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THE CHEMISTRY OF PROTACTINIUM—VII

THE FLUORO-COMPLEXES

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Abstract—Ion-exchange and conductimetric titration experiments suggest the existence of the PaF_8^{3-} anion. Pure samples of K_2PaF_7 and Na_3PaF_8 have been prepared and analysed. The salt $KPaF_6$ has been made, but a completely pure product could not be obtained from solution. Some observations have been made on the I.R. and n.m.r. spectra of the three complexes. Using an electrochemical method a preliminary set of values for the successive complexing constants k_{1-8} for the protactinium fluoro-complexes has been obtained.

THE first, and until recently the only, compound of protactinium that had been characterized by analysis was potassium fluoprotactinate (V), K_2PaF_7. GROSSE determined the potassium and protactinium contents of this substance by gravimetric analysis.[1,2] Ammonium[3] and barium[4] complex fluorides have also been reported, but no formulae or analytical data have been given. More recently an infra-red and Raman study of solutions of protactinium (V) fluoride indicated that complex fluoro-anions other than PaF_7^{2-} exist and X-ray crystallographic data and analyses suggested that a mixture of K_2PaF_7 and $KPaF_6$ had been obtained.[5] It has also been reported that salts of the series $MPaF_6$ ($M = K^+$, Rb^+ or NH_4^+) can be obtained by dissolving the oxide Pa_2O_5 in 48 per cent hydrofluoric acid, adding the calculated amount of MF and slowly evaporating the solution.[6] Even the simpler fluorides of Pa(V) have not been completely characterized, but the preparation and crystallographic properties of PaF_5, $PaF_5 \cdot 2H_2O$ and Pa_2OF_8 have recently been described.[7]

There is, however, a large body of information on the behaviour of solutions of the fluoprotactinate anions.[8] They are indeed perhaps the only relatively simple protactinium species that are thermodynamically stable with respect to hydrolysis at moderate pH values. By analogy with tantalum one would expect that $[PaF_5 \cdot H_2O]$,

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(1) A. V. GROSSE, *J. Amer. Chem. Soc.* **56**, 2501 (1934).
(2) A. V. GROSSE, *Proc. Roy. Soc.* A **150**, 363 (1935).
(3) H. E. ZAVIZZIANO, *C.R. Acad. Sci., Paris* **202**, 1053 (1936).
(4) J. GOLDEN and A. G. MADDOCK (Pt. I.), *J. Inorg. Nucl. Chem.* **2**, 46 (1956).
(5) O. L. KELLER, v. report on Gatlinburg Symposium on Protactinium Chemistry April 1963, Rapporteur C. J. Hardy A.E.R.E.-R 4382, 1963. p. 9.
(6) L. B. ASPREY and R. A. PENNEMAN, *Science*, N.Y. **145**, 924 (1964).
(7) L. STEIN, *Inorg. Chem.* **3**, 995 (1964).
(8) D. BROWN and A. G. MADDOCK, *Quart Rev.* **17**, 289 (1963).

$[PaF_6^-]$, $[PaF_8^{2-}]$ and $[PaF_\alpha^{3-}]$ might all exist in solution and the interesting questions are the values of the successive complexing constants and, especially, for which further fluoride ion is there a sharp decrease in complexing constant.

In this paper we shall present details of some observations on these complex fluorides made over the last ten years. Some of the results have been summarized elsewhere.[8]

EXPERIMENTAL

Materials

A.R. reagents were used except as specified.

Tetramethylammonium fluoride. Tetramethylammonium bromide was purified by the method of LANZA and ZAMBON[9] and a solution titrated with a solution of silver fluoride, prepared by the dissolution of silver oxide in hydrofluoric acid. The silver bromide was separated by centrifugation and the solution concentrated by evaporation in a platinum dish.

Protactinium purification. The starting material was the crude product from the solvent extraction process described previously.[10] Further purification using the same solvent extraction cycle was found unsatisfactory because of the high iron content of ordinary preparations of aluminium chloride. MOORE and REYNOLDS[11] have used oxalic acid for stripping and previous work in this laboratory has confirmed the suitability of this reagent.[12] The protactinium chlorocomplex was extracted into di-isobutyl ketone and the organic extract stripped with 0·7 M oxalic acid. Less than 0·1 per cent of the protactinium remained in the organic phase and the aqueous extract appeared quite stable. On making the oxalic extract 9 M in hydrochloric acid the protactinium could be re-extracted into the ketone with an extraction coefficient of forty-nine. It was, however, necessary to allow ten minutes for equilibrium to be established in this extraction. Three cycles using oxalic acid stripping were followed by evaporation with sulphuric acid to fuming, dilution and precipitation of the peroxide. The peroxide was dissolved in hydrochloric acid and purified by two stages of anion exchange as described in a previous publication[13] and finally converted to K_2PaF_7.

Another sample was purified by reduction and precipitation of the insoluble PaF_4, using the method of BOUISSIÈRES and HAISSINSKY.[14] The final products were all better than 99% pure compounds.

Measurements of activity

Once fairly recently purified protactinium compounds were available, extensive use was made of a scintillation counter and single channel analyser, set to span the 280–320 KeV region. The arrangement was very satisfactory for rough comparisons of the protactinium contents of samples. Where a more precise determination of the protactinium was desired and where decay products might well comprise a substantial fraction of the total α-activity, as for example in estimating the solubility of different compounds, the following procedure was used. The total α-activity was measured with a thin sample using a scintillation counter, whose efficiency was determined from time to time using a standard α-source. The total α-activity was now corrected for the protactinium fraction by measuring the alpha spectrum using a gridded Frisch ionization chamber attached to a multichannel analyser.[15]

Analyses

Protactinium. The weighed fluorocomplex was dissolved by heating in a few ml of 4 M nitric acid in a platinum dish. The solution was transferred to a polythene centrifuge tube and the protactinium

[9] P. LANZA and L. ZAMBRA, *Contribute Teorici e Sperimentali de Polarografia. Suppl. Ricerca Scientifica*, **8**, 35 (1956).

[10] A. G. GOBLE, J. GOLDEN, A. G. MADDOCK and D. J. TOMS, *Progress in Nuclear Energy, Series III. Process Chemistry* Vol. 2. p. 86. Pergamon, London (1958).

[11] F. L. MOORE and S. A. REYNOLDS, *Analyt. Chem.* **29**, 1596 (1957).

[12] A. T. CASEY and A. G. MADDOCK (Pt. V) *J. Inorg. Nucl. Chem.* **10**, 289 (1959).

[13] J. S. NAIRN, D. A. COLLINS, H. A. C. MCKAY and A. G. MADDOCK, *The Proceedings of the Second International Conference on the Peaceful Use of Atomic Energy, Geneva*, A/Conf. 15/1458. United Nations (1958).

[14] G. BOUISSIÈRES and M. HAISSINSKY, *Bull. Soc. Chim., France* **18**, 557 (1954).

[15] K. M. GLOVER and F. J. G. ROGERS, AERE/R 2971, (1959).

precipitated as hydroxide by the addition of an excess of 9 M ammonium hydroxide. The mixture was allowed to stand overnight to complete precipitation and the protactinium α-activity of the supernatant was found to have fallen to less than 0·05 γ Pa/ml. The precipitated hydroxide was separated, washed with ammonium hydroxide and finally dilute ammonium nitrate solution and finally ignited to constant weight at 800°C in a platinum micro-crucible.

Fluoride. If the alkali metal content was to be determined, the supernatant and combined washings from the above determination were made up to 50 ml and an aliquot of 20 ml taken, otherwise the whole of the supernatant and washings were used. The solution was made just alkaline to bromophenol blue with nitric acid and 1 ml of 10 per cent sodium chloride and 2 ml of 2 M hydrochloric acid added and the volume adjusted to about 75 ml. After addition of 1·67 g lead nitrate and a similar quantity of sodium acetate the mixture was digested on the steam bath for ½ hr and then left overnight. The precipitated PbClF was separated on a micro-filter stick and washed first with saturated PbClF solution and finally with a little ice water, and dried at 120°C to constant weight.

Alkali metal. The residual supernatant was now evaporated slowly in a weighed platinum crucible with sulphuric acid. Finally excess acid was fumed off and the residue heated to dull redness. After cooling the alkali sulphate was weighed.

Infrared spectra

Measurements were made using Nujol mulls between potassium bromide disks. Spectra were recorded partly using a Perkin–Elmer 521 grating spectrometer and partly with a Hilger SP 800 5. n.m.r. Measurements were made with a Varian V4300B at 40 Mc/sec. using CF_3COOH as external standard. Chemical shifts are referred to $\delta F_2 = 0$.

Electrochemical measurements

Conductimetric titrations. A known quantity of protactinium was freshly precipitated as hydroxide, separated and washed and suspended in water in a polythene cell. The cell was fitted with a magnetic stirrer and platinized platinum electrodes. The hydrofluoric acid was added from a polythene burette, made in the laboratory and controlled by a rubber teat. The cell was connected in one arm of a bridge supplied with 1000 c/s and fitted for oscilloscopic detection of the null point.

Potentiometric measurements. A five decade vernier potentiometer was used with a sensitive mirror galvanometer. Solutions were prepared containing the requisite concentrations of perchloric acid, sodium perchlorate and sodium fluoride to give the desired initial pH, $[F^-]$ and constant ionic strength of 1. The solutions were handled entirely in polythene vessels. Ten ml of the test solution was saturated with quinhydrone and connected via a saturated sodium chloride bridge to a saturated sodium chloride–calomel electrode. A platinum wire served as electrode for the test solution. Both electrode vessels dipped in a thermostatted water bath at 25°C and the whole installation was housed in a glove-box. Measurements of the potential of the cell were made before and after the addition and solution of weighed quantities of Na_3PaF_8. The test solution could be agitated by passing pure nitrogen through it. The equilibrium potential was reached after the addition of the fluoprotactinate within 15 min. At the lowest fluoride concentrations there was a subsequent slow change in potential probably due to hydrolysis under these conditions. Fortunately, with one exception, this process was sufficiently slow that no correction appeared necessary.

Under the acid conditions used there was an appreciable junction potential. This was not important for the difference measurements, for which high precision was necessary, but a correction was necessary to calculate the initial pH. A correction curve was obtained by making measurements on perchloric acid-perchlorate solutions of accurately known stoicheiometric composition and using the known pH values of such solutions.

The techniques used were essentially an adaptation of that described by VARGA and HUME[16] to a micro scale. The method is dependent on a very precise measurement of the difference of the potential of the cell before and after the addition of fluorocomplex. With the installation described the probable error in the difference in the potentials is $\pm 1{\cdot}5 \times 10^{-5}$ V.

[16] L. P. VARGA and D. N. HUME, *Inorg. Chem.*, **2**, 201 (1963).

RESULTS AND DISCUSSION

K_2PaF_7

The original analyses by A. GROSSE[1,2] included determinations of the potassium and protactinium, but not the fluorine. The precision of the analyses was such that the possibility remained of a hydroxy or even oxyfluoride complex, such as K_2PaF_6OH or even K_2PaOF_5. Two preparations of K_2PaF_7 have therefore been analysed more completely.

(a) Salt precipitated from 0·5 M hydrofluoric acid solution of protactinium by 3 M potassium fluoride. Washed with water and acetone. 60·568 mg of salt gave 61·0 Pa_2O_5 and 29·7% fluorine as PbClF (K_2PaF_7 requires 61·2 and 30·1% respectively) 71·364 mg of salt gave 61·1% Pa_2O_5 and 29·7% F as PbClF.

(b) Salt precipitated as above and recrystallized from nitric-hydrofluoric acid solution (3 M/0·2 M). 50·171 mg of salt gave 60·9% Pa_2O_5, 38·3% K_2SO_4 and 29·8 per cent of fluorine as PbClF (K_2PaF_7 requires 39·5% K_2SO_4) These results confirm the formulation of the compound as K_2PaF_7 and agree with the infrared spectra, where no trace of an OH frequency could be found, nor did the presence of a Pa=O bond appear likely.

Evidence for the PaF_8^{3-} *anion**

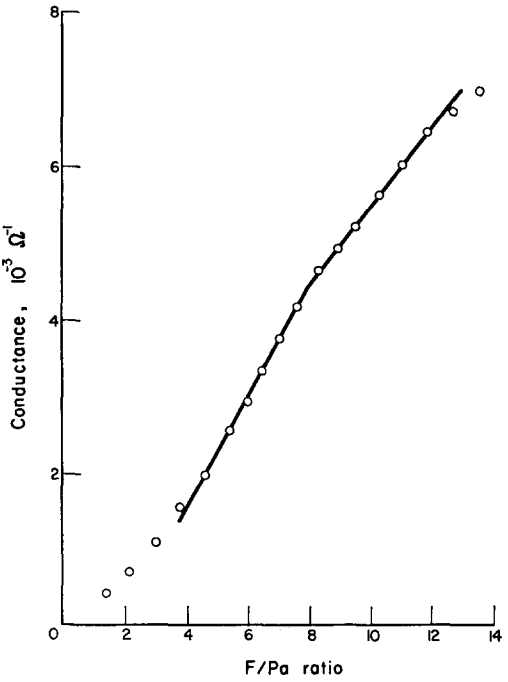

FIG. 1.—Titration of hydrated protactinium pentoxide with hydrofluoric acid 0·55 N conc of Pa $5·8 \times 10^{-3}$ M.

Conductimetric data. If a slurry of hydrated protactinium oxide is titrated conductimetrically with hydrofluoric acid one should find that the most rapid change of slope of the conductivity–F/Pa ratio plot will occur at those ratios for which there is a

* These data were reported at the XVII IUPAC meeting, Munich, 1959.

sharp change in the magnitude of the successive complexing constants of the protactinium for the fluoride ion. Similar measurements have been reported for niobium[17] and tantalum.[18]

The plot shown in Fig. 1 is representative of a number of experiments with different final concentrations of protactinium. These measurements suggest that the successive complexing constants only show one sharp break, that is for the addition of the ninth and succeeding fluoride ligands. They indicate that PaF_8^{3-} should be the dominant anion at moderately high fluoride concentrations.

Competitive anion exchange. STRICKLAND has shown[19] that if an ion, present only

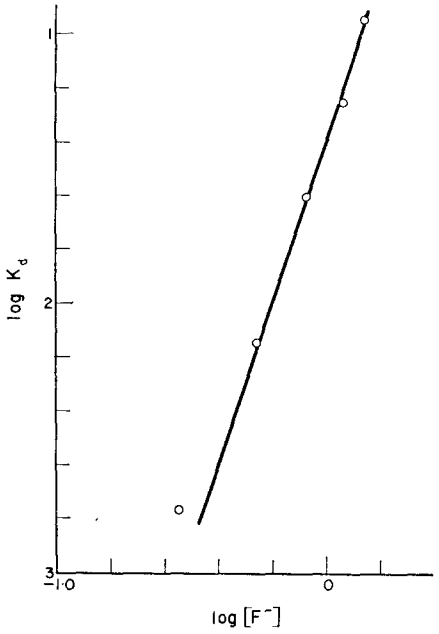

FIG. 2.

at trace concentration, competes for exchange on an ion exchange resin with an ion bearing the same sign of charge, but present at macroscopic concentration, then:

$$\log k_d = -(n \log C)/n' + A$$

where k_d is the usual distribution coefficient for the trace component, n and n' the charges carried by the trace and macroscopic ions, C the concentration of the macroscopic species in the solution and A is a constant.

Figure 2 shows data for the distribution of protactinium between the anion exchange resin Amberlite IRA 400 and an aqueous phase containing various concentrations of tetramethylammonium fluoride. The pH was maintained at 7·5, 7 ml of the solution and 0·3 g of resin in the fluoride form were used in each experiment. The slope of the plot is −3 suggesting that the protactinium is dominantly in the form of PaF_8^{3-} over the range of fluoride concentrations 0·1–1·42 M.

[17] YU BUSLAEV and N. S. NIKOLAEV, *Russian J. Inorg. Chem.* **4**, 84 (1959).
[18] YU BUSLAEV and N. S. NIKOLAEV, *Russian J. Inorg. Chem.* **4**, 210 (1959).
[19] J. D. H. STRICKLAND, *Nature, Lond.* **169**, 620 (1952).

Preparation and analysis of Na_3PaF_8

In a typical preparation 20–22 mg of protactinium pentoxide was dissolved in 4 ml of 0·35 M hydrofluoric acid and a solution of 10 mg of sodium fluoride added. The mixture was concentrated to about 1·5–2·0 ml, when the complex fluoride began to crystallize out. The crystals were washed with 0·35 M hydrofluoric acid and then acetone. Two preparations were analysed, one prepared using a few per cent excess of sodium fluoride and the other a similar deficit.

(a) Sodium fluoride deficit in preparation. 31·070 mg of the salt gave 50·6% Pa, as oxide; 15·05% Na, as sulphate and 34·6% F, as lead chlorofluoride. (Theoretical for Na_3PaF_8, 51·1%, Pa, 15·3% Na and 33·6% F.)

(b) Sodium fluoride excess in preparation. Analysis gave 50·9% Pa, 15·1% Na and 34·0% F. Na_3PaF_8 appears simple to prepare and the conditions of preparation are not critical.

Rough measurements on the solubility gave a value of $8·7 \pm 0·5$ g/l in a 0·35 M fluoride solution.

(4) *Infrared spectra of the complex fluorides.*

A sample of $KPaF_6$ was prepared by dissolving 40 mg Pa_2O_5 in concentrated hydrofluoric acid. A saturated solution containing 10 mg of KF was then added. There was no immediate precipitate but on evaporating large waxy crystals appeared. These were digested with 1 ml 40 per cent hydrofluoric acid and after further evaporation the waxy crystals were separated and washed with acetone and dried at 50°C. $CsPaF_6$ proved too soluble to prepare conveniently in this way. The infra-red spectrum and X-ray diffraction pattern of the $KPaF_6$ prepared in this way indicated it consisted substantially of $KPaF_6$, but with a little K_2PaF_7 impurity.

For comparison measurements were also made on sample of $CsNbF_6$, $CsTaF_6$, K_2NbF_7, K_2TaF_7 and Na_8TaF_8 prepared from niobium or tantalum pentoxides by published methods.[20] In no case was there evidence of bands that might be attributed to O—H or H—F stretching frequencies. The principal results, a single band in the region 3000–400 cm^{-1}, are shown in Table 1. The values quoted for NbF_6^-, NbF_7^{2-},

TABLE 1. (cm^{-1})

NbF_6^-	589	TaF_6^-	580	PaF_6^-	450 (402)
NbF_7^{2-}	524	TaF_7^{2-}	530	PaF_7^{2-}	432
		TaF_8^{3-}	490	PaF_8^{3-}	420

TaF_6^- and TaF_7^{2-} are in reasonable agreement with those reported by PEACOCK and SHARP.[21] For the MF_6^- species the frequencies quoted are most likely the $\nu_3(F_{1u})$ frequency. The PaF_6^- band was much broader than the corresponding bands for PaF_7^{2-} and PaF_8^{3-}. This may be due in part to some contamination by K_2PaF_7, but also to overlap with another band with a maximum at 402 cm^{-1}. The ν_3 values for NbF_6^- and PaF_6^- may be compared with the corresponding Raman values for ν_1 of 640 and 545 cm^{-1} quoted by KELLER.[22] As noted by PEACOCK and SHARP, and also

[20] G. S. SAVCHENKO and I. V. TANANAEV, *J. Applied Chem.*, U.S.S.R. **19**, 1093 (1946).
[21] R. D. PEACOCK and D. W. A. SHARP, *J. Chem. Soc.* 2762 (1959).
[22] O. L. KELLER. Ref. (5) p. 9.

found for the chlorocomplexes of protactinium by BAGNALL and BROWN,[23] each additional ligand unit lowers the frequency.

Estimation of the successive complexing constants for the fluorocomplexes.

Solutions were prepared containing known molarities of sodium fluoride, x, and perchloric acid, y, and sufficient sodium perchlorate to give an ionic strength of one.

Thus initially

$$y = [H^+]_i + [HF]_i + [HF_2^-]_i \quad (1)$$

$$x = [F^-]_i + [HF]_i + 2[HF_2^-]_i \quad (2)$$

$[H^+]_i$ was determined potentiometrically. On the addition of a weighed amount of Na_3PaF_8 to a known volume of the solution, a molarity z of Na_3PaF_8 was produced and the hydrogen ion concentrated became $[H^+]_f$

Hence

$$y = [H^+]_f + [HF]_f + [HF_2^-]_f \quad (3)$$

If $\bar{n}$ is the average ligand number of the complexes in the system:

$$\bar{n} = \{8z + x - [F^-]_f - [HF]_f - 2[HF_2^-]_f\}/z \quad (4)$$

$$= \{8z + ([H^+]_f - [H^+]_i)\}/z + \{([F^-]_i - [F^-]_f) + ([HF_2^-]_i - [HF_2^-]_f)\}/z \quad (5)$$

Now we shall show that under the conditions of all bar one of our experiments the second term in the right hand side of Equation (5) may be neglected.

Re-writing Equations (2) and (3) in terms of the hydrogen and fluoride ion concentrations and the dissociation constants of hydrofluoric acid and the bifluoride ion, k′ and k″, respectively, we have

$$y = [H^+]_i + \frac{[H^+]_i}{k'}[F^-]_i + \frac{[H^+]_i}{k'k''}[F^-]_i^2 = [H^+]_f + \frac{[H^+]_f}{k'}[F^-]_f + \frac{[H^+]_f}{k'k''}[F^-]_f^2. \quad (6)$$

so that

$$\frac{[H^+]_f - [H^+]_i}{[H^+]_f[H^+]_i} \cdot y = \frac{([F^-]_i - [F^-]_f)}{k'} + \frac{([F^-]_i^2 - [F^-]_f^2)}{k'k''}$$

But

$$[F^-]_i \approx [F^-]_f \text{ and } [H^+]_i \approx [H^+]_f$$

so if we call the mean values, $[F^-]_{i/f}$ and $[H^+]_{i/f}$ and put $[H^+]_f - [H^+]_i = \Delta$ we have:

$$([F^-]_i - [F^-]_f)\left(\frac{1}{k'} + \frac{2[F^-]_{i/f}}{k'k''}\right) = \frac{y \cdot \Delta}{[H^+]_{i/f}} \text{ approximately}$$

or

$$([F^-]_i - [F^-]_f) = \Delta \cdot y/[H^+]_{i/f}^2\left(\frac{1}{h'} + \frac{2[F^-]_{i/f}}{h'k''}\right)$$

$$= \Delta \cdot \alpha.$$

Using AHRLAND's values[24] of $k' = 1{\cdot}07 \times 10^{-3}$ and $k'' = 0{\cdot}32$ for 1 M perchlorate

[23] K. W. BAGNALL and D. BROWN, *J. Chem. Soc.*, 3021 (1964).

[24] S. AHRLAND, R. LARSSON and K. ROSENGREN, *Acta Chem. Scand.* **10**, 705 (1956).

solutions at 25°C, evaluation of α showed that only in one experiment, at the highest fluoride concentration, did it exceed 0·01. For the remainder of the experiments, therefore, $\bar{n}$ was calculated ignoring the second term of the right hand side of Equation (5).

The fluoride concentrations compatible with the different values of $\bar{n}$ were calculated by rearrangement of Equation (4) to give

$$\frac{2[H^+]_t[F^-]_t^2}{k'k''} + \frac{[H^+]_t[F^-]_t}{k'} + [F^-]_t = x + z(8 - \bar{n})$$

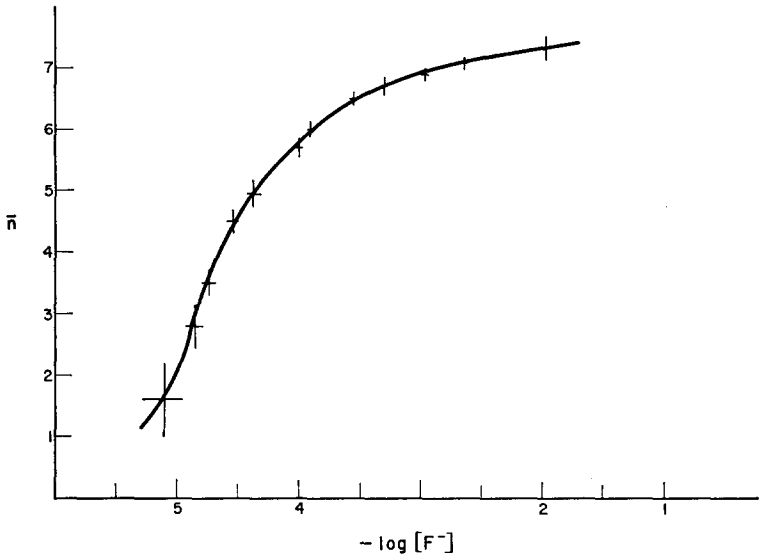

FIG. 3.—Formation curve for Pa-F complexes.

Again in all bar the one experiment, referred to above, the first term of this equation was small enough to be neglected.

Thus the measurements x, z and the e.m.f. of the cell before and after the addition of the fluorocomplex enabled us to obtain a series of values of $\bar{n}$ and $[F^-]$. These are plotted in Fig. 3. Now it is easily shown that, provided hydroxy complexes are not formed,

$$\bar{n} = \sum_{i=1}^{n} (i - \bar{n})\beta[_iF^-]^i$$

where the β's are the cumulative complexing constants so that values of β_1 can be calculated from the data shown in Fig. 3. An iterative procedure using successive approximations was used and the same technique permitted an assessment of the probable errors. Since measurements could not be made at very low values of $\bar{n}$, because of the metastability of the system with respect to hydrolysis under these conditions, the errors on the earlier β's are rather large and we prefer to quote the values of k_1, the successive complexing constants.

To prove the procedure measurements were also made on the zirconium and tantalum fluoro-complexes. The zirconium results may be compared with those of BUSLAEV[25] for 0·5 M perchlorate solutions.

	$\log k_4$	$\log k_5$	$\log k_6$
BUSLAEV 0·5 M perchlorate	1·83	1·51	0·86
This work 1·0 M perchlorate	2·8	1·9	1·35

For the tantalum, however, we do not agree very well with VARGA and FREUND's[26] data and find no evidence for TaF_9^{4-}

	k_6	k_7	k_8	k_9
VARGA and FREUND 1·0 M perchlorate	$4{\cdot}13 \times 10^3$	$2{\cdot}20 \times 10^3$	$9{\cdot}39 \times 10^2$	$3{\cdot}73 \times 10^3$
This work 1·0 M perchlorate	$5{\cdot}6 \times 10^3$	$1{\cdot}27 \times 10^3$	4·6	—

The best value for the k's for the protactinium complexes are tabulated below.

$\log k_1$, $5{\cdot}4 \pm 0{\cdot}5$*;	$\log k_2$, $5{\cdot}0 \pm 0{\cdot}5$*;	$\log k_3$, $4{\cdot}9 \pm 0{\cdot}4$;	$\log k_4$, $4{\cdot}8 \pm 0{\cdot}3$;
$\log k_5$, $4{\cdot}5 \pm 0{\cdot}2$;	$\log k_6$, $4{\cdot}4 \pm 0{\cdot}2$;	$\log k_7$, $3{\cdot}7 \pm 0{\cdot}2$;	$\log k_8$, $1{\cdot}7 \pm 0{\cdot}5$;

Measurements at different acidities justified the assumption that hydroxy complexes are not important, at least for $\bar{n} \geqslant 3{\cdot}0$. However, the errors on k_1 and k_2 (marked *) may be underestimates in that these values are greatly influenced by measurements on metastable systems. Attempts to obtain higher precision on k_{1-3} by solvent extraction or ion exchange procedures failed because of the instability of the systems at low $\bar{n}$, with respect to hydrolysis.

The precision of the data leaves much to be desired. However, in view of the paucity of quantitative data on protactinium compounds and the importance of the fluorocomplexes it has some value. There were indeed other factors than the metastability of the system at low fluoride concentrations that limit the accuracy, for example k' and k'' (the constant for HF) may well vary with the composition of the 1 M sodium perchlorate–perchloric acid mixtures used. The data confirm the high stability of these complexes and the greater tendency of protactinium than tantalum to assume higher coordination numbers. In addition, protactinium fluorocomplexes appear stable at lower $\bar{n}$ than those of tantalum.

Some n.m.r. observations on solutions of the fluorocomplexes

The fluorine resonance was examined in

(a) A solution prepared by adding one mole equivalent of sodium fluoride to a solution of hydrated protactinium pentafluoride, prepared by solution of the oxide in hydrofluoric acid and driving off the excess acid by evaporation to dryness.

(b) A solution $(NH_4)_2PaF_7$ recrystallized from a dilute hydrofluoric acid solution containing the protactinium, with two mole equivalents of ammonium fluoride.

[25] YU. BUSLAEV, *Russian J. Inorg. Chem.*, **7**, 619 (1962).
[26] L. P. VARGA and H. FREUND, *J. Phys. Chem.* **66**, 21 (1962).

(c) A solution of hydrated protactinium pentafluoride to which a small excess of sodium fluoride over that necessary for Na_3PaF_8 had been added.

In each case trifluoracetic acid was used as an external standard. All samples were around 100 mM in the complex.

(d) Measurements were also made on a solution of niobium pentoxide in hydrofluoric acid in acetonitrile and a solution of $AgNbF_6$, prepared from hydrated NbF_5 and

(e) Silver fluoride solution, in acetonitrile, containing a little HF.

The chemical shifts are quoted in p.p.m. in relation to elemental fluorine.

(a) Sharp line at 557·5 Broader line at 290·1 Similar intensities.

(b) Sharp line at 558.

(c) Sharp line at 558. Broader weraker line at 565·5.

(d) Sharp line at 556·4 and 578·1. Ratio of intensities 4:1

(e) In both solvents a decuplet was obtained with $\delta = 325{\cdot}3$ and coupling constant 343·3 c/s.

The NbF_6^- spectrum agrees well with that reported by PACKER and MUETTERTIES[27] using a solution of a complex formed by dimethylformamide and niobium pentafluoride in acetonitrile, believed to be $(CH_3)_2NOCH\ NbF_4^+ . NbF_6^-$. These authors, however, were unable to detect this spectrum in an acetonitrile solution of $AgNbF_6$. In all the other systems no sign of spin–spin coupling structure could be detected. This can either be due to quadrupole relaxation, since both niobium and protactinium have quadrupole moments, or to a sufficiently rapid fluoride ion-complex exchange. This latter possibility can be excluded because

(i) Two lines were obtained in solutions (a), (c) and (d)

(ii) The position of these lines was not sensitive to the addition of fluoride ion to the solution, although this did affect the relative intensities in solution (a).

The 4:1 ratio obtained in solution (d) taken in conjunction with the conductimetric experiments reported above, indicate that these two lines represent the two fluorine environments in $NbOF_5^{2-}$.

In solutions (a), (b) and (c) the stability constant data show that the solutions will all contain some PaF_5, PaF_6^-, PaF_7^{2-}, PaF_8^{3-} and F^-, although PaF_6^-, PaF_7^{2-} and PaF_8^{3-} will be the dominant species in (a), (b) and (c) respectively. We suggest, therefore that $\delta PaF_6^- = 290{\cdot}1$ and $\delta PaF_7^{2-} = 558$ p.p.m. Further, the position of these lines in relation to the F^- line indicates that under our conditions the mean life of a given fluorine atom in the complex before exchanging with fluoride is much greater than $1{\cdot}6 \times 10^{-5}$ sec. in the PaF_6^- and $3{\cdot}6 \times 10^{-4}$ sec in the PaF_7^{2-}. For the PaF_8^{3-} it is possible that this is suffering exchange with F^-, so that $\delta PaF_8^{3-} \geqslant 565{\cdot}5$ p.p.m. These conclusions imply that there is a single effective fluorine environment in each complex. This is reasonable for PaF_6^-, but for PaF_7^{2-} it can only happen if there is a fast intramolecular fluorine exchange.

X-ray powder diffraction photographs were also taken for our samples of Na_3PaF_8, K_2PaF_7 and $KPaF_6$. X-ray crystallographic data for Na_3PaF_8 have recently been reported by BROWN and EASEY.[28] Our results are in good agreement with their

[27] K. J. PARKER and E. K. MUETTERTIES *J. Amer. Chem. Soc.* **85**, 3035 (1963).
[28] D. BROWN and J. F. EASEY, *Nature, Lond.* **205**, 589 (1965).

report. Our data for the last salt are substantially different from those reported by ASPREY and PENNEMAN[6] and comparison of their data with our photograph for K_2PaF_7 indicate that their preparation was probably appreciably contaminated with this salt. The stability constant data given above suggest that the preparation of pure $KPaF_6$ from aqueous solution will require very carefully controlled conditions. The X-ray data for our sample of $HPaF_6$, crystallized from 40% HF, indicate that it is a purer preparation, but possibly not completely free of K_2PaF_7.

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