

119. *Complex Fluorides of Quadrivalent Osmium and Iridium and the Corresponding Free Acids.*

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Complex fluorides of osmium and iridium, $M^I_2M^{IV}F_6$, where M^I is NH_4 , Me_4N , or Na , and aqueous solutions of the corresponding fluoro-acids H_2OsF_6 and H_2IrF_6 were prepared. The lattice constants and some other properties of several of the compounds are given.

THE method of obtaining complexes of quadrivalent osmium and iridium used¹ to prepare the hexafluoro-osmates(v) and -iridates(v) and, from them by reaction with water, the corresponding hexafluoro-osmates(iv) and -iridates(iv), readily yields the sparingly soluble salts of the higher alkali metals but fails for cations whose salts are rather soluble (*e.g.*, sodium) or of which the corresponding quinquevalent complex has not been obtained (*e.g.*, ammonium, tetramethylammonium). Salts of these cations can be conveniently prepared from the appropriate free acid.

The marked resistance of the hexafluoroplatinates(iv) to hydrolysis noted by Sharpe² has been used by Clarke and Perros³ to isolate the free crystalline acid by ion exchange. A similar stability of hexafluoro-iridates(iv) and -osmates(iv) in aqueous solution allows solutions of their free acids to be prepared by ion exchange, but does not permit the isolation of the crystalline acid; all attempts to evaporate the aqueous solution resulted in decomposition. Conductivity data for hexafluoroiridic acid show that the plot of Λ against \sqrt{c} is linear below 0.0015M, and that it is an acid comparable in strength with other strong dibasic fluoro-acids of this type; this also accords with the low solubilities of its higher alkali-metal salts.

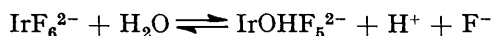
The very high equivalent conductance of the acid at infinite dilution ($\Lambda_0 = 580$

¹ Hepworth, Robinson, and Westland, *J.*, 1954, 4268.

² Sharpe, *J.*, 1950, 3444.

³ Clarke and Perros, *J. Amer. Chem. Soc.*, 1953, **75**, 5734.

ohm⁻¹ cm.²) which, if it were behaving as a dibasic acid, would represent the palpably incorrect ion conductance, λ_0^- , of 230 ohm⁻¹ cm.² for the $\frac{1}{2}\text{IrF}_6^{2-}$ anion, indicates progressive hydrolysis of the original anion. The potentiometric titration of the acid with sodium hydroxide gives a pH curve typical of a mixture containing both a strong and a weak acid. Thus the apparent basicity of the acid is raised, and when this approaches 3 the apparent ion conductance of the anion would be about the value observed. It is suggested that on dilution the hexafluoroiridate(IV) ion dissociates:



Aqueous solutions of hexafluoro-platinic, -iridic and -osmic acids are yellow, but are distinguishable by their absorption spectra. Thus the hexafluoroplatinate(IV) ion has two absorption peaks of comparable intensity (279 m μ and 318 m μ ³); the hexafluoroiridate(IV) ion a strong peak at 213 m μ and a much weaker one at 316 m μ ; and the hexafluoro-osmate(IV) ion a strong peak below 200 m μ and a very weak one at 308 m μ , so we deduced that the hexafluororhenate(IV) ion would not absorb above 200 m μ ; this has been confirmed by use of caesium hexafluororhenate, Cs₂ReF₆.

Unit-cell dimensions of the M₂PtF₆,⁴ M₂IrF₆, M₂OsF₆, and M₂ReF₆⁵ series (Å).

	Na ₂	K ₂	(NH ₄) ₂	Rb ₂	Cs ₂	(Me ₄ N) ₂
PtF ₆ ²⁻ hexagonal	<i>a</i> = 9.41, <i>c</i> = 5.16	<i>a</i> = 5.76, <i>c</i> = 4.64	—	<i>a</i> = 5.96, <i>c</i> = 4.83	<i>a</i> = 6.22, <i>c</i> = 5.01	—
IrF ₆ ²⁻ hexagonal	<i>a</i> = 9.34, <i>c</i> = 5.14	<i>a</i> = 5.80, <i>c</i> = 4.63	<i>a</i> = 5.98, <i>c</i> = 4.79	<i>a</i> = 5.97, <i>c</i> = 4.79	<i>a</i> = 6.24, <i>c</i> = 5.00	—
OsF ₆ ²⁻ hexagonal	—	<i>a</i> = 5.80, <i>c</i> = 4.62	—	—	<i>a</i> = 6.26, <i>c</i> = 5.00	<i>a</i> = 11.41
ReF ₆ ²⁻ hexagonal	—	<i>a</i> = 5.86, <i>c</i> = 4.60	<i>a</i> = 6.06, <i>c</i> = 4.77	<i>a</i> = 6.01, <i>c</i> = 4.77	<i>a</i> = 6.32, <i>c</i> = 4.99	—

Crystallographically, the salts of the hexafluoro-iridate(IV) and -osmate(IV) ions closely resemble those of other hexafluoro-(IV)-acids; the unit-cell sizes for some alkali-metal and ammonium salts are shown in the Table, for comparison with those of the hexafluoroplatinate(IV) and hexafluororhenate(IV) series.

The potassium, rubidium, and caesium salts are all of the hexagonal K₂GeF₆ type,⁶ but sodium hexafluoroiridate(IV) is isostructural with a series of sodium and lithium salts which includes sodium hexafluoroplatinate(IV).⁷

Caesium hexafluoroiridate(IV) is paramagnetic with $\mu = 1.42$ B.M., much lower than the calculated value of 1.73 B.M. required for the presence of one unpaired electron. This depression is peculiar, especially in light of the much better agreement with the theoretical value found in those hexachloroiridates(IV) which have been examined; thus in (NH₄)₂IrCl₆, $\mu = 1.67$ and in K₂IrCl₆, $\mu = 1.65$ B.M.⁸

EXPERIMENTAL

Preparation of the Free Acids.—(a) *Hexafluoroiridic.* Sodium hexafluoroiridate(V), prepared as described previously,¹ was treated with distilled water and, when reaction was complete, the solution was passed at the rate of 2—3 ml./min. through a 1.5 × 40 cm. column of Zeo-Karb 225 resin in the hydrogen form. The column was eluted with water until the eluate ceased to be yellow and acid to litmus. After dilution to a known volume, the concentration of the acid

⁴ Sharpe, *J.*, 1953, 197.

⁵ Peacock, personal communication.

⁶ Cox and Sharpe, *J.*, 1953, 1783.

⁷ Cox, *J.*, 1954, 3251.

⁸ Mellor, *J. Proc. Roy. Soc. New South Wales*, 1943, 77, 150.

in the solution was determined by evaporating an aliquot portion to dryness in a platinum dish and weighing the iridium metal produced after reduction in hydrogen.

Attempts were made to isolate the crystalline acid by (1) evaporation of the solution in a vacuum over sodium hydroxide pellets, and (2) slow evaporation in a Polythene vessel at room temperature with added hydrofluoric acid; both yielded only violet-red iridium(IV) oxide.

(b) *Hexafluoro-osmic*. An aqueous solution of this acid was made similarly from potassium hexafluoro-osmate(IV), but again the acid could not be isolated.

Potassium, Rubidium, and Cesium Hexafluoro-osmates(IV) and -iridates(IV).—These salts were prepared directly from the corresponding quinquevalent derivatives as described previously.¹ Approximate solubilities of K_2IrF_6 and Cs_2IrF_6 were obtained by measuring the concentration of their saturated aqueous solutions at room temperature (Found: K_2IrF_6 , 1.2 g./100 ml. of solution; Cs_2IrF_6 , 0.7 g./100 ml. of solution).

Sodium, Ammonium, and Tetramethylammonium Hexafluoroiridates(IV).—The calculated quantity of aqueous 0.05N-sodium hydroxide required to neutralise 20 ml. of a solution of hexafluoroiridic acid was slowly added to the latter with stirring to avoid local concentration of the alkali and thereby to minimise hydrolysis. Any suspended matter was filtered off and the filtrate evaporated to dryness in a vacuum over sodium hydroxide pellets. The residue, an almost white powder, consisted of *sodium hexafluoroiridate(IV)* (Found: Ir, 54.9; F, 32.8. Na_2IrF_6 requires Ir, 54.7; F, 32.3%). By proceeding exactly analogously and neutralising with the appropriate hydroxide, the corresponding *ammonium* and *tetramethylammonium salts* were obtained, the first as a pale violet powder and the second as large well-formed yellow cubes {Found: Ir, 56.0; F, 33.8. $(NH_4)_2IrF_6$ requires Ir, 56.3; F, 33.2%. Found: Ir, 42.0; F, 24.1. $[(CH_3)_4N]_2IrF_6$ requires Ir, 42.5; F, 25.0%}.

All these salts were readily soluble in water and easily hydrolysed in alkali. The ammonium salt was heated in a vacuum through a rising range of temperature; it decomposed suddenly at 220°, with visible volatilisation of ammonium fluoride, and left a black residue; X-ray examination revealed this to be iridium metal entirely free from any iridium trifluoride.

Absorption Spectra and X-Ray Photographs.—Ultraviolet absorption spectra of both series of salts were measured on a Model S.P. 500 Unicam spectrophotometer at 200–350 m μ with matched 1 cm. cells. Measurements were made on solutions of the free acids and their salts covering a range of concentrations; Beer's law was obeyed.

Specimens for X-ray photographs were packed in thin-walled (0.5 mm.) Pyrex glass capillaries. A 19 cm. camera, provided with iron radiation rendered monochromatic by lithium fluoride, was used.

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