

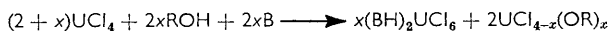
802. Reactions of Uranium Tetrachloride with 2,2'-Bipyridyl and *o*-Phenanthroline.

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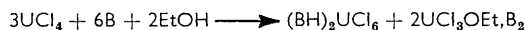
Solutions of uranium tetrachloride in alcohols undergo solvolysis in the presence of 2,2'-bipyridyl (bipy) and *o*-phenanthroline (phen). The hexachlorouranates(IV), (bipyH)₂UCl₆ and (phenH)₂UCl₆, and the addition compounds, UCl₃OEt, bipy₂ and UCl₃OEt, phen₂, have been isolated. Reactions in dimethylformamide (DMF) give the addition compounds 2UCl₄, 5DMF and UCl₄, phen₂, and oxidation of the dimethylformamide solutions gives the tetrachlorodioxouranates(VI), (bipyH)₂UO₂Cl₄ and (phenH)₂UO₂Cl₄.

URANIUM TETRACHLORIDE undergoes four important types of reaction in solution, namely, co-ordination, solvolysis, ionisation, and oxidation. Evaporation of solutions of uranium tetrachloride in the lower alcohols gives crystalline co-ordination compounds UCl₄, 4ROH (R = Me, Et, Prⁿ, Prⁱ)^{1,2} whereas solvolysed species are obtained with the butyl alcohols (R = Buⁿ, Bu^s, Bu^t).¹ Solvolysis by the lower alcohols occurs on heating or in the presence of bases such as tertiary phosphines,³ *o*-phenanthroline, or 2,2'-bipyridyl.

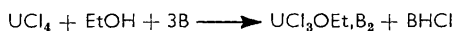
The degree of solvolysis, x , when a base, B, is added slowly to a solution of uranium tetrachloride in an alcohol until present in slight excess, is shown by the equation:



Hexachlorouranates(IV) are sparingly soluble in alcohols, except methanol in which decomposition may occur, and approximate values of x are established simply from the weight of precipitate and the initial weight of uranium tetrachloride. Observed values of x for uranium tetrachloride in various alcohols when B is 2,2'-bipyridyl are: EtOH, 0.9; PrⁿOH, 1.0; PrⁱOH, 1.5; Bu^sOH, 2.35. The observed values in ethanol when B is triethylphosphine and *o*-phenanthroline hydrate are 1.0 and 1.3, respectively, but in the latter case the solvent should be regarded as aqueous ethanol. These results suggest that the species UCl₃OEt is more resistant to solvolysis than uranium tetrachloride, and its presence in ethanol is confirmed by the formation of the compounds UCl₃OEt, bipy₂ and UCl₃OEt, phen₂ when an excess of base is added to the filtered solution. The complete reaction scheme is as follows:



The trichloroethoxyuranium(IV) addition compounds are formed also when uranium tetrachloride is added slowly to an excess of 2,2'-bipyridyl or *o*-phenanthroline in ethanol. The solutions turn red and then yellow-brown during the addition, and vivid green crystals of the compounds UCl₃OEt, 2B crystallise on standing. Further solvolysis does not occur, even in the presence of a large excess of ligand in boiling ethanol.



Monoalkoxy-pentachloro-zirconates(IV)⁴ and -niobates(IV)⁵ are known, and the compound [NbCl(OEt)₃, py]₂ is formed by solvolysis on addition of pyridine to a solution of niobium tetrachloride in ethanol.⁵

The crystal structure of uranium tetrachloride⁶ has been described as possibly

¹ Bradley, Kapoor, and Smith, *J. Inorg. Nuclear Chem.*, 1962, **24**, 863.

² Gans and Smith, unpublished results.

³ Gans and Smith, *Chem. and Ind.*, 1963, 911; preceding Paper.

⁴ Bradley, Abdel Halim, Sadek, and Wardlaw, *J.*, 1952, 2032.

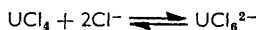
⁵ Wentworth and Brubaker, *Inorg. Chem.*, 1963, **2**, 551; 1964, **3**, 47.

⁶ Mooney, *Acta Cryst.*, 1949, **2**, 189.

indicating a compromise between an ionic and a molecular structure,⁷ and the solvolysis of uranium tetrachloride in the presence of small concentrations of base can be explained in terms of partial ionisation. Roach and Amis⁸ interpreted the conductivity of uranium tetrachloride in ethanol on the basis of uni-univalent electrolyte behaviour:

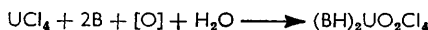


In view of the ready formation of hexachlorouranates(IV) it seems possible that a second equilibrium may be responsible for the observed deviations from strong-electrolyte behaviour:



Addition of base to an ethanol solution of uranium tetrachloride produces ethoxide ions which combine with the UCl_3^+ cations, and the protonated base forms insoluble hexachlorouranates(IV). The *s*-butoxychloro-species, where $x = 1.5$,¹ is presumably ionised in *s*-butyl alcohol since further solvolysis occurs on addition of base, whereas the UCl_3OEt species is not ionised in ethanol. Addition of concentrated hydrochloric acid to alcohol solutions of uranium tetrachloride and base gives quantitative yields of hexachlorouranates(IV).

The addition of benzene to a concentrated solution of uranium tetrachloride in dimethylformamide causes the precipitation of bis(uranium tetrachloride)-pentakis(dimethylformamide) which resembles other compounds of this type prepared by Bagnall and his co-workers.⁹ Addition of *o*-phenanthroline hydrate to a solution of uranium tetrachloride in dimethylformamide gives green crystalline uranium tetrachloride-bis(*o*-phenanthroline) but the analogous addition compound of 2,2'-bipyridyl was not obtained under these conditions. Oxidation in air of dimethylformamide solutions containing uranium tetrachloride and 2,2'-bipyridyl or *o*-phenanthroline gives yellow tetrachlorodioxouranates(VI). Traces of impurities cause intense colourations, and red or brown crystalline products are sometimes obtained.



These compounds have been prepared previously by reaction between uranyl chloride and the appropriate base in dilute hydrochloric acid.^{10,11} Alcohol solutions containing alkoxy-uranium(IV) species are particularly susceptible to oxidation, and tetrachlorodioxouranates(VI) are formed when inadequate precautions are taken.

EXPERIMENTAL

Uranium tetrachloride was prepared from uranium trioxide and hexachloropropene.¹² Solvents were purified by conventional methods, dried, and stored in molecular-sieve columns. Reactions were carried out in an atmosphere of dry nitrogen unless stated otherwise.

Bis(uranium tetrachloride)-pentakis(dimethylformamide).—Addition of benzene to a concentrated solution of uranium tetrachloride in dimethylformamide caused the precipitation of non-hygroscopic dark green needles, and recrystallisation from dimethylformamide-benzene in air gave the product (decomp.) (Found: C, 16.7; H, 3.2; N, 6.3. $\text{C}_{15}\text{H}_{35}\text{Cl}_8\text{N}_5\text{O}_5\text{U}_2$ requires C, 16.0; H, 3.1; N, 6.2%).

Compounds with 2,2'-Bipyridyl.—The same product was obtained in the presence of an excess of 2,2'-bipyridyl. Oxidation, by air, of a dimethylformamide solution containing uranium tetrachloride (1 mole) and 2,2'-bipyridyl (2 moles), and recrystallisation of the product from dimethylformamide-benzene or acetonitrile gave yellow crystalline bis-(2,2'-bipyridinium)

⁷ Wells, "Structural Inorganic Chemistry," Clarendon Press, Oxford, 3rd edn., 1962, p. 961.

⁸ Roach and Amis, *Z. phys. Chem. (Frankfurt)*, 1962, **35**, 274.

⁹ Bagnall, Deane, Markin, Robinson, and Stewart, *J.*, 1961, 1611.

¹⁰ Markov and Tsapkin, *Russ. J. Inorg. Chem.*, 1959, **4**, 1030.

¹¹ Markov and Tsapkin, *Russ. J. Inorg. Chem.*, 1961, **6**, 1052.

¹² Hermann and Suttle, *Inorg. Synth.*, 1957, **5**, 143.

[1964] *Tetrachloride with 2,2'-Bipyridyl and o-Phenanthroline.* 4179

tetrachlorodioxouranate(vi),¹⁰ m. p. 238—240° (decomp.) (Found: C, 33.4; H, 2.8; Cl, 21.6. Calc. for $C_{20}H_{18}Cl_4N_4O_2U$: C, 33.1; H, 2.5; Cl, 19.5%).

Reaction between uranium tetrachloride (1 mole), 2,2'-bipyridyl (2 moles), and concentrated hydrochloric acid in ethanol gave quantitative yields of *bis*-(2,2'-bipyridinium) *hexachlorouranate*(iv), m. p. 245—246° (from acetonitrile) (Found: C, 32.1; H, 2.4; N, 7.2. $C_{20}H_{18}Cl_6N_4U$ requires C, 31.4; H, 2.4; N, 7.3%).

A solution of 2,2'-bipyridyl (0.44 g., 2.8 mmoles) in ethanol (25 ml.) was added slowly to a stirred solution of uranium tetrachloride (1.07 g., 2.8 mmoles) in ethanol (20 ml.). The resulting precipitate of *bis*-(2,2'-bipyridinium) hexachlorouranate(iv) (0.69 g., 96%) was washed by decantation and dried *in vacuo*. A solution of 2,2'-bipyridyl (0.44 g., 2.8 mmoles) in ethanol (25 ml.) was added to the decanted solution and combined washings. Vivid green crystalline *bis*-(2,2'-bipyridyl)trichloroethoxyuranium(iv) (1.32 g., 100%) separated from the clear yellow-brown solution (Found: C, 37.6; H, 3.0; Cl, 14.5; N, 7.6. $C_{22}H_{21}Cl_3N_4OU$ requires C, 37.6; H, 3.0; Cl, 15.2; N, 8.0%). The hygroscopic crystals are insoluble in acetonitrile, nitromethane, and nitrobenzene, but dissolve in hot ethanol to give a yellow-brown solution from which the vivid green compound recrystallises unchanged on cooling.

A solution of uranium tetrachloride (0.43 g., 1.1 mmoles) in ethanol (10 ml.) was added slowly to a stirred solution of 2,2'-bipyridyl (1.42 g., 9.0 mmoles) in ethanol (20 ml.) and the mixture was boiled under reflux (2 hr.). *Bis*-(2,2'-bipyridyl)trichloroethoxyuranium(iv) (0.68 g., 87%) crystallised on cooling. Similar experiments in which the mole ratios of 2,2'-bipyridyl to uranium tetrachloride were 3 and 4 gave high yields of the same product.

Compounds with o-Phenanthroline.—Solutions of uranium tetrachloride (1 mole) and *o*-phenanthroline hydrate (1, 2, 3, and 4 moles) in dimethylformamide gave, on standing or on partial evaporation of the solvent, a green crystalline precipitate of *uranium tetrachloride-bis*-(*o*-phenanthroline), m. p. >330° (decomp.) (Found: C, 38.9; H, 2.6; Cl, 18.9; N, 7.4. $C_{20}H_{16}Cl_4N_4U$ requires C, 38.9; H, 2.2; Cl, 19.2; N, 7.6%). Attempted recrystallisation from dimethylformamide in air caused oxidation, and further recrystallisation from dimethylformamide–benzene gave yellow crystalline *bis*-(*o*-phenanthroline) tetrachlorodioxouranate(vi),¹¹ decomp. >300° (Found: C, 37.3; H, 2.6; Cl, 18.9; N, 7.4. Calc. for $C_{24}H_{18}Cl_4N_4O_2U$: C, 37.2; H, 2.3; Cl, 18.3; N, 7.2%).

Reaction between uranium tetrachloride (1 mole), *o*-phenanthroline hydrate (2 moles), and hydrochloric acid in ethanol gave a quantitative yield of green crystalline *bis*-(*o*-phenanthroline) *hexachlorouranate*(iv), decomp. >300° (Found: C, 35.9; H, 2.3; N, 6.5. $C_{24}H_{18}Cl_6N_4U$ requires C, 35.4; H, 2.3; N, 6.9%).

A solution of *o*-phenanthroline hydrate (0.62 g., 3.14 mmoles) in ethanol (25 ml.) was added slowly to a stirred solution of uranium tetrachloride (1.19 g., 3.14 mmoles) in ethanol (20 ml.). The precipitate of *bis*-(*o*-phenanthroline) hexachlorouranate(iv) (1.01 g., 1.05 mmoles) was washed by decantation and dried *in vacuo*. A solution of *o*-phenanthroline hydrate (0.62 g., 3.14 mmoles) in ethanol was added to the decanted solution and combined washings. Vivid green crystalline *trichloroethoxybis*-(*o*-phenanthroline)uranium(iv) (0.82 g., 1.09 mmoles), decomp. >200°, separated from the solution (Found: C, 41.5; H, 3.1; Cl, 14.7; N, 6.8. $C_{26}H_{21}Cl_3N_4OU$ requires C, 41.6; H, 2.8; Cl, 14.2; N, 7.5%). The same product was obtained on addition of ethanolic uranium tetrachloride (1 mole) to ethanolic *o*-phenanthroline hydrate (3 moles). This compound is not hygroscopic, and is insoluble in ethanol and other organic solvents.

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