - \sum_i n_i[(f_i(s)+\Delta f_i')^2 + (\Delta f_i'')^2 + \Phi(s)\cdot I_i^{\mathrm{inco}}(s)] \quad (1)$$

Here $s=4\pi\sin\theta/\lambda$, n_i represents the number of atom i, $f_i(s)$ the scattering factor of atom i at angle s, $\Delta f_i'$ and $\Delta f_i''$ the real and imaginary parts of the anomalous dispersion, respectively, $\Phi(s)$ the fraction of the incoherent radiation $I_i^{\mathrm{inco}}(s)$ reaching the counter.

All the calculations were referred to a stoichiometric volume of a solution containing one Pt atom.

The reduced intensities thus evaluated are shown in Fig. 1 in the form of $s\cdot i(s)$ *vs.* s.

The coherent and incoherent scattering factors for Pt were taken from Cromer and Waber[10] and from Cromer,[11] respectively. The values for anomalous dispersion of Pt were those given by Cromer and Lieberman,[12] which were corrected for the Breit-Dirac factors. The values for coherent, incoherent, and anomalous scatterings of other atoms were the same as those used in a previous paper.[6]

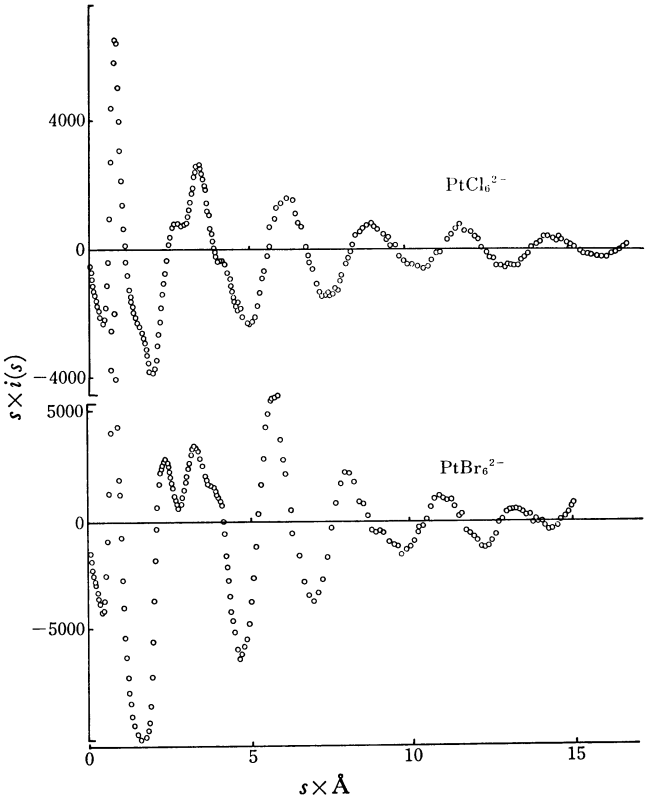

Fig. 1. Values $s\cdot i(s)$ for the chloride and bromide solutions as a function of s.

Results and Discussion

The radial distribution functions $D(r)$ were calculated from the reduced intensities $i(s)$ according to Eq. (2). The calculations were carried out with the aid of the computer program KURVLR.[13]

$$D(r) = 4\pi r^2\rho_0 + 2r\pi^{-1}\int_0^{s_{max}} s\cdot i(s)\cdot M(s)\cdot\sin(sr)ds \qquad (2)$$

Here ρ_0 denotes the average scattering density of the solution in electron units. The modification function $M(s)$ was chosen to be $(f_{Pt}^2(0)/f_{Pt}^2(s))\exp(-0.01\,s^2)$.

Spurious peaks below 1 Å in the distribution curves, which could not correspond to any interatomic distances, were used to correct the reduced intensities for low-frequency additions.

The radial distribution curves $D(r)$ for the two solutions thus calculated are shown in Fig. 2. Each distribution curve shows three peaks. The first dominant peak appeared at around 2.3 Å for the chloride solution and 2.5 Å for the bromide solution. These peaks can be identified as being due to Pt–Cl and Pt–Br distances within the complexes. The number of halide ions coordinated to a Pt(IV) ion was estimated to be about six both for the chloride and bromide solutions from the peak areas under the first peaks according to graphical procedures.[9] The second and third peaks appeared at around 3.3 Å ($\simeq$2.3 Å$\times\sqrt{2}$) and 4.6 Å ($\simeq$2.3 Å$\times$2) for the chloride solution, and at around 3.5 Å ($\simeq$2.5 Å$\times\sqrt{2}$) and 5 Å ($\simeq$2.5 Å$\times$2) for the bromide solution. These second and third peaks may be due to Cl–Cl and Br–Br contacts. The relation among the distances of

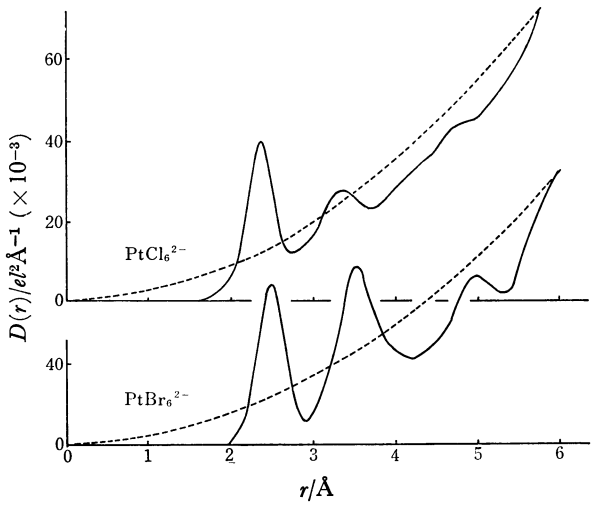

Fig. 2. Radial distribution curves for the chloride and bromide solutions. The brocken curves denote $4\pi r^2\rho_0$.

the three peaks in each $D(r)$ curve is that expected from a regular octahedral structure.

In order to refine the values for the structures of the complexes, analysis of the reduced intensity curve was carried out by means of a least squares method, in which a minimum was sought for the function $\sum s^2(i(s)-i_{calc}\cdot(s))^2$. Here, $i_{calc}(s)$ is the theoretical intensity due to interatomic interactions calculated from Eq. (3).

$$i_{calc}(s) = \sum_i\sum_j f_i(s)f_j(s)\frac{\sin(r_{ij}s)}{r_{ij}s}\exp(-b_{ij}s^2) \qquad (3)$$

where r_{ij} denotes the distance between two atoms i and j, $f_i(s)$ and $f_j(s)$ the scattering factor, and b_{ij} the temperature factor corresponding to the interaction between i and j atoms. For each interatomic interaction within the complexes the values of three parameters were refined: the distance r_{ij}, the temperature factor b_{ij}, and the frequency factor n_{ij}. For the refinement various subsets of the intensity data from different s ranges larger than 4 were used in order to detect errors in the refined parameters caused by a contribution to the intensity from the intermolecular interactions and experimental errors in the data. Two types of refinement (A and B) were carried out. In A type of refinement only the platinum–halogen bonds were included for $i_{calc}(s)$. The distance, the temperature factor, and the frequency factor were refined. In B type contacts for the platinum–halogen and the halogen–halogen at the *cis*-position were taken into account, and six parameters in all were changed simultaneously. The *trans*-halogen–halogen interactions were not included because of their small contributions to the intensities in the s ranges used for the calculations, as is seen from the theoretical intensities of interactions within the complexes in Fig. 3; the curves being calculated with the final parameter values in Table 3. Table 2 summarizes the results of the two types of refinement. As shown in Table 2 the number of the Pt–Cl and Pt–Br bonds per Pt atom does not differ from the value of 6 expected for the PtX_6^{2-} complex. The number of *cis*- Cl–Cl and Br–Br interactions (in B) was not definitely determined, but it is not so different from the expected value of 12 if the standard deviations are

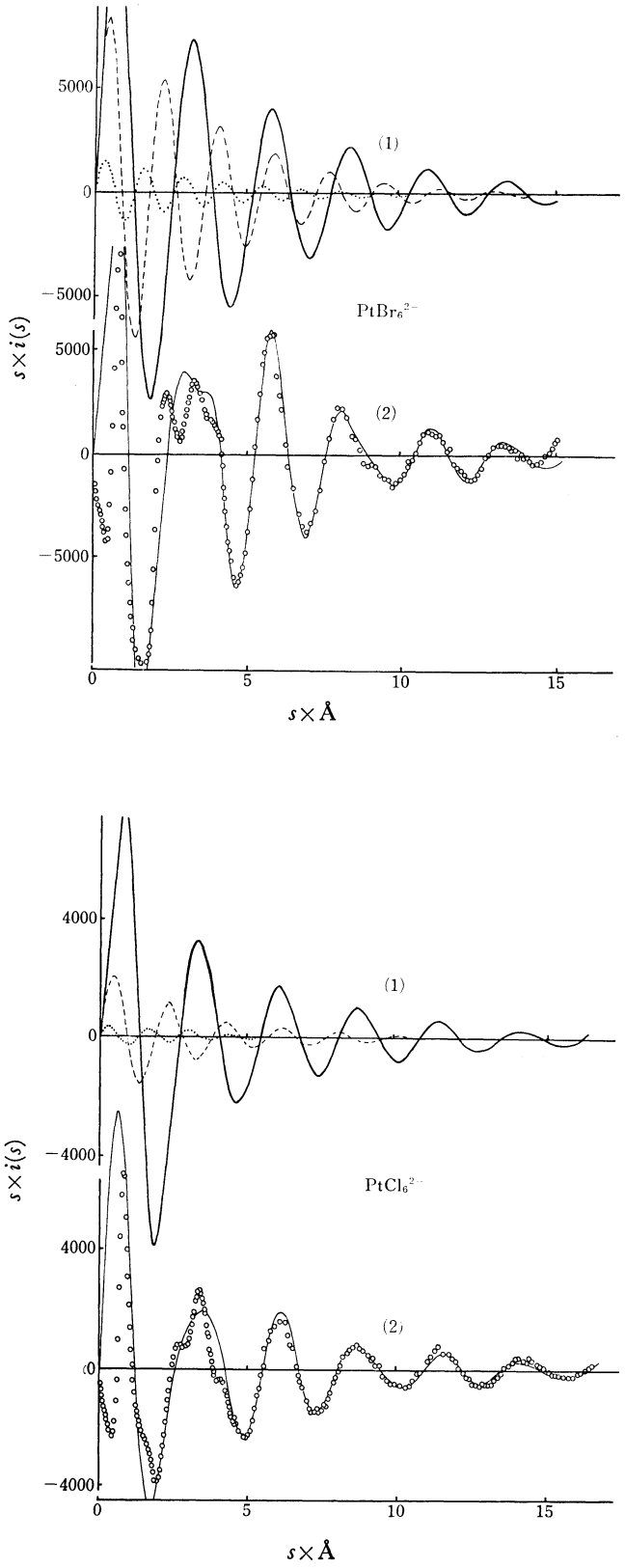

Fig. 3. Observed and calculated $s \cdot i(s)$ values for the chloride and bromide solutions.
(1) Calculated $s \cdot i(s)$ values for the interactions within the PtX_6^{2-} ions; Pt–X full drawn line, *cis*-X–X dashed line and *trans*-X–X dotted line.
(2) Comparison between observed $s \cdot i(s)$ values (circles) and calculated $s \cdot i(s)$ values (full line).

Table 2. Summary of the results of the least-squares refinements

	$PtCl_6^{2-}$	$PtBr_6^{2-}$
A	$r_{Pt-Cl}=2.332\,(5)$ Å	$r_{Pt-Br}=2.480\,(10)$ Å
	$b_{Pt-Cl}=0.0022\,(4)$ Å^2	$b_{Pt-Br}=0.0038\,(7)$ Å^2
	$n_{Pt-Cl}=6.0\,(4)$	$n_{Pt-Br}=6.1\,(4)$
B	$r_{Pt-Cl}=2.328\,(6)$ Å	$r_{Pt-Br}=2.474\,(7)$ Å
	$b_{Pt-Cl}=0.0015\,(4)$ Å^2	$b_{Pt-Br}=0.0033\,(5)$ Å^2
	$n_{Pt-Cl}=5.6\,(2)$	$n_{Pt-Br}=6.2\,(3)$
	$r_{cis-Cl-Cl}=3.30\,(4)$ Å	$r_{cis-Br-Br}=3.52\,(3)$ Å
	$b_{cis-Cl-Cl}=0.010\,(4)$ Å^2	$b_{cis-Br-Br}=0.0064\,(9)$ Å^2
	$n_{cis-Cl-Cl}=17\,(7)$	$n_{cis-Br-Br}=13\,(5)$

Numbers in the parentheses are least-squares standard deviations.

Table 3. Final parameter values for the hexachloro- and hexabromoplatinate (IV) ions

$PtCl_6^{2-}$	$PtBr_6^{2-}$
$r_{Pt-Cl}=2.33$ Å	$r_{Pt-Br}=2.47$ Å
$b_{Pt-Cl}=0.002$ Å^2	$b_{Pt-Br}=0.003$ Å^2
$n_{Pt-Cl}=6$	$n_{Pt-Br}=6$
$r_{cis-Cl-Cl}=3.30$ Å	$r_{cis-Br-Br}=3.49$ Å
$b_{cis-Cl-Cl}=0.010$ Å^2	$b_{cis-Br-Br}=0.006$ Å^2
$n_{cis-Cl-Cl}=12$	$n_{cis-Br-Br}=12$
$r_{trans-Cl-Cl}=4.66$ Å	$r_{trans-Br-Br}=4.94$ Å
$b_{trans-Cl-Cl}=0.015$ Å^2	$b_{trans-Br-Br}=0.015$ Å^2
$n_{trans-Cl-Cl}=3$	$n_{trans-Br-Br}=3$

taken into account. The ratio between the halogen–halogen and the platinum–halogen distances, which were refined independently in B, is about 1.42, which is close to the expected value of $\sqrt{2}$ for the regular octahedral configuration.

The final parameter values for the regular octahedral hexachloro- and hexabromoplatinate(IV) complexes are given in Table 3, in which the temperature factors for the halogen-halogen interactions at the *trans* position were roughly estimated from the corresponding peak shapes.

The intensities calculated by the use of the parameter values in Table 3 are compared with the observed ones in Fig. 3. It is seen that the agreement is satisfactory except at the low-angle part of the curves where the long range intermolecular interactions contribute significantly to the $s \cdot i(s)$ curves.

The theoretical peak shapes for intramolecular interactions were calculated by the use of the values in Table 3, and the peaks are compared with those of the radial distribution curves in Fig. 4. The residual curves obtained by subtraction of the calculated peaks from the radial distribution curves show two broad peaks at around 3.2 Å and 4.9 Å for the chloride solution and two distinct peaks at around 3.4 Å and 5 Å for the bromide solution. These peaks may be ascribed to the contacts between water molecules and halide ions unbonded and bonded to the platinum(IV) ions. In fact, the peak positions of 3.2 Å and 3.4 Å, respectively, are compatible with the distances of Cl–OH_2 and Br–OH_2 in the first hydration sphere so far reported.[14-15] The second peaks at 4.9 Å and 5 Å are in agreement with those found by

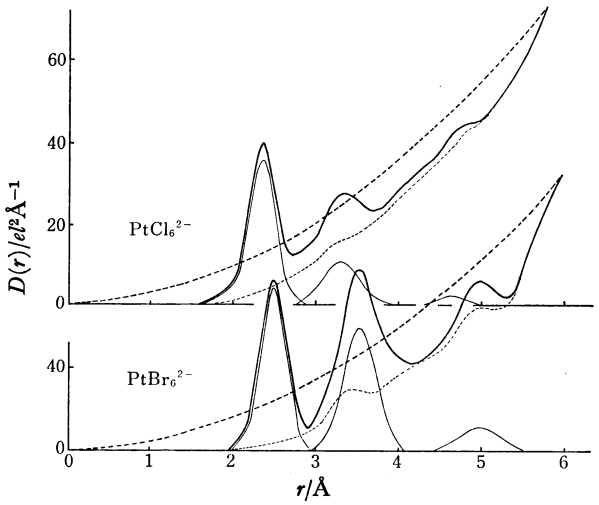

Fig. 4. Comparison between radial distribution curves and peak shapes calculated for the interactions within the PtX_6^{2-} ions using the parameter values given in Table 3. The difference between the distribution curve and the calculated peaks is shown by the dashed line.

Lawrence and Kruh in aqueous metal halide solutions.[14] They ascribed these peaks to the interactions of Cl–OH_2 and Br–OH_2 in the second hydration sphere. That the peaks for the chloride solutions are smaller than the corresponding ones for the bromide solutions is associated with the smaller scattering power of Cl than Br. No other marked peaks, which can be related to intramolecular interactions, are seen in the residual curves.

The Pt–Cl distance of 2.33 Å found in this work is shorter by 0.06 Å than that reported by Vaughan *et al.*[5] and is in good agreement with the average distance of 2.33 Å found in crystals of hexachloroplatinate (IV) compounds.[1,2] On the other hand, our Pt–Br distance of 2.47 Å is somewhat longer than that (2.43 Å) found by Vaughan *et al.* and our value agrees with the distance of 2.46 Å obtained in K_2PtBr_6 crystal.[3]

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