314. *Some Acetamide Complexes of the Actinide Tetrachlorides. Part I. Uranium, Neptunium, and Plutonium.*

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Ionic compounds of composition $MCl_4,6Ac{\cdot}NH_2$ (M = U, Np, or Pu) have been prepared in which the acetamide molecule is co-ordinated to the M^{4+} ion through the carbonyl-oxygen atom. Similar, but more stable, complexes with *NN*-dimethylacetamide, $MCl_4,2{\cdot}5Ac{\cdot}NMe_2$, have also been made; these are presumably dimeric.

THE actinides from thorium to neptunium form well-defined tetrahalides, but the only known quadrivalent plutonium halide is the tetrafluoride. Thermodynamic evidence[1] indicates that the other simple quadrivalent plutonium halides cannot be prepared, but a few derivatives of the complex chloro-acid, H_2PuCl_6, have been recorded, notably the cæsium and the pyridinium salt which are readily precipitated from aqueous solution.[2]

It seemed probable that this cæsium salt could be used in the preparation of complexes of plutonium tetrachloride and that other dicæsium actinide hexachlorides might be useful starting materials, thus avoiding the handling problems associated with anhydrous actinide tetrachlorides, so much more hygroscopic than the dicæsium salts.

Experiments showed that the uranium analogue, Cs_2UCl_6, and diethylamine gave cæsium chloride (identified by *X*-ray powder photography) and what appeared to be a uranium tetrachloride–diethylamine complex, but the two could not be separated without the latter's decomposing. Since formamide and *NN*-dimethylformamide form complexes with titanium tetrachloride,[3] solid dicæsium hexachlorouranate(IV) was mixed with a boiling solution of acetamide in acetone; this gave a green solution of a uranium tetrachloride–acetamide complex, easily separated from the insoluble cæsium chloride. On cooling, the solution deposited a green oil or, more completely, on the addition of benzene or heptane. By repeated dissolution of the crude oil in hot acetone and precipitation with hydrocarbon, uncombined acetamide was removed, the product, after drying *in vacuo* at room temperature, being an emerald-green viscous oil, or oily solid, with a composition close to $UCl_4,6Ac{\cdot}NH_2$ ($Ac{\cdot}NH_2 : U = 5{\cdot}70$—$5{\cdot}90$). On long storage over phosphorus pentoxide, it set to a green glass, m. p. ~60°, *d* 1·4.

The corresponding reddish-brown complexes $MCl_4,6Ac{\cdot}NH_2$ with neptunium and plutonium tetrachloride were made similarly. But whereas with the uranium and neptunium complexes acetone (4—5% by weight) was strongly held after prolonged drying *in vacuo*, the plutonium compound lost nearly all the excess of acetone under these conditions. As the complexes were found later to be thermally unstable, it seemed that preparation and purification in boiling acetone (56·5°) might be responsible for their slightly low acetamide content. Accordingly, ethanol was used; in this the complexes dissolve readily at room temperature and can be precipitated with isopentane or, less completely, benzene. It was found that ethanol was strongly held, but the ligand : uranium ratio was much improved. Retention of the solvent is presumably due to hydrogen-bonding with the amide-hydrogen.

The infrared spectra of the uranium complexes prepared by the acetone and by the ethanol route were identical, apart from absorptions due to the solvent.

Thermal degradation of the complexes in a vacuum on a quartz-fibre spiral thermobalance gave the curves in Fig. 1. The uranium complex appears to give a succession of

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[1] Brewer, Bromley, Gilles, and Lofgren, "The Transuranium Elements," Nat. Nuclear Energy Series, ed. Seaborg, Katz, and Manning, McGraw-Hill Book Co., Inc., New York, 1949, Vol. IV—14B, p. 873.

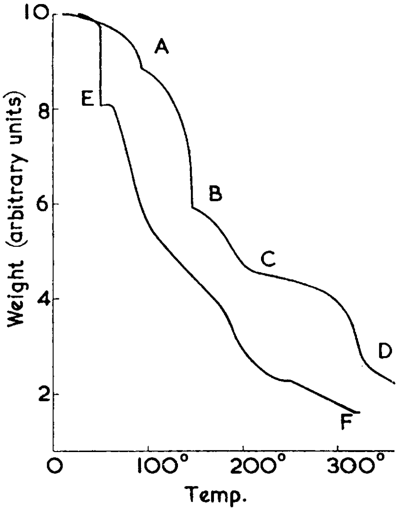
[2] Anderson, ref. 1, p. 793.

[3] Dormer and Fernelius, *Z. anorg. Chem.*, 1934, **221**, 83; Archambault and Rivest, *Canad. J. Chem.*, 1958, **36**, 1461.

lower complexes with, presumably, four, three, and two mols. of adduct and, finally, uranium tetrachloride, but the lower complexes could not be isolated. Neptunium and plutonium complexes lose acetamide continuously without definite evidence of an intermediate complex or, for the plutonium complex, of the point at which chlorine is lost to give the trichloride. Consequently, although a uranium complex can be prepared by treating dicæsium hexachlorouranate(IV) with molten acetamide, in which the complex dissolves, the high temperature required for removal of the excess of acetamide in a vacuum leads to products of very variable composition.

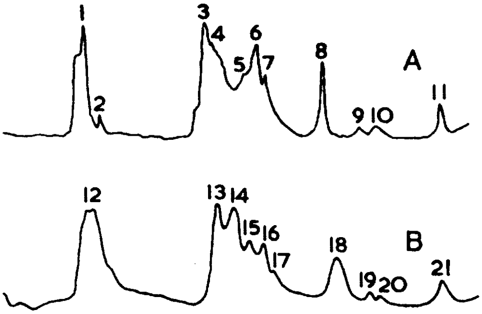
The uranium, neptunium, and plutonium complexes are soluble in hot acetone, methanol, ethanol, acetic acid, and acetic anhydride, but not in other organic solvents. They are all hygroscopic and decomposed by water. Although the complexes are precipitated from acetic acid or acetic anhydride by hydrocarbons, the composition of the product is variable. Possibly some acetylation of the amide group occurs under these conditions, for uranium tetrachloride certainly forms a complex with diacetimide.

FIG. 1.
Thermal degradation of (A—D) $UCl_4,6Ac{\cdot}NH_2$ *and* (E—F) $PuCl_4,6Ac{\cdot}NH_2$.



A, $UCl_4,5{\cdot}35Ac{\cdot}NH_2$ (?). B, $UCl_4,3{\cdot}72Ac{\cdot}NH_2$ (?). C, $UCl_4,3Ac{\cdot}NH_2$ (?). D, $UCl_4,1{\cdot}86Ac{\cdot}NH_2$ (?). E, $PuCl_4,4{\cdot}5Ac{\cdot}NH_2$ (?). F, $PuCl_3$.

FIG. 2. *Infrared spectra of* (A) *acetamide and* (B) $UCl_4,6Ac{\cdot}NH_2$.



Maxima (cm.$^{-1}$): 1, 3305, 3160 (NH); 2, 2815 (Me); 3, 1680 (C=O); 4, 1636 (δ H-N-H); 5, 1459 (δa Me); 6, 1400 (δ NH_2); 7, 1356 (δs Me); 8, 1152 (NH_2?); 9, 1048; 10, 1006; 11, 874 (C-C-N); 12, 3310, 3165 (NH); 13, 1652 (δ N-N-H); 14, 1560 (C=O); 15, 1477 (δa Me); 16, 1410 (δ NH_2); 17, 1364 (δs Me); 18, 1140 (NH_2?); 19, 1050; 20, 1023; 21, 890 (C-C-N?).

The infrared spectrum of the uranium tetrachloride complex is very similar to that of acetamide[4] (Fig. 2). In an attempt to assign the nearly coincident carbonyl stretching frequency and the H-N-H deformation band, the analogous complex with *NN*-dideuteroacetamide was prepared, but as the only solvents, acetone and ethanol, readily exchange hydrogen for deuterium, only about 50% of the original deuterium remained in the final product. The carbonyl-frequency shift ($\Delta\nu$ 120 cm.$^{-1}$) observed indicates strong bonding, being similar to that given by Susz[5] for ketonic carbonyl–metal bonding. There is also an extra band at 640 cm.$^{-1}$, possibly due to a $U \longleftarrow O$ stretching frequency or to the carbonyl-deformation frequency, since neither has been identified elsewhere. Thus the acetamide molecules appear to be co-ordinated to U^{4+} through the carbonyl-oxygen atom. This accords with the chemical evidence, for we have been unable to prepare complexes of uranium tetrachloride with either thioacetamide (where the sulphur-to-uranium co-ordination would be expected to be by a much weaker bond) or with α-chloroacetamide (where

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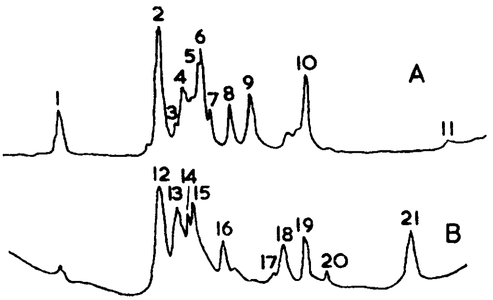
[4] Spinner, *Spectrochim. Acta*, 1959, **15**, 95.
[5] Susz, *Helv. Chim. Acta*, 1958, **41**, 634.

the electron density at the carbonyl-oxygen atom would be much reduced by the electrophilic halogen atom). Further, phthalimide did not form a complex with uranium tetrachloride, possibly for steric reasons.

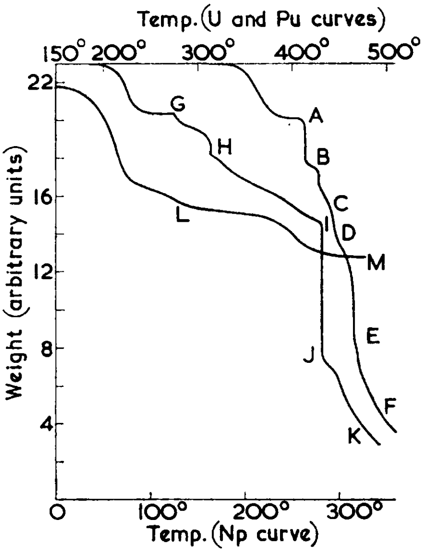
The uranium tetrachloride–acetamide complex is readily hydrolysed to products of indefinite composition which are insoluble in organic solvents. Thus it desiccates the organic solvents used in its preparation. It is fairly resistant to oxidation to uranium(VI), being unaffected by air at 190° or, in solution in acetone, by dry chlorine at 50°, but it is slowly oxidised to sexivalent uranium by ether peroxides. This behaviour differs little from that of uranium tetrachloride. Uranyl chloride–acetamide complexes are also formed, but have not yet been investigated.

FIG. 3. *Infrared spectra of* (A) NN-*dimethylacetamide and* (B) $UCl_4,2\cdot5Ac\cdot NMe_2$.



Maxima (cm.$^{-1}$): 1, 2925; 2, 1647; 3, 1548; 4, 1499; 5, 1410; 6, 1397; 7, 1355; 8, 1266; 9, 1189; 10, 1013; 11, 734; 12, 1618; 13, 1493; 14, 1427; 15, 1403; 16, 1252; 17, 1062; 18, 1032; 19, 974; 20, 917; 21, 753.

FIG. 4. *Thermal degradation of complexes* $MCl_4,2\cdot5Ac\cdot NMe_2$: A—F, M = Np; G—K, M = U; L—M; M = Pu.



A, $NpCl_4,1\cdot5Ac\cdot NMe_2$; B, $NpCl_4,Ac\cdot NMe_2$; C, $(NpCl_4,0\cdot5Ac\cdot NMe_2)$; D, $NpCl_4$; E—F, evapn. of $NpCl_4$. G, $UCl_4,1\cdot5Ac\cdot NMe_2$; H, $UCl_4,Ac\cdot NMe_2$ (?); I, UCl_4; I—K, evapn. of UCl_4. L, $PuCl_4,0\cdot5Ac\cdot NMe_2$; M, $PuCl_3$.

The electrical conductivity of the uranium tetrachloride–acetamide complex in acetone shows it to be more ionised than uranium tetrachloride in the same solvent ($\chi_{\text{complex}}/\chi_{UCl_4}$ = 1·48, 0·0313M-solutions). Migration experiments with solutions in acetone–anhydrous acetic acid proved that U^{4+} ion and acetamide accumulated at the cathode, and chloride ion at the anode. The complex is presumably ionic, the cation consisting of a U^{4+} ion surrounded by 6 molecules of acetamide co-ordinated through the carbonyl-oxygen atom, thus explaining the insolubility in most organic solvents. All the chloride ions are replaced by nitrate or perchlorate ions by metathesis with a silver salt in acetone or ethanol. These new compounds of tetrapositive uranium and its simple nitrate and perchlorate, which we have made from acetone solutions of uranium tetrachloride, will be further investigated. It may also be possible to prepare the plutonium tetrabromide and tetraiodide complexes by similar procedures.

NN-Dimethylacetamide complexes have also been prepared by treating the dicæsium actinide hexachlorides with the substituted amide in acetone; the electron density at the nitrogen atom should here be much enhanced by the two methyl groups and it is not surprising that a new series of complexes emerged. These had the composition

$MCl_4,2{\cdot}5Ac{\cdot}NMe_2$ ($M = U^{4+}$, green; Np^{4+} and Pu^{4+}, red-brown in large crystals, yellowish-brown when finely divided), in which the M^{4+} cation may be co-ordinated to both the carbonyl-oxygen and the amide-nitrogen atom. These complexes are more stable than the simple acetamide derivatives and can readily be recrystallised from acetone. They are not hygroscopic, retain little, if any, organic solvent after drying *in vacuo* and, when recrystallised from acetone, melt sharply [U(IV), 182°; Np(IV), 181°; Pu(IV), 171°; all determined in sealed tubes; molten Np(IV) and Pu(IV) complexes are dark red]. They are soluble in the same solvents as the simple acetamide complexes and also in methylene chloride.

The infrared spectrum of the uranium complex (Fig. 3) is a highly distorted *NN*-dimethylacetamide spectrum. The shift of only about 30 cm.$^{-1}$ in the carbonyl frequency suggests a rather weaker $U \longleftarrow O$ bonding than in the acetamide complex.

The thermal degradation of the *NN*-dimethylacetamide derivatives in a vacuum is more informative than that of the simple acetamide complexes; the curves (Fig. 4) show that they decompose first to $MCl_4,1{\cdot}5X$ ($X = Ac{\cdot}NMe_2$) ($M = U^{4+}$, 245—275°; Np^{4+} 240—265°) and then to a lower complex MCl_4,X ($M = U^{4+}$ 315—325°; Np^{4+}, 268—278°). The only stable lower complex of plutonium tetrachloride appears to be $PuCl_4,0{\cdot}5X$ (290—370°); there are slight inflexions at corresponding points on the decomposition curves of the uranium and neptunium complexes at 370° and 290° respectively.

Molecular-weight determinations of the uranium complex in methylene chloride and in acetone give a value somewhat in excess of the simple formula weight and, since the observed molecular weight decreases with dilution of the solute, the compound evidently ionises even in solvents of low dielectric constant. Dilute (M/18) solutions of the uranium complex in methylene chloride ($D \sim 9$) had a small, but measurable conductivity, but these results could be due to traces of water.

These results suggest that the complex has a structure in which one or more molecules of the ligand act as a bridge, co-ordination being through both the carbonyl-oxygen and the amide-nitrogen atom. The compounds are non-hygroscopic, indicating that they are co-ordinatively saturated, and since it is unlikely that quadrivalent uranium, neptunium, or plutonium is 5-co-ordinating it is possible that one or more chlorine atoms are bonded to each metal atom within the co-ordination sphere. In such a case, potentiometric titration of the chloride ion against silver perchlorate in acetone solution should reveal an inflexion at the point where the free chloride ion, external to the co-ordination sphere, has all been replaced by perchlorate ion, but no intermediate step in the titration curve could be observed experimentally. This may only mean that the chloride ion within the co-ordination sphere is extremely labile.

EXPERIMENTAL

Owing to its long half-life ($2{\cdot}2 \times 10^6$ years) ^{237}Np can be safely handled in 100 mg. amounts in a well-ventilated fume-hood. Experimental work with plutonium was done in a glove-box to minimise the hazards of a highly radioactive material. Natural uranium presents little radioactive danger.

Preparative.—(a) *Dicæsium actinide hexachlorides.* The salts were prepared by dissolving the appropriate tetrachloride (Th, U) in hydrochloric acid, adding cæsium chloride, and slowly evaporating the solution under reduced pressure at room temperature,[6] or by adding cæsium chloride in 6N-hydrochloric acid to a solution of the quadrivalent actinide (Np, Pu) in 6N-hydrochloric acid and filtering off the precipitate (cf. Anderson [2]). We found it convenient to mix solutions of the quadrivalent actinide (U, Np, Pu) and cæsium chloride in 2—11N-hydrochloric acid and to saturate the mixture with hydrogen chloride; precipitation of the complex salt is almost complete. The purity of the products was established by chemical analysis and their identity confirmed by *X*-ray powder photography.

The solutions of the quadrivalent actinides were prepared as follows:

(1) Uranium(IV). By cathodic reduction of uranyl chloride in dilute hydrochloric acid, by

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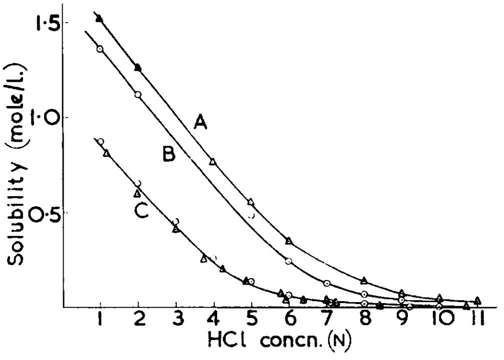
[6] Ferraro, *J. Inorg. Nuclear Chem.*, 1957, **4**, 283.

the reduction of uranyl chloride in 6N-hydrochloric acid with aluminium or with scrap metallic uranium, or by dissolving metallic uranium in concentrated hydrochloric acid; the uranium(III) first formed in the last three operations is rapidly oxidised to uranium(IV) on storage in the cold. Reduction with aluminium gives a dicæsium salt contaminated with a cæsium aluminium chloride.

(2) Neptunium(IV). By reducing a cold stock solution of Np(V)/Np(IV) (~0·5 g.) in 5N-nitric acid with hydrazine; the fawn quadrivalent hydroxide was precipitated with aqueous ammonia and, after being washed thrice with water, was dissolved in 6N-hydrochloric acid. The reduction cycle was repeated and the hydroxide redissolved in concentrated hydrochloric acid. Since the procedure occasionally gave erratic yields, later preparations were made by reduction with iodide ion (ammonium iodide) which always gave satisfactory results.

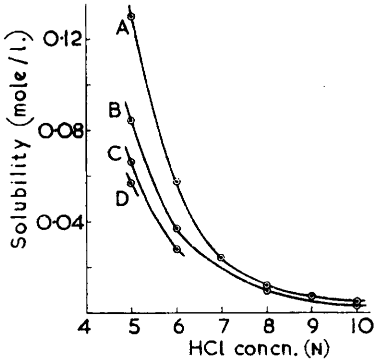
(3) Plutonium(IV). By boiling a solution of plutonium (1 g.) with concentrated nitric acid to break up the colloidal Pu(IV), and reduction to Pu(III) with formaldehyde, which also removed the excess of nitric acid; some concentrated hydrochloric acid was added to maintain acidity. Plutonium(III) hydroxide was precipitated with aqueous potassium hydroxide, and the precipitate, after being washed with water, was redissolved in concentrated hydrochloric acid and oxidised to plutonium(IV) with aqueous hydrogen peroxide. Completion of the oxidation was indicated by a colour change from bluish-violet to reddish-brown.

FIG. 5. *Solubility of* $CsMCl_6$ *in hydrochloric acid*: A, M = U, *at* 25°; B, M = Np, *at* 18°; C, M = Pu, *at* 25°.



△, *Data from ref.* 9. ○, *This work.*

FIG. 6. *Effect of added cæsium chloride on the solubility of dicæsium hexachloroplutonate in hydrochloric acid.*



Added CsCl: A, nil; B, 0·05M; C, 0·10M; D, 0·15M.

(b) *Amide complexes.* The appropriate dicæsium salt was stirred with a five-fold excess of acetamide in hot acetone or cold ethanol, the insoluble cæsium chloride was filtered off, and the complex precipitated from the filtrate by the addition of benzene, heptane, or isopentane. As the hydrocarbon was immiscible with high acetamide concentrations (>200 mg./ml.) the solution was diluted with solvent until miscibility was achieved. The reaction in ethanol was exothermal. The precipitated complex was redissolved in hot acetone or cold ethanol, and precipitation and redissolution were repeated four times to remove the excess of acetamide. The excess of hydrocarbon was evaporated in a current of dry air at room temperature and the oily product dried at 10^{-5} mm. for several hours. Ethanol is preferred as a solvent for the acetamide complexes, but acetone is better for the *NN*-dimethylacetamide complexes and was always used for them. Isopentane is the most convenient precipitant since its low b. p. makes removal easy.

Preparation of the *NN*-dimethylacetamide complexes was similar to that of the acetamide complexes in the first stages, but after the final precipitation the complex was crystallised from acetone. These crystals were collected, dried at 10^{-5} mm., powdered, and again dried in a vacuum.

(c) NN-*Dideuteroacetamide.* Pure trideuteroammonia was prepared by Hart and Partington's method [7] and liquefied in a trap, cooled in solid carbon dioxide–ethanol, containing

[7] Hart and Partington, *J.*, 1943, 104.

redistilled ethyl acetate. Redistilled acetyl chloride, from which any hydrogen chloride had been displaced by a stream of dry nitrogen at 0°, was added dropwise to the liquid ND_3–ethyl acetate mixture until reaction was complete. The product was extracted in 1 : 1 benzene–ethyl acetate in a closed system in which the solvent could be recirculated by suction.

(d) *Acetamide.* B.D.H. reagent-grade material was recrystallised from ethanol and dried *in vacuo.*

(e) NN-*Dimethylacetamide.* B.D.H. reagent-grade material was fractionated under reduced pressure, the middle, constant-boiling fraction being used.

(f) *Solvents.* Alcohols were dried by refluxing over freshly prepared barium oxide and distilled. Benzene was dried over sodium. Acetone was dried to some extent over magnesium nitride. Rigorous drying of the solvents appears to be unnecessary, however, since some of the preparation can be sacrificed as insoluble hydrolysis products.

Solubilities.—The solubility curves of the dicæsium hexachloro-uranate(IV) and -plutonate in hydrochloric acid, and the method for their determination, have been recorded;[8] the plutonium work has been repeated, with good agreement, and the curve for the neptunium analogue has also been obtained (Fig. 5). The effect of an excess of cæsium chloride on the solubility of dicæsium hexachloroplutonate is shown in Fig. 6.

Thermogravimetric Data.—These were obtained with a conventional quartz fibre thermo-balance (sensitivity 4·5 mg./cm. extension); the heating rate was 2°/min. and the operating pressure 0·02—2 × 10^{-6} mm.

Molecular-weight Determinations.—The standard Cottrell method had too much temperature drift to give reproducible results in a reasonable time and a simple spiral pump (Fig. 7) replaced the Cottrell pump after it had been tested. With this apparatus the results for naphthalene, benzophenone, and biphenyl in benzene, acetone, and dichloromethane were ~1·5% low.

The apparatus requires 30—60 min. for equilibration, but is simple to use and gives reasonably reproducible results. Those for the uranium *NN*-dimethylacetamide complex in methylene chloride ranged from 673 (14·8 g. of complex per kg. of solvent) to 625 (6·49 g./kg.), the formula weight of the monomeric complex being 598.

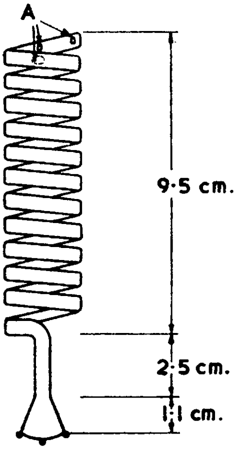


FIG. 7. *Spiral pump.* (A, *Exit holes for pumped liquid.*)

Analysis.—(a) *Chloride ion.* A weighed quantity (50—100 mg.) of the neptunium orplutonium compound was treated with dilute aqueous potassium hydroxide and the precipitated actinide hydroxide separated by centrifugation. The supernatant liquid was acidified with nitric acid, an equal volume of acetone added, and the chloride ion determined potentiometrically against silver nitrate. Addition of acetone markedly increases the sharpness of the end-point. The metal component was not separated from the uranium complex since its recovery is not obligatory.

(b) *Uranium.* Uranium(IV) was determined volumetrically by titration to uranium(VI) with dichromate,[9] and samples were checked for the presence of uranium(VI) by reduction on a lead column in 3N-hydrochloric acid,[10] but it was never found.

(c) *Neptunium and plutonium.* ^{237}Np and ^{239}Pu were determined by α-counting aliquot parts of a solution of the complex. Samples were also subjected to α-pulse analysis in order to ascertain the isotopic composition of the material and detect α-emitting impurities. The neptunium proved to contain 0·02 weight % of ^{239}Pu, and allowance was made for the α-emission from this relatively short-lived isotope.

The weights of neptunium and plutonium were calculated with 1·562 × 10^6 disintegrations $min.^{-1}$ $mg.^{-1}$ as the specific activity of ^{237}Np and 1·38 × 10^8 dis. $min.^{-1}$ $mg.^{-1}$ as that of ^{239}Pu.

(d) *Acetamide.* The amide content of the complexes was determined from a nitrogen analysis by the Kjeldahl method, the *NN*-dimethylacetamide complexes being subjected to a preliminary digestion in concentrated sulphuric acid.

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[8] Kooi, Weisskopf, and Gruen, *J. Inorg. Nuclear Chem.*, 1960, **13**, 310.

[9] Cf., *e.g.*, Rodden and Warf, "The Analytical Chemistry of the Manhattan Project," Nat. Nuclear Energy Series (ed. Rodden), McGraw-Hill Book Co., Inc., New York, N.Y., 1950, Vol. VIII—1, p. 68.

[10] Sill and Peterson, *Analyt. Chem.*, 1952, **24**, 1175.

(e) *Carbon.* Combustion analysis was attempted but the results were vitiated by the presence of organic solvent.

(f) *Results.* Owing to the retention of solvent, the results (tabulated) for the simple acetamide complexes are expressed as ligand : metal and chloride : metal ratios.

	$\mathrm{Ac{\cdot}NH_2/M(IV)}$ Found	$\mathrm{Cl^-/M(IV)}$ Found	Solvent impurity
$\mathrm{UCl_4,6Ac{\cdot}NH_2}$	6·02	4·04	4—22% (*a*)
$\mathrm{NpCl_4,6Ac{\cdot}NH_2}$	6·22	4·04	~2% (*a*)
$\mathrm{PuCl_4,6Ac{\cdot}NH_2}$	5·88	3·97	~2% (*b*)

(*a*) Ethanol. (*b*) Acetone.

	M(IV) (%)		$\mathrm{Cl^-}$ (%)		$\mathrm{Ac{\cdot}NMe_2}$ (%)	
	Found	Reqd.	Found	Reqd.	Found	Reqd.
$\mathrm{UCl_4,2{\cdot}5Ac{\cdot}NMe_2}$	39·5	39·8	23·8	23·7	35·8	36·5
$\mathrm{NpCl_4,2{\cdot}5Ac{\cdot}NMe_2}$	39·6	39·7	23·9	23·8	35·7	36·5
$\mathrm{PuCl_4,2{\cdot}5Ac{\cdot}NMe_2}$	40·5	39·9	21·5	23·7	36·7	36·4

Analyses of the plutonium compound were not very satisfactory, but spectrophotometric examination of solutions of the freshly prepared complex in dilute hydrochloric acid confirmed that the plutonium was nearly all (99%) in the quadrivalent state, the remaining 1% being plutonium(VI). In addition, *X*-ray powder photography showed that the plutonium compound was isostructural with its uranium and neptunium analogues; the reason for the low analytical results is unknown.

X-*Ray Powder Photography*.—Powder photographs were taken with a 19 cm. Unicam Debye–Scherrer camera and filtered Cu-K_α radiation. The *NN*-dimethylacetamide complexes all gave quite good *X*-ray diffraction patterns, but the complexes are evidently of low symmetry, probably monoclinic or triclinic. The uranium, neptunium, and plutonium compounds are isostructural, and the uranium compound may undergo a phase change above 180°. The crystallography of these compounds has not been further investigated.

Infrared Spectra.—Spectra of the acetamide complex were observed for very thin capillary films or melts, and the uranium tetrachloride-*NN*-dimethylacetamide complex as a melt in Fluorube and Nujol; a Hilger H800 spectrometer with sodium chloride, potassium bromide, and cæsium bromide prisms was used.

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