The Stabilisation of Plutonium Tetrabromide and Uranium Pentabromide

By D. BROWN,* D. G. HOLAH, and C. E. F. RICKARD
(*Chemistry Division, Building* 220, *A.E.R.E., Harwell, Didcot, Berks.*)

ALTHOUGH hexabromoplutonates(IV) of the type R_2PuBr_6 (R = tetralkylammonium cation) have been reported[1] plutonium tetrabromide itself is unknown. In addition, uranium pentabromide is a relatively unstable compound which is difficult to obtain pure[2] and for which few chemical properties have been reported. We describe now the preparation and some properties of the first stable complexes formed by plutonium tetrabromide and uranium pentabromide with oxygen-donor ligands.

Both plutonium tribromide and uranium tetrabromide are rapidly oxidised by liquid bromine in anhydrous methyl cyanide. In the presence of the stoicheiometric amounts of either triphenylphosphine oxide (TPPO) or hexamethylphosphoramide (HMPA) soluble complexes of the types $PuBr_4,2L$ and UBr_5,L (L = TPPO and HMPA) are formed. Whilst this work was in progress we heard from Dr. J. L. Ryan[3] that he had prepared hexabromouranates (V), $RUBr_6$ (R = tetralkylammonium cation), by methods involving bromine oxidation of uranium tetrabromide.

The bright-red, solid plutonium tetrabromide–phosphine oxide complexes are isolated by removal of the excess of oxidant and solvent *in vacuo* at room temperature. Pure products are readily obtained by washing these solids with anhydrous methylene dichloride or methyl cyanide in which they are only slightly soluble. $PuBr_4,2TPPO$ and $PuBr_4,2HMPA$ are each isostructural with their known quadrivalent actinide analogues.[4] ($PuBr_4,2HMPA$ was identified by *X*-ray powder diffraction analysis). The phosphine oxide complexes are indefinitely stable in an inert atmosphere but, in contrast, $PuBr_4,4MeCN$, which can be prepared in a similar manner, is relatively unstable and both the solid and solutions in methyl cyanide are unstable with respect to plutonium(III).

The dark-red uranium pentabromide phosphine oxide complexes are initially isolated as described for the plutonium(IV) complexes. Traces of uranium(IV) can be removed from the product by dissolving the pentabromide complexes in anhydrous, oxygen-free methylene dichloride in which they are extremely soluble and from which solvent they are quantitatively precipitated by the addition of isopentane. Uranium and plutonium were determined as described previously[5,6] and bromide was weighed as silver bromide.

X-Ray powder diffraction patterns have been recorded for these complexes but the results have not been interpreted; the number of low-angle reflections suggests that the complexes possess low symmetry. The absorption spectra of the plutonium(IV) and uranium(V) complexes dissolved in methylene dichloride (4000—30,000 cm.$^{-1}$) are very similar to those previously reported for hexabromoplutonates(IV)[1] and uranium pentachloride complexes[5] respectively. In each case only a single oxidation state has been detected and the solutions are perfectly stable for several days in an inert atmosphere.

As previously found for analogous penta- and tetra-chloride complexes, MCl_5,TPPO (M = Nb, Ta, Pa, and U)[5,7] and MCl_4,2HMPA (M = Th and U)[8] respectively, large shifts in the position of the P=O stretching vibrations are observed on co-ordination of the phosphine oxides to $PuBr_4$ and UBr_5. Thus, for $PuBr_4$,2TPPO, $PuBr_4$,2HMPA, UBr_5,TPPO, and UBr_5,HMPA $\nu_{P=O}$ and $\Delta\nu_{P=O}$ are, respectively, 1040, 1025, 960, 925, and 152, 176, 232, and 276 cm.$^{-1}$. The structure of one of the pentachloride–phosphine oxide complexes is currently being investigated in order to obtain information on the respective M^{V}–oxygen and P–oxygen bond lengths.

In addition to plutonium tetrabromide, other thermodynamically unstable actinide halides include, for example, neptunium pentachloride, neptunium pentabromide, and americium tetrabromide. Attempts to prepare phosphine oxide complexes of neptunium pentabromide and americium tetrabromide using the above method involving bromine oxidation of a stable lower bromide have been unsuccessful. Similarly, attempts to oxidise neptunium tetrachloride by passing chlorine through a suspension of $NpCl_4$,4MeCN in methyl cyanide, either alone or in the presence of TPPO or NEt_4Cl, have failed. Although the tetrachloride dissolved under these conditions the absorption spectrum of the resulting solution showed that no oxidation had taken place.

Further details of the chemical and physical properties of the plutonium tetrabromide and uranium pentabromide complexes will be published in due course together with information on analogous complexes or other actinide elements and of niobium and tantalum.

(*Received, April 24th,* 1968; *Com.* 496.)

---

[1] J. L. Ryan and C. K. Jørgenson, *Mol. Phys.*, 1963, **7**, 17.
[2] J. Prigent, *Compt. rend.*, 1954, **238**, 102; 1954, **239**, 424; *Ann. Chim. (France)*, 1960, **5**, 65.
[3] J. L. Ryan, personal communication, 1968.
[4] D. Brown, D. G. Holah, and C. E. F. Rickard, unpublished observations.
[5] K. W. Bagnall, D. Brown, and J. G. H. du Preez, *J. Chem. Soc.*, 1964, 2603; 1965, 5217.
[6] K. W. Bagnall, D. Brown, and D. G. Holah, *J. Chem. Soc. (A)*, 1968, 1149.
[7] D. Brown, J. F. Easey, and J. G. H. du Preez, *J. Chem. Soc. (A)*, 1966, 258.
[8] K. W. Bagnall, D. Brown, P. J. Jones, and J. G. H. du Preez, *J. Chem. Soc. (A)*, 1966, 737.