Formation and Characterization of Uranium(VI) Chloride Fluorides, UF_nCl_{6-n} ($n = 1—5$)

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Fluorine-19 n.m.r. measurements show that UF_6 undergoes facile halide exchange with either $SiMe_3Cl$ or UCl_6 in $CFCl_3$ or CF_2Cl_2 solution at temperatures below −60 °C. Hence all the uranium(VI) chloride fluorides in the series UF_nCl_{6-n} (n = 1—5) have been characterized virtually definitively. The visible and mass spectra of the mixed halides have been investigated also. Unlike UF_6 and UCl_6, the mixed halides decompose at temperatures above −60 °C liberating chlorine gas and giving halides of uranium(IV) or uranium(V).

Mixed uranium(VI) chloride fluorides, UF_nCl_{6-n} (n = 1—5), have been postulated recently as intermediates in the reaction of uranium hexafluoride with chlorotrimethylsilane, $SiMe_3Cl$.[1] Linear interpolation of enthalpies of formation and entropies implies that UF_5Cl and UF_4Cl_2 are thermodynamically unstable at room temperature with respect to the formation of β-UF_5 and UF_4 respectively together with gaseous chlorine. However, the only direct evidence of such species reported to date is provided by the i.r. spectra of mixtures of UF_6 with $TiCl_4$, HCl, or BCl_3 in liquid xenon held at temperatures below −60 °C.[2] Unfortunately there is no help to be gained from isotopic effects and the assignment of i.r. absorptions to particular UF_nCl_{6-n} species rests perforce on (*i*) the order of appearance of new bands and the dependence of their intensities on the relative proportions of the reagents, and (*ii*) comparisons with the wavenumbers calculated for these species.

We have prepared mixtures of the chloride fluorides UF_nCl_{6-n} (n = 1—5) by the exchange reactions of UF_6 with either $SiMe_3Cl$ or UCl_6 in a Freon solvent at temperatures below −60 °C and studied their spectroscopic properties and chemical stability. Here we report the ^{19}F n.m.r. spectra of the mixtures, the multiplet patterns and parameters of which provide an unambiguous basis for the identification of each of the species UF_5Cl, *cis*- and *trans*-UF_4Cl_2, *mer*- and *fac*-UF_3Cl_3, *cis*- and *trans*-UF_2Cl_4, and $UFCl_5$. We also describe the visible absorption spectra exhibited by such mixtures and the mass spectrum of the most volatile species UF_5Cl. The mixed halides decompose at temperatures much above *ca.* −60 °C with the release of elemental chlorine and the formation of tetra- or penta-halides of uranium.

Experimental

Apparatus.—All the samples including uranium hexafluoride were prepared using either (*i*) a metal vacuum-line constructed in ⅛-in copper tubing with brass 'Swagelok' unions and brass-bodied Hoke valves and equipped with a handling section made from Teflon-FEP tubing with Teflon unions and needle valves (Production Techniques Ltd.), or (*ii*) under an atmosphere of dry argon ($H_2O \leqslant 20$ p.p.m.) in a glove-box. Reactions were carried out in Teflon-FEP tubes (Production Techniques Ltd.) with thermally moulded ends, each fitted with a Teflon needle valve. Before use, the tubes were conditioned by admitting fluorine gas to a pressure of 1 atm (*ca.* 10^5 Pa), typically for 16 h.

Chemicals.—Uranium hexafluoride (British Nuclear Fuels Ltd.) was freshly vacuum-sublimed into a conditioned Kel-F trap held at −45 °C and its vapour pressure measured to check its purity.[3] Uranium hexachloride was prepared by the reaction of BCl_3 with UF_6 following the procedure of O'Donnell and Wilson.[4] The Freons $CFCl_3$ and CF_2Cl_2 (B.D.H. Ltd.) were initially dried over 4A molecular sieves, purified by trap-to-trap distillation *in vacuo* and stored over fresh P_2O_5. Chlorotrimethylsilane (Hopkins and Williams) was purified and stored in a similar manner. Nitrogen monoxide was used as supplied by Matheson; nitrosyl chloride was prepared by the reaction between KCl and NO_2[5] and purified by trap-to-trap distillation *in vacuo*.

Procedures and Spectrometers.—Samples for n.m.r. investigation kept at low temperature were sealed in a section of FEP tubing (length 5—10 cm, external diameter 4 mm).[6] The ends of the plastic were trimmed and the cold sample was inserted into a standard precision n.m.r. tube which also included a little CD_2Cl_2 as a 'lock'. Fluorine-19 n.m.r. spectra were recorded with the aid of a Bruker FT AM 250 or WM 250 spectrometer operating at 235.7 MHz.

Visible absorption spectra were recorded for solutions containing UF_6 and either $SiMe_3Cl$ or UCl_6 kept at low temperatures. For this purpose, the solution was contained in an FEP tube with specially flattened parallel sides which was supported in an unsilvered Dewar vessel equipped with inner and outer Pyrex windows to give optical access to the sample. The sample was cooled, typically to *ca.* −83 °C, by a stream of cold nitrogen gas produced from a liquid nitrogen boiler and the temperature was monitored using a copper–constantan thermocouple. Spectra were measured on a Perkin-Elmer Lambda 3 spectrophotometer.

Mass spectroscopic measurements were carried out with a V.G. Micromass 12B mass spectrometer operating with an electron beam of 70 eV and an accelerating voltage of 3.0 kV; the vapour sample was admitted *via* a nozzle at room temperature. The spectra were calibrated with reference to peaks due to air or 'L'-grade perfluorokerosene. Infrared spectra of vapours and solids were measured with a Pye-Unicam model SP 2000 and Raman spectra of solids with a Spex Ramalog 5 spectrophotometer.

In a typical experiment, approximately 70 mg (0.2 mmol) of UF_6, measured tensimetrically, was condensed in a conditioned FEP reaction vessel at −196 °C. About 5 cm^3 of liquid $CFCl_3$ or CF_2Cl_2 was co-condensed with the UF_6, followed by the required amount of $SiMe_3Cl$, also measured tensimetrically. The reaction mixture was then warmed up to −63 °C by supporting the vessel in a chloroform 'slush' bath and shaken periodically. As soon as the Freon melted, the mixture took on a deep red or brown colouration. With molar proportions $SiMe_3Cl : UF_6 \leqslant 6:1$, one mol of $SiMe_3F$, identified by its i.r.[7] and ^1H and ^{19}F n.m.r.[8] spectra, was produced for every mol of $SiMe_3Cl$ taken, as demonstrated for example by

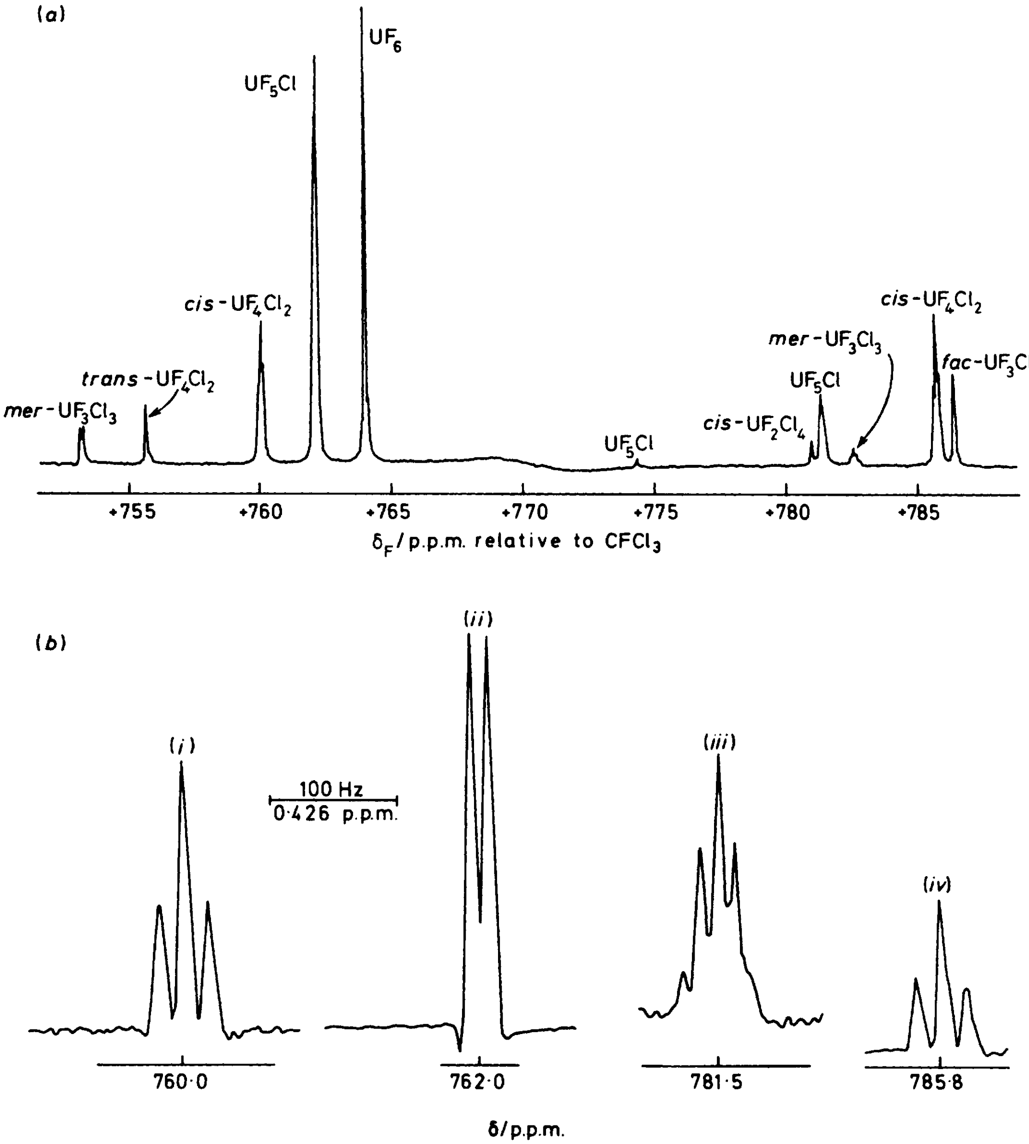

Figure 1. (*a*) Part of a ^{19}F n.m.r. spectrum (235 MHz) of a $CFCl_3$ solution containing an approximately equimolar mixture of UF_6 and $SiMe_3Cl$ at −73 °C. (*b*) Some details of the ^{19}F n.m.r. spectrum shown in (*a*): (*i*) lower frequency triplet from *cis*-UF_4Cl_2; (*ii*) doublet, and (*iii*) quintet from UF_5Cl; (*iv*) higher frequency triplet from *cis*-UF_4Cl_2

fractionation of the volatile components of the reaction mixture contained in CF_2Cl_2.

Results

Fluorine-19 *N.M.R. Spectra.*—The ^{19}F n.m.r. spectrum of a $CFCl_3$ solution containing a mixture of UF_6 and $SiMe_3Cl$ held at *ca.* −75 °C showed resonances attributable to UF_6[9] and $SiMe_3F$[8] at δ +764 and −159 p.p.m. respectively relative to $CFCl_3$. In addition there were numerous resonances, some with distinctive multiplet structures, between δ +745 and +790 p.p.m. the intensities of which varied markedly with the molar proportions $SiMe_3Cl : UF_6$.

These new resonances are illustrated in Figure 1(*a*) which shows the relevant part of the spectrum exhibited by a solution approximately 6 mmol dm^{-3} in UF_6 and having $SiMe_3Cl : UF_6$ = 1 : 1; the multiplet structures of some of the resonances are illustrated in the expanded traces of Figure 1(*b*). A solution with a similar concentration of UF_6 but with $SiMe_3Cl : UF_6$ = 1 : 3 gave a spectrum consisting essentially of the singlets at δ +764 and −159 p.p.m. due to UF_6 and $SiMe_3F$ respectively, together with a quintet centred at δ +781.5 p.p.m. and a doublet at δ +762.0 p.p.m. The quintet and doublet had relative intensities of *ca.* 1 : 4 and neither this nor the positions of the resonances varied with the reacting proportions or concentrations of UF_6 and $SiMe_3Cl$ (even with 100-fold dilution of the solution). These results give unequivocal evidence for the formation of the pseudo-octahedral molecule UF_5Cl. By contrast, a solution with the proportions $SiMe_3Cl : UF_6$ = 5 : 1 gave a strong singlet at δ +774.3 p.p.m. corresponding presumably to $UFCl_5$ and two much weaker singlets at δ +781.0 and +746.1 p.p.m. corresponding to *cis*- and *trans*-UF_2Cl_4. Systematic variations of the proportions $SiMe_3Cl : UF_6$, combined with observations of the frequencies, multiplet patterns, and relative intensities of the new resonances, allow us to identify all eight of the uranium(VI) chloride fluorides: UF_5Cl, *cis*- and *trans*-UF_4Cl_2, *mer*- and *fac*-UF_3Cl_3,

Table 1. Details of the ^{19}F n.m.r. spectra of the compounds UF_nCl_{6-n} (n = 1—6) in $CFCl_3$ solution at −73 °C

Compound	N.m.r. system	δ_F*/p.p.m.	$^2J(^{19}F-^{19}F)$/Hz
UF_6	A_6	+764.0	—
UF_5Cl	A_4X	A_4 +762.0 X +781.5	13.3 ± 0.6
cis-UF_4Cl_2	A_2X_2	A_2 +760.0 X_2 +785.8	18.8 ± 0.6
trans-UF_4Cl_2	A_4	+755.5	—
mer-UF_3Cl_3	A_2X	A_2 +753.0 X +782.6	24.0 ± 2.5
fac-UF_3Cl_3	A_3	+786.4	—
cis-UF_2Cl_4	A_2	+781.0	—
trans-UF_2Cl_4	A_2	+746.1	—
$UFCl_5$	A	+774.3	—

* ^{19}F Chemical shifts: frequency measured with reference to the resonance due to the $CFCl_3$ solvent; estimated uncertainty ±0.1 p.p.m.

cis- and *trans*-UF_2Cl_4, and $UFCl_5$. Details of the relevant n.m.r. parameters are given in Table 1.

Analogous measurements carried out with a CCl_3F solution containing a mixture of UF_6 and UCl_6, again held at *ca.* −75 °C, yielded a ^{19}F n.m.r. spectrum identical with that derived from a mixture of UF_6 and $SiMe_3Cl$ having the same proportions of fluoride and chloride, apart from the absence of a resonance due to $SiMe_3F$. Changing the proportions of UF_6 and UCl_6 had the same effect as changing the proportions of UF_6 and $SiMe_3Cl$.

The relative (integrated) intensities of the ^{19}F resonances associated with the different members of the series UF_nCl_{6-n} were estimated for mixtures with different proportions of fluoride and chloride in an attempt to assess the distribution of the products. It is of course difficult to relate the peak areas to the concentrations of the resonating nuclei without some knowledge of the relaxation times. However, we found that the integrated intensities of the quintet and doublet due to UF_5Cl were in the ratio 3.9 : 1 (as opposed to the expected ratio of 4 : 1). These two resonances span about one-half of the total range of chemical shifts exhibited by the UF_nCl_{6-n} molecules and we have therefore been encouraged to assume that there is a constant proportionality between the peak area and concentration of the resonating nucleus. For a mixture with $SiMe_3Cl : UF_6$ = *ca.* 1.3 : 1, the relative concentrations are thus estimated to be as follows: $UF_6 : UF_5Cl : UF_4Cl_2$ (both isomers) : UF_3Cl_3 (both isomers) = 1 : 2.95 : 2.78 : 1.06 (with estimated errors in the order of 5%). For a random distribution of products in such a mixture we expect $UF_6 : UF_5Cl : UF_4Cl_2 : UF_3Cl_3$ = 1 : 1.66 : 1.15 : 0.42. The ratios *cis*-UF_4Cl_2 : *trans*-UF_4Cl_2 and *fac*-UF_3Cl_3 : *mer*-UF_3Cl_3 were found for this and other mixtures to be 12 : 1 and 1.5 : 1 respectively, whereas the spectra of mixtures richer in chloride indicated that *cis*-UF_2Cl_4 : *trans*-UF_2Cl_4 = 7 : 1. Random statistics lead one to expect *cis* and *trans* isomers of pseudo-octahedral MX_4Y_2 molecules to be formed in the proportions 4 : 1 and *fac* and *mer* isomers of MX_3Y_3 molecules in the proportions 1.5 : 1.

Visible Absorption Spectra.—The effect of adding successive aliquots of $SiMe_3Cl$ to a solution of UF_6 in $CFCl_3$ was also monitored by reference to the visible absorption spectrum of the solution maintained at *ca.* −80 °C; such experiments were carried out with solutions typically 60 mmol dm^{-3} in UF_6.

Solutions rich in UF_6 exhibited a new band centred at 510 nm in addition to the strong absorption which appears at wavelengths shorter than 450 nm (see Figure 2). The position of the new band and the general appearance of the spectrum were independent of both the initial UF_6 concentration and the proportions $SiMe_3Cl : UF_6$ within the range 1 : 20 to 1 : 2.5. Under these conditions and with due allowance for the loss of a small amount of material through conditioning of the cell (leading to a lower absorbance than expected at the lowest concentrations of $SiMe_3Cl$), the absorbance of the band at 510 nm increased linearly as a function of the concentration of $SiMe_3Cl$ initially present. This indicates that the band arises from a single product, UF_5Cl, formed in accordance with equation (1). The absorption coefficient of the band, $\varepsilon_{max.}$, was estimated to be 290 ± 30 cm^2 mol^{-1}.

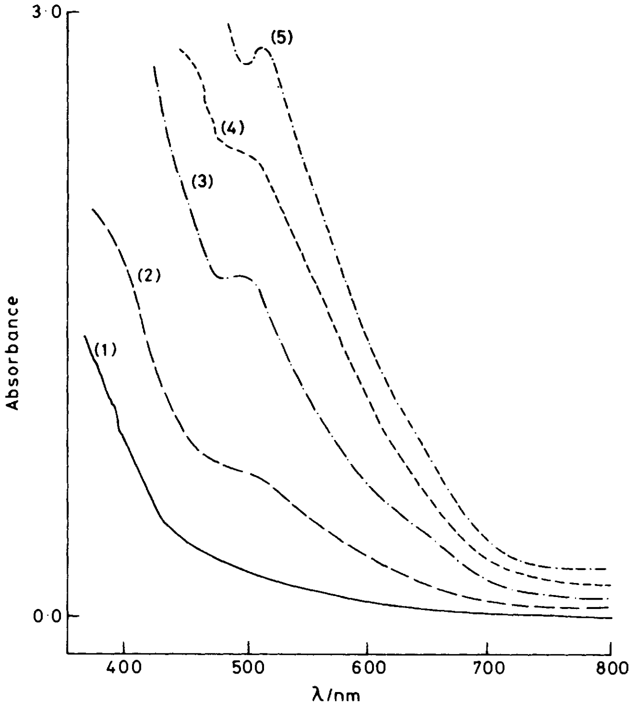

Figure 2. Visible absorption spectra of solutions containing varying amounts of $SiMe_3Cl$ added to a solution of UF_6 (30 mmol dm^{-3}) in $CFCl_3$ held at −83 °C. The proportions $UF_6 : SiMe_3Cl$ corresponding to each trace are as follows: (1) 10 : 1, (2) 5 : 1, (3) 3.3 : 1, (4) 2.5 : 1, (5) 2 : 1

$$UF_6 + SiMe_3Cl \rightleftharpoons UF_5Cl + SiMe_3F \qquad (1)$$

As the proportion of $SiMe_3Cl$ in the solution increased, the appearance of the absorption spectrum between 400 and 800 nm changed in the manner illustrated in Figure 2. When the ratio $SiMe_3Cl : UF_6$ reached or exceeded 6 : 1, the spectrum became virtually invariant with respect to the initial concentration of $SiMe_3Cl$ and was identical with that of a solution prepared from an authentic sample of UCl_6.

Mass Spectra.—A two-fold excess of UF_6 was co-condensed with a frozen $CFCl_3$ solution of $SiMe_3Cl$ in an FEP tube and the mixture maintained at −63 °C for 4 h. After all the material volatile at this temperature had been evaporated under high vacuum, the tube was connected directly to the stainless-steel gas inlet system of the mass spectrometer. With the sample at −63 °C, no mass peaks attributable to a volatile uranium compound could be detected but with the sample at −45 °C the spectrum of the vapour showed peaks originating not only in the molecular ions UF_6^+ but also in UF_5Cl^+ as well as fragments of these species. The relevant peaks are

Table 2. Mass spectrum of the vapour over the solid reaction mixture formed by UF_6 and $SiMe_3Cl$ ($UF_6 : SiMe_3Cl = 2 : 1$) and held at −45 °C

m/*e*	Relative intensity	Ion [a]
370	1.0	$UF_5{}^{37}Cl^+$
368	3.0	$UF_5{}^{35}Cl^+$
352	*b*	$UF_6{}^+$
351	3.5	$UF_4{}^{37}Cl^+$
349	10.5	$UF_4{}^{35}Cl^+$
333	*b*	$UF_5{}^+$
330	7.2	$UF_3{}^{35}Cl^+$
314	*b*	$UF_4{}^+$
311	2.9	$UF_2{}^{35}Cl^+$
295	*b*	$UF_3{}^+$
292	2.0	$UF^{35}Cl^+$
276	*b*	$UF_2{}^+$
273	1.6	$U^{35}Cl^+$
257	*b*	UF^+
238	*b*	U^+
157	*b*	$UF_4{}^{2+}$
147.5	*b*	$UF_3{}^{2+}$
138	*b*	$UF_2{}^{2+}$
128.5	*b*	UF^{2+}
119	*b*	U^{2+}

[a] U corresponds to ^{238}U, F to ^{19}F. [b] Mass peaks corresponding to $UF_n{}^+$ and $UF_n{}^{2+}$ (n = 0—6) were at least one order of magnitude more intense than those due to UF_nCl^+ (n = 0—5).

listed in Table 2. The identity of each of the ions UF_5Cl^+ and UF_4Cl^+ was confirmed by the appearance of a doublet with components having relative intensities of 1 : 3 corresponding to the abundances of the naturally occurring chlorine isotopes ^{37}Cl and ^{35}Cl respectively. However, mass peaks associated with the ions $UF_n{}^{37}Cl^+$ (n = 0—3) could not be resolved because of the high intensity of the adjacent peaks associated with the ions $UF_{2+n}{}^+$.

Chemical Studies.—$CFCl_3$ solutions containing $SiMe_3Cl$ and UF_6 in various proportions were allowed slowly to warm up from −63 °C to room temperature, with constant stirring. All the volatile components were then evaporated under vacuum and the products investigated by spectroscopic and chemical analysis.

Mixtures with $SiMe_3Cl : UF_6 \leqslant 1 : 1$ gave a pale green involatile solid which was soluble in dry acetonitrile and identified as β-UF_5 on the evidence of its i.r. and Raman spectra.[10] By contrast, a mixture with $SiMe_3Cl : UF_6 = 2 : 1$ gave a darker green solid which was insoluble in acetonitrile; elemental analysis indicated that this was UF_4, a conclusion supported by its i.r. spectrum.[11] Hence our results agree with those reported recently by Brown *et al.*[1] When the reaction mixture included an excess of $SiMe_3Cl$, with $SiMe_3Cl : UF_6 \geqslant 6 : 1$, vacuum evaporation of all the material volatile at −63 °C left what appeared to be a black solid stable at room temperature. This was shown by elemental analysis and by its i.r.,[12] u.v.-visible,[13] and mass spectra to be UCl_6.

The volatile material derived from reaction mixtures which had been allowed to warm up to room temperature included, in addition to the solvent, $SiMe_3F$, UF_6 (from mixtures rich in fluoride), and elemental chlorine (identified by the Raman spectrum of the solid condensate formed on a copper block at −196 °C [14]). Experiments were also carried out with a more volatile solvent to facilitate vaporisation at temperatures low enough to avoid significant decomposition of the uranium(VI) chloride fluorides. For example, a CF_2Cl_2 solution containing an equimolar mixture of UF_6 and $SiMe_3Cl$ was kept at −63 °C while being subjected to continuous pumping followed by trap-to-trap fractionation of the volatile material. Under these circumstances the vapour species included only the solvent, $SiMe_3F$, UF_6, and a brown product; little or no chlorine was detected. The brown product collected with UF_6 in a trap held at −83 °C; attempts to separate it from UF_6 have as yet been unsuccessful. Analysis of a typical condensate formed at −83 °C indicated that it was a mixture containing UF_6 and UF_5Cl in roughly equal proportions. When such a condensate was allowed to warm much above −60 °C, it decomposed with the formation of pale green β-UF_5 and gaseous chlorine.

Since NO reacts with UF_6 to form the nitrosonium salt $NO^+UF_6{}^-$,[15] we investigated the interaction of nitrogen monoxide with a UF_6–$SiMe_3Cl$ reaction mixture in the hope of fixing UF_5Cl or UF_4Cl_2 in the form of the corresponding hexahalogenouranate(V) anion. In fact, admission of NO to a $CFCl_3$ or CF_2Cl_2 solution having the initial composition $SiMe_3Cl : UF_6 = 1 : 1$ or $2 : 1$ and held at −70 °C gave only NOCl (identified by its i.r. spectrum [16]) and either β-UF_5 or UF_4 formed in accordance with an equation such as (2).

$$UF_5Cl + NO \longrightarrow UF_5 + NOCl \qquad (2)$$

Evidently UF_5 and NOCl do not interact even at −70 °C.

Discussion

Our results demonstrate that facile halide exchange occurs between UF_6 and either $SiMe_3Cl$ or UCl_6 in Freon solutions at temperatures below −60 °C. The solutions vary in colour from red to almost black according to the concentrations and the relative proportions of chloride and fluoride. With the aid of the ^{19}F n.m.r. spectra it has been possible to identify all the members of the series UF_nCl_{6-n} (n = 1—5). The facility of halide exchange tends to frustrate any attempt to separate individual species, although mixtures rich in UF_6 and containing essentially only UF_6 and UF_5Cl may yet prove amenable to low-temperature fractionation.

The assignment of some of the ^{19}F resonances summarised in Table 1 and illustrated in Figure 1 follows directly from the multiplet patterns. This is the case with (*i*) UF_5Cl characterized by a doublet and a quintet with relative intensities of 4 : 1, (*ii*) *cis*-UF_4Cl_2 characterized by two triplets of equal intensity, and (*iii*) *mer*-UF_3Cl_3 characterized by a doublet and a triplet with relative intensities of 2 : 1. However, the other products each contain fluorine in a single magnetic environment and exhibit only a single ^{19}F resonance. We have identified these resonances by reference to the way in which the intensity varies with the relative proportions of chloride and fluoride. Thus the singlet due to *trans*-UF_4Cl_2 grows in step with the distinctive multiplets due to the *cis* isomer and likewise the singlet due to *fac*-UF_3Cl_3 grows in step with the distinctive multiplets due to the *mer* isomer. $UFCl_5$ is identified as the source of the only ^{19}F resonance to persist in solutions containing a large excess of chloride. To distinguish the resonances arising from *cis*- and *trans*-UF_2Cl_4, we have constructed a Dean–Evans plot [17] showing how the chemical shift varies with the number of fluorine substituents *cis* to the resonant fluorine atom (Figure 3). Smooth curves are obtained only if the resonance at lower frequency is assigned to *trans*-UF_2Cl_4.

The Dean–Evans plot brings to light three features of interest in relation to molecules of the type UF_nCl_{6-n}. (*i*) We note that fluorine atoms *trans* to chlorine resonate at consistently higher frequencies than fluorine atoms *trans* to a second fluorine atom. Similar behaviour is found for fluorine *trans* to OMe in individual molecules of the type $UF_n(OMe)_{6-n}$[18] but does not necessarily extend from one member

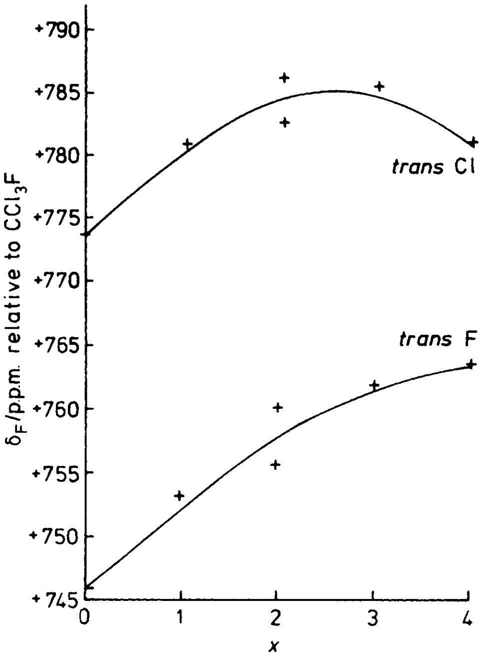

Figure 3. Plot of the ^{19}F resonance frequency, δ_F, *vs.* number of fluorine atoms (x) *cis* to the resonant fluorine in the series UF_nCl_{6-n} (n = 1—6). The upper curve relates to a resonant fluorine which is *trans* to a chlorine and the lower curve to a resonant fluorine which is *trans* to another fluorine

of the series to another. By contrast, the reverse frequency pattern applies, *mutatis mutandis*, to molecules in the series $UF_n(OTeF_5)_{6-n}$[19] and WF_nCl_{6-n}.[20] (*ii*) It appears that the resonance of a linear F–U–F moiety moves to higher frequency as the number of *cis*-fluorine atoms increases. Again this parallels the behaviour of molecules in the series $UF_n(OMe)_{6-n}$[18] but is opposed to the trend exhibited by the series $UF_n(OTeF_5)_{6-n}$[19] and WF_nCl_{6-n}.[20] (*iii*) The resonance frequency of a linear F–U–Cl moiety first increases, reaches a maximum and then decreases as the number of *cis*-fluorine atoms increases. Such a trend is intermediate between those displayed by the series $UF_n(OMe)_{6-n}$[18] and $UF_n(OTeF_5)_{6-n}$.[19]

The ^{19}F resonance frequencies of octahedral or pseudo-octahedral species of the type $[SnF_nX_{6-n}]^{2-}$ (*e.g.* X = Cl, Br, I, OR, NCO, NCS, or N_3) led Dean and Evans[17] to the empirical expression (3) for the resonance frequency of nucleus Z, δ_Z, where p is the number of fluorine atoms *cis* and

$$\delta_Z = pC + qT \qquad (3)$$

q the number *trans* to Z, and C and T are constants for a particular system. This simple linear relation gives a tolerable account of δ_F for the members of the series $UF_n(OMe)_{6-n}$,[18] $UF_n(OTeF_5)_{6-n}$,[19] and WF_nCl_{6-n}[20] but Figure 3 shows it to be wide of the mark for the series UF_nCl_{6-n}.

The relative intensities of the ^{19}F resonances due to the molecules UF_nCl_{6-n} suggest non-random scrambling, with the equilibria favouring somewhat the mixed halides UF_5Cl, UF_4Cl_2, and UF_3Cl_3. Hence there is probably a small but significant enthalpy change associated with reactions of type (4). It is noteworthy also that although the isomers *fac*- and

$$\frac{n}{6}UF_6 + \frac{6-n}{6}UCl_6 \rightleftharpoons UF_nCl_{6-n} \qquad (4)$$

mer-UF_3Cl_3 are formed in proportions consistent with random statistics, this is not the case with UF_4Cl_2 and UF_2Cl_4, the *cis* isomers of which are 2—3 times more abundant than random statistics would lead us to expect. This possibly reflects the additional dipolar contributions made by interactions between the *cis* isomers and the CCl_3F solvent molecules.

The visible absorption spectrum associated with UF_5Cl in $CFCl_3$ solution (see Figure 2) displays two significant features: (*i*) the distinctive new band centred at *ca.* 510 nm, and (*ii*) the marked increase in absorption at shorter wavelengths ($\leqslant$450 nm). In view of the ambiguity about the correct ordering of the molecular orbitals in the symmetrical UCl_6 molecule,[21] it is difficult to give an unequivocal interpretation of this spectrum. However, comparisons with the absorption spectra of gaseous UF_6 ($\lambda_{max.}$ = 369 nm)[22] and UCl_6 in either the gas phase ($\lambda_{max.}$ = *ca.* 485 nm)[13] or in $CFCl_3$ solution ($\lambda_{max.}$ = 495 nm)[23] suggest that the band at 510 nm has significant Cl→U charge-transfer character. Presumably the absorption at shorter wavelengths involves mainly F→U charge transfer and the increased intensity reflects the reduction in symmetry of UF_5Cl compared with UF_6 although some admixture of Cl→U charge transfer cannot be discounted. The weak band at 369 nm exhibited by gaseous UF_6 has been ascribed to forbidden $a_{1g}\rightarrow t_{2u}$ and $t_{1g}\rightarrow a_{2u}$ transitions;[24] under C_{4v} symmetry, the corresponding transitions of UF_5Cl are allowed ($a_1\rightarrow e$ and $e\rightarrow b_2$). This is consistent with the observed absorption coefficients, with $\varepsilon_{max.}$ = *ca.* 54 cm^2 mol^{-1} for UF_6 at λ = 369 nm[21] and $\varepsilon \geqslant$ 460 cm^2 mol^{-1} for UF_5Cl at $\lambda \leqslant$ 400 nm. Unfortunately the absorption of the Teflon-FEP cell precluded measurements at wavelengths shorter than 400 nm.

Conclusions

Uranium hexafluoride reacts rapidly with either chlorotrimethylsilane or uranium hexachloride in Freon solution at temperatures below −60 °C to produce uranium(VI) chloride fluorides of the type UF_nCl_{6-n} (n = 1—5) which have been characterized by their ^{19}F n.m.r. and visible absorption spectra. Unlike the hexafluoride and hexachloride, the chloride fluorides decompose at room temperature with the evolution of gaseous chlorine and the formation of uranium(IV) or uranium(V) halides. They react with nitrogen monoxide to form not the appropriate nitrosonium hexahalogenouranate(V), $NO^+UF_nCl_{6-n}^-$ (*cf.* UF_6^-), but nitrosyl chloride and a lower-valent uranium halide.

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