# 317. *Uranium*(IV) *Perchlorate.*

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A uranium tetraperchlorate–dimethylacetamide complex, $U(ClO_4)_4,6Ac{\cdot}NMe_2$, and its trihydrate have been prepared. The complex is stable, much more so than those formed by methylacetamide, which appear to have 6 and 8 molecules of ligand severally and are hygroscopic. Uranium tetraperchlorate is itself unstable and has not been obtained pure.

ALTHOUGH solutions of uranium(IV) in perchloric acid are easily made by electrolytic reduction of acid solutions of uranyl perchlorate[1] or by dissolution of uranium(IV) hydroxide in perchloric acid,[2] the only recorded solid perchlorate is the hydrated phosphate perchlorate compound, $U(H_2PO_4)_2(ClO_4)_2$, obtained by shaking hydrated uranium(IV) monohydrogen phosphate with 10M-perchloric acid for several days.[3] Previously[4] we found that a solution of uranium(IV) perchlorate–amide complex resulted from metathesis of the chloride complex with silver perchlorate in acetone. This reaction, and the corresponding one with uranium tetrachloride, have now been further investigated.

Pure uranium tetraperchlorate could not be made. Treating an acetone solution of uranium tetrachloride, or solid dicæsium uranium(IV) hexachloride, with silver perchlorate in acetone and precipitating the uranium compound from the filtrate with isopentane gave a green hygroscopic viscous oil in which the uranium(IV) : perchlorate ratio was close to 1 : 4. The product, after several dissolutions in acetone and precipitations by isopentane, was a mixture of uranium tetraperchlorate and uranyl perchlorate ($<30\%$). Infrared spectroscopy showed the presence of water and an organic component, possibly strongly bonded acetone, neither of which could be removed in a vacuum at room temperature. Heating the oil at 55° in a vacuum gave a shock-sensitive, explosive green solid. The uranium(IV) component in the oil is not oxidised appreciably on storage but is oxidised quite rapidly in aqueous acetone or mineral acid; this suggests that the partial oxidation to uranium(VI) occurs during its preparation and that a pure product is not to be expected.

The oil was an unsuitable starting material from which to make the more stable amide complexes. These are easily prepared by metathesis of the corresponding chloride derivatives with silver perchlorate in an acetone–amide solution, the product being precipitated from the filtrate with isopentane. The dimethylacetamide complex was purified by crystallisation from its solution in nitromethane on addition of isobutyl methyl ketone or diethyl ketone. Unlike the chloride[4] and nitrate[5] analogues, it crystallises with six molecules of ligand. The dark green anhydrous complex melts at about 132°,

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[1] See, *e.g.*, Lawrence, *J. Amer. Chem. Soc.*, 1934, **56**, 778.

[2] See, *e.g.*, Sidgwick, " The Chemical Elements and their Compounds," Oxford, Clarendon Press, 1950, p. 1083.

[3] Schreyer and Phillips, *J. Phys. Chem.*, 1956, **60**, 588.

[4] Bagnall, Deane, Markin, Robinson, and Stewart, *J.*, 1961, 1611.

[5] Bagnall, Robinson, and Stewart, *J.*, 1961, 4060.

with some decomposition, to a green liquid which is completely oxidised to uranium(VI) at 160°. When rapidly heated above that point it deflagrates violently. The solid is oxidised slowly at room temperature in dry air [about 5% of uranium(VI) formed in 30 days], but at 100° in a vacuum its oxidation to a uranyl perchlorate complex is complete in 7 hr.; it is also rapid at 100° in air. The amount of ligand in the oxidation products was variable. In moist air, it becomes the paler green trihydrate in about 2 hr.; this water is easily removed under a vacuum ($10^{-2}$ mm.) at room temperature and is gradually lost in air below 100°, but not when kept over phosphorus pentoxide at room temperature.

The infrared spectra of the hydrated and the anhydrous compound show organic ligand frequencies almost identical with those of the chloride complex. Water in the hydrate is bonded in a fairly well-defined manner, and gives four distinct peaks in the region of OH stretching vibrations; possibly the band pairs at 3535, 3415 and 3320, 3185 cm.$^{-1}$ are the symmetric and antisymmetric vibrations ($\nu_1$, $\nu_3$) of water molecules in two different positions within the complex. In the anhydrous compound the perchlorate groups absorb at 1091, 1027, 640, and 623 cm.$^{-1}$, which may indicate some covalent character,[6] for the free ion should show only two bands, at about 1100 and 630 cm.$^{-1}$. The hydrate has perchlorate absorptions at 1112, 1065, 1032, and 623 cm.$^{-1}$, again possibly indicating some covalent character. The changes in frequency are related to the presence of water, but since this is not strongly held, it may be hydrogen-bonded to the ligand rather than to either cation or anion. The electron density at the amide nitrogen atom is enhanced by nucleophilic methyl groups and since the ligand does not seem to form a bridge as might occur with the chloride analogue,[4] it is reasonable to suppose that the water molecules are shared between adjacent pairs of ligand molecules by hydrogen bonding to the amide nitrogen atoms. This would account for no more than three molecules of water being taken up. The *X*-ray powder patterns of the anhydrous and the hydrated complex also do not differ much; both show low symmetry.

It was also of interest to prepare the *N*-methylacetamide derivative of uranium tetraperchlorate since the chloride analogue differs from the acetamide and *NN*-dimethylacetamide complexes in having the composition $UCl_4$,4Ac·NHMe.[7] It was obtained by a similar metathesis with silver perchlorate in acetone–amide solution; the product from cold solutions had the composition $U(ClO_4)_4$,7·4—7·68Ac·NHMe, with 1·2—3·1% of unidentified impurity, probably organic since analysis showed the absence of water. It was extremely hygroscopic and at 102° appeared to exude liquid which was probably free ligand; it melted (or dissolved) at 115—120°. When the original material was recrystallised from nitromethane–isobutyl methyl ketone or heated with an excess of ligand at 70° for 15 min., its composition approached $U(ClO_4)_4$,6Ac·NHMe (m. p. 146—154°); again there was appreciable impurity present and this material was also very hygroscopic. Both complexes are more readily oxidised than the *NN*-dimethylacetamide derivative, about 25% oxidation to uranium(VI) occurring in 12 days at room temperature. *X*-Ray powder photographs indicated that at least two different species were present; the first was presumably mainly $U(ClO_4)_4$,8Ac·NHMe and the second, $U(ClO_4)_4$,6Ac·NHMe. This was not pursued because of the ready oxidation to uranium(VI).

## EXPERIMENTAL

*Preparative.*—(a) *Uranium tetraperchlorate.* Uranium tetrachloride was titrated potentiometrically against silver perchlorate, both in acetone. Isopentane was added to the filtrate and the green oil which separated was subjected to 3 acetone dissolution–isopentane precipitation cycles. The product was vacuum-dried, but remained an oil, even over phosphorus pentoxide during several days. Similar material was obtained when methyl acetate was used as solvent and also by treating dicæsium uranium(IV) hexachloride with the calculated quantity of silver perchlorate in acetone. This oil is soluble in acetone, ethyl, methyl, or pentyl acetate, heptan-1-ol, isobutyl methyl ketone, and nitromethane. Although insoluble in cold diethyl

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[6] Hathaway and Underhill, *J.*, 1961, 3091.

[7] Bagnall and Robinson, to be published.

carbonate, it dissolves when warmed, to a green solution from which an oil separates on cooling; when this solution is heated for 30 min. at 60° the uranium is oxidised to the sexivalent state. The oil also dissolved, and was oxidised to uranium(VI), in cold tetrahydrofuran, t-pentyl alcohol, and di-isopropyl ketone, and in warm nitrobenzene. Warming with dioxan produced a sludge of black uranium oxides. Treatment of the oil, or its solution in nitromethane, with di-isobutyl ketone precipitated a little unidentified green solid, but addition of isopentane or propyl or butyl chloride to the solution caused the perchlorate oil to separate, as did isopentane when added to solutions in other solvents. Methanol proved an unsatisfactory solvent for the preparation.

(b) *Uranium tetraperchlorate*–NN-*dimethylacetamide complex.* The chloride analogue (200—400 mg.) was dissolved in hot acetone (~10 ml.) and the calculated amount of silver perchlorate in acetone (10 ml.), was added. Excess of ligand was added to the filtrate, and the complex was precipitated as a green oil with isopentane. The acetone–isopentane cycle was repeated five times and the final product washed with isopentane and vacuum-dried. The resulting green solid was about 96% pure. Recrystallisation of the crude product from heptanol led to some oxidation of the uranium, but the addition of isobutyl methyl ketone or diethyl ketone to solutions of the complex in nitromethane slowly precipitated purer crystals in 50% yield. These were washed with isopentane (2 × 15 ml.) and vacuum-dried ($2 \times 10^{-4}$ mm.); analysis showed a purity >99%. With larger (gram) scale preparations the crude product separated as a solid rather than as an oil; it was washed with ethyl acetate (3 × 15 ml.) to remove the excess of ligand and purified as before. It is soluble in acetone, acetonitrile, ethanol, ethyl methyl ketone, formamide, methanol, 50% v/v methanol–methyl acetate, nitroethane, and nitromethane; it is slightly soluble in t-pentyl alcohol and insoluble in "Butex," diethyl carbonate, diethyl ether, diethyl ketone, di-isobutyl ketone or halogenated hydrocarbons. It is moderately soluble in hot heptan-1-ol, but some oxidation occurs, and analysis of the product recovered from the solution suggests that it is a mixture of $U(ClO_4)_4,6Ac{\cdot}NMe_2$ and $UO_2(ClO_4)_2,4Ac{\cdot}NMe_2$.

The trihydrate and trideuterate were prepared by exposing the anhydrous compound to the vapour of water and heavy water, respectively.

(c) *Uranium tetraperchlorate*–N-*methylacetamide complexes.* These were prepared by a similar metathesis with silver perchlorate, $U(ClO_4)_4,8Ac{\cdot}NHMe$ being formed in the cold and precipitated as an oil with isopentane. It was vacuum-dried ($10^{-3}$ mm.) to a green solid and finally washed with ethyl acetate. Sometimes the product had to be washed with ethyl acetate before it would solidify. $U(ClO_4)_4,6Ac{\cdot}NHMe$ was obtained by treating it, in nitromethane, with isobutyl methyl ketone or by heating it with an excess of ligand at 70°, followed by an isopentane wash and vacuum-drying as before.

*Analysis.*—(*a*) Uranium(IV) and amides were determined as already described.[4] (*b*) Water was determined by the Karl Fischer method,[8] the results being in agreement with the increase in weight due to hydration. (*c*) Perchlorate was weighed as the tetraphenylarsonium salt [9] after the removal of uranium as hydroxide with ammonia, since uranium(IV) is precipitated by this reagent under the conditions for perchlorate precipitation.

*Results.*—(*a*) *NN*-Dimethylacetamide complex; Found: U(IV), 20·5; $ClO_4^-$, 34·5; $Ac{\cdot}NMe_2$, 44·7. $U(ClO_4)_4,6Ac{\cdot}NMe_2$ requires U(IV), 20·5; $ClO_4^-$, 34·4; $Ac{\cdot}NMe_2$, 45·1%. The trihydrate; Found: $H_2O$, 4·6. Requires $H_2O$, 4·5%.

(*b*) *N*-Methylacetamide complexes. The analytical results are expressed as ratios owing to the irreproducible amounts of impurity present in all preparations. $U(ClO_4)_4,8Ac{\cdot}NHMe$: Found, U(IV) : $ClO_4^-$ : Ac·NHMe = 1 : 4·0 : 7·4—7·7 (impurity 1·2 to 3·1%). $U(ClO_4)_4,6Ac{\cdot}NHMe$: Found, U(IV) : $ClO_4^-$ : Ac·NHMe = 1 : 4·0 : 5·85—6·45 (impurity 1·8 to 6%).

*Infrared Spectra.*—Spectra of the tetraperchlorate and the amide complexes were observed as mulls in Fluorube and Nujol; a Hilger H800 spectrometer with sodium chloride and cæsium bromide prisms was used.

X-*Ray Powder Photography.*—Powder photographs were taken with a 19-cm. Unicam Debye–Scherrer camera and filtered Cu-*K*α radiation.

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[*Received, October 9th*, 1961.]

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[8] Vogel, "A Text-book of Quantitative Inorganic Analysis," 2nd Edn., Longmans, Green and Co., Ltd., London, 1951, p. 698.

[9] Willard and Smith, *Ind. Eng. Chem. Analyt.*, 1939, **11**, 186, 305.