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ACETONITRILE AND TRIPHENYLPHOSPHINE OXIDE COMPLEXES OF THE URANIUM  
PENTAFLUORIDE - ANTIMONY PENTAFLUORIDE AND URANIUM TETRAFLUORIDE  
OXIDE - ANTIMONY PENTAFLUORIDE ADDUCTS

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SUMMARY

The new ternary adducts,  $UF_4O \cdot SbF_5 \cdot 2CH_3CN$ ,  $UF_4O \cdot 2SbF_5 \cdot 6L$ ,  $UF_5 \cdot SbF_5 \cdot 2L$  ( $L = CH_3CN$  or  $(C_6H_5)_3PO$ ) and  $UF_5 \cdot 2SbF_5 \cdot 5CH_3CN$ , have been prepared and studied by infrared,  $^{19}F$  n.m.r. and e.s.r. spectroscopy, mass spectrometry, X-ray powder diffraction and chemical analysis. The infrared spectra strongly suggest an ionic formulation with the uranium cationic species preferentially coordinated by the organic ligand.

INTRODUCTION

The adducts  $UF_4O \cdot nSbF_5$  ( $n = 1-3$ ) [1] and  $UF_5 \cdot nSbF_5$  ( $n = 1,2$ ) [2,3] have recently been prepared. Crystal structure determinations on representatives of both classes,  $UF_4O \cdot 2SbF_5$  [1] and  $UF_5 \cdot 2SbF_5$  [2,3], have shown that they contain fluorine-bridged networks related to those in the parent uranium compound. We have now shown that addition of dry acetonitrile brings about drastic alteration to the bonding and gives rise to new room temperature-stable adducts (see Table 1).

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\* Dedicated to the memory of the late Professor Jozse Šlivnik

TABLE 1

Reactions of  $UF_4O \cdot SbF_5$  and  $UF_5 \cdot SbF_5$  adducts with  $CH_3CN$ 

Initial adduct	Product of Reaction with $CH_3CN$
$UF_4O \cdot SbF_5$ $\longrightarrow$	$UF_4O \cdot SbF_5 \cdot 2CH_3CN$ (orange)
$UF_4O \cdot 2SbF_5$ $\longrightarrow$	$UF_4O \cdot 2SbF_5 \cdot 6CH_3CN$ (pale brown)
$UF_4O \cdot 3SbF_5$ $\longrightarrow$	$UF_4O \cdot 2SbF_5 \cdot 6CH_3CN$ (pale brown)
$UF_5 \cdot SbF_5$ $\longrightarrow$	$UF_5 \cdot SbF_5 \cdot 2CH_3CN$ (pale green)
$UF_5 \cdot 2SbF_5$ $\longrightarrow$	$UF_5 \cdot 2SbF_5 \cdot 5CH_3CN$ (pale green)

All of these adducts are moisture sensitive. On heating under vacuum there is no gradual loss of  $CH_3CN$  to give lower adducts, and the eventual simultaneous loss of all the  $CH_3CN$  ligands is accompanied by complete decomposition.

Reactions of the binary adducts,  $UF_4O \cdot 2SbF_5$  and  $UF_5 \cdot SbF_5$  with triphenylphosphine oxide (TPPO) in dry acetonitrile solution give  $UF_4O \cdot 2SbF_5 \cdot 6TPPO$  (orange) and  $UF_5 \cdot SbF_5 \cdot 2TPPO$  (green). The reaction of the ternary acetonitrile adducts  $UF_4O \cdot 2SbF_5 \cdot 6CH_3CN$  and  $UF_5 \cdot SbF_5 \cdot 2CH_3CN$  with various stoichiometries of TPPO in dry  $CH_3CN$  solution results in the successive replacement of  $CH_3CN$  ligands until  $UF_4O \cdot 2SbF_5 \cdot 6TPPO$  and  $UF_5 \cdot SbF_5 \cdot 2TPPO$  are again produced.

Preliminary data on some of this work has already been reported [4].

## EXPERIMENTAL

### Reagents and Apparatus

Unless otherwise stated, apparatus, materials and techniques used were as described previously [1,5]. Acetonitrile of spectroscopic grade (B.D.H. Ltd.) was repeatedly distilled onto and refluxed over phosphorus pentoxide, and was stored over 4A molecular sieves. The effectiveness of the drying process was monitored by Raman spectroscopy and by examining the behaviour of the solvent with  $UF_6$ . Triphenylphosphine oxide (Aldrich Chemical Co. Ltd.) was used without purification. Electron spin resonance

spectra were recorded on a Bruker ER200 spectrometer with a solution of the sample in dry  $\text{CH}_3\text{CN}$  in a sealed quartz tube. Mass spectra were run on a VG Micromass 16B spectrometer, the samples being inserted directly into the prefluorinated ionization chamber.

Preparation of the Adducts,  $\text{UF}_4\text{O}\cdot\text{SbF}_5\cdot 2\text{CH}_3\text{CN}$ ,  $\text{UF}_4\text{O}\cdot 2\text{SbF}_5\cdot 6\text{CH}_3\text{CN}$ ,  $\text{UF}_5\cdot\text{SbF}_5\cdot 2\text{CH}_3\text{CN}$  and  $\text{UF}_5\cdot 2\text{SbF}_5\cdot 5\text{CH}_3\text{CN}$

The preparations were carried out in Pyrex glass or FEP reaction tubes. The solvent was distilled onto the solid binary adducts,  $\text{UF}_4\text{O}\cdot\text{SbF}_5$ ,  $\text{UF}_4\text{O}\cdot 2\text{SbF}_5$ ,  $\text{UF}_4\text{O}\cdot 3\text{SbF}_5$ ,  $\text{UF}_5\cdot\text{SbF}_5$  and  $\text{UF}_5\cdot 2\text{SbF}_5$  ( $\sim 2$  mmol), and the orange ( $\text{UF}_4\text{O}\cdot\text{SbF}_5$ ) or blue-green ( $\text{UF}_5\cdot\text{SbF}_5$ ) solutions were allowed to stand at room temperature for up to one hour before removal of the excess of acetonitrile by pumping. The solids were pumped to constant weight. For each reaction a weight-loss versus time-of-pumping curve was plotted which showed that no intermediate phases were formed. The reactions, which yielded four new ternary adducts, are summarized in Table 1. The reaction stoichiometries were obtained from the pumping curves and were checked by chemical analysis. X-ray powder photography also showed that each of the four compounds was a distinct phase. It is noteworthy that the reactions of  $\text{UF}_4\text{O}\cdot 2\text{SbF}_5$  and  $\text{UF}_4\text{O}\cdot 3\text{SbF}_5$  yield the same product. This was confirmed by vibrational spectroscopy, X-ray powder photography and chemical analysis.

Preparation of the Adducts,  $\text{UF}_4\text{O}\cdot 2\text{SbF}_5\cdot 6\text{TPPO}$  and  $\text{UF}_5\cdot\text{SbF}_5\cdot 2\text{TPPO}$

The adducts were prepared in two ways. In the first, reaction of the binary adducts,  $\text{UF}_5\cdot\text{SbF}_5$  and  $\text{UF}_4\text{O}\cdot 2\text{SbF}_5$  ( $\sim 1$  mmol), with TPPO in dry acetonitrile yielded the two ternary adducts  $\text{UF}_5\cdot\text{SbF}_5\cdot 2\text{TPPO}$  (green) and  $\text{UF}_4\text{O}\cdot 2\text{SbF}_5\cdot 6\text{TPPO}$  (orange). These were characterized by weight analysis, X-ray powder diffraction and vibrational spectroscopy. In the second, reaction of the ternary acetonitrile adducts  $\text{UF}_5\cdot\text{SbF}_5\cdot 2\text{CH}_3\text{CN}$  and  $\text{UF}_4\text{O}\cdot 2\text{SbF}_5\cdot 6\text{CH}_3\text{CN}$  ( $\sim 1$  mmol) with a range of stoichiometries of TPPO in dry  $\text{CH}_3\text{CN}$  solution resulted in successive replacement of the  $\text{CH}_3\text{CN}$  ligands by TPPO. Ultimately, all the  $\text{CH}_3\text{CN}$  ligands are replaced and  $\text{UF}_5\cdot\text{SbF}_5\cdot 2\text{TPPO}$  and  $\text{UF}_4\text{O}\cdot 2\text{SbF}_5\cdot 6\text{TPPO}$  were produced.

Analytical Data

Chemical analysis for the  $\text{UF}_4\text{O} \cdot 2\text{SbF}_5 \cdot 6\text{CH}_3\text{CN}$  adduct was good (found C,14.27; H,1.79; N,8.27; F,26.65; Sb,24.66; U,24.11.  $\text{UF}_4\text{O} \cdot 2\text{SbF}_5 \cdot 6\text{CH}_3\text{CN}$  requires C,14.26; H,1.78; N,8.32; F,26.35; Sb,24.12; U,23.58%) while those for the other  $\text{UF}_4\text{O}$  and  $\text{UF}_5$  adducts were poor. For example, the solid product obtained from the reaction of the  $\text{UF}_5 \cdot \text{SbF}_5$  with acetonitrile gave an analysis 4% lower in fluoride than that calculated for  $\text{UF}_5 \cdot \text{SbF}_5 \cdot 2\text{CH}_3\text{CN}$  (found C,8.05; H,1.06; N,4.77; F,25.85; U,39.76; Sb,20.43.  $\text{UF}_5 \cdot \text{SbF}_5 \cdot 2\text{CH}_3\text{CN}$  requires C,7.60; H,0.95; N,4.43; F,30.07; U,37.68; Sb,19.27%). This implies the composition  $\text{U}_{1.00} \text{Sb}_{1.00} \text{C}_{4.02} \text{N}_{2.04} \text{H}_{6.35} \text{F}_{8.15}$  and, although the possibility that the adduct is  $\text{UF}_5 \cdot \text{SbF}_5 \cdot 2\text{CH}_3\text{CN}$  or  $\text{UF}_5 \cdot \text{SbF}_3 \cdot 2\text{CH}_3\text{CN}$  cannot be ignored, the weight-loss versus time-of-pumping curve was in accord with the  $\text{UF}_5 \cdot \text{SbF}_5 \cdot 2\text{CH}_3\text{CN}$  formulation, a  $^{19}\text{F}$  n.m.r. study of the  $\text{CH}_3\text{CN}$  solvent removed from the reaction shows no evidence of fluorine derivatives, mass spectra of the solid show  $[\text{SbF}_5]^+$  fragments, and e.s.r. spectra of the adduct in  $\text{CH}_3\text{CN}$  exhibits the characteristic  $\text{U}^{\text{V}}$  signal. For the same reasons, the product of the reaction of  $\text{UF}_5 \cdot 2\text{SbF}_5$  with  $\text{CH}_3\text{CN}$ , which analysed to give the mole ratios  $\text{Sb}/\text{U} = 2.03$  and  $\text{C}/\text{U} = 9.96$  (found C,13.20; H,1.59; Sb,27.27; U,26.30; F,25.24.  $\text{UF}_5 \cdot 2\text{SbF}_5 \cdot 5\text{CH}_3\text{CN}$  requires C,12.36; H,1.56; Sb,25.06; U,24.49; F,29.33%), is formulated  $\text{UF}_5 \cdot 2\text{SbF}_5 \cdot 5\text{CH}_3\text{CN}$  despite low fluoride analysis. Similarly, the product of the reaction of  $\text{UF}_4\text{O} \cdot \text{SbF}_5$  with  $\text{CH}_3\text{CN}$ , which analysed to give the mole ratios  $\text{Sb}/\text{U} = 0.98$ ,  $\text{C}/\text{U} = 4.1$ ,  $\text{N}/\text{U} = 2.1$ , is formulated as  $\text{UF}_4\text{O} \cdot \text{SbF}_5 \cdot 2\text{CH}_3\text{CN}$ . Low fluoride analysis is not uncommon in such systems [6] and may arise because of interference of the two heavy metals, U and Sb, in the analytical scheme.

The stoichiometries of the TPPO adducts were obtained by mass balance.

Vibrational Spectra of the Adducts

Raman spectra could not be obtained for the solid ternary adducts between 25 and  $-196^\circ\text{C}$ , probably because of their poor crystallinity. Infrared data for the  $\text{CH}_3\text{CN}$  adducts are similar and the positions of the ligand bands are as expected for coordinated acetonitrile. Table 2 compares the principal infrared peaks associated with  $\text{UF}_5 \cdot 2\text{SbF}_5 \cdot 5\text{CH}_3\text{CN}$  with those for the related adduct  $[\text{Mn}(\text{CH}_3\text{CN})_6]^{2+} 2[\text{SbCl}_6]^-$  [7,8]. The table also shows the shift ranges for all the modes of vibration of

acetonitrile coordinated via nitrogen in similar compounds. The shift to higher frequency for the  $\text{-C}\equiv\text{N}$  stretching mode is a strong indication of coordination of acetonitrile and all the new adducts exhibit this phenomenon.

In the infrared spectrum of  $\text{UF}_4\text{O}\cdot 2\text{SbF}_5$  [1] there are many bands in the  $700\text{-}500\text{ cm}^{-1}$  region which can be attributed to U-F and Sb-F bonds in accord with the known fluorine-bridged structure. In the product of reaction with acetonitrile there are fewer bands, indicating that the fluorine-bridged structure has been destroyed or its extent reduced.

The strong peak at  $912\text{ cm}^{-1}$ , attributable to the  $\text{U}=\text{O}$  stretch in  $\text{UF}_4\text{O}\cdot 2\text{SbF}_5$ , is at higher frequency than the equivalent band in  $\text{UF}_4\text{O}$  itself, indicating contributions to the bonding from ionic structures involving  $[\text{UF}_2\text{O}]^{2+}$ . The position of the  $\text{U}=\text{O}$  stretch in the spectra of the  $\text{CH}_3\text{CN}$  adducts, however, is difficult to deduce. Since a shoulder at  $945\text{ cm}^{-1}$  in the spectrum of  $\text{UF}_4\text{O}\cdot 2\text{SbF}_5\cdot 6\text{CH}_3\text{CN}$  is completely reproducible and is absent from the spectra of the  $\text{UF}_5$  ternary adducts this has been tentatively assigned to the  $\text{U}=\text{O}$  stretch. Its appearance at higher frequency than in the binary adducts implies an increased ionic contribution in the bonding of the ternary compounds. This is reasonable if the adducts have ionic formulations similar to those postulated [9] for the  $\text{UF}_5\cdot n\text{CH}_3\text{CN}$  ( $n = 1,2$ ) adducts (i.e.  $[\text{UF}_4(\text{CH}_3\text{CN})_4]^+[\text{UF}_6]^-$  and  $[\text{UF}_4(\text{CH}_3\text{CN})_2]^+[\text{UF}_6]^-$ ).

All four of the new ternary adducts exhibit two bands in the C-C stretching region. In the spectrum of  $\text{UF}_5\cdot 2\text{SbF}_5\cdot 5\text{CH}_3\text{CN}$  there are strong bands at  $978(\text{vs})$  and  $942(\text{s})\text{cm}^{-1}$ , and for  $\text{UF}_4\text{O}\cdot 2\text{SbF}_5\cdot 6\text{CH}_3\text{CN}$  there are bands at  $975$  and  $938\text{ cm}^{-1}$ , in addition to the  $\text{U}=\text{O}$  stretch at  $945\text{ cm}^{-1}$ . It is tempting to explain the appearance of an extra band by assuming uranyl formation in all these cases. Other factors suggest that this is unlikely. Firstly, compounds such as  $\text{UF}_5\cdot n\text{CH}_3\text{CN}$  ( $n = 1,2$ ) [9,10],  $\text{M}(\text{BF}_4)_2\cdot 4\text{CH}_3\text{CN}$  ( $\text{M} = \text{Zn}, \text{Mn}$ ) [11] and  $\text{SnCl}_4\cdot 2\text{CH}_3\text{CN}$  [12] all exhibit two strong bands in this region and, similarly, the two bands present in the new ternary adducts can be attributed to C-C

TABLE 2

Comparison of Infrared Data ( $\text{cm}^{-1}$ ) for  $\text{UF}_5 \cdot 2\text{SbF}_5 \cdot 5\text{CH}_3\text{CN}$  and  $[\text{Mn}(\text{CH}_3\text{CN})_6]^{2+} \cdot 2[\text{SbCl}_6]^{-}$  <sup>a</sup>

Vibrational mode	$\text{CH}_3\text{CN}$ ( $\ell$ ) <sup>a</sup>	$[\text{Mn}(\text{CH}_3\text{CN})_6]^{2+} \cdot 2[\text{SbCl}_6]^{-}$ <sup>a</sup>	$\text{UF}_5 \cdot 2\text{SbF}_5 \cdot 5\text{CH}_3\text{CN}$	Shift range for coordinated acetonitrile in ternary adducts <sup>a</sup>
$\text{C}\equiv\text{N}$ str. ( $\nu_2$ )	2257	2286	2310	2321-2266
$\text{CH}_3$ def. ( $\nu_3$ )	1376	1370	1370	1374-1360
C-C str. ( $\nu_4$ )	920	939	942	980-924
comb. ( $\nu_5+\nu_4$ )	2297	2316	2335	2355-2300
$\text{CH}_3$ rock. ( $\nu_7$ )	1040	1055	1055	1038-1025
comb. ( $2\nu_4+\nu_8$ )	2208	2243	2282	2278-2216
overtone 2( $\nu_8$ )	750	778	795	825-750
C-CN bend ( $\nu_8$ )	380	390	400	420-380

<sup>a</sup> Refs. [7,8].

stretching modes. Secondly, the bands observed are sharp whereas uranyl bands tend to be broad. Furthermore, the anaerobic, anhydrous conditions for the synthesis of the new adducts coupled with the constant appearance and constant relative intensity of the peaks in the many preparations, militate against uranyl formation, and exposure of the adducts to small quantities of moist air resulted in the observation of a broad band at about  $950\text{ cm}^{-1}$ , due to uranyl formation, and not sharp bands at  $975$  or  $940\text{ cm}^{-1}$ .

Further evidence was provided by e.s.r. spectroscopy. Solutions of the  $\text{UF}_5\text{-SbF}_5$  adducts in  $\text{CH}_3\text{CN}$  gave the characteristic signal of uranium(V), the intensity of which did not decrease with respect to time. Solutions of  $\text{UF}_4\text{O-SbF}_5$  adducts in  $\text{CH}_3\text{CN}$  gave no signal. This militates against reduction of U(VI) to U(V).

Finally, the two bands in question have been shown to be due to the attached ligand  $\text{CH}_3\text{CN}$ , and not due to uranium-oxygen species since the infrared spectra of the TPPO adducts, prepared by reaction of the binary adducts  $\text{UF}_4\text{O-SbF}_5$  and  $\text{UF}_5\text{-SbF}_5$  with the ligand in the same dry acetonitrile solvent as that used in the preparation of the ternary acetonitrile adducts (see below), contained no bands around  $975\text{ cm}^{-1}$  and  $940\text{ cm}^{-1}$ .

Infrared data for  $\text{UF}_5\text{-SbF}_5\cdot 2\text{TPPO}$  and  $\text{UF}_4\text{O}\cdot 2\text{SbF}_5\cdot 6\text{TPPO}$  are recorded in Table 3 together with data for  $\text{UF}_5\cdot\text{TPPO}$  and free TPPO. The spectrum of  $\text{UF}_5\cdot\text{SbF}_5\cdot 2\text{TPPO}$  exhibits a P=O stretch at  $1055\text{ cm}^{-1}$  (c.f.  $1045\text{ cm}^{-1}$  in  $\text{UF}_5\cdot\text{TPPO}$ ), a shift of  $138\text{ cm}^{-1}$  down from that in free TPPO ( $1193\text{ cm}^{-1}$ ). Although much smaller shifts are observed in TPPO transition-metal halide complexes and complexes involving the typical elements, such large shifts are common for actinide adducts, and shifts of up to  $230\text{ cm}^{-1}$  have been reported previously [13]. The large shift in the P=O stretching frequency on complex formation reflects an overall decrease in bond order of the P=O probably due to a large decrease in the  $\text{p}\pi\text{-d}\pi$  bonding as a result of the coordination of the TPPO to the metal via the oxygen and the great affinity of U(V) for oxygen.

The infrared spectrum for  $\text{UF}_4\text{O}\cdot 2\text{SbF}_5\cdot 6\text{TPPO}$  exhibits a P=O stretching band at  $1065\text{ cm}^{-1}$  originating from TPPO coordination to uranium and, as there is a possibility of differently coordinated ligands, the shoulder at  $1130\text{ cm}^{-1}$  may represent a P=O stretch for TPPO bonded to antimony or some solid-state effect. The U=O stretch is observed at  $922\text{ cm}^{-1}$ , a shift of  $10\text{ cm}^{-1}$  to higher frequency from that in the binary adduct, suggesting a greater withdrawal of electron density from the  $\text{UF}_4\text{O}$ .

TABLE 3

Infrared data for  $UF_5 \cdot SbF_5 \cdot 2TPPO$ ,  $UOF_4 \cdot 2SbF_5 \cdot 6TPPO$ ,  $UF_5 \cdot TPPO$  and  $TPPO$  ( $cm^{-1}$ )

TPPO	$UF_5 \cdot TPPO$	$UF_5 \cdot SbF_5 \cdot 2TPPO$	$UOF_4 \cdot 2SbF_5 \cdot 6TPPO$	Assignment
1487 m	1485	1484 m	1484 mw	$\nu(C-C)$
1444 s	1440	1440 vs	1438 s	$\nu(C-C)$
1410 w br				
1335 vw	1340 w	1340 w	not visible	$\nu(C-C)$
1314 m	1310 w	1314 mw	" "	comb.
1281 w				$\beta(C-H)$
1193 vs				$\sim(P=O)$
1188 sh	1185 vw	1190 vw	1188 w	$\beta(C-H)$
1168 m	1165 w	1165 vw sh	1165 vw	$\beta(C-H)$
			1150 vw	
			1130 sh	$\nu(P=O)?$
			1120 vs	
1122 vs	1120 vs	1122 vs		comb.
1097 m				$\beta(C-H)$
1074 m	1070 w sh		1070 sh	$\nu(P=O)$
	1045 s	1055 s	1065 s	$\beta(C-H)$
1028 m	1020 ms	1026 m	1025 w	
		1014 w		
997 m	995 m	996 m	995 mw	ring
		990 mw sh		
973 vw	972 vw			$\gamma(C-H)$
			922 s	$\nu(U=O)$
918 vw		930 vw		$\gamma(C-H)$
860 w	850 w	850 w br	845 vw br	$\gamma(C-H)$
843 w		822 w		
755 m	755 sh	756 m sh	758 sh	$\gamma(C-H)$
750 sh	750 ms	750 m	750 ms	
721 vs	730 s	730 s	724 vs	
698 s	690 ms	692 ms	692 s	$\phi(C-C)$
		660 s	655 vs	$\sim(Sb-F)$
619 w		618 vw		$\alpha(C-C-C)$
	600 ms	602 mw		
	550 s sh	$\sim 560$ sh		$\nu(U-F)$
542 vs	540 vs	540 vs	540 vs	
	530 s sh	520 m sh	$\sim 520$ sh	$\nu(U-F)$
507 w	505 s	500 w		
457 m	470 w	$\sim 460$ vw br	460 vw br	
451 m	450 sh			
	445 w	$\sim 440$ vw br	440 vw br	$\phi(C-C)$
$\sim 395$ vw	405 w	$\sim 415$ vw br		



In the spectra of both new ternary adducts the U-F stretching bands are observed in the expected 560-520  $\text{cm}^{-1}$  region, although somewhat masked by the ligand band around 540  $\text{cm}^{-1}$ . The strong sharp band observed at approximately 660  $\text{cm}^{-1}$  is attributable to Sb-F stretching, and all other bands are attributable to ligand vibrations involving the phenyl groupings, which are virtually undisturbed. As with the ternary  $\text{CH}_3\text{CN}$  adducts fewer fluorine-bridging bands are observed than in the binary  $\text{UF}_5 \cdot \text{SbF}_5$  and  $\text{UF}_4\text{O} \cdot 2\text{SbF}_5$  adducts. No evidence of uranyl formation was observed.

### $^{19}\text{F}$ n.m.r. Studies

$\text{UF}_4\text{O}$  is insoluble in  $\text{CH}_3\text{CN}$ , while uranium and antimony pentafluorides dissolve in and react with dry acetonitrile;  $\text{UF}_5$  produces a blue-green solution in which at least two solvent molecules are coordinated to the metal, whereas  $\text{SbF}_5$  forms a neutral 1:1 adduct with the solvent. The  $\text{SbF}_5 \cdot \text{NCCH}_3$  adduct is well characterized by vibrational spectroscopy [14,15] and  $^{19}\text{F}$  n.m.r. studies give the spectra shown (Figure 1a) which, in addition to a signal at 97 ppm which may be attributable to  $2\text{SbF}_5 \cdot \text{NCCH}_3$ , shows a quintet and a doublet characteristic of the octahedral  $\text{C}_{4v}$  symmetry expected for the fluorines about antimony in  $\text{SbF}_5 \cdot \text{NCCH}_3$ . The spectrum of  $\text{UF}_4\text{O}$  in excess of  $\text{SbF}_5$  was recorded at  $-40^\circ\text{C}$  (Figure 1b) and exhibited one broad line at 94 ppm, attributed to fluorines associated with both metals in addition to the lines due to  $\text{SbF}_5$  itself (Figure 1c) [1]. Solutions of the  $\text{UF}_4\text{O} \cdot \text{SbF}_5$  and  $\text{UF}_5 \cdot \text{SbF}_5$  adducts in acetonitrile were prepared and their  $^{19}\text{F}$  n.m.r. spectra were recorded from 0 to  $-48^\circ\text{C}$  (e.g. Figure 1d). The spectra were related in all five cases, giving reproducible broad bands scattered from 212 ppm to 39 ppm from  $\text{CFCl}_3$  as reference. On scanning the usual F-on-U region of the spectrum ( $\sim 740$  ppm) no signal was observed, and it seems likely that the lines due to fluorine on uranium are in the string of bands further upfield. The results are inconclusive but infer that polymeric species or equilibria involving a number of fluorine species with a variety of different fluorine environments are present.

In the spectrum of the solvent removed from these reactions no evidence of  $\text{CF}_3\text{CN}$  or other fluorine derivatives of  $\text{CH}_3\text{CN}$  was observed.

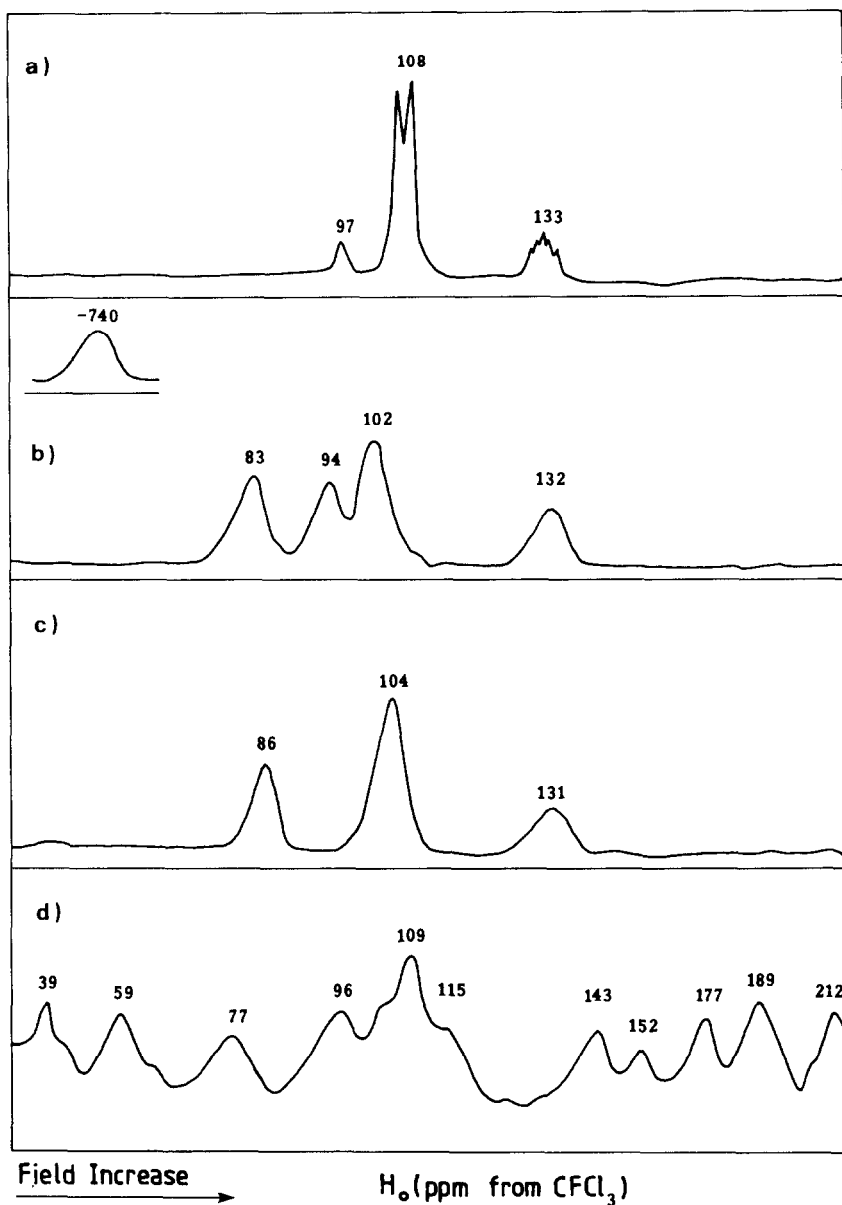


Fig. 1.  $^{19}\text{F}$  n.m.r. spectra of a)  $\text{SbF}_5$  in  $\text{CH}_3\text{CN}$  ( $-75^\circ\text{C}$ ); b)  $\text{UOF}_4$  in  $\text{SbF}_5$  ( $-40^\circ\text{C}$ ), + F-on-U ( $-30^\circ\text{C}$ ); c)  $\text{SbF}_5$  ( $0^\circ\text{C}$ ); d)  $\text{UOF}_4 \cdot 2\text{SbF}_5$  in  $\text{CH}_3\text{CN}$  ( $0^\circ\text{C}$ ).

(the chemical shift,  $\delta$ , is expressed in ppm with positive value upfield with respect to  $\text{CCl}_3\text{F}$  as external reference).

## Mass Spectrometry

Mass spectra of the solid ternary adducts exhibited stepwise fragmentation patterns of  $[\text{SbF}_5]^+$  to  $\text{Sb}^+$ , confirming the presence of  $\text{SbF}_5$ . The fragmentation pattern of acetonitrile was also present. However, no uranium species were observed, presumably due to their involatility. An interesting feature of the spectra is the presence of the  $[\text{Sb}_3]^+$  and  $[\text{Sb}_4]^+$  ions.

## X-ray Powder Diffraction Studies

The patterns obtained for the solid products of reaction of  $\text{CH}_3\text{CN}$  with  $\text{UF}_4 \cdot n\text{SbF}_5$  ( $n = 1-3$ ) and  $\text{UF}_5 \cdot n\text{SbF}_5$  ( $n = 1,2$ ) evidenced poor crystallinity but clearly showed that reaction had occurred. Identical patterns were obtained for the products of the reactions of  $\text{UF}_4 \cdot 0.2\text{SbF}_5$  and  $\text{UF}_4 \cdot 0.3\text{SbF}_5$  with  $\text{CH}_3\text{CN}$ . The TPPO adducts were all amorphous.

## DISCUSSION

Ternary adducts involving pentahalides such as  $\text{SbCl}_5$ , metal halides and acetonitrile are formed by chloride ion transfer between the metal halide and the pentachloride and yield solvated cations and  $[\text{SbCl}_6]^-$ . For example, the reaction of  $\text{MnCl}_2$  with  $\text{SbCl}_5$  in  $\text{CH}_3\text{CN}$  yields the complex  $[\text{Mn}(\text{CH}_3\text{CN})_6]^{2+} 2[\text{SbCl}_6]^-$  [7,8]. It is not always the case that all the halide ions are transferred from the metal and the higher the charge on the metal the less likely this is to occur. For example, the  $\text{FeCl}_3\text{-SbCl}_5\text{-CH}_3\text{CN}$  reaction yields  $[\text{FeCl}(\text{CH}_3\text{CN})_5]^{2+} 2[\text{SbCl}_6]^-$  and the  $\text{BiCl}_3\text{-SbCl}_5\text{-CH}_3\text{CN}$  reaction yields  $[\text{BiCl}_2(\text{CH}_3\text{CN})_6]^+ [\text{SbCl}_6]^-$  [16].

Vibrational spectroscopy shows that, in solution, the binary adducts of  $\text{SbF}_5$  with  $\text{UF}_4\text{O}$  or  $\text{UF}_5$  break up and fluorine-bridged bonds are no longer evident. The solids  $\text{UF}_5 \cdot 2\text{SbF}_5$  and  $\text{UF}_4 \cdot 0.2\text{SbF}_5$  have contributions to their bonding from structures such as  $[\text{UF}_3][\text{SbF}_6]_2$  and  $[\text{UF}_2\text{O}][\text{SbF}_6]_2$  [1-3]. It may be that, in  $\text{CH}_3\text{CN}$ , this tendency towards fluorine ion donation is enhanced by the electron density supplied to the pseudo cation by the coordinating solvent and dissociation of the binary adduct occurs accordingly. Thus  $\text{UF}_5 \cdot \text{SbF}_5$ , having a tendency towards  $[\text{UF}_4][\text{SbF}_6]$  in the solid, may dissociate in  $\text{CH}_3\text{CN}$  solution to yield  $[\text{UF}_4(\text{CH}_3\text{CN})_x]$  and solvated  $[\text{SbF}_6]$  so that the solid ultimately removed from solution is probably best formulated as  $[\text{UF}_4(\text{CH}_3\text{CN})_2][\text{SbF}_6]$ .

The appearance of a sharp, symmetrical Sb-F stretching band in the infrared spectra of all the ternary adducts, attributable to the  $\nu_3$  vibration of the octahedral  $[\text{SbF}_6]^-$  anion, gives additional weight to this interpretation.

The  $^{19}\text{F}$  n.m.r. data are also indicative of the complexity of the solution phase and imply the occurrence of polymeric species or the coexistence of a variety of adducts.

The X-ray powder and analytical data have confirmed the unique character of each adduct and the mass spectra have demonstrated the presence of the  $\text{SbF}_5$  moiety in each. It is possible, therefore, to suggest the formulations  $[\text{UF}_4(\text{CH}_3\text{CN})_2][\text{SbF}_6]$ ,  $[\text{UF}_3(\text{CH}_3\text{CN})_5]2[\text{SbF}_6]$ ,  $[\text{UF}_3\text{O}(\text{CH}_3\text{CN})_2][\text{SbF}_6]$  and  $[\text{UF}_2\text{O}(\text{CH}_3\text{CN})_6]2[\text{SbF}_6]$  for the ternary adducts. The uranium (V) compounds would exhibit coordination numbers of 6 and 8 respectively and  $\text{UF}_4\text{O}\cdot\text{SbF}_5\cdot 2\text{CH}_3\text{CN}$  would also contain six-coordinate uranium. However, in  $[\text{UOF}_2(\text{CH}_3\text{CN})_6][\text{SbF}_6]_2$  nine coordination is implied which seems unlikely. It may be that like  $\text{AlCl}_3\cdot 3\text{CH}_3\text{CN}$  [17], which is reported as  $[\text{AlCl}(\text{CH}_3\text{CN})_5]^{2+}2[\text{AlCl}_4]^- \cdot \text{CH}_3\text{CN}$ , one of the  $\text{CH}_3\text{CN}$  molecules is contained in the crystal lattice.

For  $\text{UF}_5\cdot\text{SbF}_5\cdot 2\text{TPPO}$ , comparison of the position of the P=O stretch in the infrared with literature values for TPPO coordinated to uranium and antimony halides shows that in the ternary adduct the TPPO is coordinated to uranium only. Furthermore, the existence of only one P=O stretch confirms that all the ligands are coordinated to the same metal. The Sb-F stretch is again observed as a sharp band at  $660\text{ cm}^{-1}$  and many of the fluoride-bridging bands observed in the spectrum of the binary adduct are lost. The complex may therefore be formulated as  $[\text{UF}_4(\text{TPPO})_2][\text{SbF}_6]$  involving six coordinate U(V).

For  $\text{UF}_4\text{O}\cdot 2\text{SbF}_5\cdot 6\text{TPPO}$  it is difficult to envisage a nine coordinate uranium species incorporating six large TPPO ligands. The complexity of the infrared spectrum in the P=O stretching region suggests that there may be two types of TPPO present.

The true nature of the bonding in the ternary adducts reported in this work, and of many of those reported in the literature will remain uncertain until their structures are determined by X-ray crystallography. Other ligands such as dimethyl sulphoxide, dimethylformamide, other phosphine oxides and nitriles, may form crystalline ternary adducts suitable for single crystal work.

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