

increased by 1 to accommodate the water molecule. Presumably, steric crowding prevents the total coordination number from increasing beyond 9.

The structure⁹ of the complex $\text{Ca}(\mathbf{1a})_2\text{Cl}_2$ reveals that the Ca(II) is in a site of D_2 symmetry, coordinated to the ether and carbonyl groups of the ionophore to attain a total coordination number of 8. Our studies on $[\text{Eu}(\mathbf{1b})_2](\text{BF}_4)_3$ are entirely consistent with an identical structure for the analogous Eu(III) complex.

Lanthanide ions exhibit high coordination numbers, with 8 and 9 being the most common.¹⁴ A marked preference for

oxygen donors has been demonstrated for Ln(III) ions. The facts that only one water molecule can bind to the ionophore complex, that only non-coordinating anions are present, and that no solvent (CH_3CN) remains upon formation of the complex suggest that the Eu(III) is coordinated in a fashion similar to that of the analogous Ca(II) system (i.e., to the eight available oxygen donor atoms of the ionophore). The splittings in the excitation and emission spectra are also consistent with the symmetry found⁹ for Ca(II) in the analogous complex (D_2 for Ca(II); $\leq D_{2h}$ for Eu(III)).

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Registry No. $[\text{Eu}(\mathbf{1b})_2](\text{BF}_4)_3$, 87050-40-6; Eu, 7440-53-1.

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Nuclear Magnetic Resonance and Chemical Studies of Uranium(V) Alkoxides

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The following uranium(V) alkoxides have been synthesized: $\text{U}(\text{OR})_5$, $\text{R} = \text{CH}_3, \text{CH}_2\text{CH}_3, \text{C}_6\text{H}_5$; $\text{U}(\text{OR}_f)_4(\text{OC}_2\text{H}_5)(\text{HOC}_2\text{H}_5)$, $\text{R}_f = \text{C}_4\text{F}_9, \text{C}_3\text{HF}_6$; $\text{U}(\text{OC}_6\text{F}_5)_5(\text{HOC}_2\text{H}_5)$. The compounds have been characterized by high-resolution ^{13}C , ^{19}F , and ^1H NMR spectroscopy. Well-resolved, temperature-dependent ^{13}C spectra were obtained for $\text{U}(\text{OEt})_5$ and $\text{U}(\text{OPh})_5$, indicative of rapid ligand exchange at ambient temperatures and slower exchange and/or molecular association beyond dimeric at lower temperatures. Reactions of $\text{U}(\text{OEt})_5$ with SO_2 , pyridine, THF, CH_3CN , O_2 , NO, 18-crown-6, and HF are discussed.

Introduction

Uranium(V) and uranium(VI) alkoxides, $\text{U}(\text{OR})_5$ and $\text{U}(\text{OR})_6$, form a fairly extensive but incompletely characterized class of uranium compounds. These alkoxides were first prepared by Gilman and co-workers,¹⁻⁴ who reported syntheses, analyses, relative volatilities/stabilities, and a few chemical properties. These reports were followed by work by Bradley et al.,⁵⁻⁸ who prepared additional $\text{U}(\text{OR})_5$ and $\text{U}(\text{OR})_6$ compounds and reported ebullioscopic molecular weights in addition to volatilities. Derivative reactions of certain uranium alkoxides were reported by other groups in the 1960s.⁹⁻¹¹ Some infrared⁸ and proton NMR¹² data have been reported for $\text{U}(\text{OEt})_5$ and $\text{U}(\text{O}-i\text{-Pr})_5$, and a preliminary X-ray structure has shown the penta-*tert*-butoxide compound to be

dimeric.¹³ Most uranium(V) alkoxides appear to be oligomeric, but otherwise little is known about their physical and chemical properties. Recently, $\text{U}(\text{OCH}_3)_6$ has been used in a laser isotope separation experiment to enrich uranium.¹⁴ A related uranium(VI) compound, $\text{U}(\text{OTeF}_5)_6$, has been synthesized and shown to possess octahedral geometry,¹⁵ and mixed complexes stable only at very low temperatures, $\text{UF}_x(\text{OCH}_3)_{6-x}$, have been reported.^{16,17}

We prepared $\text{U}(\text{OR})_5$ compounds containing polyfluoroaryl and polyfluoroalkyl groups to study the stabilities and volatilities of such new compounds. Also, we wanted to characterize more definitively the chemical properties and the feasibility of NMR characterization of these paramagnetic (f^1) systems. Herein we report our characterization of several U(V) alkoxides, including several new compounds containing fluoroalkoxide groups.

Experimental Section

Standard high-vacuum, Schlenk, and inert-atmosphere glovebox procedures were used throughout this study. Unless otherwise noted, solvents and chemicals were of commercial reagent grade and were purified by vacuum distillation. Ethanol and hydrocarbons were freshly distilled over sodium. Polyfluoro alcohols were obtained from Peninsular Chemical Co. and were purified by vacuum sublimation or distillation. Elemental analyses for C, H, and N were performed by Galbraith Laboratories, Inc. Combustion analyses for the fluoroalkoxides, however, were often highly variable, presumably due to difficulties in completely burning these fluorocarbon materials. Therefore, additional analytical methods were also used. Uranium was determined by hydropyrolysis at 850 °C on a Perkin-Elmer TGS-2 thermogravimetric system. Ethanol:fluoro alcohol ratios were de-

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terminated by hydrolyzing the mixed-ligand complexes in 5 M aqueous HCl and measuring relative peak areas in ^{19}F and ^1H NMR spectra relative to an added standard ($\text{CF}_3\text{CH}_2\text{OH}$). The ethanol:fluoro alcohol ratios were also determined by acidifying the complexes with butyric acid and measuring relative alcohol peak areas in gas chromatograms. A Varian Aerograph Series 2700 gas chromatograph (Poropak N column) was used. Electronic spectra were obtained on a Carey 14 spectrometer, and infrared spectra (supplementary material) of Nujol mulls were obtained with a Perkin-Elmer 521 instrument. Mass spectral characterization of the new compounds was unsuccessful, decomposition being observed in the mass spectrometer. Fourier transform ^{13}C NMR spectra were obtained at 25.2 MHz with a Varian XL-100 spectrometer interfaced to a Data General Nova 1210 or Super Nova computer, with a resolution of at least one spectral point per 2.5 Hz. Broad-band proton noise decoupling was employed in most spectra (exceptions are noted). T_1 relaxation times were determined at 25 °C for both the methyl and methylene carbons in $\text{U}(\text{OC}_2\text{H}_5)_5$ by using the $180^\circ\text{-}\tau\text{-}90^\circ$ pulse train method. T_1 values were taken from a nonlinear least-squares fit of the equation

$$A_\tau = A_\infty(1 - 2\alpha e^{-\tau/T_1})$$

Other experimental details of the NMR data acquisition and treatment are as reported in Ref 18.

CW ^{19}F and ^1H NMR spectra were obtained with a Varian EM 390 instrument. Chemical shifts are quoted relative to CFCl_3 (^{19}F) and tetramethylsilane (^1H).

Preparation of the Compounds. $\text{U}(\text{OC}_2\text{H}_5)_5$ was prepared by published methods^{1,19} and was used to prepare the other compounds via alcohol exchange. $\text{U}(\text{OCH}_3)_5$ was also prepared by a published procedure.²

$\text{U}(\text{OC}_2\text{H}_5)_5$. Uranium pentaethoxide (1.03 g, 2.22 mol) was added to a cold (-30°C) suspension of freshly sublimed phenol (2.60 g, 27.7 mmol) in 30 mL of pentane. The mixture was allowed to warm to room temperature and stirred for 2.5 h, producing a brown-black microcrystalline precipitate, and volatiles were stripped off under vacuum. Anal. Calcd for $\text{U}(\text{O}_6\text{H}_5)_5$: C, 52.21; H, 3.58. Found: C, 50.99; H, 3.60. The compound shows some decomposition above 140 °C, and rapidly melts at $\sim 165\text{--}170^\circ\text{C}$.

$\text{U}(\text{OC}_4\text{F}_9)_4(\text{OC}_2\text{H}_5)(\text{HOC}_2\text{H}_5)$. Ca. 4 mL of nonafluoro-2-methyl-2-propanol was condensed onto 1.00 g (2.16 mmol) of $\text{U}(\text{OC}_2\text{H}_5)_5$. When the mixture was warmed to room temperature, a lime green solution resulted, from which crystals readily formed on slight cooling. After standing for several hours, the solution was subjected to vacuum for 15 h, giving a green-yellow crystalline product. Solution in nonafluoro-2-methyl-2-propanol and volatiles removal was repeated three more times to give 2.6 g (93% yield) of crystalline yellow product. An identical product was obtained when the reaction was carried out in pentane solution. Anal. Calcd: U, 18.7; C, 18.95; H, 0.87; F, 53.89. Found: U, 18.7; C, 18.61; H, 0.81; F, 53.70. Fluoroalkoxide:ethoxide ratio observed: 4.0:2.0 (NMR). The formula was confirmed by single-crystal X-ray diffraction.^{20,21} The compound gradually decomposes above $\sim 130^\circ\text{C}$.

$\text{U}(\text{OC}_3\text{F}_6\text{H})_4(\text{OC}_2\text{H}_5)(\text{HOC}_2\text{H}_5)$. Ca. 4 mL of hexafluoro-2-propanol was condensed onto 0.927 g (2.00 mmol) of $\text{U}(\text{OC}_2\text{H}_5)_5$. When the mixture was warmed to room temperature, a tan solution was obtained. The solution was stirred several hours, and volatiles were removed by vacuum pumping for ca. 15 h, giving a red-brown gum. Solution in hexafluoro-2-propanol followed by vacuum pumping was repeated three more times to give 1.9 g [Calcd 2.0 g for $\text{U}(\text{OC}_3\text{F}_6\text{H})_4(\text{OC}_2\text{H}_5)(\text{HOC}_2\text{H}_5)$] of tan solid. Anal. Calcd: U, 23.9. Found: U, 23.0. Observed fluoroalkoxide:ethoxide ratio: 4.0:1.7 (NMR). The compound gradually decomposes above $\sim 130^\circ\text{C}$.

$\text{U}(\text{OC}_6\text{F}_5)_3(\text{HOC}_2\text{H}_5)$. Pentafluorophenol (~ 10 mmol) was condensed onto a solution of uranium pentaethoxide (1.0 g, 2.2 mmol) in several milliliters of CFCl_3 . When the mixture was warmed to room temperature, a red-brown solution formed. After the solution was stirred for 4 h, volatiles were pumped away overnight. Three more

Table I. ^{13}C NMR Shifts and Line Widths for $\text{U}(\text{OC}_2\text{H}_5)_5$ Complexes^a

solvent	$\delta 1$ (fwhh)	$\delta 2$ (fwhh)	δ (ligand)
C_6D_6	85.9 (88)	30.2 (21)	
CFCl_3	79.0 (70)	30.5 (23)	
1:1 py/ CFCl_3 ^b	86.0 (110)	30.1 (20)	149.7, 134.9, 123.2
10:1 py/ CFCl_3 ^b	83.8 (80)	29.1 (27)	149.9, 135.3, 123.5
1:1 THF/ CFCl_3 ^c	85.6 (110), 74.0 (110)	29.8 (24)	
10:1 THF/ CFCl_3 ^c	87.4 (~ 100), 73.9 (~ 61)	30.3 (~ 43)	67.1, 26.0
SO_2 / CFCl_3	83.2 (~ 235)	28.4 (~ 124)	
$\text{Na}[\text{U}(\text{OC}_2\text{H}_5)_6]$ ^d	81.1 (73)	31.7 (12)	

^a Spectra were run at 15 °C. Chemical shift values were calculated in ppm downfield relative to external neat tetramethylsilane (Me_4Si) measured under similar conditions and are accurate to ± 0.1 ppm. $\delta 1$ = methylene chemical shift, $\delta 2$ = methyl chemical shift, and fwhh = full width at half-height. ^b ^{13}C resonances in neat pyridine occur at 150.4, 136.1, and 134.1 ppm. ^c ^{13}C resonances in neat THF occur at 67.5 and 25.9 ppm. ^d Acetonitrile solution. The ^{13}C resonance for the cyanide carbon occurs at 117.2 ppm for pure acetonitrile and at 117.8 ppm for the $\text{Na}[\text{U}(\text{OC}_2\text{H}_5)_6]$ solution.

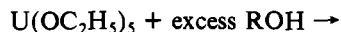
times a similar charge of CFCl_3 and pentafluorophenol was added, the solution was stirred several hours at room temperature, and volatiles were pumped away. The product is a moderately air-sensitive, dark red-brown solid that is very soluble in benzene, CFCl_3 , heptane, and ether. Anal. Calcd: U, 19.8. Found: U, 20.9. Observed pentafluorophenoxide:ethanol ratio: 5.0:0.9 (NMR). The compound gradually softens above 120 °C and melts rapidly above $\sim 160\text{--}165^\circ\text{C}$.

$\text{Na}[\text{U}(\text{OC}_2\text{H}_5)_6]$. Sodium (0.43 g, 1.8 mmol) was dissolved in ~ 5 mL of ethanol. Uranium pentaethoxide (0.50 mL, 0.86 g, 1.8 mmol) was added to form a pale green solution. After the mixture was stirred for 1–2 h, solvent was stripped off under vacuum. When the solvent volume reached several milliliters, nearly colorless needle crystals up to 2 mm in length resulted, but when they were pumped to dryness, a very pale green powder resulted (yield 0.80 g, 84%). The compound melts at $56\text{--}59^\circ\text{C}$ to a light green liquid.

Reaction of $\text{U}(\text{OEt})_5$ with HF. Onto a frozen solution of uranium pentaethoxide (0.30 mL, 0.51 g, 1.1 mmol) in several milliliters of heptane in a Kel-F tube was condensed 1.1 mmol of HF. The mixture was allowed to warm to $\sim -20^\circ\text{C}$, producing two layers. An additional 2.2 mmol of HF was added, and the mixture was allowed to warm to room temperature, giving a green precipitate. After the mixture was stirred for ca. 15 h, volatiles were removed under vacuum. Anal. Calcd for $\text{U}(\text{OC}_2\text{H}_5)_2\text{F}_3$: C, 12.48; H, 2.62; F, 14.80; U, 61.80. Found: C, 11.61; H, 2.50; F, 16.12; U, 60.89. When a large (100-fold) excess of liquid HF was added to $\text{U}(\text{OC}_2\text{H}_5)_5$, the reaction course was very similar.

Results and Discussion

The uranium(V) alkoxides were prepared by alkoxide exchange of $\text{U}(\text{OC}_2\text{H}_5)_5$ with a large excess of the appropriate liquid alcohol or a mixture of the appropriate solid alcohol with an inert solvent, followed by removal of volatile constituents.



$$x = 0, 1$$

$\text{U}(\text{OC}_2\text{H}_5)_5$. The behavior of uranium pentaethoxide in the presence of several coordinating ligands and solvents was investigated. Changes in the visible spectrum, indicative of complexation to uranium(V), were observed when acetonitrile, THF, pyridine, and SO_2 were added to solutions of $\text{U}(\text{OC}_2\text{H}_5)_5$ in pentane (supplementary material). Evidence for complexation was also afforded by the observation of substantial shifts in the alkoxide magnetic resonances when these bases were added to $\text{U}(\text{OC}_2\text{H}_5)_5$ solution (Table I). Substantial changes in ethoxide and coordinating solvent line widths, in-

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(20) Crystal data for $\text{U}(\text{OC}_4\text{F}_9)_4(\text{OC}_2\text{H}_5)(\text{HOC}_2\text{H}_5)$: space group $C2/c$, $a = 10.594$ (3) Å, $b = 18.595$ (3) Å, $c = 18.771$ (5) Å, $\beta = 100.34$ (2)°, $Z = 4$, $R = 0.100$ for 2044 reflections with $I \geq 2\sigma(I)$. Details of data treatment and structure refinement are as given in ref 21.

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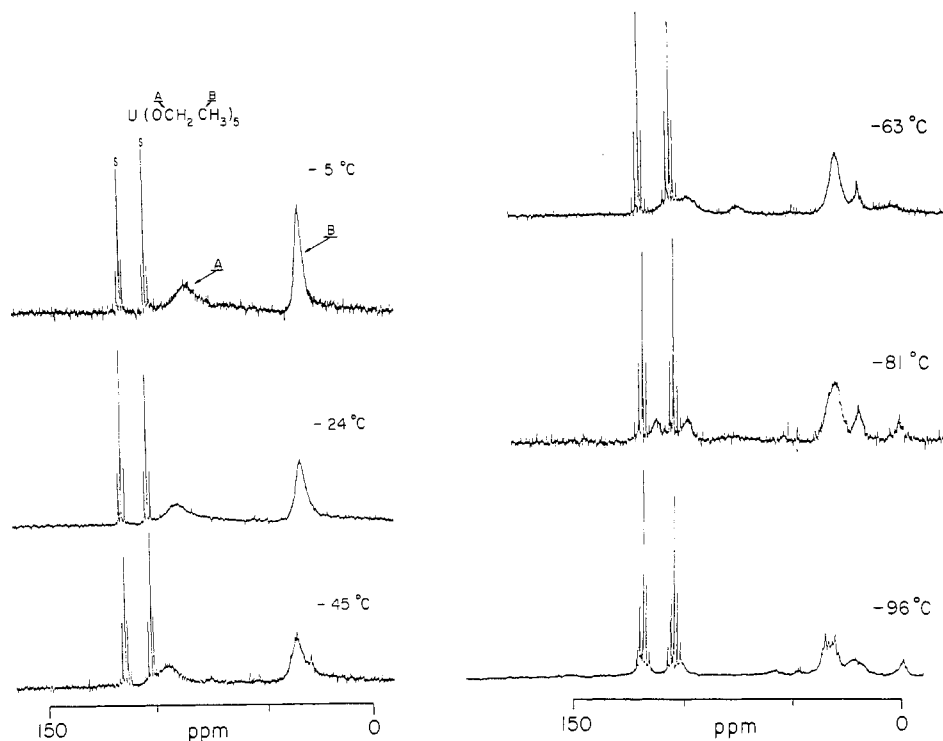


Figure 1. Natural-abundance ^{13}C NMR spectra of $\text{U}(\text{OC}_2\text{H}_5)_5$ in CFCl_3 (-5 to -96 °C). The sharp multiplets labeled "S" are due to solvent peaks and associated spinning side bands. Spectra in pentane were very similar.

dicative of ligation, also were observed. In each case the parent $\text{U}(\text{OC}_2\text{H}_5)_5$ was recovered when volatile components were pumped away at room temperature.

With SO_2 , a bright green oil was obtained initially on incomplete solvent removal and green crystals could be obtained in liquid SO_2 at -20 °C. The infrared spectrum of the green oil contained strong, new absorptions at 1238 and 950 cm^{-1} , assignable to S–O frequencies. According to SO_2 infrared correlations, these frequencies are in the range for side-on or end-on bonded SO_2 ligands.²² However, other structures are possible, e.g., with a primary U–OSO linkage with sulfur bridging to an adjacent alkoxide oxygen.

No reaction of $\text{U}(\text{OC}_2\text{H}_5)_5$ was observed with H_2 , NO , or 18-crown-6. The addition of dry O_2 to a $\text{U}(\text{OC}_2\text{H}_5)_5$ /18-crown-6 solution led to a yellow crystalline uranyl complex containing crown ether, although this compound does not necessarily imply coordination of the uranyl by the crown ether.²³

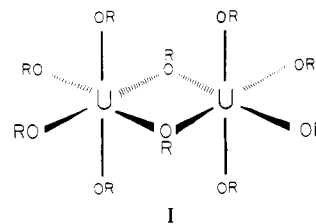
The reaction of $\text{U}(\text{OC}_2\text{H}_5)_5$ with anhydrous HF gave a mixed fluoroalkoxide instead of the expected UF_5 . The analytical data and observance of strong infrared bands near 962 and 1017 cm^{-1} confirmed the presence of ethoxide groups. The mixed fluoroalkoxide $\text{UF}_3(\text{OC}_2\text{H}_5)_2$ resulted when either a large (100:1) or stoichiometric (3:1) ratio of HF:pentaethoxide was used. The tan, moderately air-sensitive product is insoluble in common organic solvents and probably is polymeric.

$\text{U}(\text{OC}_6\text{H}_5)_5$. Bagnall et al. reported that a 100% excess of phenol reacted with uranium pentaethoxide in benzene at reflux for 9 h to form the mixed-alkoxide $\text{U}(\text{OPh})_4(\text{OEt})$.¹¹ In contrast, we find that the reaction in pentane at room temperature using a 12:1 ratio of phenol to uranium pentaethoxide produces, after removal of volatiles, a black-brown product, analyzing closely for the fully substituted product $\text{U}(\text{OPh})_5$. The infrared spectrum showed no peaks attributable to ethoxy groups, and the ^{13}C NMR spectrum in CFCl_3 ,

CH_2Cl_2 , and C_6D_6 over the range ± 240 ppm (relative to Me_4Si) contained only peaks attributable to phenoxy carbons. In view of the difference in $\text{p}K_a$'s for ethanol and phenol, 15.9 and 10.0, respectively,²⁴ and the fact that the solid-state structure of the sterically more congested compound $\text{U}(\text{O}-t\text{-Bu})_5$ is dimeric,^{7,13} we feel that the generation of fully substituted $\text{U}(\text{OPh})_5$ under the above conditions is reasonable.

Our $\text{U}(\text{OPh})_5$ compound has high solubility in toluene, benzene, methylene chloride, and fluorotrichloromethane and moderate solubility in pentane. The compound decomposes without sublimation on heating under high vacuum, and a mass spectrum contained no peaks above $m/e \sim 318$. For short periods of time in the solid state (~ 1 h) and in solution (several minutes), the compound appeared unchanged when exposed to dry air, but on long exposure it decomposed to a gray powder. On storage for a few weeks in a loosely capped container, phenol was observed above the sample.

NMR Studies of $\text{U}(\text{OC}_2\text{H}_5)_5$ and $\text{U}(\text{OC}_6\text{H}_5)_5$. $\text{U}(\text{OC}_2\text{H}_5)_5$. Karraker and co-workers found that above -40 °C, the ethoxide groups of $\text{U}(\text{OC}_2\text{H}_5)_5$ are proton NMR equivalent.¹² Paramagnetic line broadening and line shifting were observed, but usable spectra were easily obtained. At -65 °C a four-line pattern was observed, consistent with a dimeric structure (I)



containing edge-bridged octahedra and bridging ethoxides, which are magnetically nonequivalent to terminal ethoxides. Below -65 °C the pattern became complex, and formation of higher oligomers was postulated. For $\text{U}(\text{O}-i\text{-C}_3\text{H}_7)_5$ the proton

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NMR spectrum was interpreted in terms of a monomer-dimer equilibrium at room temperature, with a predominance of dimer at lower temperatures. Free energy ligand-exchange barriers were estimated to be 10–15 kcal/mol.¹²

The temperature-dependent ¹³C NMR spectra of U(OC₂H₅)₅ in CFCl₃ solution are presented in Figure 1. Qualitatively, the ¹³C NMR spectra are consistent with the published proton data. At temperatures above -5 °C, only a broad peak at approximately 28 ppm (fwhh = 12–27 Hz) and a much broader peak at lower field (~83 ppm, fwhh = 40–120 Hz) were observed, indicating rapid ligand exchange in this (presumed) dimeric system. The degree of broadening and shifting of the individual resonances reflects the distance of the respective carbon atoms from the paramagnetic uranium center. The peak near 28 ppm is the resonance assignable to the methyl carbon and the peak near 83 ppm is assignable to the methylene carbon. This assignment was confirmed by the spectrum observed in a proton-coupled ¹³C NMR experiment, where a broad quartet (¹J(¹³C-¹H) = 110 Hz) due to ¹³C-H coupling was observed for the 28 ppm (methyl) resonance. The methylene carbon peak at 83 ppm was so broadened that a coupling constant was not resolved. By comparison, the methylene carbon and methyl carbon resonances for NaOC₂H₅ occur at 57.3 and 17.9 ppm, respectively, in neat ethanol. As expected for these paramagnetic samples, relaxation times were short and saturation effects were unimportant under our experimental conditions. T₁ values of 185 (±6) and 60 (±6) ms were observed for the methyl and methylene carbons, respectively.

A limiting ¹³C NMR spectrum for U(OC₂H₅)₅ was approached at 70 °C. At -24 °C and lower temperatures, additional peaks become evident, with a four-band pattern being discernible at -45 °C. It was not possible to obtain accurate integrations on these broad peaks, but the pattern is consistent with the 4:1 ratio observed by Karraker et al. in the -65 °C proton NMR spectrum of U(OC₂H₅)₅ and is consistent with a dimeric structure in which terminal alkoxides are equivalent to each other but distinct from the bridging alkoxides. Additional bands are present in the spectra at -63 °C, and at -81 °C at least three bands in the methyl region and three very broad bands in the methylene region are evident. This pattern could correspond to a dimeric structure in which each of the three types of alkoxide groups is distinct on the NMR time scale. However, at lower temperatures (-96 °C), the spectrum becomes even more complex, indicating the possible formation of higher oligomers.

U(OC₆H₅)₅. The temperature-dependent ¹³C NMR spectra of U(OPh)₅ in dichloromethane solution are shown in Figure 2. A pattern of only four peaks is observed at temperatures above -45 °C, indicating rapid equilibration of the five phenoxide groups on the NMR time scale. The four resonances differ greatly in line width and chemical shift, reflecting the distance of the respective carbon atoms from the paramagnetic metal. From 15 to 73 °C, the chemical shifts and line widths continue to change in the pattern set by the +15 and -5 °C spectra. However, when the solution is cooled to -25 °C, additional structure begins to grow in and by -65 °C a complex set of peaks is observed. The spectra are consistent with the hypothesis that at the lower temperatures, as for U(OC₂H₅)₅, ligand equilibration rates are slow on the NMR time scale and association to higher oligomers occurs.

The ¹³C NMR spectrum of 90% ¹³C-enriched uranium pentamethoxide (prepared by U(OC₂H₅)₅ exchange with ¹³CH₃OH) in CFCl₃ contained three broad peaks indicative of nonequivalent methoxide groups. This result is in contrast to the spectra of U(OC₂H₅)₅ and U(OC₆H₅)₅, which exhibited complete NMR equivalence at room temperature and above. These results are consistent with a more rigid structure for

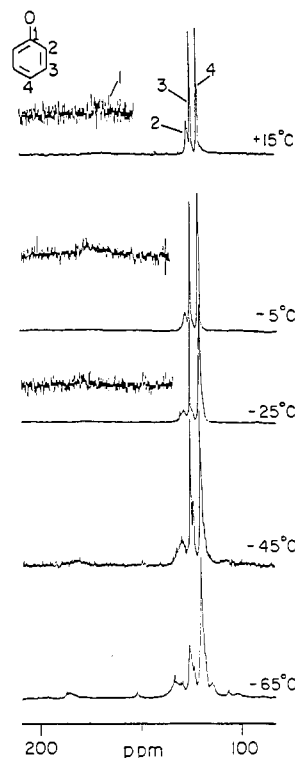


Figure 2. Natural-abundance ¹³C NMR spectra of U(OC₆H₅)₅ in CH₂Cl₂ (+15 to -65 °C).

U(OCH₃)₅, but further structural assignment must await results of an X-ray study.²⁵ Low-temperature spectra were not recorded due to the low solubility of the compound.

Na[U(OC₂H₅)₆]. Sodium hexaethoxyuranium(V) formed in nearly quantitative yield by direct reaction of NaOEt and U(OEt)₅. Well-formed, almost colorless crystals of an ethanol solvate were obtained, but a powdery, very pale green solid resulted when the product was exposed to high vacuum. The solid rapidly (<1 min) turned yellow-tan on air exposure (especially when moist with solvent) to give an ill-defined uranium oxide species with low carbon and hydrogen content. A solution of Na[U(OC₂H₅)₆] in ethanol appeared unchanged when exposed to dry oxygen for 5 min but when exposed to air darkened very rapidly. The ¹³C NMR spectrum of Na[U(OC₂H₅)₆] in THF closely resembled that of U(OC₂H₅)₅. A solution of Na[U(OC₂H₅)₆] in ethanol gave an EPR signal at g = 0.76 ± 0.01, indicative of an f¹ complex with closely octahedral geometry.²⁶

Polyfluoroalkoxides. The compounds U(OC₄F₉)₄(OC₂H₅)(HOC₂H₅) and U(OC₃HF₆)₄(OC₂H₅)(HOC₂H₅) were prepared by direct reaction of the respective fluoro alcohols with U(OC₂H₅)₅. The presence of C-H bonds in these two compounds was shown unambiguously by the presence of C-H stretching modes at 2956 (m), 2931 (ms), and 2860 (m) cm⁻¹ for the OC₄F₉ compound and 2944 (m) and 2930 (ms) cm⁻¹ for the OC₃HF₆ compound. In addition, the presence of O-H groups was indicated by the appearance of medium-intensity bands at 3583 and 3590 cm⁻¹, respectively. The ¹H NMR spectrum of the pure materials indicated no unbound ethoxy or ethanol groups to be present. On dissolution of the samples in oxygenated 5 M HCl, the ratios of fluoro alcohol:ethanol were determined by NMR integration and found to be consistent with the indicated formulas. Samples of U(OC₄F₉)₄-

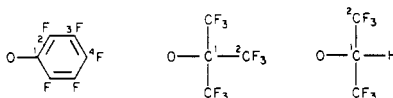
(25) Crystals obtained by sublimation are triclinic with the cell of dimensions a = 7.215 (6) Å, b = 8.686 (4) Å, c = 16.29 (2) Å, α = 89.55 (7)°, β = 90.79 (7)°, and γ = 90.60 (5)°.

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Table II. Carbon-13 NMR Parameters for Uranium(V) Alkoxide Compounds^{a-c}

	$\delta 1$ (fwhh)	$\delta 2$ (fwhh)	$\delta 3$ (fwhh)	$\delta 4$ (fwhh)
$U(OC_6F_5)_5$	157.7 (120)	149.0 (86)	139.5 (55)	129.6 (86)
HOC_6F_5	143.3 (30)	133.7 (10)	133.0 (10)	131.3 (30)
Δ	14.4 (90)	15.3 (76)	6.5 (45)	-1.7 (56)
$U(OC_4F_9)_4(OC_2H_5)(HOC_2H_5)$...	129.6 (~30)	$J(2F) = 287$	
HOC_4F_9	77.2 (2)	120.3 (<5)	$J(2F) = 287;$ $J(1F) = 32$	
Δ		9.3 (~25)		
$U(OC_3F_6H)_4(OC_2H_5)(HOC_2H_5)$	108.8 (100)	137.8 (150)	$J(2F) = 284$	
HOC_3HF_6	69.8 (3)	121.5 (<3)	$J(2F) = 280;$ $J(1F) = 34$	
Δ	39.0 (97)	16.3 (~147)		

^a Spectra were run at 15 °C in $CFCl_3$ solution. Full widths at half-height (fwhh) are given in parentheses. The numbering system is as follows:



Δ is the difference in chemical shift between the alcohol and the corresponding alkoxide complex. ... indicates resonance not assigned.

^b Chemical shifts are relative to internal tetramethylsilane, adjusted to a D_2O lock signal at 25 °C. Fwhh and J values are in Hz. ^c HOC_4F_9 and HOC_3HF_6 were run as neat liquids.

$(OC_2H_5)(HOC_2H_5)$ and $U(OC_4HF_6)_4(OC_2H_5)(HOC_2H_5)$ were acidified, and the volatile constituents were separated and injected into a gas chromatograph. Again, approximately the correct area ratios were observed for the ethanol and fluoro alcohol peaks. Finally, the identity of $U(OC_4F_9)_4(OC_2H_5)(HOC_2H_5)$ was verified by single-crystal X-ray diffraction.²⁰ This study showed the presence of a *monomeric*, six-coordinate structure with cis ethoxides and only minor angular distortions from octahedral geometry. The observed U—O— C_4F_9 angles are near 172°, compared to the smaller values around 157° observed for the U— OC_2H_5 moieties, consistent with the severe steric requirements of the OC_4F_9 groups. Thus, it appears that the steric bulk of the perfluoro groups prevents the oligomerization observed for the compounds $U(OR)_5$ ($R = Me, Et, Ph$). Accurate molecular models are consistent with this conclusion, showing the difficulty of further substitution of OC_2H_5 by OC_4F_9 and indicating the steric situations for the cis and trans geometries to be similar. At the present stage of the structure refinement, the ethoxides are equivalent and the hydroxylic proton (assumed to be hydrogen bonded between the cis ethoxides) has not been located. In the proton NMR spectrum only one type of ethoxide was detected. Due to its comparable properties, the OC_3HF_6 compound is assumed to have a similar structure.

Both $U(OR)_4(OC_2H_5)(HOC_2H_5)$ compounds, $R_f = C_4F_9$ and C_3HF_6 , are air- and moisture-sensitive materials that are stable for many months in an inert atmosphere. They readily dissolve in Freons, chlorocarbons, and many hydrocarbons to give stable yellow-green or tan solutions. They do not sublime without massive decomposition.

The compound $U(OC_6F_5)_5(HOC_2H_5)$ was prepared as a red-brown solid that could be recrystallized from benzene/heptane. The infrared spectrum contained peaks at 3600, 2975, and 2925 cm^{-1} , confirming the presence of ethanol. Like the fluoroalkoxides described above, it is moderately air sensitive, soluble in $CFCl_3$, benzene, and heptane, and decomposes without sublimation when heated under high vacuum.

The ^{13}C NMR spectra of $U(OC_6F_5)_5(HOC_2H_5)$, $U(OC_4F_9)_4(OC_2H_5)(HOC_2H_5)$, $U(OC_3F_6H)_4(OC_2H_5)(HOC_2H_5)$, and the corresponding polyfluoro alcohols are given in Figure 3 and Table II. The spectrum of nonafluoro-2-methyl-2-propanol (Figure 3A) consists of a quartet ($^1J(^{13}C-^{19}F) = 287$ Hz) at 120.3 ppm due to the trifluoromethyl carbons and a ten-line pattern ($^2J(^{13}C-^{19}F) = 32$ Hz) at 77.2 ppm due to the tertiary carbon. In $U(OC_4F_9)_4(OC_2H_5)(HOC_2H_5)$ the quartet has moved downfield by 9.3 ppm compared to that of

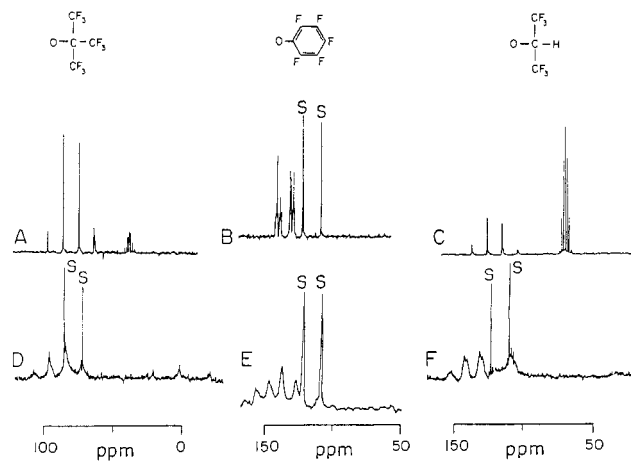


Figure 3. Natural-abundance ^{13}C NMR spectra of some polyfluoro alcohols (A, B, C) and their corresponding uranium(V) compounds (D, E, F). Spectra A and C are for neat alcohols and spectra B, D, E, and F are for $CFCl_3$ solutions. Peaks labeled "S" are due to $CFCl_3$.

the free alcohol, and the line widths have broadened to ~30 Hz (fwhh) (Figure 3D). The tertiary carbon resonance was not located definitely for the uranium complex but is expected to be paramagnetically broadened and shifted, perhaps occurring as a very broad peak under the quartet envelope. The ethanol peaks, expected to be broad and weak, were not definitely located but may be the weak, broad peaks at higher field. Although at room temperature the fluoroalkoxy groups are equivalent by ^{13}C NMR, the ^{19}F NMR spectrum for $U(OC_4F_9)_4(OC_2H_5)(HOC_2H_5)$ was unusually complex. At ambient temperature five ^{19}F NMR peaks were observed in the range +71.3 to +73.6 ppm (+72.8 ppm for full ligand) with full widths at half-height (fwhh) 7–20 Hz and approximate area ratios 2.5:7.0:2.8:1.0:3.6. At 68 °C, the practical high-temperature limit for these samples, only three broad peaks were seen (fwhh \approx 30 Hz), whereas the spectrum at 0 °C is more complex and more broadened. These results suggest restricted rotation of the CF_3 groups. The 1H NMR spectrum contained no peaks assignable to free ethanol but did contain peaks assignable to coordinated ethoxy groups at -3.4 ppm (fwhh \approx 27 Hz) and -1.5 ppm (fwhh \approx 8 Hz).

The ^{13}C NMR spectrum of hexafluoro-2-propanol (Figure 3C) consists of a quartet due to trifluoromethyl carbons ($^1J(C-F) = 280$ Hz) at 121.5 ppm and a septet due to the secondary carbon ($^2J(C-F) = 34$ Hz) at 69.8 ppm. In the com-

plex $U(OC_3F_6H)_4(OC_2H_5)(HOC_2H_5)$, the quartet has broadened (fwhh ≈ 150 Hz) and shifted +16.3 ppm, while the secondary carbon has broadened (fwhh ≈ 100 Hz) and shifted +39.0 ppm (Figure 3F). Ethanol peaks were not definitively assignable, again presumably due to broadening, but could be the broad, weak absorption near 32 ppm and/or lie under the OC_3HF_6 absorption envelope. Thus, the fluoroalkoxide ligands appear to be equivalent by ^{13}C NMR at ambient temperature. The ^{19}F NMR spectrum at ambient temperature contained two broad peaks (fwhh = 37 and 56 Hz) of approximately equal intensity at +74.7 and +75.2 ppm (+75.4 ppm for ligand). At 70 °C, these peaks occur 2–3 ppm further upfield, have sharpened (fwhh ≈ 18 Hz), and have relative intensities of 1:3.8. When the solution is cooled to -35 °C the peaks broaden noticeably and remain about equal in intensity. As for $U(OC_4F_9)_4(OC_2H_5)(HOC_2H_5)$, some restricted rotation of CF_3 groups is indicated. The 1H NMR spectrum contains no free ethanol peaks but does exhibit peaks at 2.0 ppm (fwhh ≈ 38 Hz) and 1.20 and 0.83 ppm (fwhh ≈ 8 Hz) attributable to coordinated ethoxy groups.

The ^{13}C NMR spectrum of C_6F_5OH (Figure 3B) contains four multiplets, occurring over the range 131.3–143.3 ppm, broadened 10–30 Hz by C–F spin–spin coupling. In $U(OC_6F_5)_5(HOC_2H_5)$ (Figure 3E), the ^{13}C NMR resonances have shifted to the range 129.6–157.7 ppm and the full widths at half-height have increased to 55–120 Hz. No peaks attributable to ethanol were assigned. Again, at room temperature the OR_f ligands seem to be equivalent by ^{13}C NMR. The ^{19}F resonances occurred in the range +155.6–158.7 ppm (fwhh = 27–54 Hz) compared to the sharp resonances in the range

+160.4–165.5 ppm for the pentafluorophenol. The 1H NMR spectrum showed no free ethanol to be present and had peaks at -3.6 ppm (fwhh ≈ 90 Hz) and -1.2 ppm (fwhh ≈ 20 Hz), which could be attributable to coordinated ethoxy groups.

Conclusions

The newly prepared uranium(V) fluoroalkoxide compounds are thermally stable, air-sensitive materials of low volatility. High-resolution ^{13}C NMR spectra are reported here for the first time for f^1 compounds and found to be useful for characterizing carbon-containing f^1 complexes. The ^{13}C spectra indicate temperature-dependent oligomeric structures in solution for $U(OC_2H_5)_5$ and $U(OC_6H_5)_5$. The fluoroalkoxide compounds are shown to be monomeric mixed-ligand complexes, whose NMR spectra indicate restricted CF_3 rotation.

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Registry No. $U(OC_6H_5)_5$, 86853-81-8; $U(OC_4F_9)_4(OC_2H_5)(HOC_2H_5)$, 86862-67-1; $U(OC_3F_6H)_4(OC_2H_5)(HOC_2H_5)$, 86853-83-0; $U(OC_6F_5)_5(HOC_2H_5)$, 86853-84-1; $Na[U(OC_2H_5)_6]$, 64653-58-3; $U(OC_2H_5)_5$, 10405-34-2; $U(OCH_3)_5$, 83178-45-4; $UF_3(OC_2H_5)_2$, 86853-82-9.

Supplementary Material Available: Tables of infrared spectra of uranium(V) alkoxides and near-IR-visible spectra of $U(OC_2H_5)_5$ and $U(OC_6H_5)_2$ (2 pages). Ordering information is given on any current masthead page.

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Magnetic Susceptibility and EPR Study of Bis(β -alaninium) Tetrabromocuprate(II)

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The structural, magnetic, and EPR properties of bis(β -alaninium) tetrabromocuprate(II), $(\beta\text{-alaH})_2CuBr_4$, are reported. The salt crystallizes in a monoclinic space group, $I2/c$, with $a = 7.661$ (1) Å, $b = 8.027$ (1) Å, $c = 24.295$ (7) Å, and $\beta = 92.49$ (2)°. It contains two-dimensional layers of square-planar $CuBr_4^{2-}$ anions separated by the organic cations. The compound exhibits ferromagnetic intralayer interactions with $J/k = 21.2$ K. Three-dimensional ordering occurs at $T_c = 10$ K. Magnetization studies reveal the existence of an Ising type anisotropy, with the easy axis normal to the layers. A substantial rhombic component also exists. The EPR spectrum consists of a single exchange-narrowed line of axial symmetry with $g_{\parallel} = 2.044$ and $g_{\perp} = 2.098$. The EPR line widths are strongly temperature dependent with phonon modulation of the spin anisotropies being the principal source of line broadening.

Introduction

Two-dimensional square-planar magnets of the type $(RNH_3)_2CuX_4$ ($X = Cl^-, Br^-$) have been of current interest in the study of the low-dimensional magnetic systems,¹⁻⁵ as well as model systems for lipid bilayers.^{6,7} These salts are

characterized by strong, nearly isotropic, ferromagnetic intralayer exchange interactions (J) and a very small ratio of inter- to intralayer exchange couplings ($|J'/J| \approx 10^{-3}$ – 10^{-4}).³ In the chloride salts, the intralayer coupling is typically of the order $J/k \approx 15$ – 20 K with a small XY-like anisotropy. Both ferro- and antiferromagnetic interlayer exchange couplings have been reported.^{2,3} The intralayer coupling is slightly larger for the bromide salt, $J/k \approx 20$ – 25 K, and the small anisotropic component of the exchange is now Ising-like. A smaller rhombic component to the anisotropy is also present in both types of salts. A renewed interest in the bromide salts has arisen due to the recent observation of large interlayer exchange coupling in the alkyldiammonium analogues, $(NH_3R_nH_{2n}NH_3)CuBr_4$, $n = 2$ – 4 .⁸

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