791. *The Uranium*(IV) *Nitrates.*

By K. W. BAGNALL, P. S. ROBINSON, and M. A. A. STEWART.

An amide complex of uranium tetranitrate, $U(NO_3)_4,2{\cdot}5Ac{\cdot}NMe_2$, has been prepared and the complex nitrates $Cs_2U(NO_3)_6$ and $(Et_4N)_2U(NO_3)_6$ have been investigated; none of the compounds is hygroscopic but all are thermally unstable. Attempts to prepare uranium tetranitrate and uranium(IV) oxynitrate have been made.

THERE have been several unsuccessful attempts to isolate uranium(IV) nitrates from aqueous solution, which have all resulted in uranyl compounds.[1,2] A basic nitrate, $UO(NO_3)_2$, said to be stable to 100°, has, however, been reported as being precipitated during the photochemical reduction of an aqueous-ethanolic solution of uranyl nitrate [3] and also, more recently, a hydrated form, $UO(NO_3)_2,4H_2O$, has been said to be precipitated when uranium(IV) in 2N-nitric acid is treated with dioxan.[4] We have been unable to repeat either of these preparations.

Uranium(IV) is fairly resistant to oxidation in 5N-nitric acid when reagents which destroy nitrite, such as sulphamic acid, are present [5] and this stability increases with the nitric acid concentration, probably owing to the formation [6] of complex anions such as $U(NO_3)_6^{2-}$. Since the plutonium analogues of this anion give relatively insoluble salts with alkali-metal cations, of the form [7] $M_2^IPu(NO_3)_6$, an attempt has been made to prepare the uranium analogues and also uranium tetranitrate or its amide complex in non-aqueous media by a method already described.[8]

We tried to prepare uranium tetranitrate by reaction of uranium tetrachloride in acetone with silver nitrate in acetonitrile; the green solution, after removal of silver chloride, was evaporated under a vacuum at room temperature, but as the green solid product separated in the last stages of the evaporation it was oxidised spontaneously to uranium(VI); similarly, evaporation *in vacuo* of solutions of uranium(IV) in 2N-nitric acid yielded a green solid which was oxidised spontaneously. Strong cooling of solutions of the tetranitrate in acetonitrile did not lead to separation of a solid. We also failed to

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[1] Späth, *Monatsh.*, 1912, **33**, 857.
[2] Aloy and Rodier, *Bull. Soc. chim. France*, 1922, **31**, 246.
[3] Benrath, *Z. wiss. Phot.*, 1917, **16**, 259.
[4] Sahoo and Patnaik, *Current Sci.*, 1960, **29**, 16.
[5] See, *e.g.*, Jenkins and Streeton, A.E.R.E. report R-3158, 1959.
[6] Ryan, *J. Phys. Chem.*, 1960, **64**, 1375.
[7] Anderson, " The Transuranium Elements," Nat. Nuclear Energy Series, ed. Seaborg, Katz, and Manning, McGraw-Hill Book Co., Inc., New York, 1949, Vol. IV-14B, p. 964.
[8] Bagnall, Deane, Markin, Robinson, and Stewart, *J.*, 1961, 1611.

obtain a basic nitrate; azeotropic distillation of uranium(IV) in dilute nitric acid with diethyl ether yielded a black sludge of oxide, and removal of acid and water by repeatedly shaking similar solutions with ethyl acetate ultimately gave a ~3% yield of a green solid of composition $UO(NO_3)_{1\cdot03-1\cdot54}$, 2·4—4·9 H_2O which evolved oxides of nitrogen at 80° and was oxidised to uranium(VI) at 100° in air. It seems unlikely that the compound previously reported [3] to be stable at 100° was a uranium(IV) nitrate.

The *NN*-dimethylacetamide complex was prepared by treating an acetone solution of the chloride derivative, UCl_4,2·5Ac·NMe_2, in the presence of an excess of ligand, with the calculated quantity of silver nitrate in acetonitrile. After evaporation of the supernatant liquid *in vacuo* to small volume, the solution was diluted with acetone, and the complex was precipitated as a green oil by adding isopentane. Repetition of the acetone-dissolution–isopentane-precipitation cycle removed the last traces of silver salts, and the oil was dried under a vacuum to a green solid. This was ground with ethyl acetate to remove the last traces of free ligand and again dried *in vacuo*. The compound can also be prepared, but in poor yield, from the cæsium complex salt, $Cs_2U(NO_3)_6$, by following the procedure used for the chloride complex.[8]

The pale green complex, $U(NO_3)_4$,2·5Ac·NMe_2, is non-hygroscopic and soluble in acetone, acetonitrile, *NN*-dimethylacetamide, dioxan, ethanol, methanol, and nitromethane. It is slightly soluble (~10 g./l.) in ethyl acetate, very slightly soluble in isobutylmethyl ketone, and insoluble in benzene, diethyl carbonate, diethyl ether, and di-isobutyl ketone. It can be recovered as an oil from its solutions in organic solvents, other than methanol, by precipitation with isopentane, acetone being added where necessary to achieve miscibility with the hydrocarbon. The complex is not very stable, the evolution of oxides of nitrogen being detectible at 65°; it melts to a green liquid at 80—82° and oxidation to uranium(VI) is complete at 90—95°. It is slowly oxidised on storage (about 6% in one month).

The ligand infrared spectrum is almost identical with that of the ligand in the corresponding chloride complex; [8] six nitrate bands were observed, at 1517, 1277, 1020, 807, and 702 cm.$^{-1}$, and one band split at 743, 739 cm.$^{-1}$, indicating covalent nitrate groups.[9]

Both cæsium and tetraethylammonium hexanitratouranate(IV) are precipitated in good yield when the appropriate nitrate in concentrated nitric acid saturated with sulphamic acid is added to uranium(IV) in 8M-nitric acid–sulphamic acid at 0°.

They are both white solids with a faint green cast. The cæsium salt is also produced by treating solid dicæsium hexachlorouranate(IV) with an acetonitrile solution of silver nitrate; when the solution is diluted with acetone and isopentane is added, the product separates in rather poor yield.

At this stage of the work, Dr. Ryan informed us that he was shortly describing [10] the preparation of the tetraethylammonium salt, which he had obtained by the addition of an excess of tetraethylammonium nitrate in concentrated nitric–sulphamic acid to a solution of uranium(IV) in perchloric acid at 0°, together with data on the absorption spectra in acetone and in nitromethane. We had found that the compound is also soluble in acetonitrile, *NN*-dimethylacetamide, and hot methanol, slightly soluble in hot ethanol, and insoluble in diethyl carbonate, dioxan, ethyl acetate, and ethyl methyl ketone. We had also shown that it is slowly oxidised to uranium(VI) if kept in organic solvents and that it can be recovered from solutions in these solvents by precipitation with isopentane, acetone being added in order to achieve miscibility with the hydrocarbon where necessary. The compound is best recrystallised from hot methanol or hot acetone.

The compound is non-hygroscopic, and stable at room temperature for many weeks, but Ryan found some signs of decomposition after 18 months; [10] it decomposes at 120—125°, oxides of nitrogen being detectable, and at 150° oxidation to uranium(VI) is rapid. The oxidised product melts at 162—164°, releasing trapped oxides of nitrogen. The

[9] See, *e.g.*, Ferraro, *J. Mol. Spectroscopy*, 1960, **4**, 99.

[10] Ryan, *J. Inorg. Nuclear Chem.*, in the press.

melting point corresponds to that reported [10] for $(Et_4N)_2UO_2(NO_3)_4$. If rapidly heated, it decomposes violently. The nitrate bands in the infrared spectrum of the quadrivalent salt indicate covalent nitrate groups, as in the tetranitrate complex.

The cæsium salt is slightly soluble in acetonitrile and very slightly soluble in hot acetone and in methanol, but is readily oxidised to uranium(VI) in the last solvent; it is insoluble in pentyl acetate, dioxan, ethanol, ether, methyl acetate, or nitromethane. It decomposes very slowly at room temperature, more rapidly when heated, oxides of nitrogen being detectable at 100—105°; decomposition is very rapid at 155—165°, with oxidation of the uranium to the sexivalent state. The salt dissolves in formamide to an emerald solution from which cæsium nitrate is precipitated by acetone; repeated washing of the supernatant liquid with benzene to remove the excess of formamide ultimately gives a green solid in very poor yield; this is presumably a uranium(IV) nitrate–formamide complex.

EXPERIMENTAL

Preparative.—(a) *Uranium tetranitrate.* Uranium tetrachloride was dissolved in acetone. The calculated amount of silver nitrate, in acetonitrile, was added. The filtrate was evaporated to dryness under a vacuum at room temperature or below.

(b) *Uranium tetranitrate–amide complex.* The chloride complex, $UCl_4,2{\cdot}5Ac{\cdot}NMe_2$, (1—2 g.) was dissolved in hot acetone (20 ml.), cooled, and, after addition of an excess of ligand (1—2 ml.), the calculated amount of silver nitrate, in acetonitrile, was added. The filtrate was evaporated under a vacuum to small bulk, acetone (2 vol.) was added, and the complex precipitated as a green oil with isopentane (10 vol.). The acetone–isopentane cycle was repeated, 5—6 times, small amounts of silver salts being removed at each of the earlier acetone dissolution stages. The final oily product was dried in a vacuum and ground with ethyl acetate, and the solid dried again (yield, 50—60%). Preparations made by treating dicæsium uranium(IV) hexanitrate as in the preparation of the chloride complex [8] only solidified on vacuum-drying after being washed with benzene; the *product* was then treated with ethyl acetate as above [Found: U(IV), 33·2; NO_3^-, 35·2; $Ac{\cdot}NMe_2$, 30·5. $U(NO_3)_4,2{\cdot}5Ac{\cdot}NMe_2$ requires U(IV), 33·8; NO_3^-, 35·3; $Ac{\cdot}NMe_2$, 30·9%].

(c) *Hexanitratouranium*(IV) *salts.* Since sulphamic acid is much less soluble in concentrated than in dilute nitric acid, solutions in dilute nitric acid were prepared by diluting those in concentrated acid. Freshly prepared uranium(IV) hydroxide was dissolved in 8M-nitric acid–sulphamic acid at 0° and an excess of cæsium or tetraethylammonium nitrate in 16M-nitric acid, saturated with sulphamic acid, was added slowly, with stirring, at 0°. The precipitate was filtered off after being kept for 15 min. at 0°. The *cæsium salt* was dissolved in N-nitric acid–sulphamic acid and reprecipitated with concentrated acid as before, washed with ethanol (3 × 5 ml.), ether (1 × 5 ml.), and dried at 10^{-3} mm. for 8 hr. [Found: U(IV), 27·2; NO_3^-, 42·8; Cs, 30·7. $Cs_2U(NO_3)_6$ requires U(IV), 27·2; NO_3^-, 42·5; Cs, 30·4%]. The *tetraethylammonium salt* was washed with ethanol (5 ml.), recrystallised from hot methanol or acetone, and dried *in vacuo* as above [Found: U(IV), 27·6; NO_3^-, 42·3; total N, 12·8; C, 22·4; H, 4·6. $(Et_4N)_2U(NO_3)_6$ requires U(IV), 27·3; NO_3^-, 42·7; total N, 12·9; C, 22·2; H, 4·6%].

(d) Starting materials were prepared as previously described.[8]

Analysis.—(a) *NN*-Dimethylacetamide was determined as already described.[8]

(*b*) Nitrate was weighed as nitron nitrate,[11] since the Kjeldahl method gave rather low results.

(*c*) Uranium(IV) was determined by titration to uranium(VI) with permanganate or dichromate. Nitrate ion is reported to interfere with the dichromate titration, but we found that titration in the presence of sulphamic acid gave concordant results with both reagents.

(*d*) Cæsium was weighed as hexachlorostannate,[12] uranium having first been removed by precipitation as hydroxide by calcium hydroxide.

(*e*) Tetraethylammonium ion. Nitrogen determinations by the Kjeldahl method were

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[11] Vogel, "Textbook of Quantitative Inorganic Analysis," Longmans, Green and Co., London, 1953, p. 505.

[12] Treadwell and Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York, 1945, Vol. II, p. 286.

low even after prolonged digestion. Total nitrogen by the Dumas method gave better results; carbon and hydrogen were found by combustion.

Infrared Spectra.—Spectra of the tetranitrate–dimethylacetamide complex were observed as mulls in Fluolube and Nujol; a Hilger H800 spectrometer with sodium chloride and cæsium bromide prisms was used.

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