Reaction of UF_6 with Methanol to form UF_5OMe

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Summary The compound F_5UOMe has been prepared by the reaction of UF_6 with MeOH in $CFCl_3$ solvent at −90 °C and has been characterized by ^{13}C, ^1H, and ^{19}F n.m.r. methods.

URANIUM(VI) alkoxides of the type $U(OR)_6$, (R = Et, Pr, or Me), have been known to exist for some time[1] and the extensive metathetical chemistry of the main group and transition metal fluoride is also well known as typified by the compounds, $WF_x(OMe)_{6-x}$.[2,3] Other transition metal mixed fluoride–alkoxide compounds[4,5] have been well characterized. In spite of the large amount of literature on the chemistry of UF_6[6] there has been very little reported on U^{VI} mixed ligand fluoride-containing compounds, the recent synthesis[7] of the series $UF_x(OTeF_5)_{6-x}$ ($x = 0$—5) and the structural result[8] on the $x = 0$ species being unique in this regard. No evidence has been reported to suggest the existence of mixed fluoride alkoxide U^{VI} species, and this stimulated our interest in the synthesis of mixed-ligand compounds.

In order to extend the basic knowledge of the chemistry of uranium and to synthesize and characterize new, often unstable, species, we have been studying the interaction chemistry of uranium^{VI} with various ligands. In one of our first attempts at forming mixed fluoride alkoxide U^{VI} compounds, we studied the reaction of UF_6 with simple alcohols under a variety of conditions of concentration and temperature. This route has proven successful in reactions of TeF_6 with alcohols.[9] The driving force for the formation of any substituted UF_6 species would presumably be the formation of a covalent fluoride (HF) as well as the propensity for uranium to bind to oxygen donors [*e.g.* $U(OTeF_5)_6$ is formed from $F_3Si(OTeF_5)$ or $B(OTeF_5)_3$ resulting in SiF_4 or BF_3 as the gaseous product].[7]

The reaction of UF_6 with a stoicheiometric amount of MeOH at −90 °C in $CFCl_3$ solvent results in a red-brown solution whose n.m.r. spectra demonstrate the formation of the mono-substituted species of UF_5OMe as in equation (1).

$$UF_6 + MeOH \rightarrow UF_5OMe + HF \qquad (1)$$

No evidence for further substitution has been observed but mixed species of the type $F_xU(OR)_{6-x}$ cannot be ruled out in light of the stability of the end members of the series. However, amounts of MeOH in excess of stoicheiometry for equation (1) cause more rapid decomposition.

The n.m.r. evidence indicates that at the early stages of the reaction a single U^{VI} species is formed. The ^{19}F n.m.r. spectrum at −100 °C in $CFCl_3$ shows an AB_4 pattern expected for a mono-substituted octahedral molecule with δ_A +56·3 (±0·3) p.p.m. from internal UF_6 and δ_B +117 (±0·5) p.p.m. The fluorine *trans* to the methoxy ligand (A) is split into a quintet and the *cis* fluorines (B) are split into a doublet with J(F–F) 16·9(±0·3) Hz. The equatorial fluorines resonate upfield of the axial multiplet in UF_5OMe as is the case with TeF_5OR[9] whereas the reverse is true for other compounds.[3,7,10]

The ^1H n.m.r. spectrum at −100 °C shows a peak at 7·70 (±0·05) p.p.m. downfield from MeOH, which is attributed to the methyl protons of UF_5OMe. The ^1H-decoupled ^{13}C n.m.r. spectrum of a sample, prepared with 93% enriched $^{13}CH_3OH$, displays a prominent peak at 46·9 p.p.m. downfield from MeOH, which is assigned to UF_5OMe. This peak develops into a quartet in the proton coupled experiment with $J(^{13}C–^1H)$ 151·3(±0·5) Hz. This same coupling constant is observed for the peak attributed to UF_5OMe in the ^1H n.m.r. spectrum and is unusually large for a methoxide compound. Both ^1H and ^{13}C chemical shifts are also unusually large for a methoxide compound and yet not surprising considering the large ^{19}F chemical shift observed for UF_6 (764 p.p.m. downfield from $CFCl_3$).

Upon warming the reaction solution to room temperature, a green solid precipitates out and the solution becomes clear and colourless. A rough estimate of the decomposition temperature has been made and the material appears to decompose readily at −60 °C.

The reaction of UF_6 with MeOH at −90 °C to produce UF_5OMe is not unique and preliminary experiments indicate that other alcohols as well as phenols undergo similar reactions with UF_6.

N.m.r. techniques have proven especially useful in the previous studies of transition metal and main group mixed-ligand species to determine stereochemical features as our n.m.r. evidence in the present study demonstrates.

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