values of $J_{F_a\text{-}F_e}$ and the relative chemical shifts together with the experimental transitions were then iterated with use of ITRACL to give the best fit for the experimentally observed set of transitions. Root-mean-square errors of less than 1.0 Hz were achieved in one or two iterations.

Variable-temperature studies were carried out with use of a Bruker temperature controller. Temperatures were measured with a copper–constantan thermocouple inserted directly into the sample region of the probe and were accurate to ±1 °C.

**Laser Raman Spectroscopy.** A Spectra Physics Model 164 argon-ion laser giving up to 900 mW at 5145 Å was used to excite the Raman spectra. The spectrometer was a Spex Industries Model 14018 double monochromator equipped with 1800 groves/mm Holographic gratings. An RCA C31034 phototube detector in conjunction with a pulse count system consisting of pulse amplifier, analyzer, and ratemeter (Hamner NA-11, NC-11, and N-780A, respectively) and a Texas Instruments Model FSOZWBA strip chart recorder were used to record the spectra. The spectrometer was periodically calibrated by recording the discharge lines from an argon lamp over the spectral range of interest; the Raman shifts quoted are estimated to be accurate to $\pm 1\ \text{cm}^{-1}$. Slit widths depended on the scattering efficiency of the sample, laser power, etc., with $1.3\ \text{cm}^{-1}$ being typical.

Cylindrical sample tubes were mounted vertically. The angle between the incident laser beam and the sample tube was 45°, and Raman scattered radiation was observed at 45° to the laser beam or 90° to the sample tube direction.

Low-temperature spectra were recorded at −196 °C by mounting the sample vertically in an unsilvered Pyrex glass Dewar filled with liquid nitrogen.

**Registry No.** $XeOTeF_5^+AsF_6^-$, 27680-14-4; $XeOTeF_5^+Sb_2F_{11}^-$, 77079-64-2; $XeF_2{\cdot}BrOF_2^+AsF_6^-$, 77071-47-7; $FXeFXeOTeF_5^+$, 77079-65-3; $XeOSO_2F^+$, 77070-48-5; $Xe(OTeF_5)_2$, 25005-56-5; $SbF_5$, 7783-70-2; $BrF_5$, 7789-30-2; $HOSO_2F$, 7789-21-1; $BrOF_2^+$, 62521-26-0; $BrOF_3$, 61519-37-7; $(FXe)_2F^+$, 37366-73-7; $HOTeF_5$, 57458-27-2; $Xe(OSO_2F)_2$, 25523-77-7; $XeF^+$, 47936-70-9; $TeF_6$, 7783-80-4; $AsF_5$, 7784-36-3.

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# Uranium Hexamethoxide and Mixed Methoxyuranium(VI) Fluorides: Facile Syntheses from $UF_6$ and a Nuclear Magnetic Resonance Investigation of Structure and Chemical Dynamics

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*Received October 3, 1980*

Efficient, one-step scalable syntheses of uranium hexamethoxide, $U(OCH_3)_6$, starting from readily available $UF_6$ and $NaOCH_3$ or $CH_3Si(OCH_3)_3$ are described. In addition, the reaction of appropriate quantities of $(CH_3)_3SiOCH_3$ or $U(OCH_3)_6$ with $UF_6$ produces a series of mixed methoxyuranium(VI) fluorides, $U(OCH_3)_nF_{6-n}$, $n = 1$–5, the degree of substitution being determined by control of stoichiometry. Characterization of the complexes by both $^1H$ and $^{19}F$ NMR indicates that all the species possess a monomeric, six-coordinate geometry and undergo rapid, intermolecular ligand exchange. A surprisingly large solvent and temperature dependence of the $^{19}F$ chemical shifts is interpreted in terms of charge-transfer complex formation. The solution-phase electronic spectrum of $U(OCH_3)_6$ is interpreted in terms of both ligand- and solvent-to-metal charge transfer.

## Introduction

High-valent uranium alkoxides[1] are of current interest as organic medium-compatible precursors for new uranium compounds[2] and as subjects for isotopically selective infrared photochemical studies.[3,4] In particular, our recent success in laser-induced uranium isotope separation[4] using uranium hexamethoxide, $U(OCH_3)_6$, prompted the development of efficient syntheses for uranium hexaalkoxides and the related mixed methoxyuranium(VI) fluorides, as well as a detailed exploration of their chemical and physicochemical properties. Although the hexaalkoxides have been known for some time,[5] the existing syntheses are tedious and inefficient, typically requiring five steps starting from $UCl_4$.[5a] Also, little has been reported concerning the spectroscopic properties of these materials. We report here simple, one-step syntheses of $U(OCH_3)_6$ starting from $UF_6$. Other hexaalkoxides are then readily accessible by transalkoxylation[1,5] (eq 1). We also

$$U(OCH_3)_6 + \text{excess ROH} \rightarrow U(OR)_6 + 6CH_3OH \qquad (1)$$

report here the syntheses of the new methoxyfluorouranium(VI) series $U(OCH_3)_nF_{6-n}$, $n = 1$–5. The interesting properties we demonstrate for these species include rapid intermolecular ligand exchange and an unusually large solvent and temperature dependence of the $^{19}F$ chemical shifts. The electronic spectrum of $U(OCH_3)_6$ and optical absorption trends of the $U(OCH_3)_nF_{6-n}$ series are interpreted on the basis of the known

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electronic structures of $UF_6$ and $UCl_6$ and optical absorption trends of mixed-metal halides and the $W(OCH_3)_nCl_{6-n}$ series.

## Experimental Section

All sample manipulations and preparations were carried out either under high vacuum on a grease-free vacuum line or under an atmosphere of prepurified nitrogen, with the use of standard vacuum-line and Schlenk techniques[6] and a Vacuum Atmospheres Corp. HE-43-2 "Dri-Lab" glovebox fitted with a HE-193-1 "Dri-Train" atmosphere recirculating unit. All solvents were freshly distilled under an atmosphere of prepurified nitrogen from the appropriate drying agents.[7] Uranium hexafluoride (Allied Chemical) was sublimed under reduced pressure from the shipping cylinder into a cooled, flame-dried Pyrex tube fitted at one end with a Kontes Teflon stem valve. The $UF_6$ could be stored safely at room temperature over sodium fluoride for a prolonged period (>1 year). The manipulation and reactivity of $UF_6$ are described in detail elsewhere.[8] Sodium methoxide was prepared from sodium and dry methanol. Methoxymethylsilanes were either purchased from Petrarch Systems or prepared from the appropriate chloromethylsilanes (Aldrich Chemical Co.) and $NaOCH_3$.[1a] $^1H$ NMR spectra were recorded on Perkin-Elmer R-20B (60 MHz, CW) or Varian CFT-20 (80 MHz, FT) spectrometers. $^{19}F$ NMR spectra were recorded on a JEOL FX-90Q FT instrument operating between 84.31 and 84.38 MHz. Serum-capped 10-mm Pyrex NMR tubes (Wilmad 513-5PP) with concentric 4- or 5-mm Pyrex inserts centered with a notched Teflon collar and containing acetone-$d_6$ as the deuterium lock were used for the $^{19}F$ studies. The $^{19}F$ chemical shifts are reported in ppm and were found by dividing the difference in resonance frequencies between the compound of interest and neat $CFCl_3$ (at the appropriate temperature) by 84.36. We find that neat $CFCl_3$ resonates at $94\,094\,005 \pm 1$ Hz at 20 °C with respect to 0.5% internal $(CH_3)_4Si$ at 100 MHz, in good agreement with the value reported by Brownstein and Bornais.[9] Infrared spectra were recorded on Perkin-Elmer 267 or 283 spectrometers using Nujol mulls on KBr plates. Mass spectra were recorded on Hewlett-Packard 5930A or 5985 spectrometers. Electronic spectra were recorded on a Cary 17D spectrophotometer using a 1-cm path length anaerobic quartz cell. Repetitive scans and deliberate exposure of the sample to air were carried out to ascertain their effect on the optical spectra. No indication of sample decomposition could be detected. Melting points were determined in sealed, nitrogen-filled capillaries and are uncorrected. Elemental analyses and molecular weight determinations were performed by Dornis and Kolbe Microanalytical Laboratories, Mülheim a. d. Ruhr, West Germany.

**Synthesis of $U(OCH_3)_6$. Method A.** A 9.36-g (26.2-mmol) quantity of $UF_6$ was freshly sublimed into a reaction vessel held at −78 °C. A 150-mL quantity of $CH_2Cl_2$ was then added and the $UF_6$ dissolved. This solution was slowly introduced into a stirred suspension of 9.0 g (170 mmol) of $NaOCH_3$ in 250 mL of $CH_2Cl_2$ at −78 °C through a stainless-steel cannula under a positive nitrogen pressure. The deep red-brown reaction mixture was allowed to warm slowly to 0 °C (ca. 1.5 h), and the resulting deep red solution was stirred for an additional 1.5 h to ensure complete reaction. The solid residue was filtered off and the $CH_2Cl_2$ removed from the dark red filtrate in vacuo to yield an oily red solid. The solid was dissolved in 50 mL of pentane and refiltered. The pentane was then removed in vacuo, leaving 4.6 g (42%) of extremely moisture-sensitive purple-red platelets. The product can be recrystallized from pentane at −130 °C; mp 70–72 °C (lit.[5a] mp 62–64 °C). The compound readily sublimes (with minor decomposition) at 30 °C ($10^{-3}$ mm).

Anal. Calcd for $C_6H_{18}O_6U$: C, 16.99; H, 4.28; mol wt 424. Found: C, 17.21; H, 4.25; mol wt 472 (cryoscopic in benzene).

Infrared spectrum (Nujol solution, $cm^{-1}$): 1051 s, 465 s.

Mass spectrum (10 eV): strong *m/e* values at 393, $U(OCH_3)_5^+$; 362, $U(OCH_3)_4^+$; 347, $UO(OCH_3)_3^+$; 332, $UO_2(OCH_3)_2^+$; 331, $U(OCH_3)_3^+$; 316, $UO(OCH_3)_2^+$; 301, $UO_2(OCH_3)^+$; 300, $U(OCH_3)_2^+$; 285, $UO(OCH_3)^+$; 270, $UO_2^+$.

**Method B.** To 5.0 mL (35 mmol) of $CH_3Si(OCH_3)_3$ in 250 mL of $CH_2Cl_2$ at −95 °C was added 5.28 g (15 mmol) of $UF_6$ dissolved in 150 mL of $CH_2Cl_2$ as above. The workup and purification procedure described in method A was then followed, yielding 4.58 g (72%) of purple-red platelets.[10]

**Synthesis of $U(OCH_3)_nF_{6-n}$, $n = 1–5$.** The individual mixed methoxyuranium(VI) fluorides were prepared as dilute solutions by mixing the appropriate stoichiometric quantities of $UF_6$ with either $(CH_3)_3SiOCH_3$ or $U(OCH_3)_6$ at low temperature in halogenated hydrocarbon solvents. The thermal characteristics and intermolecular ligand-exchange reactions (vide infra) exhibited by these compounds necessitated characterization by low-temperature $^1H$ and $^{19}F$ NMR spectroscopy. Only $U(OCH_3)_5F$ was isolated. The typical procedures utilized in preparing the $U(OCH_3)_nF_{6-n}$ species are illustrated for $U(OCH_3)F_5$[11] and $U(OCH_3)_5F$ below.

**I. $U(OCH_3)F_5$. Method A.** To 0.50 g (1.4 mmol) of $UF_6$ dissolved in 50 mL of $CFCl_3$ at −78 °C was added a solution of 0.20 mL (1.4 mmol) of $(CH_3)_3SiOCH_3$ dissolved in 50 mL of $CFCl_3$ at −78 °C. Reaction was immediate to form a red-brown solution, which decomposed rapidly above approximately −60 °C.

**Method B.** To 0.05 g (0.12 mmol) of $U(OCH_3)_6$ dissolved in 10 mL of $CFCl_3$ at −78 °C was added 8.4 mL of a solution of 0.5 g (1.4 mmol) of $UF_6$ dissolved in 20 mL of $CFCl_3$ at −78 °C. Reaction was immediate to form $U(OCH_3)F_5$. Alternatively, a $U(OCH_3)_6$ solution can be added to the $UF_6$.

**II. $U(OCH_3)_5F$.** A $CH_2Cl_2$ solution of $U(OCH_3)_5F$ was prepared by either method A or method B above for $U(OCH_3)F_5$. Removal of the $CH_2Cl_2$ in vacuo left a red oil. This was dissolved in pentane, the solution filtered, and the filtrate cooled to −130 °C to yield a red crystalline solid. The solvent was syringed off and the solid dried under vacuum. A chemical analysis was not obtained due to significant sample decomposition after 1 day at 25 °C.

Mass spectrum (10 eV): strong *m/e* values at 393, $U(OCH_3)_5^+$; 381, $U(OCH_3)_4F^+$; 362, $U(OCH_3)_4^+$; 350, $U(OCH_3)_3F^+$; 347, $UO(OCH_3)_3^+$; 332, $UO_2(OCH_3)_2^+$; 331, $U(OCH_3)_3^+$; 319, $U(OCH_3)_2F^+$; 304, $UO(OCH_3)F^+$; 301, $UO_2(OCH_3)^+$; 300, $U(OCH_3)_2^+$; 289, $UO_2F^+$; 288, $U(OCH_3)F^+$; 285, $UO(OCH_3)^+$; 273, $UOF^+$; 270, $UO_2^+$; 269, $U(OCH_3)^+$.

Infrared spectrum (Nujol solution, $cm^{-1}$): 1041 br, s; 607 br, w; 459 br, s.

## Results

**Synthesis, Optical Spectra, and Thermal Stability.** Uranium hexamethoxide can be prepared in a single step by the reaction of $UF_6$ with either of the methoxylating reagents $NaOCH_3$ and $CH_3Si(OCH_3)_3$ at low temperature in halogenated hydrocarbon solvents, as shown in eq 2 and 3. The methoxyfluorouranium(VI) complexes, $U(OCH_3)_nF_{6-n}$, $n = 1–5$, can be prepared in a similar manner as shown in eq 4 and 5.

$$UF_6 + 6NaOCH_3 \xrightarrow[CH_2Cl_2]{-78\ °C} U(OCH_3)_6 + 6NaF \qquad (2)$$

$$UF_6 + 2CH_3Si(OCH_3)_3 \xrightarrow[CH_2Cl_2]{-78\ °C} U(OCH_3)_6 + 2CH_3SiF_3 \qquad (3)$$

$$UF_6 + n(CH_3)_3SiOCH_3 \xrightarrow[CH_2Cl_2]{-78\ °C} U(OCH_3)_nF_{6-n} + n(CH_3)_3SiF \qquad (4)$$

$$UF_6 + nU(OCH_3)_6 \xrightarrow[CH_2Cl_2]{-78\ °C} (1 + n)U(OCH_3)_{6n/(1+n)}F_{6/(1+n)} \qquad (5)$$

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(6) Shriver, D. F. "The Manipulation of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969.

(7) $P_2O_5$ for $CCl_4$, $CFCl_3$, $CHCl_3$, $CH_2Cl_2$, and $CH_3Cl$; Na–K/benzophenone for *p*-dioxane, THF, ethyl ether, toluene, and pentane; Mg for $CH_3OH$. (a) Vogel, A. I. "Textbook of Practical Organic Chemistry", 4th ed.; Furniss, B. S., Hannaford, A. J., Rogers, V., Smith, P. W. G., Tatchell, A. R., Eds.; Longmans, Green and Co.: London, 1978; pp 264–279. (b) Jolly, W. L. "The Synthesis and Characterization of Inorganic Compounds"; Prentice-Hall: Englewood Cliffs, NJ, 1970; pp 114–121.

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(10) Occasionally the crystals isolated by this procedure appear "damp" and are not free flowing. Redissolving the crystals in 50 mL of pentane, adding ~1 mL $CH_3Si(OCH_3)_3$, and stirring at 0 °C overnight followed by filtering and recrystallization at −130 °C then give a pure product.

(11) Vergamini, P. J. *J. Chem. Soc., Chem. Commun.* **1979**, 54.

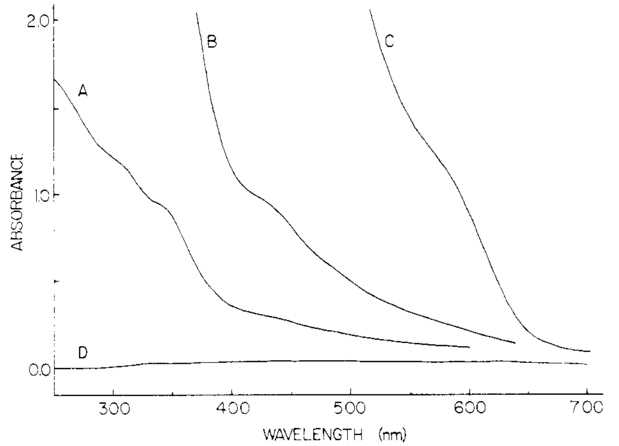

**Figure 1.** Electronic spectrum of $U(OCH_3)_6$ in $CH_2Cl_2$: (A) $\sim 1 \times 10^{-4}$ M; (B) $\sim 1 \times 10^{-3}$ M; (C) $5.5 \times 10^{-3}$ M; (D) base line.

Reacting methanol with $UF_6$ as previously reported for $U(OCH_3)F_5$[11] did not yield any of the other members of the series. All of the complexes are extremely moisture sensitive.

The members of the $U(OCH_3)_nF_{6-n}$ series exhibit interesting optical characteristics, ranging from colorless through amber, orange, and finally red for 0.01 M $CFCl_3$ solutions of $UF_6$, $U(OCH_3)F_5$, $U(OCH_3)_2F_4$, and $U(OCH_3)_6$, respectively. Concentrated solutions of all the species are deep red, except $UF_6$, which is colorless. Assuming that the electronic structures of the $U(OCH_3)_nF_{6-n}$ compounds are similar to that of $UF_6$,[12] the colors noted above can be attributed to the tail of the optical absorption by $O_{2p} \rightarrow U_{5f}$ ligand-to-metal charge-transfer (LMCT) transitions. On the basis of the optical electronegativities[13] of fluoride (3.9[13]) and that estimated for methoxide (~3.0–3.5[13,14]), the observed color trend is consistent with the optical spectra of a number of mixed-metal halides,[15] where the LMCT bands systematically shift to lower energy as the number of less optically electronegative halide ligands bound to the metal increases.

The electronic spectrum of $U(OCH_3)_6$, which has never been reported, is shown as a $CH_2Cl_2$ solution in Figure 1. The spectrum exhibits four unresolved absorption maxima at 300, 340 ($\epsilon \approx 3500 \pm 2500$), 430 ($\epsilon \approx 100$), and 580 nm ($\epsilon \approx 120 \pm 80$). Because of the severe overlap of these transitions, the extinction coefficients are only approximate. On the basis of the estimated optical electronegativity of the methoxide ligand,[13,14] optical absorption trends in the $W(OCH_3)_nCl_{6-n}$[16] series, and the diffraction-determined local $O_h$ symmetry of the U—O framework in $U(OCH_3)_6$,[17] it is reasonable to expect the LMCT transitions of $U(OCH_3)_6$ to be of energy intermediate between those of $UF_6$ (weak absorption from 360 to 400 nm ($\epsilon \approx 10$); much stronger absorption beginning at $\lesssim$340 nm)[12,18] and $UCl_6$ (weak absorption from 480 to 510 nm; much stronger absorption beginning at $\lesssim$400 nm).[19,20] The solution spectrum of $U(OCH_3)_6$ is in general agreement with this prediction, except for the weak absorption at ~580 nm (Figure 1), which appears to be too low in energy to be ascribed to an intramolecular LMCT transition, on the basis of the preceding arguments. This absorption may be due to charge-transfer interactions with the solvent (vide infra).[21] Analogous low-energy transitions (absent in gas-phase spectra) have been similarly assigned in the electronic spectra of $UF_6$ solutions.[21d] Due to the thermal instability of the non-$U(OCH_3)_6$ members of the series, their electronic spectra were not investigated.

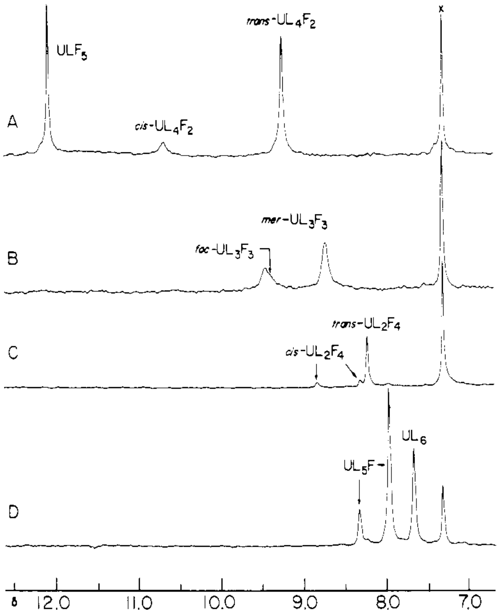

**Figure 2.** $^1H$ FT NMR spectra of $U(OCH_3)_nF_{6-n}$ compounds as 1–5 mM solutions in $CD_2Cl_2/CDCl_3$ (2:1) at −80 °C. The peak at $\delta$ 7.30 marked with an × is $CHCl_3$. Spectrum A shows the result of adding ~0.35 equiv of $U(OCH_3)_6$ to 1 equiv of $UF_6$. Spectra D, C, and B illustrate the successive addition of $UF_6$ to $U(OCH_3)_6$.

While the decomposition of $U(OCH_3)_6$ is only slight over prolonged periods at 0 °C in the absence of light,[22] thermal stability progressively decreases as the number of fluorine atoms per $U(OCH_3)_nF_{6-n}$ molecule increases. Thus, methylene chloride solutions of $U(OCH_3)_5F$ undergo little decomposition at 20 °C over a period of several hours, while methylene chloride solutions of $U(OCH_3)F_5$ decompose rapidly above approximately −60 °C. The exact nature of the decomposition products was not investigated. The complexes where $n = 1$–3 give a clear, colorless solution and a green precipitate upon warming to room temperature. However, when $n = 4$ or 5, the solutions remain red at room temperature and precipitates ranging in color from light green through beige slowly deposit. The $^1H$ NMR spectra at 34 °C of the latter samples as fresh 0.5–1.0 M solutions in $CDCl_3$ exhibit a single, broadened resonance at $\delta$ 8.2 (±0.1) when $n = 4$ and at $\delta$ 8.0 (±0.1) when $n = 5$ due to intermolecular ligand exchange (vide infra). As the decomposition progresses, this resonance gradually moves

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(14) We employ $\chi_{opt}(OH^-)$ as a reasonable approximation to $\chi_{opt}(OCH_3^-)$. $\chi_{opt}(OH^-)$ is estimated to lie between $\chi_{opt}(Cl^-)$ (3.0) and $\chi_{opt}(H_2O)$ (3.5) on the basis of the observed and calculated values of the thermochemical electronegativity of the $OH^-$ group (Huheey, J. E. "Inorganic Chemistry: Principles of Structure and Reactivity", 2nd ed.; Harper and Row: New York, 1978; pp 159–173, 178–180) as well as LMCT energies of analogous ligands.[13]

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(22) Thermal degradation does not become significant until approximately 40 °C. Although not extremely light sensitive, $U(OCH_3)_6$ decomposition is accelerated by fluorescent lights or sunlight.

**Table I.** NMR Spectral Data for $U(OCH_3)_nF_{6-n}$ Complexes

| compd | NMR system[a] | $^1H$ chem shift[b] | $^{19}F$ chem shift[c] | $^{19}F$ chem shift[d] |
|---|---|---|---|---|
| $UF_6$ | $X_6$ | | 766.5 | 764.3 |
| $U(OCH_3)F_5$ | $M_3VX_4$ | 12.13 | 690.3 ($F_V$)[f]<br>627.2 ($F_X$)[f] | 706.2 ($F_V$)[f]<br>643.5 ($F_X$)[f] |
| *cis*-$U(OCH_3)_2F_4$ | $(M_3)_2V_2X_2$ | 10.73 | 578.1 ($F_V$)[g]<br>512.5 ($F_X$)[h] | [i] |
| *trans*-$U(OCH_3)_2F_4$ | $(A_3)_2X_4$ | 9.29 | 512.5 | 542.8 |
| *fac*-$U(OCH_3)_3F_3$ | $(M_3)_3V_3$ | 9.50[e] | 483.0 | [i] |
| *mer*-$U(OCH_3)_3F_3$ | $(A_3)_2M_3VX_2$ | 9.57 ($H_M$)<br>8.79 ($H_A$) | 486.5 ($F_V$)[g]<br>418.2 ($F_X$)[g] | 526.7 ($F_V$)[g]<br>459.6 ($F_X$)[g] |
| *cis*-$U(OCH_3)_4F_2$ | $(A_3)_2(M_3)_2V_2$ | 9.01 ($H_M$)<br>8.42 ($H_A$) | 397.4 | 453.2 |
| *trans*-$U(OCH_3)_4F_2$ | $(A_3)_4X_2$ | 8.32 | 337.8 | 385.3 |
| $U(OCH_3)_5F$ | $(A_3)_4M_3V$ | 8.37 ($H_M$)<br>8.02 ($H_A$) | 330.5 | 388.2 |
| $U(OCH_3)_6$ | $(A_3)_6$ | 7.74 | | |

[a] Key: A, methoxide ligand trans to a methoxide ligand; M, methoxide ligand trans to a fluoride ligand; V, fluoride ligand trans to a methoxide ligand; X, fluoride ligand trans to a fluoride ligand. [b] Chemical shifts in ppm downfield from internal $(CH_3)_4Si$. Recorded on 1-5 mM solutions in $CD_2Cl_2/CDCl_3$ (2:1) at −80 °C; estimated uncertainty of ±0.04 ppm. [c] Chemical shifts in ppm downfield from external $CFCl_3$. Recorded on $CH_2Cl_2$ solutions at −80 °C that were 10 mM; estimated uncertainty of ±0.2 ppm. [d] Recorded on $CFCl_3$ solutions at −80 °C that were 10 mM and referenced to $CFCl_3$; estimated uncertainty of ±0.3 ppm. [e] Shoulder. [f] $J_{F-F} = 17.0 \pm 2.5$ Hz. [g] $J_{F-F}$ not observed. [h] Assumed degenerate with *trans*-$U(OCH_3)_2F_4$ resonance. [i] Isomer not observed.

upfield, ultimately (2-3 days) coinciding with that of $U(OCH_3)_6$.

**NMR Studies. Characterization and Structure.** Because of rapid, intermolecular ligand exchange (vide infra) and thermal instability, it was necessary to characterize the $U(OCH_3)_nF_{6-n}$ complexes by NMR spectroscopy on dilute solutions (1-15 mM) at −80 °C. The $^1H$ and $^{19}F$ NMR spectra of the members of the $U(OCH_3)_nF_{6-n}$ series are presented in Figures 2 and 3, respectively. Resonance positions are compiled in Table I. The spectra shown illustrate the mixing of $U(OCH_3)_6$ and $UF_6$ solutions. Through careful control of stoichiometry, complexes containing 1-5 methoxy ligands can be prepared.

The NMR spectral results are consistent with a monomeric, quasi-octahedral geometry for all members of the $U(OCH_3)_nF_{6-n}$ series as already established for $UF_6$[23] and $U(OCH_3)_6$.[17] In addition, all possible isomers are observed in $CH_2Cl_2$. As an aid in the assignment of the spectra, the chemical shift of each resonance in $CH_2Cl_2$ is presented (Figure 4) in Dean-Evans plots[24] (eq 6). Here $\delta(Z)$ is the

$$\delta(Z) = pC + qT \qquad (6)$$

resonance position of a particular ligand Z, $p$ and $q$ are the number of fluorine atoms cis and trans to Z respectively, and $C$ and $T$ are parameters characteristic of the ligand Z. As with similar plots for $SnL_nF_{6-n}{}^{2-}$,[24] $WCl_nF_{6-n}$,[25] $W(OCH_3)_nF_{6-n}$,[16,26] $Te(OH)_nF_{6-n}$,[27] and $U(OTeF_5)_nF_{6-n}$,[28] both the fluorine and proton resonances in the present case fall on two smooth curves: one where Z is trans to a fluorine ligand and one where Z is trans to a methoxy ligand. These empirical relationships allow for a consistent interpretation of the spectral data in high-symmetry cases where each isomer of a given species is only expected to exhibit a single resonance. For example, $U(OCH_3)_2F_4$ exists as both the cis isomer (approximate $C_{2v}$ symmetry) and the trans isomer (approximate $D_{4h}$ symmetry); therefore each will exhibit a single proton resonance (Figure 2). Only assignment of the low-field resonance as the cis isomer will lead to smooth curves in Figure 4. Additional support for the spectral assignments comes from studies of isomer distribution as a function of solvent polarity. Thus, the more polar members of the trifluoro and tetrafluoro isomer pairs *fac*-$U(OCH_3)_3F_3$ and *cis*-$U(OCH_3)_2F_4$ are favored in polar $CH_2Cl_2$ (Figure 3, $\epsilon$(20 °C) = 9.14[29]), are less

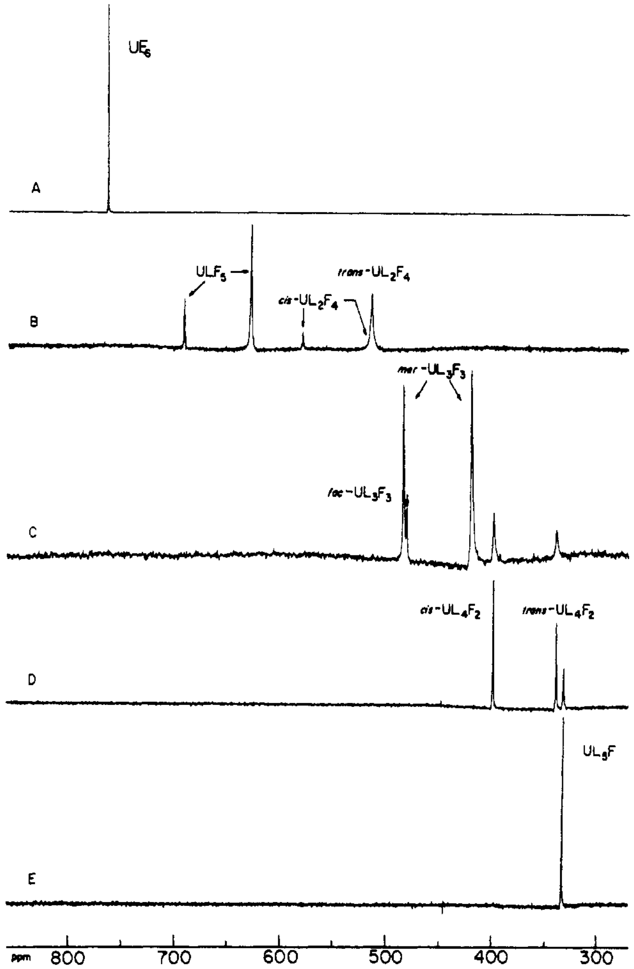

**Figure 3.** $^{19}F$ FT NMR spectra of $U(OCH_3)_nF_{6-n}$ compounds as 10 mM solutions in $CH_2Cl_2$ at −80 °C. Spectrum B shows the result of adding ~0.3 equiv of $U(OCH_3)_6$ to 1 equiv of $UF_6$. Spectra E, D, and C illustrate the successive addition of $UF_6$ to $U(OCH_3)_6$.

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(23) Levy, J. H.; Taylor, J. C.; Wilson, P. W. *J. Chem. Soc., Dalton Trans.* **1976**, 219.

(24) (a) Dean, P. A. W.; Evans, D. F. *J. Chem. Soc. A* **1968**, 1154. (b) L = $OH^-$, $OCH_3^-$, $OEt^-$, O-*n*-$Pr^-$. (c) L = $Cl^-$, $Br^-$, $I^-$, $NCO^-$, $NCS^-$, $NCSe^-$, $N_3^-$.

(25) Fraser, G. W.; Gibbs, C. J. W.; Peacock, R. D. *J. Chem. Soc. A* **1970**, 1708.

(26) Noble, A. M.; Winfield, J. M. *J. Chem. Soc. A* **1970**, 2574.

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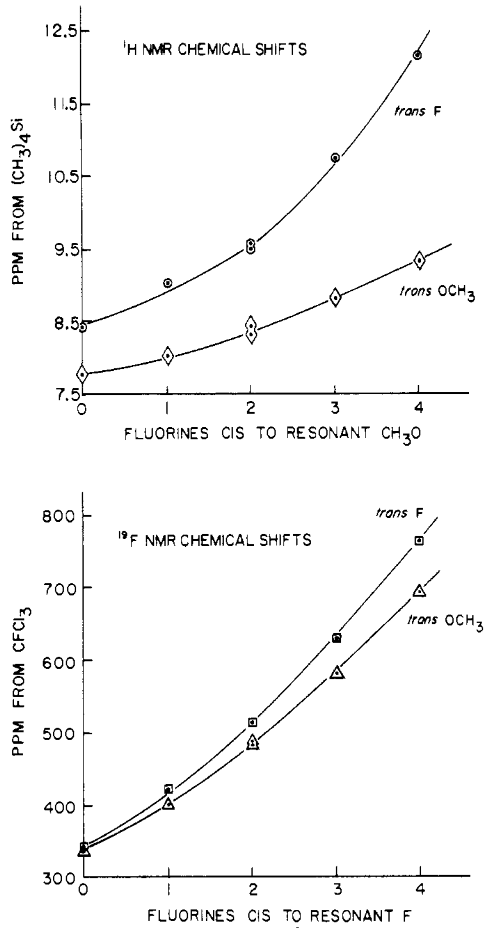

**Figure 4.** Plots of $\delta(Z)$ vs. number of fluorines cis to resonant Z in the series $U(OCH_3)_nF_{6-n}$: upper diagram, Z = H; lower diagram, Z = F. In both diagrams the upper curve is for molecules containing a fluorine atom trans to Z, $q = 1$; the lower curve is for molecules containing a methoxy group trans to Z, $q = 0$.

favored in less polar $CHCl_3/CH_2Cl_2$ (Figure 2, $\epsilon(CHCl_3, 25\ °C) = 4.89$[29]), and are not observed in $CFCl_3$ (Table I, $\epsilon(20\ °C) = 2.27$[29]).

**NMR Studies. Intermolecular Exchange Reactions.** Low-temperature ¹H NMR spectra of a 0.18 M solution of $U(OCH_3)_5F$ (Figure 5) exhibit the 4:1 methoxide resonance pattern expected for a $C_{4v}$ quasi-octahedral geometry. That the ligand exchange observed at higher temperatures is predominantly intermolecular in character is confirmed by dilution experiments (the exchange-broadened line shapes revert to the slow-exchange-limit pattern). Small quantities of both *trans*-$U(OCH_3)_4F_2$ and $U(OCH_3)_6$ are also observed. Figure 6 shows the temperature dependence of a mixture (ca. 0.02 M total) of $U(OCH_3)_4F_2$ and $U(OCH_3)_5F$; again, rapid ligand exchange is observed. These observations indicate solution equilibria such as those in eq 7 and 8, where L = $OCH_3$.

$$2UL_5F \rightleftharpoons UL_4F_2 + UL_6 \qquad (7)$$

$$UL_4L'F + UL_3L''F_2 \rightleftharpoons UL_4L''F + UL_3L'F_2 \qquad (8)$$

These processes interconvert both compounds and isomers. Isomer interconversion is not observed in the absence of compound interconversion. Still lower concentrations, in the range of 5 mM, are necessary to resolve the respective isomers of a mixture of $U(OCH_3)_3F_3$ and $U(OCH_3)_4F_2$. Similar processes are observable in the fluorine NMR spectra.

**NMR Studies. Solvent and Temperature Effects on the ¹⁹F Chemical Shift.** Solvent effects[30] are typically described as contributing an amount $\sigma_s$ to the observed nuclear shielding, where $\sigma_s$ is given by[31]

$$\sigma_s = \sigma_b + \sigma_a + \sigma_w + \sigma_e + \sigma_c \qquad (9)$$

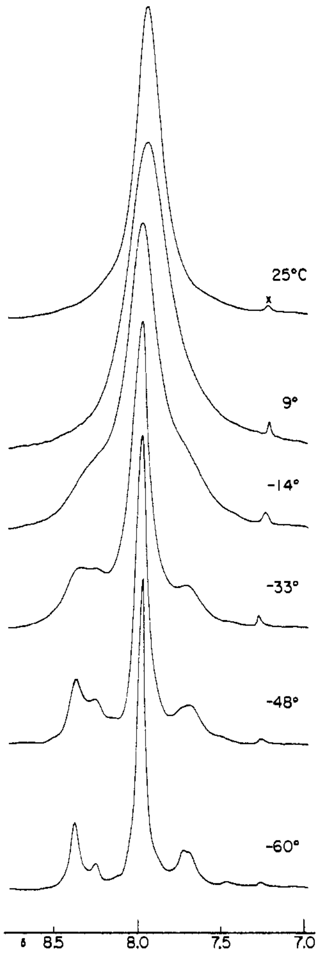

**Figure 5.** Variable-temperature ¹H FT NMR spectra of $U(OCH_3)_5F$ as a 0.18 M solution in $CDCl_3$. The resonances at δ 8.32 and 7.75 are due to small quantities of *trans*-$U(OCH_3)_4F_2$ and $U(OCH_3)_6$, respectively. The peak marked with an × is $CHCl_3$.

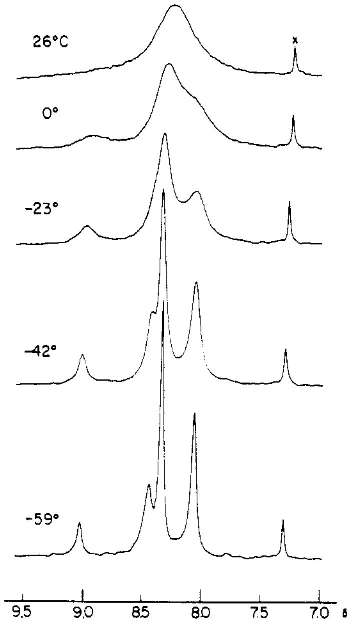

**Figure 6.** Variable-temperature ¹H FT NMR spectra of a mixture of $U(OCH_3)_4F_2$ and $U(OCH_3)_5F$ in $CDCl_3$; total concentration of species 0.02 M. The peak marked with an × is $CHCl_3$.

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(29) Landolt-Börnstein. "Zahlenwerte und Funktionen", 6th ed.; Springer-Verlag: Berlin, 1959; Vol. II, Part 6, pp 665–686.

**Table II.** Variation of $^{19}$F Chemical Shifts[a] of $U(OCH_3)_nF_{6-n}$ with Temperature in Various Solvents

| compd | solvent | concn, M | temp, °C −100 | −90 | −80 | −70 | −60 | −50 | −40 | −30 | −20 | −10 | 0 | 10 | 20 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $U(OCH_3)_5F$ | $CH_2Cl_2$ | 0.02 | | 327.4 | 330.8 | | 337.1 | | 342.9 | | 349.2 | | 354.2 | | 358.9 |
| | $CH_2Cl_2$ | 0.5 | | 330.7 | 333.5 | 336.4 | 339.2 | | 345.6 | | 350.9 | | 355.9 | 358.4 | 360.7 |
| | $CH_2Cl_2$ | 1.5 | | 332.6 | 335.5 | 338.1 | 340.8 | 343.7 | 346.7 | 349.7 | 352.1 | 354.7 | 357.3 | 359.4 | 361.6 |
| | $CFCl_3$ | 0.08 | | 384.4 | 387.4 | | 393.4 | | 399.6 | | 404.8 | | 409.1 | | 412.7 |
| | toluene | 0.07 | | 390.8 | | 394.7 | | 398.3 | | 401.9 | | 404.7 | 406.0 | | 408.4 |
| | ether | 0.08 | | 401.1 | | 404.4 | | 407.2 | | | 411.1 | | 413.7 | | 415.3 |
| | $CH_3Cl$ | 0.08 | | 359.3 | 362.1 | 364.8 | | 370.1 | | 374.9 | | | | | |
| | THF | 0.07 | | | | | 394.1 | 395.4 | 397.1 | 398.2 | 399.6 | 400.7 | 401.9 | 403.0 | 404.0 |
| | $CHCl_3$ | 0.08 | | | | | | 325.2 | | 333.8 | | 341.0 | 344.2 | 347.5 | 350.2 |
| | pentane | 0.07 | | | | | | | 425.0 | 427.0 | 428.1 | 429.5 | 430.6 | 431.5 | 432.1 |
| | $CCl_4$ | 0.08 | | | | | | | | | | 406.7 | 408.6 | 410.2 | 412.0 |
| | dioxane | 0.08 | | | | | | | | | | | | | 393.0 |
| *cis*-$U(OCH_3)_4F_2$ | $CH_2Cl_2$ | 0.02 | | 395.6 | 398.8 | | 404.1 | | 409.2 | | 415.6 | | | | |
| | $CFCl_3$ | 0.01 | | | 453.2 | | | | | | | 467.0 | | | |
| *trans*-$U(OCH_3)_4F_2$ | $CH_2Cl_2$ | 0.02 | | 336.0 | 339.1 | | 344.3 | | 349.4 | | 357.0 | | | | |
| | $CFCl_3$ | 0.01 | | | 385.2 | | | | | | | 405.8 | | | |
| *fac*-$U(OCH_3)_3F_3$ | $CH_2Cl_2$ | 0.02 | | 478.0 | 480.2 | 482.1 | | | | | | | | | |
| *mer*-$U(OCH_3)_3F_3$ ($2F_X$)[b] | $CH_2Cl_2$ | 0.02 | | 415.5 | 417.4 | 420.8 | | | | | | | | | |
| *mer*-$U(OCH_3)_3F_3$ ($F_V$)[b] | $CH_2Cl_2$ | 0.02 | | 480.7 | 482.9 | 484.0 | | | | | | | | | |
| *cis*-$U(OCH_3)_2F_4$ ($2F_V$)[b] | $CH_2Cl_2$ | 0.02 | | 576.8 | 578.0 | 579.1 | 581.1 | | | | | | | | |
| *trans*-$U(OCH_3)_2F_4$ | $CH_2Cl_2$ | 0.02 | | 511.1 | 512.4 | 513.4 | 515.1 | | | | | | | | |
| $U(OCH_3)F_5$ ($4F_X$)[b] | $CH_2Cl_2$ | 0.02 | | 626.6 | 627.2 | 627.5 | 628.4 | | | | | | | | |
| | $CFCl_3$ | 0.01 | 643.1 | | 643.8 | | | | | | | | | | |
| $U(OCH_3)F_5$ ($F_V$)[b] | $CH_2Cl_2$ | 0.01 | | 689.9 | 690.3 | 690.7 | 691.1 | | | | | | | | |
| | $CFCl_3$ | 0.01 | 706.3 | | 706.4 | | | | | | | | | | |
| $UF_6$ | $CH_2Cl_2$ | 0.01 | | | 766.5 | | 766.2 | | 765.9 | | 765.6 | | 765.3 | | |
| | $CFCl_3$ | 0.01 | 764.6 | | 764.3 | | 764.0 | | 763.6 | | 763.3 | | 763.1 | | |

[a] In ppm downfield from external $CFCl_3$; estimated uncertainty of ±0.2 ppm. [b] Spin system defined in Table I.

The bulk magnetic susceptibility of the solvent ($\sigma_b$), diamagnetic anisotropy of the solvent ($\sigma_a$), solvent–solute van der Waals interactions ($\sigma_w$), and electric field interactions ($\sigma_e$) generally account for a 5–10 ppm solvent effect on fluorine chemical shifts.[32,33] Other effects such as complex formation or hydrogen bonding are ascribed to $\sigma_c$. The unusually large magnitude of the solvent (Tables I and II) and temperature effects (Table II) on the $U(OCH_3)_nF_{6-n}$ $^{19}$F chemical shifts appeared to be totally unprecedented for diamagnetic systems and therefore warranted further investigation.

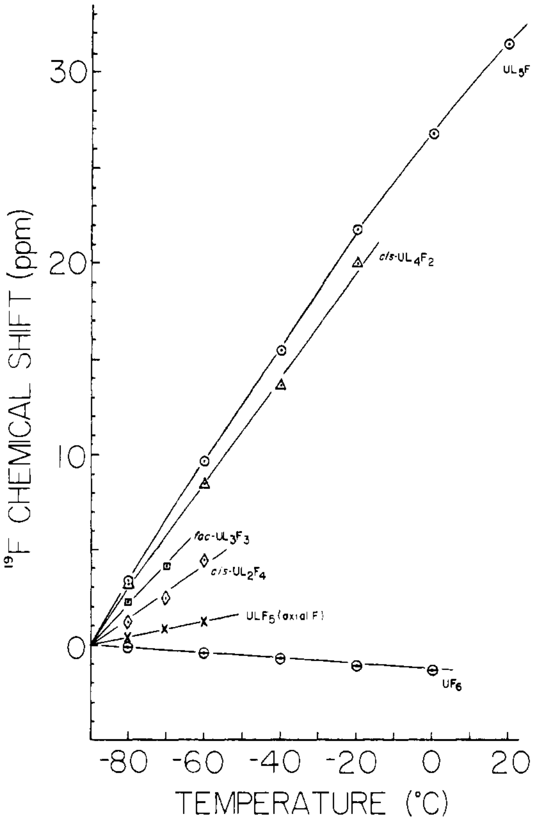

**Figure 7.** $^{19}$F chemical shifts of some $U(OCH_3)_nF_{6-n}$ species as 0.01–0.02 M solutions in $CH_2Cl_2$ as a function of temperature. The zero for each species is the $^{19}$F resonance position vs. external $CFCl_3$ at −90 °C.

Fluorine chemical shift effects were investigated most thoroughly for $U(OCH_3)_5F$ since this is the most stable of the fluorine-containing complexes and exhibits the largest changes in chemical shift with solvent and temperature. The solvent dependence of the fluorine chemical shift of $U(OCH_3)_5F$, from high field to low (Table II), is in the order $CHCl_3 > CH_2Cl_2 \gg CH_3Cl >$ *p*-dioxane > THF > toluene > $CCl_4 > CFCl_3$ > ether ≫ pentane. The chemical shifts are not corrected for $\sigma_b$, $\sigma_a$, $\sigma_w$, or $\sigma_e$. However, the sum of these effects should be far smaller than the observed chemical shift differences for $U(OCH_3)_5F$ in the various solvents. Typically, for the solvents used in this study, corrections for $\sigma_b$ range from approximately +0.14 to −0.24 ppm,[34] $\sigma_a \sim 0.5$ ppm for toluene and 0 for the others,[35] and $\sigma_e \sim 0$.[36,37] Although the overall magnitude of $\sigma_w$ is typically ca. 10 ppm,[38] the difference in $\sigma_w$ among the above solvents should be considerably smaller and is not expected to alter the above order. No correlation exists between

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(30) (a) Homer, J. *Nucl. Magn. Reson.*, **1978**, *7*, 318. (b) Foreman, M. I. *Ibid.* **1977**, *6*, 233. (c) Homer, J. *Appl. Spectrosc. Rev.* **1975**, *9*, 1. (d) Laszlo, P. *Prog. Nucl. Magn. Reson. Spectrosc.* **1967**, *3*, 231.

(31) Buckingham, A. D.; Schaefer, T.; Schneider, W. G. *J. Chem. Phys.* **1960**, *32*, 1227.

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(34) Magnetic susceptibility data taken from: Landolt-Börnstein. "Zahlenwerte und Funktionen", 6th ed.; Springer-Verlag: Berlin, 1967; Vol. II, Part 10, pp 66–140.

(35) Lambert, J. B.; Shurvell, H. F.; Verbit, L.; Cooks, R. G.; Stout, G. H. "Organic Structural Analysis"; Macmillan: New York, 1976; pp 31–49.

(36) Muller, N. *J. Magn. Reson.* **1977**, *25*, 111.

(37) Petrakis, L.; Bernstein, H. J. *J. Chem. Phys.* **1963**, *38*, 1562.

(38) Rummens, F. H. A. *NMR: Basic Princ.* **1975**, *10*.

the fluorine chemical shifts of the $U(OCH_3)_nF_{6-n}$ species and the static[29] or nonstatic[40] dielectric constants of the solvents (i.e., $\sigma_e$) or solvent polarizability[41b] or ionization potential[41c,42b] (i.e., $\sigma_w$). Figure 7 shows a plot of the $^{19}F$ chemical shifts of the $U(OCH_3)_nF_{6-n}$ series in $CH_2Cl_2$ vs. temperature. $UF_6$[39] and presumably the other members of the series display temperature-independent paramagnetism. Therefore, the strong, reversible temperature dependences of the chemical shifts are especially noteworthy.

Possible explanations for the large solvent and temperature dependence of the $U(OCH_3)_nF_{6-n}$ fluorine chemical shifts include (1) the presence of paramagnetic impurities or decomposition products that are in rapid (on the NMR time scale) equilibrium with the diamagnetic species, (2) monomer–dimer equilibria, (3) a large temperature dependence of intermolecular exchange equilibria (eq 7), and/or (4) the formation of solute–solvent charge-transfer molecular complexes.[43] The first three explanations can be readily eliminated.

It is unlikely that paramagnetic species or decomposition products in rapid equilibrium with the $U(OCH_3)_nF_{6-n}$ species are responsible for the observed solvent and temperature dependence. The $U(OCH_3)_5F$ fluorine chemical shift and line width at any temperature are virtually independent of concentration[44] (Table II). This concentration independence is not the case for intermolecular ligand exchange (vide supra) and is not expected for intermolecular electron transfer. For $U(OCH_3)_5F$ in pentane, decomposition products precipitate with time, and both broad and sharp resonances appear upfield of $CFCl_3$. These impurities do not affect the position or temperature behavior of the resonance of interest. The resonance positions of all the $U(OCH_3)_nF_{6-n}$ species are also independent of the mode of preparation.

In regard to monomer–dimer equilibria, it is noted that all spectra can be interpreted on the basis of monomers and that the spectra are virtually independent of concentration.[44] Furthermore, the sensitivity of the $U(OCH_3)_5F$ fluorine chemical shift to coordinating solvents does not follow the trend expected for the anticipated disruption of molecular association. Thus, the resonance positions in THF and dioxane lie between those of more poorly coordinating toluene and $CH_3Cl$.

The temperature dependence of the $U(OCH_3)_nF_{6-n}$ spectra cannot be explained in terms of the temperature dependence of intermolecular exchange (eq 7) equilibrium constants. For example, if the concentration of $U(OCH_3)_4F_2$ increased with increasing temperature, the time averaging of the $U(OCH_3)_4F_2$ and $U(OCH_3)_5F$ fluorine resonances would give rise to a singlet that would progressively shift downfield of the original, low-temperature resonance position for $U(OCH_3)_5F$. However, the magnitude of the $^{19}F$ chemical shift of $U(OCH_3)_5F$ to lower field with increasing temperature is the same in both $CH_2Cl_2$ and $CFCl_3$, despite the fact that the centers of gravity of the *cis*- and *trans*-$U(OCH_3)_4F_2$ signals are further downfield in $CH_2Cl_2$.

**Table III.** Chemical Shifts[a] of $U(OCH_3)_5F$ in Pentane/$CH_2Cl_2$ Mixtures at Various Temperatures

| initial mole fraction of $CH_2Cl_2$ | temp, °C | | | | |
|---|---|---|---|---|---|
| | 20 | 0 | −20 | −50 | −90 |
| 0 | 432.23 | 430.64 | 428.38 | 423.2[b,c] | 412.8[b,d] |
| 0.0430 | 421.91 | 417.71 | 412.27 | | |
| 0.0825 | 413.54 | 408.36 | 401.60 | | |
| 0.152 | 403.39 | 397.29 | 390.05 | | |
| 0.212 | 396.82 | 390.85 | 383.52 | | |
| 0.265 | 392.63 | 386.30 | 379.20 | | |
| 0.471 | 381.09 | 375.36 | 369.03 | | |
| 0.640 | 374.15 | 369.04 | 363.09 | | |
| 0.779 | 367.99 | 363.28 | 358.03 | | |
| 0.900 | 362.72 | 357.65 | 353.17 | 344.48 | 330.12 |
| 0.947 | 361.31 | 356.65 | 352.04 | 343.56 | 329.50 |
| 0.973 | 360.44 | 355.57 | 350.75 | 341.97 | 328.08 |
| 1.000 | 359.57 | 355.11 | 350.07 | 342.02 | 327.67 |

[a] In ppm downfield from external $CFCl_3$; estimated uncertainty ±0.1 ppm. [b] Extrapolated from a plot of chemical shift vs. temperature as in Figure 7. The solubility of $U(OCH_3)_5F$ in pentane is low at these temperatures. [c] Estimated uncertainty of ±0.2 ppm. [d] Estimated uncertainty of ±3.0 ppm.

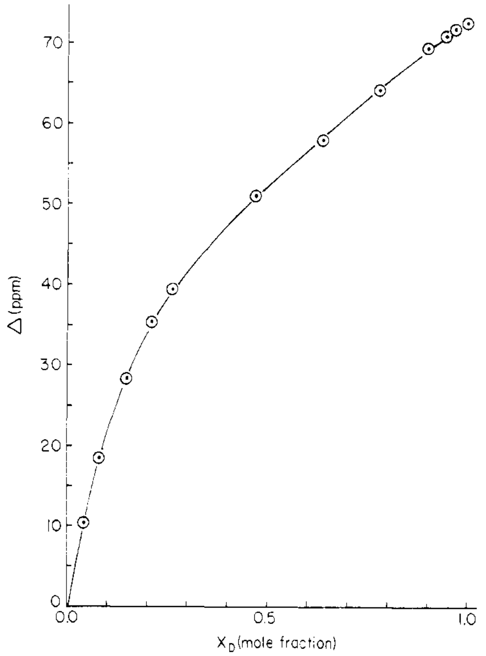

**Figure 8.** $^{19}F$ chemical shift of $U(OCH_3)_5F$ as a function of solvent composition for several pentane/$CH_2Cl_2$ mixtures at 20 °C.

The preceding discussion leaves charge-transfer complex formation[43] as the most plausible explanation for the observed $^{19}F$ chemical shift effects. In all cases where NMR data are available,[36,45–47] charge-transfer complex formation induces an upfield shift of the acceptor $^{19}F$ resonances. In the present case, all $U(OCH_3)_5F$ solvent shifts are upfield of those observed with the solvent that is expected to be the weakest donor, pentane (alkane charge-transfer complexes with $I_2$[48] and $WF_6$[21d] are exceedingly weak). Oxygen-containing donors such as THF and dioxane have a relatively high affinity for hard Lewis acids such as U(VI) and not unexpectedly induce

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(39) (a) Hutchison, C. A.; Tsang, T.; Weinstock, B. *J. Chem. Phys.* **1962**, *37*, 555. (b) Henkel, P.; Klemm, W. *Z. Anorg. Allg. Chem.* **1935**, *222*, 70.

(40) Approximated as the square of the refractive index: Becconsall, J. K.; Hampson, P. *Mol. Phys.* **1965**, *10*, 21. Tables of refractive indexes can be found in ref 41a and 42a.

(41) (a) Landolt-Börnstein. "Zahlenwerte und Funktionen", 6th ed.; Springer-Verlag: Berlin, 1962; Vol. II, Part 8, pp 573–675. (b) Landolt-Börnstein. *Ibid.*, 6th ed.; Springer-Verlag: Berlin, 1951; Vol. I, Part 3, pp 515–517. (c) Landolt-Börnstein. *Ibid.*, 6th ed.; Springer-Verlag: Berlin, 1951; Vol. I, Part 3, pp 363–367.

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(43) Rose, J. "Molecular Complexes"; Pergamon Press: Oxford, 1967.

(44) The relatively small concentration dependence of $U(OCH_3)_5F$ in $CH_2Cl_2$ (Table II) may be due to the presence of minor amounts of fluorine-bridged, associated species at the higher concentrations: (a) McFarlane, W.; Noble, A. M.; Winfield, J. M. *J. Chem. Soc. A* **1971**, 948. (b) Rupp, H. H.; Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 613.

(45) Larsen, D. W.; Allred, A. L. *J. Phys. Chem.* **1965**, *69*, 2400.

(46) Foster, R.; Fyfe, C. A. *Prog. Nucl. Magn. Reson. Spectrosc.* **1968**, *4*, 1.

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(48) Evans, D. F. *J. Chem. Soc.* **1957**, 4229.

**Table IV.** Equilibrium Constants and Chemical Shift Parameters for $U(OCH_3)_5F\cdots CH_2Cl_2$ Complexes in Pentane

| $T$, °C | $K$, (mole fraction)$^{-1}$ | $\Delta_0$ | $\Delta_c$ | $\Delta$ |
|---|---|---|---|---|
| | | Method A[a] | | |
| 20 | 3.17 ± 0.19 | 87.9 ± 5.0 | 66.8 ± 4.8 | 72.7 |
| 0 | 4.32 ± 0.17 | 83.5 ± 3.1 | 67.8 ± 3.1 | 75.5 |
| −20 | 5.80 ± 0.19 | 81.5 ± 1.4 | 69.5 ± 1.5 | 78.3 |
| | | Method B[b] | | |
| 20 | 1.51 ± 0.11 | 121 ± 3 | 72.6 ± 3.9 | 72.7 |
| 0 | 2.08 ± 0.37 | 112 ± 6 | 75.6 ± 8.0 | 75.5 |
| −20 | 1.61 ± 0.32 | 127 ± 8 | 78.4 ± 10.7 | 78.3 |
| −50 | 1.93 ± 0.73[c] | 124 ± 12 | 81.6 ± 17.0 | 81.2 |
| −90 | 2.31 ± 0.78[c] | 122 ± 10 | 85.1 ± 14.2 | 85.1 |

[a] Data for 0 ⩽ mole fraction of $CH_2Cl_2$ ⩽ 0.265. [b] Data for 0.900 ⩽ mole fraction of $CH_2Cl_2$ ⩽ 1.000. [c] The error due to using extrapolated values for the fluorine chemical shift of $U(OCH_3)_5F$ in pentane at low temperature is approximately ±0.2 ppm.

relatively large upfield shifts of the fluorine resonance in $U(OCH_3)_5F$. The observed charge-transfer complexation order toluene > $CCl_4$ > $CFCl_3$ is consistent with the electronic spectral trends of these solvents with high-valent metal halides.[21] It is interesting that the upfield shift of $U(OCH_3)_5F$ in $CHCl_3$, $CH_2Cl_2$, and $CH_3Cl$ is much larger than would be expected purely on the basis of coordinating ability, polarizability, ionization potential, and analogy to $CCl_4$ and $CFCl_3$. Similar anomalies have been reported in the solvent-dependent $^{19}F$ chemical shifts of *p*-nitro- and *p*-nitrosofluorobenzene[49] and the $^{13}C$ chemical shifts of molybdenum and tungsten carbonyl complexes.[50] This suggests that there are hydrogen–oxygen[51] and/or hydrogen–fluorine[32,52] interactions taking place between these solvents[53] and $U(OCH_3)_5F$ that enhance charge-transfer complex formation.

Additional evidence for charge-transfer complex formation comes from a determination of the $^{19}F$ chemical shift of $U(OCH_3)_5F$ as a function of solvent composition for pentane/$CH_2Cl_2$ mixtures at several temperatures. The results are presented in Table III, and a representative plot is shown in Figure 8. The strong, nonlinear dependence of the fluorine chemical shift of $U(OCH_3)_5F$ with solvent composition is significantly in excess of that expected solely on the basis of nonbonded screening interactions. The strength of the proposed charge-transfer interaction can be estimated from the Benesi–Hildebrand relationship[30c,36]

$$\Delta/X_D = K(\Delta_0 - \Delta) \tag{10}$$

Here $\Delta$ (assumed to arise from 1:1 complex formation) is the observed chemical shift difference of the fluorine resonance position of $U(OCH_3)_5F$ dissolved in the pentane/$CH_2Cl_2$ mixture minus the fluorine resonance position of $U(OCH_3)_5F$ dissolved in pentane, $\Delta_0$ is the chemical shift difference between the $U(OCH_3)_5F\cdots CH_2Cl_2$ complex in pentane and unbound $U(OCH_3)_5F$ in pentane, $X_D$ is the initial concentration of added $CH_2Cl_2$ in mole fraction, and $K$ is the equilibrium quotient. There is controversy over which solvent composition regions eq 10 is valid,[30c] therefore $\Delta/X_D$ vs. $\Delta$ was plotted for $0 < X_D < 0.3$ (method A) and $X_D > 0.90$ (method B). The plots are linear in both regions. Derived values for $K$, $\Delta_0$, and $\Delta_c$ are presented in Table IV; those determined by method B are probably more accurate.[30c] Here the $\Delta_c$ values are the contact charge-transfer[54] corrected values of $\Delta_0$[36] (eq 11). The

$$\Delta_c \cong K\Delta_0/(1 + K) \tag{11}$$

values of $K$ are similar to those of several organic[36,45,46] and inorganic[21] systems where weak charge-transfer complexes are postulated. From a least-squares plot of ln $K$ vs. $1/T$ (method A), the values $\Delta H = -2.24 \pm 0.12$ kcal/mol and $\Delta S = -5.33 \pm 0.44$ eu are calculated for the equilibrium. These values compare favorably with those previously reported for organic[36,45,46] and inorganic systems.[21] The large errors in the $K$ values prohibit such an analysis of the data obtained by method B; the magnitude of the values would clearly be somewhat smaller.

Solvent effects were also sought in the electronic spectrum of $U(OCH_3)_6$, but no significant changes could be detected between a spectrum recorded in $CH_2Cl_2$ (Figure 1) and one recorded in pentane. The only difference is in the 300–350 nm region, where a single broad shoulder at 320 nm is observed in pentane instead of the two distinct absorptions in $CH_2Cl_2$. It therefore appears that $^{19}F$ NMR spectroscopy is a more sensitive probe of such interactions.

## Discussion

Many interesting differences and parallels can be drawn between the chemistry of the $U(OCH_3)_nF_{6-n}$, $n$ = 0–6, series and that of analogous hexavalent metal series such as those of $WCl_nF_{6-n}$,[25] $W(OCH_3)_nF_{6-n}$,[16,26] $W(OCH_3)_nCl_{6-n}$,[16] $W(OR)F_5$,[55] and $U(OTeF_5)_nF_{6-n}$.[28] The most striking differences are the high reactivity of $UF_6$ toward methoxylating reagents and the rapid intermolecular ligand exchange among the $U(OCH_3)_nF_{6-n}$ species. Uranium hexamethoxide can be synthesized in a matter of minutes from $CH_3Si(OCH_3)_3$ at −78 °C, whereas the formation of $W(OCH_3)_6$ from $WF_6$ and $(CH_3)_3SiOCH_3$ proceeds only to a limited extent after 1–2 days of heating at 120 °C in $C_6F_6$.[16] Similar trends in the reactivity of $UF_6$ vs. $WF_6$ have been noted previously.[8b] The analogous Mo(VI) species should be of intermediate reactivity.[8b,57] Likewise, while intermolecular ligand exchange does occur in the tungsten and $U(OTeF_5)_nF_{6-n}$ series mentioned above, it appears to be slow on the NMR time scale. The only conditions under which peak broadening is observed is in the room-temperature $^{19}F$ NMR spectrum of *neat* $WCl_2F_4$.[25] It is likely that the exchange in all of these systems proceeds via bridging intermediates,[1,25] seven- and eight-coordinate complexes being well-known for U(VI)[58,59] but rare for W(VI).[47,58,60]

The progressive upfield shift of both the $^1H$ and $^{19}F$ NMR absorptions of the $U(OCH_3)_nF_{6-n}$ species with increasing $n$ parallels that of the $W(OCH_3)_nF_{6-n}$[16,26] series. Fluorine chemical shifts[32] are generally assumed to be dominated by the local paramagnetic shielding tensor, $\sigma_p$. All approximations

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for $\sigma_p$[32,61] rely on the inverse excitation energies of the molecule, with lower excitation energies resulting in downfield shifts. Adopting a similar formalism for the methoxy ligand, we find that the large overall shift of both the $^1H$ and $^{19}F$ resonances to lower field in the $U(OCH_3)_nF_{6-n}$ series with respect to the $W(OCH_3)_nF_{6-n}$[16,26] series is consistent with the lower LMCT excitation energies in $U(OCH_3)_nF_{6-n}$[12,18] vs. $W(OCH_3)_nF_{6-n}$.[62] However, the trends among the individual members of the series will depend largely upon such factors as changes in the excitation energies, changes in the electron density on the atoms in question, and intramolecular electric field effects.[24,35] Detailed calculations of the electronic structures and charge distributions for any of these systems are not available.

Interestingly, for a given member of the $U(OCH_3)_nF_{6-n}$ series, the fluorine resonance of a fluorine atom trans to a methoxy ligand is always downfield of the fluorine resonance for a fluorine atom trans to another fluorine ligand (Figure 3). This same trend is observed in $IOF_5$,[63] $TiF_5{\cdot}ROH^-$,[64] $Te(OH)_nF_{6-n}$,[27] $Te(OR)F_5$,[56] and $SnL_nF_{6-n}^{2-}$.[24a,b] The opposite trend is observed in $WOF_5^-$,[47] $ReOF_5$,[63] $OsOF_5$,[63] $WCl_nF_{6-n}$,[25] $W(OCH_3)_nF_{6-m}$[16,26] $W(OR)F_5$,[55] $SnL_nF_{6-n}^{2-}$,[24a,c] $Ti(OR)F_5^{2-}$,[65] and $U(OTeF_5)_nF_{6-n}$.[28] Shielding of the axial fluorine in $ReOF_5$ and the $W(OR)F_5$ complexes was attributed to $p\pi$–$d\pi$ bonding between the filled fluorine 2p orbitals and unoccupied $(n-1)$d orbitals in Re(VII)[63] and W(VI).[55] The $(n-1)$d orbitals are filled in Sn(IV) and I(VII), and the observed trends are assigned to intramolecular electric field effects.[24,63] The reason for the trend observed in the $U(OCH_3)_nF_{6-n}$ species is not clear since $p\pi$–$d\pi(f\pi)$ bonding is likely to be important in these molecules.

The present study also demonstrates the remarkable sensitivity toward both solvent and temperature that the $^{19}F$ chemical shifts of U(VI) complexes can display. Charge-transfer interactions between the solvent and solute presently offer the best explanation of these effects. That such large differences in the fluorine chemical shifts can occur with solvent and temperature in U(VI) complexes (and likely other metal complexes as well) should be borne in mind when one interprets or calculates the fluorine NMR spectra of metal complexes.

**Acknowledgment.** We thank the National Science Foundation (T.J.M.; Grants CHE76-84494 A01 and CHE-8009060), the Electric Power Research Institute (Contract RP506-7), and the Northwestern University Office of Research and Sponsored Projects for support of this research. We are grateful to Professor Eric Weitz for stimulating discussions. We also thank Allied Chemical for a gift of $UF_6$ and Dr. S. S. Miller for assistance with the mass spectral measurements. T.J.M. is a Camille and Henry Dreyfus Teacher-Scholar.

**Registry No.** $UF_6$, 7783-81-5; $U(OCH_3)F_5$, 71186-40-8; *cis*-$U(OCH_3)_2F_4$, 77241-89-5; *trans*-$U(OCH_3)_2F_4$, 77286-40-9; *fac*-$U(OCH_3)_3F_3$, 77255-89-1; *mer*-$U(OCH_3)_3F_3$, 77286-92-1; *cis*-$U(OCH_3)_4F_2$, 77241-90-8; *trans*-$U(OCH_3)_4F_2$, 77286-41-0; $U(OCH_3)_5F$, 77241-91-9; $U(OCH_3)_6$, 69644-82-2; $CH_3Si(OCH_3)_3$, 1185-55-3.

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# Conformations of (1,3-Diamine)platinum(II) Chelates As Studied by $^{13}C$ and $^1H$ NMR Spectroscopy

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*Received July 8, 1980*

The $^{13}C$ NMR spectra of a series of aqueous solutions of square-planar platinum(II) chelates, Pt(2,2′-bipyridine)(aliphatic 1,3-diamine)$^{2+}$, have been obtained for eight different diamines. The $^{13}C$ chemical shifts of the bpy carbons resemble quite closely the bpy $^{13}C$ shifts of the analogous 1,2-diamine chelates which we reported earlier (*Inorg. Chem.* **1975**, *14*, 3007). Only the $C_6$ carbon exhibits a significant difference in chemical shift between the two series with an ≈2 ppm upfield shift in the present series, which is attributable to increased steric crowding around the $C_6$–$H_6$ bonds by the coordinated amine substituents in the 1,3-diamine chelates. Evidence is presented that the six-membered chelate ring is in a distorted-chair conformation, flattened in the region between the PtNN and NCCN planes. In the limit of severe flattening, an envelope conformation, as found in the *N*,*N′*-dimethyl-1,3-propanediamine (*N*,*N′*-$Me_2$tn) chelates, results. In such envelope conformations the *N*,*N′*-methyl groups stereoselectively form meso complexes with the methyl groups pointing inward toward the envelope as determined from analysis of $^3J_{HNCN}$ data. As found earlier, $^3J_{PtNCC}$ data follow a Karplus-like dihedral angle relationship and along with $^3J_{PtNCH}$ and $^3J_{HCCH}$ provide the basis for assigning conformational preferences of methyl substituents. For example, for the 1,3-diaminobutane complex, the equilibrium distribution is estimated to consist of 80% equatorial-methyl group preference in a flattened-chair conformation in solution. In the racemic 2,4-diaminopentane chelate the diequatorial skew boat predominates over the axial–equatorial dimethyl chair conformation in solution. $J_{PtC}$ values involving diamine ring $\beta$-carbons provide further evidence for multipath coupling, i.e., algebraic additivity of two or more independent coupling paths that link two nuclei to give the observed $J_{PtC}$.

## Introduction

In earlier papers in this series we used carbon-13 NMR spectra to probe the configuration and conformation of some $\alpha$-amino acid[2,3] and 1,2-diamine[4] complexes of platinum(II). These works[2-4] and the findings of others[5,6] have shown the

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