52. *Iodo-complexes of Thorium*(IV) *and Uranium*(IV).

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Complexes of the type $R_2M^{IV}I_6$ ($R = Bu_4N^+$, Ph_4As^+; M^{IV} = Th, U) and the adduct $ThI_4,4CH_3CN$ have been prepared by reactions in anhydrous methyl cyanide. Magnetic properties are reported for tetraphenylarsonium hexaiodouranate(IV) and hexachlorouranate(IV).

ALTHOUGH the hexachloro-,[1,2a] hexabromo-[3] and hexanitrato-complexes [2b,4] of thorium(IV) and uranium(IV) have been characterised, no successful preparation of the analogous hexaiodo-complexes has so far been reported. Thorium and uranium tetraiodides are readily hydrolysed,[2a] even in the solid state, and it is unlikely that anhydrous hexaiodo-complexes can be isolated pure from aqueous solution. Recently Ryan and Jørgensen [3] have examined the absorption spectra of methyl cyanide solutions of a uranium(IV) iodide in the presence of tributylpropylammonium iodide. The uranium(IV) iodide was obtained by oxidation of the tri-iodide by a deficit of iodine. They concluded, from a comparison with the spectra of the hexachloro- and hexabromo-complexes, that UI_6^{2-} ions were present. However, they were unable to obtain solid complexes from such solutions or from a similar system in aqueous mixtures of hydriodic acid, methanol, and acetone.

We now report the preparation of the tetrabutylammonium and tetraphenylarsonium

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[1] Ryan, *J. Phys. Chem.*, 1961, **65**, 1856.

[2] Seaborg and Katz, " The Actinide Elements," Nat. Nucl. Energy Series, Div. IV, **14***A*, McGraw-Hill, New York, 1954, (*a*) p. 84, (*b*) p. 81, (*c*) pp. 85 and 154.

[3] Ryan and Jørgenson, *Mol. Phys.*, 1963, **7**, 17.

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

hexaiodo-complexes of thorium(IV) and uranium(IV), $(Bu_4N)_2MI_6$ and $(Ph_4As)_2MI_6$, from methyl cyanide solutions of the metal tetraiodides.

Thorium tetraiodide undergoes an exothermic reaction with anhydrous methyl cyanide at room temperature to give the solid adduct, $ThI_4,4CH_3CN$, a pale yellow, moisture-sensitive compound, which is only slightly soluble in methyl cyanide in the absence of free iodine. It readily loses methyl cyanide even at 50° in a vacuum; thermogravimetric analysis shows that all four molecules are lost at 160° and there is no indication of thermally stable complexes between $ThI_4,4CH_3CN$ and ThI_4. The analogous uranium(IV) complex cannot be isolated pure, presumably owing to the ready loss of iodine in methyl cyanide solution in the absence of alkylammonium iodides. Low iodine : uranium ratios are always observed (~3·7 : 1) even when the reaction is performed in an atmosphere of argon. Although uranium tetraiodide itself is unstable in dry air, we find that it can be safely handled in dry argon.

The tetraphenylarsonium hexaiodocomplexes of thorium(IV) (yellow) and uranium(IV) (red) crystallise when a methyl cyanide solution of the components is cooled to 0°. They are slowly hydrolysed in moist air, initially turning brown and green, respectively, but are indefinitely stable in a dry atmosphere. They are soluble in acetone, and are decomposed rapidly by water or dilute acids to give a solution of the metal ion and insoluble tetraphenylarsonium iodide. The complexes are moderately stable to heat, but iodine is liberated above 200°; although they are obtained as large crystals from methyl cyanide solution, they give poor quality *X*-ray powder-diffraction photographs. The tetraphenylarsonium hexaiodouranate(IV) is temperature-independent paramagnetic between 300 and 84°K, a behaviour similar to that previously observed for hexachlorouranates(IV) [5,6] and hexabromouranates(IV).[7] The molar susceptibility, $\chi_m = 2146 \pm 30 \times 10^{-6}$ c.g.s. units, is very similar to that of the cæsium and tetramethylammonium hexachlorouranates(IV), 2063 (or [5] 1944) and 2243×10^{-6} c.g.s., respectively. We have also examined the magnetic properties of tetraphenylarsonium hexachlorouranate(IV), and again find temperature-independent paramagnetism between 300 and 84°K. The molar susceptibility in this instance is $2053 \pm 16 \times 10^{-6}$ c.g.s. units.

Care is necessary in the preparation of the tetraphenylarsonium hexaiodo-complexes in order to avoid the presence of free iodine, which would lead to the formation of tetraphenylarsonium periodide, Ph_4AsI_3, which crystallises as large black plates from methyl cyanide. Thus, it is essential that the tetraiodides used for these preparations should be completely free from excess of iodine, a condition that is readily fulfilled for thorium(IV) by use of the methyl cyanide adduct. The most satisfactory published preparation [8] of uranium tetraiodide involves complicated apparatus, and we find that an extremely pure product is obtained by using a vessel that consists simply of two sections of glass tubing joined through a constriction. Iodine, in 50% excess, is placed with uranium metal turnings in one section and the whole of the vessel evacuated. The empty section is heated to 140° and the iodine–uranium mixture is then gradually heated to 530° by means of a second furnace, and maintained at this temperature for several hours. On simultaneous cooling of the two sections the excess of iodine is quantitatively sublimed out of the section containing uranium tetraiodide. Reactions carried out with uranium metal and iodine initially in separate sections were less satisfactory, the product being contaminated with uranium tri-iodide.

Addition of tetrabutylammonium iodide in methyl cyanide to the thorium tetraiodide–methyl cyanide adduct or to uranium tetraiodide gave yellow and dark red solutions, respectively, from which no crystalline solids were obtained on prolonged cooling in ice. However, on vacuum evaporation of solutions containing stoicheiometric quantities of the

[5] Bagnall, Brown, and Colton, *J.*, 1964, 2527.

[6] Candela, Hutchinson, and Lewis, *J. Chem. Phys.*, 1959, **30**, 246.

[7] Day, personal communication.

[8] Katz and Rabinowitch, " The Chemistry of Uranium," Part I, Nat. Nuclear Energy Series, Div. VIII, Vol. 5, McGraw-Hill, New York, 1951, p. 253.

reactants $(Bu_4N)_2ThI_6$ (orange) and the extremely unstable $(Bu_4N)_2UI_6$ (red) were obtained. Both complexes are sensitive to moisture and the uranium(IV) compound, although stable in a vacuum, rapidly liberates iodine even in dry argon. The absence of lines due to tetrabutylammonium iodide on the *X*-ray powder-diffraction photographs of the thorium(IV) complex precludes the possibility that the products are merely intimate mixtures of the reactants. Solutions of tetrabutylammonium hexiodouranate(IV) in methyl cyanide are unstable in air, rapidly depositing a green solid, which is presumably a hydrolysis product.

EXPERIMENTAL

Uranium tetraiodide was prepared as described in the discussion, and thorium tetraiodide was prepared according to the published [9] method. The uranium compounds were handled in a dry argon box, but an argon atmosphere was unnecessary for the thorium reactions. Anhydrous methyl cyanide was obtained as described previously,[10] and tetraphenylarsonium iodide was prepared from the chloride.[11]

Thorium Tetraiodide–Methyl Cyanide Complex.—Anhydrous methyl cyanide (4 ml.) was added to thorium tetraiodide (2 g.) and the pale yellow solid that immediately formed was washed with methyl cyanide (3 × 3 ml.) and vacuum dried at room temperature (Found: Th, 25·7; I, 56·2; N, 6·1. $ThI_4,4CH_3CN$ requires Th, 25·8; I, 56·0; N, 6·2%).

Tetraphenylarsonium Hexaiodo-complexes.—These were prepared by heating (70°) uranium tetraiodide or the thorium tetraiodide–methyl cyanide complex (1 g.) with excess of tetraphenylarsonium iodide in methyl cyanide (10 ml.). The crystalline products obtained on cooling the solutions in ice were washed with ice-cold methyl cyanide (1 × 2 ml.) and vacuum dried at room temperature [Found: U, 13·3; I, 43·0. $(Ph_4As)_2UI_6$ requires U, 13·5; I, 43·1. Found: Th, 13·3; I, 43·1. $(Ph_4As)_2ThI_6$ requires Th, 13·2; I, 43·3%].

Tetrabutylammonium Hexiodo-complexes.—These were prepared by dissolving stoicheiometric amounts (2 : 1) of tetrabutylammonium iodide (1 g.) and either uranium tetraiodide or the thorium tetraiodide–methyl cyanide complex in methyl cyanide (10 ml.) and evaporating the resulting solution to dryness *in vacuo*. The products retained methyl cyanide at room temperature, and this was removed by prolonged heating at 80° in a vacuum. Even under these conditions, the uranium complex was never more than 98% pure [Found: U, 15·6; I, 50·2. $(Bu_4N)_2UI_6$ requires U, 16·0; I, 51·3. Found: Th, 15·8; I, 50·9. $(Bu_4N)_2ThI_6$ requires Th, 15·7; I, 51·5%].

Tetraphenylarsonium Hexachlorouranate(IV).—Prepared from hydrochloric acid solution as previously described [12] for the cæsium salt, this compound was purified by crystallisation from methyl cyanide [Found: U, 19·5; Cl, 17·5. $(Ph_4As)_2UCl_6$ requires U, 19·6; Cl, 17·5%].

Thermogravimetric Measurements.—These were made with a conventional quartz-fibre thermobalance as described previously.[12] The samples were slurried in methyl cyanide to afford protection from atmospheric moisture during mounting, the excess of methyl cyanide being removed under vacuum at room temperature before any measurements were made. The operating pressure was 3×10^{-4} mm. and the temperature was increased at a rate of 0·5°/min.

Magnetic Susceptibilities.—These were measured on a Gouy balance described previously.[13] Samples of the hexaiodo-complex were packed in a previously calibrated quartz tube in a dry atmosphere, and the tube was stoppered with a polythene bung to exclude moisture during measurements. The susceptibilities of the tetraphenylarsonium chloride and iodide were determined directly, and it was found that these compounds contained small amounts of a temperature-independent paramagnetic impurity, $\chi_m = 73$ and 139×10^{-6} c.g.s. units, respectively. The observed susceptibilities of the uranium(IV) complexes were corrected for the diamagnetism [14,15] of the uranium(IV) chloride and iodide atoms but, since the slight paramagnetism of the tetraphenylarsonium chloride and iodide was unchanged on repeated recrystallisation from methyl cyanide, the measured correction was applied in these instances.

[9] Anderson and D'Eye, *J.*, 1949, S.244.
[10] Bagnall, Brown, and Jones, *J.*, 1964, 2396.
[11] Blicke and Monroe, *J. Amer. Chem. Soc.*, 1935, **57**, 720.
[12] Bagnall, Deane, Markin, Robinson, and Stewart, *J.*, 1961, 1611.
[13] Brown and Colton, *J.*, 1964, 714.
[14] Lewis and Wilkins, " Modern Co-ordination Chemistry," Interscience Publ. Inc., New York, 1960.
[15] Selwood, " Magnetochemistry," Interscience Publ. Inc., New York, 1956.

Thus, the magnetic susceptibilities of the hexachloro- and hexaiodouranates(IV), although similar to those of other hexachlorouranates(IV), should only be accepted with reserve.

X-*Ray Powder-diffraction Photographs.*—These were taken with a Debye-Scherrer 19-cm. camera with filtered Cu-K_α radiation. The specimens were sealed in glass capillaries in a dry atmosphere.

Analysis.—Uranium [5] and thorium [16] were determined as described previously; chloride was titrated against standard silver nitrate solution, and nitrogen was determined by the Kjeldahl method.[17a] Iodine in the methyl cyanide complex and tetrabutylammonium salts was determined gravimetrically as silver iodide or by titration against standard potassium iodate solution,[17b] after removal of uranium and thorium as hydroxides. However, owing to interference by the tetraphenylarsonium cation, these methods were unsuitable for analysis of the tetraphenylarsonium complexes. Consequently, these were decomposed by water and dissolved completely in a mixture of water and acetone, and the iodide was determined by the Volhard [17c] method.

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[16] Bagnall, Brown, Jones, and Robinson, *J.*, 1964, 2531.

[17] Vogel, " A Textbook of Quantitative Inorganic Analysis," Longmans, London, 1953, (*a*) p. 248, (*b*) p. 361, (*c*) p. 259.