Chemistry of the Trivalent Actinoids. Part IV.[1] Nephelauxetic Effects as a Guide to Complex Formation for Uranium(III) and Neptunium(III)

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In the absence of oxygen, neptunium(III) is much more stable towards oxidation than uranium(III) in aqueous solutions of complexing agents. Nephelauxetic shifts have been found for both metal ions and used as a guide to complex formation for the tri- and quadri-valent states; those for neptunium are less than those for uranium in each oxidation state. An improved method for the production of Np^{III} is described.

COMPOUNDS of uranium(III) have proved difficult to isolate from solution [1-3] because of the ready oxidation of the metal ion, even in the absence of oxygen. Little is known of aqueous neptunium(III) chemistry.

The nephelauxetic effect [4,5] is a useful tool for assessing the interactions with potential complexing agents. By comparing the spectra obtained with that of the fully hydrated metal ion it is possible to order various ligands in their ability to shift the absorption bands relative to a standard condition. The order is much the same for many metal ions. Red shifts are observed relative to the hydrated ion except for fluoride. The red (or occasionally blue) shifts observed in the present work were assumed to derive from nephelauxetic effects. Thus, for metal ions which are readily oxidised by oxygen, the spectral measurements, which can be relatively easily carried out under nitrogen, are a simple guide to which types of ligand are worthy of further study. The results were internally consistent in that no marked blue shifts were observed except for $UF_3{\cdot}OH_2$ and the effects for neptunium were smaller than for uranium and larger in all cases than for the corresponding lanthanoid ions as previously [6] supposed.

The solution chemistry of the actinoids has been extensively reviewed recently.[7] The hydrated trivalent actinoid ions are thought to be nine-co-ordinate in solution. There are no crystallographic structures for hydrated trivalent uranium and neptunium compounds and very few for the quadrivalent state where the preferred co-ordination number of the hydrated ion is eight. This was found in $U(SO_4)_2{\cdot}4OH_2$.[8] Stability constants confirm that the tri- and quadri-valent actinoid ions have marked class A character, forming strongest complexes with fluoride- and oxygen-containing anions.

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[1] Part III, R. Barnard, J. I. Bullock, B. J. Gellatly, and L. F. Larkworthy, *J.C.S. Dalton*, 1973, 604.

[2] R. Barnard, J. I. Bullock, and L. F. Larkworthy, *J.C.S. Dalton*, 1972, 964.

[3] R. Barnard, J. I. Bullock, B. J. Gellatly, and L. F. Larkworthy, *J.C.S. Dalton*, 1972, 1932.

[4] C. K. Jorgensen, ' Modern Aspects of Ligand Field Theory,' North-Holland, Amsterdam, 1971, p. 293.

[5] B. N. Figgis, ' Introduction to Ligand Fields,' Interscience, New York, 1966, p. 243.

[6] J. L. Ryan in *MTP Internat. Rev. Sci.*, ' Inorganic Chemistry,' series 1, vol. 7, ed. K. W. Bagnall, Butterworths, London, 1972, p. 327.

[7] S. Ahrland, J. O. Liljenzin, and J. Rydberg, in ' Comprehensive Inorganic Chemistry,' vol. 5, ed. A. F. Trotman-Dickenson, Pergamon, Oxford, 1973, pp. 465—635.

[8] P. Kierkgard, *Acta Chem. Scand.*, 1956, **10**, 599.

RESULTS AND DISCUSSION

All manipulations with the trivalent ions were made in an atmosphere of nitrogen. The admission of oxygen was a useful method of preparing the corresponding quadrivalent metal-ion solutions (see Experimental section).

The Stability of Neptunium(III) *towards Oxidation* (*Table* 1).—Unlike neptunium(III), neptunium(IV) absorbed strongly at 13 700 cm^{-1} and this served as a diagnostic test for Np^{IV} in the present work. The band obeys Beer's law in perchloric [9] and sulphuric [10] acid solutions. The electrolytic method of reduction and subsequent handling technique consistently produced 100% Np^{III} solutions so that spectra were obtained in aqueous HCl and H_2SO_4 for the first time in the absence of Np^{IV} impurity.

TABLE 1

Stability of the hydrated neptunium(III) and uranium(III) ions

(a) With various anions (Np)

Anion	Stability
$[SO_4]^{2-}$	Stable [a]
Cl^-	Stable [a]
$MeCO_2^-$	Stable [a]
HCO_2^-	Stable [a]
Citrate	Stable [a]
$[SCN]^-$	Stable [a]
$C_2O_4^{2-}$	Oxidation [b]

(*b*) With various complexing agents in water–methanol (Np)

Complexing agent	Stability
Pentane-2,4-dione	Oxidation [b]
4-Phenylpentane-2,4-dione	Stable [a]
1-Thienyl-3-trifluoromethylpropane-1,3-dione	Stable [a]
$Na[S_2CNEt_2]$	Oxidation [b]
N-Benzoyl-*N*-phenylhydroxylamine	Oxidation [c]
Hquin	Stable [a]
$PO(NMe_2)_3$	Stable [a]
dppo	Stable [a]

(*c*) With various anions (U)

	Stability [d]	
Anion	0.3M-HCl [e]	Water [f]
$MeCO_2^-$	Stable	Oxidation
HCO_2^-	Stable	Oxidation
Citrate	Stable	Oxidation
$[BF_4]^-$	Stable	Oxidation
Lactate	Stable	Oxidation
$[SCN]^-$	Stable	Oxidation

[a] For 12 h under nitrogen. [b] In 5—15 min. [c] Immediate. [d] See text. [e] Present work. [f] Ref. 3.

Neptunium(III) in aqueous HCl solution (0.6M) * showed only a negligible trace of oxidation after 1 week under nitrogen in a sealed spectrophotometric cell. Using the hydrogen-reduction technique [9] a similar result was found in aqueous $HClO_4$ (1M). In aqueous H_2SO_4 solution (1M), Np^{III} was less stable and some oxidation had occurred after 24 h (*ca.* 20%), although oxidation was not complete even after 1 week. In similar experiments some degree of stability was found for a further 11 environments (Table 1). The β-diketones are usually used in solutions of high pH necessary to dissociate the protons. For Np^{III}, addition of sodium hydroxide caused rapid oxidation, as would be expected,[7] and hydrolysis.

The Stability of Uranium(III) *towards Oxidation* (Table 1).—The anions listed in Table 1(*c*) were previously [1] found to oxidise uranium(III) when added as aqueous solutions to an aqueous solution of red ammonium uranium(III) chloride pentahydrate. When a dilute acidic solution of U^{III} was used there was no detectable oxidation (from the spectrum) after 2 h and *ca.* 30% oxidation after 24 h for the ions listed, although oxalate, sulphide, borate, phosphate, and ethylenediaminetetra-acetate gave rapid oxidation for both conditions. Colour changes for the stable solutions (except for tetrafluoroborate) were similar to those observed [3] for U^{III} in concentrated HCl and methanol, suggesting complex formation had occurred.

Uranium(III) *Spectra* (*Table* 2).—The overall appearance of the *f–f* transitions was much the same in all cases. There was little or no uranium(IV) impurity as the 6 500 cm^{-1} absorption was absent.[2] In general, no marked splittings attributable to crystal-field effects were observed. Spectroscopic shifts were seen for all the *f–f* transitions, although as expected the magnitude of the effect varied for the different absorption bands. The selected bands were compared in frequency with the equivalent band for the ion in dilute HCl solution. The results in Table 2 express the difference as a simple percentage of the standard frequencies. A negative sign indicates a red shift. The spaces in Table 2 indicate that either a charge-transfer band obscured the *f–f* transition or that splitting of the standard absorption was observed.

TABLE 2

Nephelauxetic shifts (% wavenumber) for uranium(III) compared with the ion in water [a]

Band for the hydrated ion (cm^{-1})	13 680	11 300	10 220	
	Nephelauxetic shift			Average
$[BF_4]^-$ (aq)	−0.6	−0.9	−0.7	−0.75
Lactate (aq)	−0.95	−0.9	−1.15	−1.0
HCO_2^- (aq)	−0.95	−0.9	−1.15	−1.0
$MeCO_2^-$ (aq)	−1.3	−0.9	−1.65	−1.3
Citrate (aq)	−2.4	−1.75	−3.15	−2.45
$[SCN]^-$	−2.05	−1.8	−2.15	−2.0
Cl^- (aq) [b]	−0.55	0	−0.7	−0.4
Br^- (aq) [b]	−0.55	+0.9	−0.2	+0.05
I^- (aq) [b]	−0.55	+0.45	−0.7	−0.25
$[SO_4]^{2-}$ (aq) [b]	−0.15		0	−0.05
$UF_3{\cdot}OH_2$ [c]	+1.6	+3.1		+2.35
UCl_3 [c]	−2.8	−1.35	−3.15	−2.45
UBr_3 [c]	−3.15	−0.9	−4.1	−2.7
UI_3 [c]		−2.65	−6.05	−4.35
$U_2[SO_4]_3{\cdot}8OH_2$	−0.2	−0.45	−0.7	−0.45
$K_2U_2[SO_4]_4{\cdot}10OH_2$ [c]	0		−0.2	−0.1
$[NH_4]UCl_4{\cdot}5OH_2$ (red) [c]	−2.05		−1.65	−1.85
$[NH_4]UCl_4{\cdot}6OH_2$ (green) [c]	−3.15	−0.45	−2.65	−2.1
$[NH_4]UCl_4{\cdot}5OH_2$ (red), in water	−0.3		0	−0.15
$[NH_4]UCl_4{\cdot}5OH_2$ (red), in methanol		−1.7	−0.4	−1.05
$[U(dppo)_6][BPh_4]_3$ [c]		−4.85	−8.05	−6.45
$[NH_4]_2U_2[SO_4]_3{\cdot}9OH_2$, in 11M-HCl [d]	−0.8	−1.8	−1.4	−1.35

[a] 0.3M-HCl. [b] 1M Acid solution. [c] Reflectance spectra at room temperature. [d] 7.30 × 10^{-3}M-U.

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* 1M = 1 mol dm^{-3}.

[9] R. Sjoblom and J. C. Hindman, *J. Amer. Chem. Soc.*, 1951, **73**, 1744.

[10] J. I. Bullock and D. G. Tuck, unpublished work.

(a) *Diffuse-reflectance spectra of the solid compounds.* The simple sulphate, $U_2[SO_4]_3 \cdot 8OH_2$, and the double sulphate, $K_2U_2[SO_4]_4 \cdot 10OH_2$, had very small shifts which were comparable with the probable experimental errors and these contain the simple hydrated U^{III} ion. This confirmed our earlier conclusion[2] which was based on the i.r. spectrum of the sulphate ion in these compounds (which was that expected for the T_d non-co-ordinated anion). The same result was found for other sulphates and double sulphates of similar formula described in ref. 2.

The red double chloride, $[NH_4]UCl_4 \cdot 5OH_2$, which had[3] a strong absorption at 18 000 cm^{-1} assigned to a charge-transfer transition and U–Cl stretching frequencies in the far-i.r. spectrum, had large red shifts which confirm the presence of a complex chlorouranium(III) ion in this and other[3] related compounds. Dissolution in methanol preserved the complex chloro-ion to some extent since both the large nephelauxetic effects and the 18 000 cm^{-1} absorption were retained, whilst in aqueous solution the complex species broke down to give the spectrum of the hydrated ion with little or no shift observable. The double sulphate, $[NH_4]_2U_2[SO_4]_4 \cdot 9OH_2$, was partly converted into the chloro-species in 11M-HCl solution. Unexpectedly the green double chloride, $[NH_4]UCl_4 \cdot 6OH_2$, had larger red shifts than the red series of chlorides. The absences of the 18 000 cm^{-1} absorption and U–Cl stretching frequencies in the far-i.r. spectrum had previously[2] led us to suppose that this contained the simple hydrated ion. This is unlikely and we propose that this complex has a lower co-ordination number towards water as ligand than the aqua-ion. We found no evidence for chloride-ion co-ordination. There was some evidence to support this for the 2,3-dimethyl-1-phenylpyrazol-5-one (dppo) complex, $[U(dppo)_6][BPh_4]_3$, which may well be six-co-ordinate, and which had very large red shifts. In this complex there is no possibility of a co-ordinated anion.

The nephelauxetic shifts for the halides fell in the expected order, namely $UF_3 \cdot OH_2 < UCl_3 < UBr_3 < UI_3$. The effects were larger than for the lanthanoid ions.[11]

(b) *Solution spectra.* For the anions tetrafluoroborate to citrate (Table 2) the order of red shifts was fluoroborate < lactate ≈ formate < acetate < citrate. A similar series was found[11] for praseodymium(III) and neodymium(III), although the effects for U^{III} were larger. The stability constants, K_1, for other actinoid(III) ions indicated[7] that some complex formation was to be expected, except for the weakly co-ordinating $[BF_4]^-$ for which no values are available, but since the wavenumbers were reproducible to less than 50 cm^{-1} all the shifts were significant.

Relatively large shifts were observed for thiocyanate although relevant stability constants are small,[7] but for the mineral, acid solutions (HX; X = Cl, Br, or I) which had low U : X ratios neither significant shifts nor the 18 000 cm^{-1} absorption were observed so these contained the hydrated metal ion. Stability constants[7] for halide ion with trivalent actinoids and lanthanoids are small (where known), but those for sulphate, where no red shift occurred, are higher and comparable with those for acetate and formate (see below).

Uranium(IV) *Spectra* (*Table* 3).—Most results in Table 3 were obtained by oxidising the U^{III} solutions with air. It was immediately apparent that, for comparable systems, the shifts were, on average, larger than for U^{III}. Whilst the U^{IV} complexes would be more easily formed since the stability constants are higher, the observation that larger shifts were also found in the diffuse-reflectance spectra of the anhydrous halides confirms that the covalency of the uranium(IV)–ligand bond is largest. The nephelauxetic ordering was lactate < oxalate ≈ formate < acetate < citrate. As with U^{III}, small nephelauxetic effects were found for sulphate systems. The tetrahydrate is eight-co-ordinate[8] with a square-antiprismatic structure completed by four unidentate water molecules and four oxygen atoms from bridging sulphate ligands. This result may imply that $[SO_4]^{2-}$ ion produces nephelauxetic shifts very similar to those of water.

TABLE 3

Nephelauxetic shifts (% wavenumber) for uranium(IV) compared with the ion in water[a]

Band for the hydrated ion (cm^{-1})	18 300	15 400	9 200	
	Nephelauxetic shift			Average
Lactate (aq)	−1.3	−0.95	−0.55	−0.95
HCO_2^- (aq)	−1.95	−1.95	−2.95	−2.3
$MeCO_2^-$ (aq)	−2.7	−3.25	−3.15	−3.05
$C_2O_4^{2-}$ (aq)	−1.9	−3.25	−1.65	−2.25
Citrate (aq)	−2.75	−3.4	−3.7	−3.3
$[SCN]^-$ (aq)	−2.7	−2.75	−2.15	−2.55
Br^- (aq)[b]	−1.5	−0.95	−0.5	−1.0
UCl_4[c]	−1.75	−2.65	−4.95	−3.2
UBr_4[c]		−2.95	−4.4	−2.6
UI_4[c]		−3.95	−8.25	−6.1
$U[SO_4]_2 \cdot 8OH_2$[c]	+0.25	+0.15	−1.85	−0.5
$U[SO_4]_2 \cdot 8OH_2$ in H_2SO_4(1M)	−0.55	−0.45	+0.35	−0.2
$U[SO_4]_2 \cdot 4OH_2$[c]	−1.1	−2.3	−1.1	−1.5

[a] 0.3M-HCl. [b] 1M Acid solution. [c] Diffuse reflectance at room temperature.

Neptunium(III) *Spectra* (*Table* 4).—For citrate, formate, and thiocyanate small but significant red shifts were observed, but the result for acetate was close to experimental error. No change in the spectrum was found for a 1M-H_2SO_4 solution. The shifts were smaller but comparable with those for U^{III} and increasing atomic number gave[11] decreased effects for the lanthanoids.

Of the organic ligands, only dppo and tris(dimethylamino)phosphine oxide provided evidence for complex formation when methanolic solutions of the ligands were mixed with acidic aqueous solutions of Np^{III}. The sulphur ligand 1-thienyl-3-trifluoromethylpropane-1,3-dione (ttpd), the β-diketones, and 8-hydroxyquinoline (Hquin) gave no shifts, but these would not be significantly ionised in dilute acidic solution. The lack of complex formation was illustrated by the inability of Np^{III} to distribute between acidified aqueous and

[11] C. K. Jorgensen, *Progr. Inorg. Chem.*, 1962, **4**, 73.

TABLE 4

Nephelauxetic shifts (% wavenumber) for neptunium-(III) and -(IV) compared with the ions in water [a]

(*i*) Neptunium(III)

Band for the hydrated ion (cm^{-1})	17 950	15 000	12 500	9 850	
	Nephelauxetic shift				Average
HCO_2^- (aq) [b]	−0.7	−0.65	−1.05	−0.8	−0.8
$MeCO_2^-$ (aq) [b]	−0.05	+0.35	−0.4	−0.5	−0.15
Citrate (aq) [b]	−1.85	−1.75	−1.05	−0.2	−1.2
$[SCN]^-$ (aq) [b]	−0.55	−0.65	0	−1.0	−0.55
$[SO_4]^{2-}$ (aq) [c]	0	0	+0.8	+0.5	+0.3
dppo [d]	−0.4	−0.35			−0.4
$PO(NMe_2)_3$ [d]	−0.95	−1.25	−0.25		−0.8
ttpd [d]	+0.3	0	0		+0.1
pd [d]	−0.3	0	0		−0.1
ptpd [d]	0	0	0	+0.5	+0.1
Hquin [d]	0	+0.35	0		+0.1

(*ii*) Neptunium(IV)

Band for the hydrated ion (cm^{-1})	16 670	13 700	11 800	10 250	
	Nephelauxetic shift				Average
HCO_2^- (aq) [b]	−1.1	−0.8		−1.15	−1.0
$MeCO_2^-$ (aq) [b]	−0.3	−0.15		−1.0	−0.5
$C_2O_4^{2-}$ (aq) [b]		−1.45	−2.95	−2.15	−2.2
$[SCN]^-$ (aq) [b]	−1.0	−0.75	−2.15	−1.0	−1.25
Citrate (aq) [b]	−1.55	−2.85	−2.95	−2.25	−2.4
Cl^- (aq) [c]	+0.5	0	−0.5	0	0
SO_4^{2-} (aq) [c]	−0.7	−0.75	+0.85	−1.0	−0.4
dppo [d]	−0.4	−0.65	−1.25	−1.0	−0.85
ttpd [d]	−0.4	−0.75	−0.75	−0.8	−0.7
ptpd [d]	−0.35	−0.65	−1.7	−0.7	−0.85
Hquin [d]	−0.55	−0.75	−1.55	−0.7	−0.9
pd [d]	−0.4	−0.75	−0.7	−0.5	−0.6

ttpd = 1-Thienyl-3-trifluoromethylpropane-1,3-dione, pd = propane-2,4-dione, ptpd = 1-phenyl-3-trifluoromethylpropane-1,3-dione, and Hquin = 8-hydroxyquinoline.

[a] 0.3M-HCl. [b] See text. [c] 1M Acid solutions. [d] Methanol–water.

organic solutions of these complexing agents.[12] For the lanthanoids, distribution coefficients are very much conditioned by pH for similar ligand systems.[7]

Neptunium(IV) *Spectra* (*Table* 4).—Oxidation of the Np^{III} solutions produced analogous Np^{IV} solutions. The shifts were larger than for Np^{III} but smaller than for U^{IV}. For the carboxylate anions the order of nephelauxetic effects was acetate < formate < oxalate < citrate. The neptunium–acetate bonds were apparently less covalent than those of uranium in both oxidation states. As with uranium, larger effects were found for $[SCN]^-$, and Np^{IV}, like U^{III} and U^{IV}, was found[12] to extract into tri-n-butyl phosphate solutions from aqueous acidic $[SCN]^-$.

For the five organic ligands, used as methanolic solutions, evidence of complex formation was found in all cases. The self ionisation of the four ligands with hydroxyl functions would be increased as the oxidation state of the metal ion increased. For dppo significantly higher shifts were found for the quadrivalent state. A tentative ordering of the red shifts was pd < ttpd < dppo ≈ ptpd ⩽ Hquin.* The spaces in both parts of Table 4 indicate that splitting of the band for the aquaion had occurred.

EXPERIMENTAL

The trivalent ions were manipulated in nitrogen atmospheres with carefully deoxygenated solutions. The use of pure reagents significantly reduced the degree of oxidation. Both uranium(III) and neptunium(III) were rapidly oxidised in the presence of oxygen.

Neptunium(IV) *Solutions*.—Neptunium-237 (100 mg, isotopic purity greater than 99%) was supplied as neptunium(V) in aqueous nitric acid solution (10 cm^3, 1M) by A.E.R.E., Harwell. The Np^V solution (5 cm^3) was diluted with aqueous sulphuric acid (5 cm^3, 2M), and reduced to neptunium(IV) by passage of sulphur dioxide for 30 min. Excess of SO_2 was removed by passing nitrogen through the solution for the same time. Propan-2-ol (20 cm^3) was added dropwise to the reduced solution. The solution was cooled in ice and after 96 h precipitation of dark grey-green crystals was complete, further addition of alcohol and cooling resulting in no precipitation. This precipitate was likely to be a neptunium(IV) sulphate. The precipitate was collected, washed with propan-2-ol, and dissolved in either aqueous H_2SO_4 (50 cm^3, 1M) or HCl (50 cm^3, 0.6M) to give stock solutions containing *ca*. 1 g l^{-1} of neptunium(IV). Alternatively, Np^{IV} solutions were produced by aerial oxidation of neptunium(III).

Neptunium(III) *Solutions*.—Neptunium(III), unlike uranium(III), is not oxidised by water under anaerobic conditions but oxidation is rapid in the presence of oxygen. A chemical method for the reduction of Np^{IV} with sodium methanesulfinate, $Na[SO_2Me]\cdot 2OH_2$,[13,14] gave 95% reduction at 60 °C in the presence of hydrazine in aqueous HCl solution. Hydrazine alone will not reduce Np^V but it was necessary since $Na[SO_2Me]\cdot 2OH_2$ gave a maximum of 78% reduction. Additionally the method produced solutions containing excess of reducing agent and the products of its oxidation.

Hydrogen[9] and deuterium[15] reduction at a platinum surface gave complete[9] or nearly complete[15] reduction, but the catalyst was placed[9] in the spectrophotometric cell and only small-scale reductions were thus possible. Later the hydrogen-reduction method was said[16] to be inconsistent but the relative redox potentials were favourable. Although an electrolytic technique with a mercury cathode was more reliable[16] it has not been extended previously to a larger scale.

One purpose of the present work was to find a reliable method for the production of Np^{III}. The electrolytic technique with a mercury cathode described here was adapted from a successful design[2] for U^{III} and suffered no obvious disadvantage, producing 100% Np^{III} solutions on a relatively larger scale. An electrolytic cell (diameter 7.5 cm, height 7.5 cm) with four ground-glass inlets was set up in a nitrogen-filled glove-box. The cathode was purified mercury (650 g) to which external electrical connection was made by a platinum-wire dipping electrode. The platinum-foil anode (0.3 cm^2) was contained in a glass tube which held dilute acid at the electrolyte concentration and was separated from the bulk electrolyte by a grade 3 sinter. The electrodes were connected by tungsten leads to a stabilised power supply which gave a maximum current of 5 A and voltage of 30 V. The cell was thoroughly flushed with nitrogen before use and nitrogen

* ptpd = 1-phenyl-3-trifluoromethylpropane-1,3-dione.

[12] J. I. Bullock and M. E. King, unpublished work.

[13] P. G. Hagan and J. M. Cleveland, *J. Inorg. Nuclear Chem.*, 1966, **28**, 2905.

[14] A. D. Gel'man and M. P. Mefod'eva, *Soviet J. Atomic Energy*, 1958, **4**, 361.

[15] W. C. Waggener, *J. Phys. Chem.*, 1958, **62**, 382.

[16] J. C. Hindman, J. C. Sullivan, and D. Cohn, *J. Amer. Chem. Soc.*, 1958, **80**, 1812.

was passed through the solution during electrolysis. The four inlets were gas tight.

The Np^{IV} stock solution (30 cm^3) in aqueous H_2SO_4 (1M) was electrolysed at a voltage of 20 V, which generated a current of 0.7 A. Under these conditions, the initial green solution was pale lilac-purple after 10—15 min but the electrolysis was continued for a total of 30 min to ensure complete reduction. In aqueous HCl acid (0.6M), electrolysis of Np^{IV} (30 cm^3) at 12 V generated an initial current of 0.7 A which rapidly decreased to 0.35 A. The pale lilac-purple colour was produced after 5—7 min, but electrolysis was continued as before for 30 min.

Uranium(III) was more difficult to produce. Uranyl chloride (0.008M) in aqueous HCl solution (30 cm^3, 0.6M) was reduced in the same cell. The initial current (0.7 A) produced at 20 V soon decreased (0.35 A). After reduction to U^{IV}, 25 min elapsed before electrolysis produced the characteristic wine-red colour of U^{III}.

The Np^{III} solutions used for Tables 1 and 3 were prepared as follows: (*a*) an aqueous HCl solution (3.5 cm^3, 0.3M) of Np^{III} (1×10^{-3}M), which was also used for measuring the standard spectra, was added to an aqueous solution of potassium thiocyanate (0.5 cm^3, 4M); (*b*) an aqueous HCl solution (2 cm^3, 0.5M) of Np^{III} (3×10^{-3}M) was added to dilute HCl acid solutions (1 cm^3, 0.1M) of the sodium or potassium salts of the organic acids (0.5M); and (*c*) an aqueous HCl solution (2 cm^3, 0.5M) of Np^{III} (2×10^{-3}M) was added to a methanolic solution (2 cm^3) of the organic ligands (0.5M) (footnote *d* in Table 4).

Uranium(III) *Solutions*.—(*a*) For tetrafluoroborate, lactate, formate, acetate, and citrate, a uranium(III) solution (0.016M) in dilute HCl (5 cm^3, 0.3M), prepared by electrolytic reduction at a mercury cathode under nitrogen, was added to a solution of the sodium or potassium salt of the anions in aqueous HCl (15 cm^3, 0.5M). The resulting solutions were 0.5M with respect to the anions. (*b*) Uranium(III) (0.080M) in aqueous HCl solution (5 cm^3, 0.3M) was added to aqueous K[SCN] solution (20 cm^3, 1.5M). (*c*) The solutions marked *b* in Table 2 were prepared by electrolytic reduction under nitrogen and were 0.15M with respect to U^{III}. (*d*) Other solutions were prepared as previously described.[3] (*e*) The standard solution was 0.3M in HCl.

Uranium(IV) solutions were obtained by aerial oxidation of the corresponding U^{III} solution. Uranium-(III) and -(IV) compounds were prepared as previously described.[1-3]

Spectroscopic Measurements.—Spectra were measured at 20 ± 1 °C, either by transmission or diffuse-reflectance techniques, with a Unicam SP 700 C recording spectrophotometer. Silica cells fused *via* graded seals to Pyrex vacuum taps were used for the air-sensitive solutions. Routine precautions were observed when handling the α-emitting ^{237}Np isotope. The spectrophotometer was calibrated from time to time against the 15 327 cm^{-1} line of deuterium to ±20 cm^{-1}. Since the *f–f* transitions were so sharp a confidence level of *ca.* ±50 cm^{-1} was readily obtained. This represented ±0.5% at 10 000 cm^{-1} and ±0.25% at 20 000 cm^{-1}. A small number of spectra were recorded with a Beckman DK 2a spectrophotometer using similar precautions.

Counting Techniques.—Neptunium-237 was determined by α assay of aliquot portions of known volume (specific activity [17] 1.562×10^6 α decays min^{-1} mg^{-1}).

We thank Professor K. W. Bagnall, Dr. B. J. Gellatly, and Dr. L. F. Larkworthy for their help.

[4/2598 *Received*, 12*th December*, 1974]

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[17] F. P. Brauer, U.S. Report HW-59642, 1959.