41. *The Chemistry of the Platinum Metals. Part II.* Fluoropalladates and Fluoroplatinates.*

By A. G. SHARPE.

The compounds K_2PdF_6, Rb_2PdF_6, Cs_2PdF_6, Rb_2PtF_6, and Cs_2PtF_6 are obtained by interaction of the corresponding complex chlorides and bromine trifluoride. The ions PdF_6^{2-} and PtF_6^{2-} are similar in size and magnetic properties, but PdF_6^{2-} differs from PtF_6^{2-} in being immediately hydrolysed by water. Rb_2PtF_6 and Cs_2PtF_6 are isomorphous with K_2PtF_6 and hence with K_2GeF_6; Cs_2PdF_6 has the K_2PtCl_6 structure. The occurrence of the K_2GeF_6 and K_2PtCl_6 structures among complex halides is discussed.

THE chemistry of potassium hexafluoroplatinate was described in some detail in Part I,* where evidence was presented to show that reactions of the PtF_6^{2-} ion with water and iodide ion are thermodynamically possible but extremely slow. It was also shown that bromine trifluoride converts palladium dichloride into the trifluoride, and potassium tetrachloropalladite into a complex fluoride which is rapidly decomposed by water. At that time, it was assumed that the complex would be a derivative of palladium trifluoride. No definite compound was obtained, however; and it has since become apparent that at the temperatures (200—280°) employed for the removal of bromine trifluoride from the complex, some decomposition had taken place.

Further investigation showed that if potassium tetrachloropalladite or hexachloropalladate is treated with bromine trifluoride and the product of the reaction is heated to constant weight at 150°, the pale yellow residue has the composition $K_2PdF_6,0{\cdot}1BrF_3$. This residue is diamagnetic, and therefore resembles potassium hexafluoroplatinate (Nyholm and Sharpe, *J.*, 1952, 3579) and potassium hexafluoronickelate, K_2NiF_6 (Hoppe, *Angew. Chem.*, 1950, **62**, 339). Rubidium and cæsium chloropalladates and bromine trifluoride yield, under similar conditions, the pure fluoropalladates Rb_2PdF_6 and Cs_2PdF_6. The fluoropalladates are immediately decomposed by water: $PdF_6^{2-} + 2H_2O = PdO_2 + 4H^+ + 6F^-$. Since palladium dioxide is not redissolved by hot concentrated hydrofluoric acid (though it is readily soluble in hydrochloric acid), the hydrolysis appears to be irreversible. The oxidation state of the palladium is shown to remain constant by the formation of potassium hexachloropalladate if the precipitated oxide is filtered off, dissolved in hydrochloric acid, and added to a solution of potassium chloride.

It is shown below that the PdF_6^{2-} and PtF_6^{2-} ions are of about equal size, and since the bond type in these ions (as deduced from their magnetic susceptibilities, which indicate that the 4*d* and 5*d* orbitals respectively are all full) is the same, comparison of their rates of reaction with water is of some interest in connection with theories of the mechanism of substitution in complex ions, a subject which has recently been extensively reviewed by Taube (*Chem. Reviews*, 1952, **50**, 69), who considered a series of complex ions in which the central atoms had the same charge and co-ordination number (six) and differed only slightly in size. Since, for replacement of fluorine or chlorine in the complex ions by water, the rates vary widely, he deduced that an electronic factor must be involved, and concluded that an empty *d* orbital in the outermost but one shell is usually associated with rapid substitution. For attack on PdF_6^{2-} or PtF_6^{2-} with co-ordination on to the central atom as the rate-determining step, steric and electronic factors should be the same for both ions; and even consideration of the known higher valencies of metals of the third transition series appears to favour substitution in the platinum-containing ion, provided that the mechanism of substitution in the two ions is the same. The experimental data appear to show that this last condition is not fulfilled, and that PdF_6^{2-} (and presumably also NiF_6^{2-}) hydrolyse by a mechanism different from that for PtF_6^{-2}. Dissociation of the complex ion, rather than substitution, may perhaps be the governing process for ions of high oxidation states such as Ni^{iv} and Pd^{iv}. It should be noted that the rate-determining step for hydrolysis of

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* *J.*, 1950, 3444, is considered Part I of this series.

the SiF_6^{2-} ion is the first-order process $SiF_6^{2-} \longrightarrow SiF_4 + 2F^-$ (Hudleston and Bassett, *J.*, 1921, **119**, 403; Rees and Hudleston, *J.*, 1936, 1334), and that substitutions such as $PtF_6^{2-} + 6I^- \longrightarrow PtI_6^{2-} + 6F^-$, which proceed at measurable speed only in the presence of hydrogen ions, have orders higher than unity. The speed of hydrolysis of PdF_6^{2-} unfortunately makes determination of the order of reaction almost impossible. This difference between PdF_6^{2-} and PtF_6^{2-} emphasizes the need for caution in classifying substitution processes until more is known of the mechanisms, as distinct from the rates, of such reactions.

The structure of potassium hexafluoroplatinate has recently been described by Mellor and Stephenson (*Austral. J. Sci. Res.*, 1951, **4**, *A*, 406): K_2PtF_6 is isomorphous with K_2GeF_6 (Hoard and Vincent, *J. Amer. Chem. Soc.*, 1939, **61**, 2849), the dimensions of the hexagonal unit cells being respectively $a = 5{\cdot}76$, $c = 4{\cdot}64$, and $a = 5{\cdot}62$, $c = 4{\cdot}65$ Å. The rubidium and cæsium salts have now been prepared by the action of bromine trifluoride on the chloroplatinates. A preliminary examination of their structures by the powder method indicates that both are isomorphous with K_2PtF_6: for Rb_2PtF_6, $a = 5{\cdot}96$, $c = 4{\cdot}83$ Å; for Cs_2PtF_6, $a = 6{\cdot}22$, $c = 5{\cdot}01$ Å. The structure of Rb_2PdF_6 has not been elucidated, but Cs_2PdF_6 is isomorphous with K_2PtCl_6, with $a = 9{\cdot}01$ Å. For Cs_2GeF_6, which also has this structure, Wyckoff and Müller (*Amer. J. Sci.*, 1927, **13**, 347) reported $a = 8{\cdot}99$ Å. From the lattice constants of K_2GeF_6, K_2PtF_6, Cs_2GeF_6, and Cs_2PdF_6 we may therefore reasonably conclude that the ions GeF_6^{2-}, PdF_6^{2-}, and PtF_6^{2-} are similar in shape and size.

In K_2GeF_6 (Hoard and Vincent, *loc. cit.*) each K^+ ion has nine F at 2·85 Å and three F at 3·01 Å: and the environment of the K^+ ions in the isomorphous K_2TiF_6 (Siegel, *Acta Cryst.*, 1952, **5**, 683) is also unsymmetrical. In Rb_2GeF_6 (which is also hexagonal) each Rb^+ ion has twelve almost equidistant F neighbours (Vincent and Hoard, *J. Amer. Chem. Soc.*, 1942, **64**, 1233); in Cs_2GeF_6 (cubic) the twelve Cs–F distances are, so far as is known, identical. This variation has been generally attributed to the relatively small size of the K^+ ion (see, *e.g.*, Wells, "Structural Inorganic Chemistry," Oxford, 1950), but this explanation ceases to be convincing when we recall that in K_2PtBr_6 the K^+ ion can have twelve much larger Br atoms as nearest neighbours. Furthermore, in the series K_2PtF_6, K_2PtCl_6, K_2PtBr_6, only the salt with the smallest anion is non-cubic, and, despite the closeness in unit cell dimensions of K_2PtF_6 and K_2GeF_6, Mellor and Stephenson attribute the structure of K_2PtF_6 to the relative smallness of the *anion*.

The relation of the K_2PtCl_6 structure to cubic close-packing is admirably discussed by Wells (*op. cit.*), who shows that K_2SiF_6 (which has this structure) may be described from the point of view of pure geometry as a lattice of cubic close-packed layers of suitably arranged halogen and alkali-metal atoms in numerical ratio of 3 : 1, with one half of the octahedral holes occupied by silicon atoms. Wells and Hoard and Vincent have also drawn attention to the fact that in K_2GeF_6 and Rb_2GeF_6 the packing of alkali-metal and fluorine atoms approximates to hexagonal close-packing. It is now suggested that in addition to the cubic K_2PtCl_6 structure for complex halides of general formula A_2BX_6 (where A is a large cation such as K, Rb, Cs, or NH_4) there is an ideal hexagonal structure in which the packing of the layers containing the A and X atoms is hexagonal (instead of cubic) close-packing. There is, of course, no reason why there should not be some deviation from the ideal structure, such as is found in K_2GeF_6 and K_2TiF_6; but it is suggested that such deviations are comparatively unimportant. If this hypothesis is accepted, there should be little difference in energy between the cubic and hexagonal structures, and the significance of their distribution should be something like that of the distribution of cubic and hexagonal close-packing in the structures of metals.

In spite of the much greater ionic radius of cæsium, K_2PtF_6 and Cs_2PtF_6 are isomorphous; Cs_2PdF_6 and Cs_2PtF_6 are not isomorphous, although the octahedral radii of Pd^{IV} and Pt^{IV} are equal; in the series K_2SiF_6 (dimorphic, cubic, or hexagonal), K_2GeF_6 (hexagonal), K_2PtF_6 (hexagonal), K_2PtCl_6 (cubic), there is no regular variation in structure with increasing anion size. These facts are quite incapable of simple explanation based solely on radius ratio effects, but present no difficulty if we accept the possibility of two ideal structures differing only slightly in energy content, and in which the co-ordination numbers of the atoms are identical.

Hitherto, the K_2GeF_6 structure for complex salts A_2BX_6 has been identified by *X*-ray methods only in one form of $(NH_4)_2SiF_6$ (Gossner and Kraus, *Z. Krist.*, 1934, **88**, 223), $(NH_4)_2GeF_6$ (Hoard and Vincent, *loc. cit.*), Cs_2PuCl_6 (Zachariasen, *Acta Cryst.*, 1948, **1**, 268), and the compounds mentioned above. A systematic search should, however, reveal that it is much more common than has formerly been supposed; the results of such a search will be reported in a later communication.

EXPERIMENTAL

Reaction involving bromine trifluoride and analyses of palladium and platinum compounds were carried out by methods described or referred to in Part I.

Hexafluoropalladates.—The sparingly soluble hexachloropalladates of potassium, rubidium, and cæsium were made by warming solutions of the tetrachloropalladites with sodium chlorate and hydrochloric acid. The complex chlorides were treated with bromine trifluoride, and the reaction products were heated to constant weight at 150°.

Rubidium and cæsium hexafluoropalladates were thus obtained free from chlorine or bromine, but attempts to obtain the potassium salt free from bromine were unsuccessful; heating above 200° produced decomposition (Found, for Rb salt: Pd, 28·0; F, 28·0. Rb_2PdF_6 requires Pd, 27·4; F, 29·1%. Found, for Cs salt: Pd, 21·7; F, 23·8. Cs_2PdF_6 requires Pd, 21·9; F, 23·4%. Found, for K salt: Pd, 34·5; F, 37·9; Br, 2·5. Calc. for K_2PdF_6: Pd, 35·7; F, 38·2%; Br, nil). The analytical data given for the potassium salt (typical of several preparations) correspond with an approximate composition $K_2PdF_6,0{\cdot}1BrF_3$, indicating slight solvolysis; the instability of the fluoropalladates unfortunately precludes further purification.

The three hexafluoropalladates are all pale yellow salts soluble in hot, sparingly soluble in cold, bromine trifluoride. They are immediately hydrolysed by cold water, and rapidly turn brown on exposure to the atmosphere. Treatment with concentrated hydrochloric acid at once produces the hexachloropalladates. The magnetic susceptibility of the (slightly impure) potassium salt at 20° is $-0{\cdot}23 \times 10^{-6}$ c.g.s. units.

X-Ray powder photographs were taken with Cu-K_α radiation; samples were filled into Pyrex capillaries by using the " dry box " technique, and the capillaries were at once sealed off with warm picein wax. All of the lines on the photograph of the cæsium salt could be indexed on the basis of a face-centred cubic unit cell with $a = 9{\cdot}01$ Å. The relative intensities of the lines (visually estimated) corresponded with those on the powder pattern of a sample of Cs_2PdCl_6 [Found: $a = 10{\cdot}17$ Å. Ketelaar and van Walsem (*Rec. Trav. chim.*, 1938, **57**, 964) give $a = 10{\cdot}16$ Å] in which fluorine is replaced by another relatively light element; Cs_2PdF_6 and Cs_2PdCl_6 are therefore isomorphous. The powder pattern of the rubidium salt could not be indexed.

Hexafluoroplatinates.—*Rubidium* and *cæsium hexafluoroplatinates* were made by interaction of the chloroplatinates and bromine trifluoride, followed by heating of the residue at 200°. The pale yellow, very sparingly soluble salts were recrystallised from water (Found, for Rb salt: Pt, 40·0. Rb_2PtF_6 requires Pt, 40·7%. Found, for Cs salt: Pt, 34·4. Cs_2PtF_6 requires Pt, 34·4%). Reactions of these salts with potassium iodide and with hydrochloric acid are exactly like those of the potassium salt, described in Part I.

X-Ray powder photographs of the potassium, rubidium, and cæsium salts showed similar patterns, all of which could be indexed on the basis of hexagonal unit cells. For K_2PtF_6, values $a = 5{\cdot}76$, $c = 4{\cdot}64$ Å were found, in agreement with Mellor and Stephenson: cell constants for Rb_2PtF_6 and Cs_2PtF_6 are quoted above.

Grateful acknowledgment is made to Professor R. S. Nyholm for a determination of magnetic susceptibility, and to Messrs. Johnson, Matthey, and Company, Limited, for the loan of compounds of palladium and platinum.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.

[*Received, October 2nd*, **1952**.]