Chemistry of the Trivalent Actinides. Part III.[1] Some Chemical and Physical Properties of Hydrated Uranium(III) Fluoride and the Anhydrous Chloride, Bromide, and Iodide. The Stability of Uranium(III) in Aqueous Solution and in Organic Solvents

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The halides UX_3 (X = Cl, Br, or I) have been prepared and their electronic spectra measured at room and liquid nitrogen temperatures. The interactions of the halides with a large number of organic solvents are given. Hydrated uranium(III) fluoride, UF_3,H_2O, and a carbonate and hydroxide of uncertain compositions have been recognised. The extreme reactivity of uranium(III) to most anions and organic solvents in which it is soluble severely limits the chemistry of this oxidation state even if oxygen is rigorously excluded.

UNTIL recently no well characterised uranium(III) compounds had been prepared from aqueous solution. Sulphates [2,3] and chlorides [1] are now known. This paper describes a previously prepared [4] hydrated fluoride and substances which are probably the carbonate and hydroxide. The stability of uranium(III) in aqueous solution with 25 anions and of the anhydrous halides in organic solvents is described qualitatively in order to demonstrate the limited chemistry of this oxidation state. There are very few studies of the rate of oxidation of uranium(III). In the absence of oxygen, aqueous solutions of uranium(III) are known [1,5] to be stable for several days in 1M hydrochloric acid, but become unstable [1,6] as the acid concentration is increased. Oxidation is spontaneous in the absence of oxygen and it has been shown [7] that in hydrochloric acid solution this process is first order with respect to uranium but is a complex function of the hydrogen and chloride ion concentrations. The rate is low in dilute hydrochloric and sulphuric acids but is greater for dilute perchloric, acetic, and ethylenediaminetetra-acetic acids and on the addition of electrolyte, such as lithium chloride. Other studies [8,9] confirm these results. These studies and the present work show that it is very unlikely that uranium(III) will form many of the typical salts of a tervalent cation.

The anhydrous halides UX_3 (X = Cl, Br, or I) have been prepared [10-12] previously but there are few reports of their physical and chemical properties. The preparation [13] of an adduct, $U(CH_3CN)Cl_3$, could not be repeated and the bromide is even more unstable.

RESULTS AND DISCUSSION

Hydrated Uranium(III) *Fluoride*.—The isolation of this salt [4] is in marked contrast to the chloride, bromide, and iodide systems where the only compounds isolable from aqueous solution were [1] two series of double uranium(III) chlorides. The water content of the fluoride is low and it is far more reactive than the anhydrous salt which has [14] a moderate stability in air. The diffuse reflectance spectra of the compound and its oxidation product show that UF_3,H_2O contains a very small quantity of uranium(IV) since a weak band is observed at 6500 cm^{-1}. The magnetic susceptibility measurements (Table 1) are typical [1,2] for uranium(III) with a room temperature moment slightly over 3 B.M. and a high θ value. Again [1,2] curvature below the Curie–Weiss line is observed at low temperatures.

TABLE 1

Variation with temperature of atomic susceptibilities (c.g.s.u.) and magnetic moment (B.M.) of UF_3,H_2O

Diamagnetic correction = -96×10^6 c.g.s.u; $\theta = 74°$

T/K	295·5	262·5	230·5	198
$10^6\chi_A$	3847	4181	4598	5136
$\mu_{eff.}$ [a]	3·02	2·96	2·91	2·85
T/K	166	135	103	98·5
$10^6\chi_A$	5840	6782	8180	9006
$\mu_{eff.}$ [a]	2·78	2·71	2·60	2·54

[a] $\mu_{eff.} = 2{\cdot}828\sqrt{\chi_A T}$.

The Carbonate and Hydroxide.—These were too unstable to allow characterisation, but both contained much uranium(III) immediately after preparation. Uranium(III) is a great deal more unstable in alkaline than in acid solution.

Diffuse Reflectance Spectra of the Anhydrous Halides.—These have been recorded over the range 30,000—4100 cm^{-1} for the first time. Details of the spectra have been deposited in Supplementary Publication No. SUP 20624 (4 pp.).† The quality of the spectra was much improved

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† For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

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at low temperature when several new shoulders appeared and better resolution was obtained. Below 10,000 cm^{-1} the three halides have very similar spectra but that of the chloride was best resolved. A very weak peak (*ca.* 0·5% of the 18,550 cm^{-1} absorption) was observed at 6500 cm^{-1} in the chloride which is due to uranium(IV). This could not be detected analytically.

The lowest observed frequency (*ca.* 4400 cm^{-1}) is commonly assumed [15,16] to be the first multiplicity-allowed transition of uranium(III), $5f^3$, but a lower frequency has been predicted.[17] The positions of the bands below 10,000 cm^{-1} change little in different environments.

Above 10,000 cm^{-1} there are differences as the more intense, presumably *f–d* absorption bands move progressively towards lower frequency as the atomic weight of the halogen increases. This is possibly reflected in the stabilities of the compounds towards oxidation in dry air. The chloride (green) is fairly stable, the bromide (brown) oxidises readily, and the iodide (violet) reacts explosively. Uranium(III) chloride and bromide are isostructural whilst UI_3 has a layer structure with a lower co-ordination number. A $5f^n$ to $5f^{n-1}6d$ transition may imply partial oxidation and in a similar way,[18] the positions of the intense $5f^n$ to $5f^{n-1}6d$ transitions in tervalent uranium, neptunium, plutonium, and americium in perchloric acid solution progressively shift to higher energy as the atomic number and the stability of the oxidation state increases. For americium(III) the corresponding allowed band is above 50,000 cm^{-1}.

The Reactivity of Uranium(III) *in Solution.*—(a) *Aqueous solution.* Table 2 summarises the results for 25 anions. Other than for the halogenic, sulphuric, and perchloric acids, which can also be used as media for the electrolytic reduction of uranium(IV), uranium(III) is oxidised to uranium(IV) within 5 min at the prevailing concentrations and usually complete oxidation is even more rapid than this. For tartrate, citrate, and lactate, dark green solutions, which are orange by transmitted light, are initially formed; these colour effects would suggest [2] that complex uranium(III) species are present. However, the colour of these solutions soon changes to the pale green of uranium(IV). Ion-exchange and other procedures have been used to identify plutonium(III) citrate,[19] tartrate,[19] and acetate [20] complexes, americium(III) [21] oxalate complexes, and complexes of the heavier trivalent actinides with citrate,[22] in solution.

Uranium(III) formate, $U(HCOO)_3$, has been isolated [23] from anhydrous formic acid but very rapid oxidation occurs in dilute aqueous solutions of both formate and acetate. When glacial acetic acid was added to a solution of uranium(III) sulphate, $U_2(SO_4)_3,8H_2O$, in sulphuric acid (M) a green-brown precipitate was obtained. This was the uranium(III) starting material. The hydrated sulphate was insoluble in anhydrous formic acid.

TABLE 2

Stability of the hydrated uranium(III) ion with various anions

Anion	Stability
Fluoride	Stable [a]
Chloride	Stable [b]
Bromide	Stable [b]
Iodide	Stable [b]
Sulphate	Stable [b]
Perchlorate	Stable [b]
Phosphate, PO_4^{3-}	Oxidation [c]
Hydrogen phosphate, HPO_4^{2-}	Oxidation [c]
Dihydrogen phosphate, $H_2PO_4^-$	Oxidation [c]
Carbonate	Oxidation [a,d]
Hydroxide	Oxidation [a,c]
Thiocyanate	Oxidation [c]
Nitrate	Oxidation [c]
Nitrite	Oxidation [c]
Sulphite	Oxidation [c]
Thiosulphate	Oxidation [c]
Ethylenediaminetetra-acetate	Oxidation [c]
Borate	Oxidation [c]
Fluoroborate	Oxidation [d]
Formate	Oxidation [c]
Acetate	Oxidation [c]
Oxalate	Oxidation [c]
Tartrate	Oxidation [d]
Citrate	Oxidation [d]
Lactate	Oxidation [d]

[a] Solid uranium(III) compound formed. [b] Stable for 24 h at 0°. [c] Immediate oxidation to uranium(IV). [d] Oxidation to uranium(IV) within 5 min.

The addition of potassium thiocyanate solutions to aqueous uranium(III) solutions caused rapid oxidation. However, if a solution of uranium(III) in aqueous hydrochloric acid (0·4M) prepared [1] by electrolytic reduction, was put in contact with an aqueous solution of ammonium thiocyanate in equilibrium with a benzene solution of triethylphosphate then a bright blue organic layer was obtained which contained uranium(III). The red aqueous layer slowly evolved hydrogen and the uranium(III) was completely oxidised in both layers in 2 h to give the typical pale green of uranium(IV) (Figure, Curve B). The spectrum (Figure, Curve A) of the unoxidised organic layer has a strong band centred at 17,600 cm^{-1} like the uranium(III) phenazone and chloro-complexes [1] but this is absent in uranium(IV) and most uranium(III) spectra. The absorption partly obscures the *f–f* spectrum as is the case for UI_3 (Figure, Curve C). This strong band moves to higher energy as the stability of the compound towards oxidation increases. Thus, it is at 13,400 cm^{-1} for UI_3, near [24] 20,000 cm^{-1} for UBr_3,

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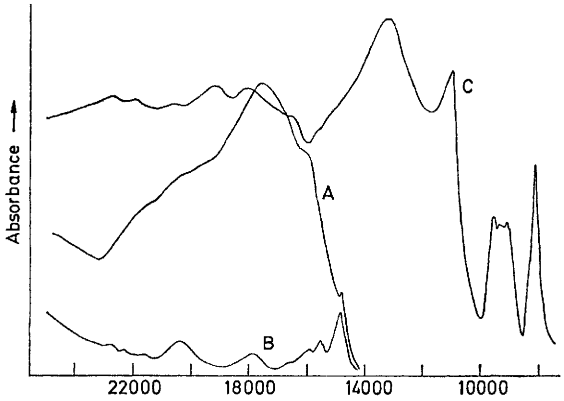
and at over 20,000 cm^{-1} in [25] UCl_3, the hydrated sulphates [2] and the green double chlorides [1] of uranium(III).

The nature of the extracted species is unknown but presumably is of the form $U(SCN)_3,[(C_2H_5O)_3PO]_n,xH_2O$.

(b) *Organic solvents.* Table 3 lists the observations made. Uranium(III) iodide is extremely reactive towards oxygen and moisture so that a smaller number of tests was carried out. In methanol, ethanol, and water transient red solutions are formed with UCl_3 and UBr_3 but these evolve hydrogen and give green uranium(IV) within half a minute.

It has been stated [23] that none of the halides is soluble in organic solvents without oxidation to uranium(IV).



Absorption spectra: Curve A, U^{III} in triethyl phosphate and benzene; Curve B, U^{IV} spectrum from A by aerial oxidation; Curve C, UI_3 at 90 K (by reflectance)

This is clearly not the case for UBr_3 and UI_3 but we did not find a suitable organic solvent for UCl_3, the most stable of the halides prepared. Although the iodide was found to be fairly soluble in methanol, ethanol, ethyl acetate, dimethylacetamide, and acetic acid, the general preparative and handling problems are very much greater than for the other halides. Having reviewed the reactivity of uranium(III) towards potential types of organic and inorganic ligands, it would appear that the extreme reactivity of uranium(III) will limit the numbers and types of compound formed. A neutral organic ligand with an oxygen donor atom and no acidic hydrogen atom stabilises uranium(III) and complexes of ligands with these properties have been precipitated [1] with a large anion from solutions in organic solvents. Sulphates [2] and double chlorides [1] have been isolated from aqueous solution and a few other compounds, *e.g.*, $U(HCOO)_3$,[23] from non-aqueous solutions. It is possible that further studies of the iodide in non-aqueous solvents, and of fused systems would yield uranium(III) compounds. The preparation of complexes with π-bonding ligands has yet to be fully investigated.

EXPERIMENTAL

All operations were performed under nitrogen and with de-oxygenated solvents. Analytical methods were standard.

TABLE 3

Solubility of uranium(III) halides in various solvents

Solvent	UCl_3	UBr_3	UI_3
Diethyl ether	IS	IS	
Tetrahydrofuran	IS	O	O
Dioxan	O	O	
Methanol	O	O	S
Ethanol	O	O	S
Water	O	O	O
Pyridine	IS	IS	O
Acetonitrile	IS	O	O
Phosphorus trichloride	IS	IS	
Phosphorus tribromide	IS	IS	
Arsenic trichloride	IS	IS	
Carbon disulphide	IS	IS	
Ethyl acetate	IS	IS	S
Acetone	IS	IS	O
Dimethylformamide	IS	IS	O
Dimethylacetamide	IS	S	S
Propylene carbonate	O	O	
Acetic acid	IS	S	S
Phosphorus oxychloride	O	O	
Tri-n-butyl phosphate	IS	IS	
Hexamethylphosphoramide	IS	IS	
Nitromethane	O	O	
Nitrobenzene	IS	IS	
Thionyl chloride	O	O	
Dimethyl sulphoxide	IS	IS	
Benzene	IS	IS	
n-Hexane	IS	IS	
Carbon tetrachloride	IS	IS	IS
Chloroform	IS	IS	
Dichloromethane	IS	IS	
Silicon tetrachloride	IS	IS	

S = Soluble; red solution formed, stable for 5 min or more. O = Spontaneous oxidation within 1 min. IS = Insoluble.

Uranium(III) *Fluoride Monohydrate*, UF_3,H_2O.—A solution of uranium(III) sulphate,[2] $U_2(SO_4)_3,5H_2O$ (3 g) in hydrochloric acid (M, 150 ml) was added slowly to a solution of ammonium fluoride (1 g) in hydrochloric acid (M, 50 ml). The green precipitate was shaken for 15 min, filtered off, washed with cold, dry acetone (100 ml), and dried for 3 h *in vacuo* at room temperature and sealed in evacuated tubes. The product was brown in white, non-fluorescent light, contained water (by i.r.), and was very reactive, oxidising in air immediately to give a pale green uranium(IV) substance. Yield 1·5 g (71%) (Found: F, 18·4; U, 75·8; F/U = 3·04. UF_3,H_2O requires F, 18·2; U, 76·0%; F/U = 3·00). Previous workers [4] reported similar precipitation methods but used uranium(III) solutions prepared by reduction with zinc amalgam.

A Uranium(III) *Carbonate*.—A solution of sodium carbonate (0·2 g) in water (30 ml) was added to a solution of potassium uranium(III) chloride,[1] $KUCl_4,5H_2O$ (1 g) in water (100 ml). A yellow-brown, gelatinous precipitate was slowly formed and a considerable amount of gas was evolved. The compound oxidised before it could be isolated as did a similar substance prepared from the ammonium chloride,[1] $NH_4UCl_4,5H_2O$, and sodium bicarbonate. The colour of the yellow-brown material changed to pale green immediately on exposure to air. The compound is difficult to filter off rapidly because of its gelatinous nature, and a sample which had turned green after 3 h filtration still warmed up and smoked considerably on exposure to air to give a yellow product which contained no uranium(III) (reflectance spectrum).

A suspension of the initial yellow-brown precipitate when dissolved in hydrochloric acid (11M) gave the characteristic red colouration of uranium(III). The solution spectrum indicated much uranium(III) was present.

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A Uranium(III) *Hydroxide*.—The addition of an ammonia solution (2M) to an aqueous solution of ammonium uranium(III) chloride, $NH_4UCl_4,5H_2O$, gave an immediate black-brown precipitate in agreement with an earlier observation of Loebel.[26] This evolved hydrogen and within a few minutes gave a pale green oxidised product. Aqueous solutions of ethylenediamine gave the same reaction.

Uranium(III) *Chloride*.—This was prepared by the action of hydrogen chloride on uranium(III) hydride at 250°. Uranium metal (5 g) was cleaned with nitric acid (6M), washed with water and acetone, and placed in the reaction tube which had been out-gassed at 500° and 10^{-5} Torr, for 2 h. Hydrogen was passed over the metal for 3 h at 225° to give the black hydride. Dry hydrogen chloride was passed over this for 1 h at 250°. The olive-green product was heated to 480° at 10^{-5} Torr to remove impurities (UCl_4 and NH_4Cl). The product was stored under nitrogen. Yield 6·5 g (90%) (Found: Cl, 30·15; U, 68·75; Cl/U = 2·95. UCl_3 requires Cl, 30·9; U, 69·1%; Cl/U = 3·00).

Uranium(III) *Bromide*.—This was prepared from the hydride by passing dry hydrogen bromide over it for 1 h at 300°. The brown product was heated at 450° at 10^{-5} Torr and stored as before. Yield 8·5 g (85%) (Found: Br, 49·5; U, 49·25%; Br/U = 2·99. UBr_3 requires Br, 50·2; U, 49·8%; Br/U = 3·00).

Uranium(III) *Iodide*.—Methyl iodide was passed over the hydride in a stream of hydrogen for 2 h at 300°. The violet-black product was treated as for the bromide. Yield 10·2 g (78%) (Found: U, 37·1. UI_3 requires 38·45%).

Reactions with Acetonitrile.—A compound UCl_3,CH_3CN has been reported.[13] Attempts to repeat the preparation and to prepare the bromide were unsuccessful as the reaction did not go to completion and oxidation of uranium(III) occurred. Uranium(III) chloride was heated at 80° with a 20-fold excess of dry acetonitrile in a sealed tube for 4 days. The tube was broken in nitrogen and the brown solid was filtered off, washed with dry carbon tetrachloride and dry light petroleum, and dried under vacuum for 2 h at room temperature [Found: C, 5·3; H, 0·85; N, 3·1; U, 64·05. $U(CH_3CN)Cl_3$ requires C, 6·25; H, 0·8; N, 3·65; U, 61·75%]. Some uranium(IV) was present (reflectance spectrum) and the analytical figures indicated that the reaction had not gone to completion. A longer reaction time (8 days) gave a product containing a great deal of uranium(IV) and the acetonitrile was partially degraded.

Attempts to repeat the preparation with UBr_3 gave products containing only uranium(IV).

Solubility Tests.—A small amount of the anhydrous halide (*ca.* 10 mg) was added to the carefully deoxygenated organic solvents (5 ml) under nitrogen. Small volumes (5 ml) of aqueous solutions (*ca.* 0·1M) of ammonium uranium(III) chloride were mixed with solutions of sodium or ammonium salts (*ca.* 0·2M) as shown in Table 2. The extraction experiments were performed in all glass apparatus under nitrogen.

[2/2160 *Received*, 18*th September*, 1972]

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