The Oxidising and Fluoride Ion Acceptor Properties of Uranium Hexafluoride in Acetonitrile †

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Metallic copper, cadmium, and thallium are oxidised by uranium hexafluoride in acetonitrile at ambient temperatures to give solutions of copper(II), cadmium(II), and thallium(III) hexafluorouranates(V). After removal of solvent, these salts were obtained as solvates. Copper(II) fluoride reacts with uranium hexafluoride in acetonitrile to give copper(II) heptafluorouranate(VI).

ACETONITRILE is a good solvent for molybdenum and tungsten hexafluorides [1] and in this solvent it is possible to oxidise metals to solvated cations whilst at the same time reducing the hexafluorides to hexafluorometallates(V). In this solvent tungsten hexafluoride acts as an acid to fluoride ions and heptafluorotungstates(VI) are formed.[2] The corresponding reactions involving uranium hexafluoride are now described. The inert solvents C_7F_{16} and tetrachloroethane have been previously used for reactions involving uranium hexafluoride [3] and chlorine trifluoride has also been used as a solvent for this substance [4] although in this case there is the strong possibility of the formation of ionised adducts of the type $(ClF_2)_n(UF_{6+n})$ as intermediates.

Uranium hexafluoride dissolves in acetonitrile to give a clear yellow solution which, although stable for short periods, gradually darkens during a period of hours as attack of uranium hexafluoride on the solvent initiates polymerisation of the MeCN. In these respects the present results are completely consistent with previous observations [5] on this system. During the polymerisation there is an increase in the linewidth of the ^1H n.m.r. signal of the solvent (5 to 250 Hz during 12 h) consistent with a gradual increase in the concentration of paramagnetic species in the solution. It has been previously postulated [5] that the polymerisation of the solvent involves the reduction of uranium(VI) to uranium(V) either *via* the solvent or dissolved water or oxygen and these present observations support this strongly.

A solution of uranium hexafluoride in acetonitrile reacts readily with the metals copper, cadmium, and thallium to give green solutions of metal hexafluorouranates(V); an excess of metal was, therefore, used in each experiment. In each case the metal was oxidised to the highest state, Cu^{II}, Tl^{III}, that might be expected in such a solvent and there was no sign of Cu^I and Tl^I salts as has been observed during the formation of hexafluoromolybdates(V) and hexafluorotungstates(V).[1] The oxidation of metallic silver by the solution of uranium hexafluoride in acetonitrile is extremely fast and undefined black products, containing much polymerised acetonitrile, are formed even at low temperatures. On removal of solvent from the acetonitrile solutions green hexafluorouranates(V), $M[UF_6]_2\cdot5MeCN$ (M = Cu or Cd) and $Tl[UF_6]_3\cdot5MeCN$ are obtained. These salts hydrolyse in moist air and are soluble in acetonitrile without decomposition; they lose acetonitrile when heated but give ill-defined products.

Hexafluorouranates(V) have been previously prepared by reduction of uranium hexafluoride with ammonia, nitric oxide, or hydrazinium or hydroxylammonium fluoride,[6] the reactions being carried out by direct interaction of the gases or in anhydrous hydrogen fluoride. Hexafluorouranates(V) also result from the interaction of alkali, silver(I), and thallium(I) fluorides with UF_5 either directly or in acetonitrile.[7] The use of acetonitrile as solvent appears to have inherent advantages for the formation of transition-metal derivatives since the conditions used are mild and involve use of a solvent which is easy to handle.

The electronic absorption spectra ‡ of the green solutions of copper(II), cadmium(II), and thallium(III) hexafluorouranates(V) in acetonitrile are very similar to those previously observed [8] for solid caesium hexafluorouranate(V), $Cs[UF_6]$, and for tetraphenylarsonium hexafluorouranate(V), $[AsPh_4][UF_6]$, as a solid and in acetonitrile solution.

The Raman spectra ‡ of solutions of the hexafluorouranates(V) show intense polarised bands at 613 cm^{-1} and the Raman spectra of the solids measured at 77 K also show intense bands at this frequency together with a less intense band at 194 cm^{-1}. The i.r. spectra of the solids show bands at 520 cm^{-1} whilst an additional band is observed at 145 cm^{-1} in the spectrum of $Tl[UF_6]_3\cdot5MeCN$ (the other solids were not examined in this region). The spectra indicate common species in both solution and in

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‡ See Supplementary Publication No. SUP 20653 (3 pp.). For further details see Notice to Authors No. 7, in *J.C.S. Dalton*, 1975, Index issue (items less than 10pp. are supplied as full size copies).

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the solid state. An octahedral $[UF_6]^-$ ion would be expected to have six fundamental modes of vibration and the absorption at 613 cm^{-1} is assigned to ν_1, the A_{1g} mode previously observed in $[UF_6]^-$ species in anhydrous hydrogen fluoride at 628 cm^{-1}. The frequency of this mode is considerably higher than that assigned[8] from the vibronic spectra of hexafluorouranates(V). The weak band at 194 cm^{-1} is assigned to the ν_5 mode. The ν_3 and ν_4 vibrational modes of the $[UF_6]^-$ ion have been previously assigned at 525 and 170 cm^{-1} respectively;[8] the frequencies observed for these modes in the present work are in fair agreement with this. The *N*-co-ordination of acetonitrile in the solid complexes is indicated by the increase in frequency of the C≡N stretching mode when comparing the i.r. spectra of the complexes with the spectrum of the free ligand.[9]

No signal was observed in the e.p.r. spectrum of solid $Tl[UF_6]_3{\cdot}5MeCN$ at 77 K. This is consistent with there being very little, if any, distortion from full O_h symmetry in hexafluorouranates(V).[10]

The formation of thallium(III) species when the metal is oxidised by uranium hexafluoride in acetonitrile shows the oxidising power of this system to be comparable with that of molybdenum hexafluoride and greater than that of tungsten hexafluoride.[1] Previous workers[7] have claimed a rather ill-defined thallium(I) hexafluorouranate(V) but this was in the absence of acetonitrile and in that solvent excess of thallium metal does not reduce the thallium(III), and indeed a solution of uranium hexafluoride in acetonitrile reacts with thallium(I) fluoride to give solutions of thallium(III) hexafluorouranate(V). Similarly, although solutions of $Cu[MF_6]_2$ (M = Mo or W) are readily reduced to copper(I) species by the action of excess of copper, the solutions of copper(II) hexafluorouranate(V) are stable in the presence of an excess of the metal although there is no evidence for further reduction of the $[UF_6]^-$ ions. In this series of reactions, as in the corresponding reactions with molybdenum and tungsten hexafluorides, there is no evidence for reduction of the hexafluorometallates to the +4 oxidation state although this state is well known for uranium.

Reaction between copper(II) fluoride and uranium hexafluoride in acetonitrile gives a blue solution from which blue crystalline copper(II) heptafluorouranate(VI), $Cu[UF_7]_2{\cdot}5MeCN$, can be obtained. This reaction of uranium hexafluoride is analogous to those observed for tungsten hexafluoride.[2] The spectra of both solutions show the absence of $[UF_6]^-$ species. The Raman spectra of both solid and solution show a strong polarised band at 594 cm^{-1} indicating that the heptafluorouranate(VI) species is present in the same form in both phases. The i.r. spectrum of the copper salt shows bands typical of co-ordinated acetonitrile and in addition bands at 530s, br, 505s, br and 450w cm^{-1}. There is no definitive structural information on heptafluorouranates(VI) and there have been no vibrational studies on the heptafluorouranates(VI) previously prepared to allow comparison to be made with the present results. Sodium fluoride reacts with uranium hexafluoride in acetonitrile to form yellow-green crystals which decompose on final removal of solvent. This is apparently a fluorouranate(VI) but the stoicheiometry was not determined reproducibly and the stoicheiometry of the product must be accidental.

If slightly moist acetonitrile is used as the reaction medium reduction occurs even with metal fluorides and hexafluorouranates(V) are formed. The products with copper(II) and thallium(I) fluorides are identical with those previously described; mercury(II) fluoride gives a mercury(II) hexafluorouranate(V) solvate. This marked effect of the presence of traces of water is consistent with the studies on the polymerisation of acetonitrile by uranium hexafluoride mentioned earlier.

^{18}F Exchange studies on reactions between uranium hexafluoride and copper hexafluorouranate(V) or copper heptafluorouranate(VI) show that ^{18}F exchange is complete after 15 min; the corresponding reactions involving tungsten are also fast.[1,2] In the $[UF_7]^-$ case the fraction exchanged[11] after 1 h was 0.8225 ± 0.029 although the value after 15 min was 1.025 ± 0.003. The exchange kinetics are, however, made more complex by the slow reaction which occurs between uranium hexafluoride and acetonitrile.

Although uranium hexafluoride does not give stable solutions in acetonitrile, heptafluorouranate(VI) and hexafluorouranate(V) species appear to be stable indefinitely in this solvent.

EXPERIMENTAL

The experimental methods used are those described elsewhere.[1,2] Visible–near i.r. spectra were recorded on a Pye–Unicam SP 700C spectrophotometer; samples were prepared *in vacuo* and were transferred on the vacuum line to a 1-cm cell.

Uranium hexafluoride (U.K.A.E.A.), was purified in sufficient quantity for each reaction by double distillation from sodium fluoride which had been dried by pumping at 390 K and 10^{-3} Torr for 12 h. Copper(II) fluoride (Ozark Mahoning) and thallium(I) and mercury(II) fluorides (Alfa) were used as received but were handled in an inert atmosphere box (<15 p.p.m. water). Metals were cleaned with abrasive paper and handled in the inert atmosphere box. ^{18}F-Labelled uranium hexafluoride was prepared as follows. Caesium fluoride, labelled as previously described,[11] was shaken with boron trifluoride in a stainless steel (75 ml) Hoke pressure vessel fitted with a Hoke needle valve for 30 min. The labelled boron trifluoride was removed by vacuum distillation and shaken with uranium hexafluoride in another vessel. The labelled uranium hexafluoride was separated by vacuum distillation.

For the reactions between uranium hexafluoride and metals an excess of metal was used in each case. A mixture of uranium hexafluoride and acetonitrile was distilled

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Analyses (%) of the solid products: Found (calculated)

Compound	C	H	F	N	U	M
$Cu[UF_6]_2\cdot5MeCN$ [a]	12.1 (12.3)	1.5 (1.6)	23.2 (23.4)	7.0 (7.2)	49.0 (48.9)	6.4 (6.5)
$Cu[UF_6]_2\cdot5MeCN$ [b]	12.4 (12.3)	1.5 (1.6)	23.2 (23.4)	7.4 (7.2)	48.6 (48.9)	6.4 (6.5)
$Cd[UF_6]_2\cdot5MeCN$	11.8 (11.8)	1.6 (1.5)	22.3 (22.3)	6.7 (6.8)	46.6 (46.6)	10.8 (11.0)
$Tl[UF_6]_3\cdot5MeCN$ [c]	8.3 (8.2)	1.0 (1.0)	23.1 (23.3)	3.7 (4.8)	49.1 (48.7)	
$Tl[UF_6]_3\cdot5MeCN$ [d]	8.4 (8.2)	1.0 (1.0)	23.3 (23.3)	3.7 (4.8)	48.9 (48.7)	
$Hg[UF_6]_2\cdot6MeCN$ [e]	11.0 (12.5)	1.4 (1.6)	18.9 (19.8)		40.2 (41.4)	16.6 (17.4)
$Cu[UF_7]_2\cdot5MeCN$	12.6 (11.9)	1.7 (1.5)	24.9 (26.3)	7.3 (6.9)	44.5 (47.1)	6.2 (6.3)
$NaF–UF_6$			39.7		35.9	24.2

[a] Product from reaction for 1 h. [b] Product from reaction for 4 days. [c] From Tl + UF_6. [d] From TlF + UF_6. [e] From 'wet' acetonitrile.

on to the metal which had been degassed for at least 30 min. Reactions occurred at ambient temperature and were generally complete within 2 h. In one experiment involving copper the reaction mixture was set aside for 4 days but the product was identical with that obtained after 30 min.

The reaction between copper(II) fluoride (0.015 g), uranium hexafluoride (0.178 g), and acetonitrile (1.0 g) was carried out with shaking for several hours. A blue solution was isolated which gave a blue solid (0.14 g) after removal of volatile material.

Analyses are by Bernhardt.

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