

the square-planar complex $\text{Ni}[(1,4,8,11)[14]\text{aneN}_4](\text{ClO}_4)_2$ can be isolated from the six-coordinate square-planar equilibrium in water.

Experimental Section

Materials. $(1,4,7,11)[14]\text{aneN}_4$,²² $\text{Ni}[(1,4,7,11)[14]\text{aneN}_4](\text{ClO}_4)_2$,¹⁴ and $\text{Ni}[(1,4,8,11)[14]\text{aneN}_4](\text{ClO}_4)_2$ ¹⁰ were made according to standard procedures.

Synthesis of Dichloro(1,4,7,11-tetraazacyclotetradecane)nickel(II) Hemihydrate. To a solution of 0.50 g (0.0025 mol) of $(1,4,7,11)[14]\text{aneN}_4$ in 50 mL of methanol was added 0.62 g of nickel acetate tetrahydrate. The violet mixture was warmed on a steam bath for 15 min. An excess of LiCl, 0.3 g (0.0071 mol), was added and the warming continued for 10 min. The product was rotoevaporated to dryness to yield a purple solid. The solid was dissolved in a minimum amount of chloroform, and the solution was filtered and evaporated to dryness. This product was then recrystallized from warm acetonitrile; yield 0.71 g (84%). Anal. Calcd for $\text{Ni}(\text{C}_{10}\text{H}_{24}\text{N}_4)\text{Cl}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$: C, 35.44; H, 7.43; N, 16.53. Found: C, 35.56; H, 7.30; N, 16.33.

Synthesis of (Diisothiocyanato)(1,4,7,11-tetraazacyclotetradecane)nickel(II). To 50 mL of water in a 100-mL round-bottom flask was added 0.25 g (0.0012 mol) of $(1,4,7,11)[14]\text{aneN}_4$. After the ligand was dissolved, 0.31 g (0.0012 mol) of nickel acetate tetrahydrate was added. The solution was heated on a steam bath for 15 min, during this time the solution changed from light green to dark blue. An excess, 0.29 g (0.003 mol), of LiSCN was added, and a lavender precipitate formed. The product was centrifuged from the suspension and recrystallized from a minimum amount of hot water; yield 0.25 g (53%). Anal. Calcd for $\text{Ni}(\text{C}_{10}\text{H}_{24}\text{N}_4)(\text{NCS})_2$: C, 38.41; H, 6.45; N, 22.40. Found: C, 38.48; H, 6.60; N, 22.32.

Physical Measurements. Conductance measurements were made by using an American Instrument Co. Model 5-2050 conductivity bridge in conjunction with a Beckman Model C1-BB1 conductivity cell. The cell constant was 1.00/cm. Solvents used for making measurements were water, methanol, acetonitrile, and nitromethane. The mass susceptibility was determined by the Evans method by using a Varian A-60 NMR with coaxial NMR tubes. The solvent was water

with 2% *tert*-butyl alcohol as the reference. The complex dissolved in solvent was placed in the outer tube, and solvent alone was placed in the inner tube. Concentrations of 4.15–18.93 mg/mL were used depending on the magnitude of the magnetic moment. Diamagnetic corrections were made by using Pascals' constants. A Perkin-Elmer Model 337 spectrophotometer was used to record all infrared spectra. The spectra of complexes were obtained on both Nujol mulls and KBr pressed pellets. The spectra were calibrated by using polystyrene. A Beckman Acta MIV UV-visible near-IR spectrophotometer with 1-cm and 10-cm matched cells was used to obtain visible and near-infrared spectra. The visible spectra of solids were measured in Nujol mulls. The mull was placed on Sharkskin filter paper in the sample beam, and a similar piece of filter paper with Nujol was placed in the reference beam. The electronic spectra were taken at 77 K with a Cary 14 using Nujol mulls at the University of Toledo. Equilibrium constants were calculated from spectra data obtained on a Beckman Acta MIV UV-visible near-IR spectrophotometer. The data were obtained at 470 nm. The 0.1 M NaClO_4 was obtained by titrating 1 M HClO_4 against a standard NaOH solution and then diluting. The temperature was controlled by using a Haake Model FK thermostated water bath.

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Registry No. $\text{Ni}[(1,4,7,11)[14]\text{aneN}_4]\text{Cl}_2$, 72765-27-6; $\text{Ni}[(1,4,7,11)[14]\text{aneN}_4](\text{SCN})_2$, 72893-71-1; $\text{Ni}[(1,4,8,11)[14]\text{aneN}_4]\text{Cl}_2$, 15333-47-8; $\text{Ni}[(1,4,8,11)[14]\text{aneN}_4](\text{ClO}_4)_2$, 15220-72-1; $\text{Ni}[(1,4,7,11)[14]\text{aneN}_4](\text{OH}_2)_2^{2+}$, 68317-92-0; $\text{Ni}[(1,4,7,11)[14]\text{aneN}_4\text{H}](\text{OH}_2)^{3+}$, 72893-72-2; $\text{Ni}[(1,4,7,11)[14]\text{aneN}_4](\text{ClO}_4)_2$, 68344-01-4.

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Preparation and Characterization of a Volatile Uranyl Compound, Bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)dioxouranium-Tetrahydrofuran

G. M. KRAMER,* M. B. DINES, R. B. HALL, A. KALDOR, A. J. JACOBSON, and J. C. SCANLON

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A volatile uranyl compound $\text{UO}_2[(\text{CF}_3\text{CO})_2\text{CH}]_2 \cdot \text{THF}$ with a vapor pressure of 0.7 torr at 100 °C has been prepared. The compound has high thermal stability and is suitable for studies of laser-induced isotope separation. The compound has been characterized by its IR, UV, NMR, fluorescence, and mass spectra and other physical and chemical properties including an X-ray structural determination. The molecule contains a linear uranyl ion equatorially surrounded by a pentagon of oxygen atoms. The chelating anions are tilted slightly in a boatlike configuration from this plane. The crystals are monoclinic, $P2_1/c$, with $a = 8.540$ (3) Å, $b = 9.110$ (4) Å, $c = 28.884$ (11) Å, $\beta = 94.26$ (3)°, and $Z = 4$.

Introduction

Recently we reported on an unusually efficient multiple photon CO_2 laser driven unimolecular decomposition of a volatile uranyl compound, $\text{UO}_2[(\text{CF}_3\text{CO})_2\text{CH}]_2 \cdot \text{THF}$.¹ A key facet of this work was the synthesis of a sufficiently volatile compound. In this report we will discuss its preparation and characterization.

The objective of the synthetic work was to prepare a uranyl compound with a vapor pressure of about 0.1 torr or greater at a temperature below 150 °C. To be suitable for isotope

separation studies with a CO_2 laser, it must have an asymmetric UO_2^{2+} stretch in roughly the 900–1100- cm^{-1} region that is spectrally isolated from other vibrations of the molecule. At the inception of this work the volatility requirement seemed particularly difficult to attain because of the low vapor pressure of existing uranyl compounds. The THF complex of uranyl hexafluoroacetylacetonate is an unexpectedly volatile and stable complex, which, however, meets these requirements.

A literature search revealed limited vapor pressure data for uranyl compounds. Schlesinger et al.³ found that the uranyl β -diketonate prepared with 1,1,1-trifluoro-2,4-pentanedione

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had a vapor pressure of 2.7×10^{-3} torr at 125°C , which was higher than that of any nonfluorinated homologue.

Gilman et al.⁴ described 14 uranyl 1,3-dicarbonyl chelates. Some were partially fluorinated, some contained a coordinated molecule of solvent (water or an alcohol), and all were reported to decompose completely when distillations were attempted at reduced pressure.

Belford, Martell, and Calvin⁵ described the preparation and IR spectra of $\text{UO}_2[(\text{CF}_3\text{CO})_2\text{CH}]_2\cdot(\text{H}_2\text{O})_4$. Upon being heated under vacuum, this compound was found to decompose and form a red-orange substance. This material can, however, be treated to form a sublimable anhydrous uranyl hexafluoroacetylacetonate.⁶ The $[(\text{CF}_3\text{CO})_2\text{CH}]_2^-$ anion, FAA^- , is well-known as a volatilizing chelating reagent for metal ions, presumably because of its ability to surround the cations with a shell whose outer surface has a substantial negative charge. The intermolecular repulsion of the shells tends to keep other chelated cations from approaching closely and acts as a shield to intermolecular interactions which would reduce volatility.⁷

The problem of obtaining a volatile uranyl derivative is principally one of forming a well-shielded uranyl ion. The uranyl ion is known to prefer a coordination number of either 5 or 6 and a geometry in which these sites lie in an equatorial plane perpendicular to the linear UO_2^{2+} system. Occupying these sites with suitable ligands is thus the key to volatility.

At this time, numerous species with a coordination number of 5, some of which are sublimable or transportable during thermal gravimetric analyses, are known. These include compounds using the FAA^- anion and having a $\text{UO}_2(\text{FAA})_2\cdot\text{B}$ formula where B is a Lewis base like dibutyl sulfoxide,⁸ pyridine *N*-oxide,⁹ tributyl phosphate,¹⁰ and trimethyl phosphate.¹¹ However, while several reviews¹² of the copious and recent literature are available there is a paucity of information concerning volatility.

Other uranyl derivatives of low volatility have also recently been reported, such as the phthalocyanine complexes prepared by Marks and Stojakovic.¹³

This report deals with a complex that appears to be more volatile than any of the above, the tetrahydrofuran adduct of uranyl hexafluoroacetylacetonate, $\text{UO}_2(\text{FAA})_2\cdot\text{THF}$ (I). The THF molecule has sufficient basicity to form a stable sublimable adduct which is easily volatilized below 100°C . This is a bright yellow compound with a vapor pressure of 0.7 torr at 100°C .

- (4) H. Gilman, R. G. Jones, E. Bindshadler, D. Blume, G. Karmes, G. A. Martin, Jr., J. F. Nobis, J. R. Thitle, H. L. Yale, and F. A. Yoeman, *J. Am. Chem. Soc.*, **78**, 2790 (1956).
- (5) R. L. Belford, A. E. Martell, and M. Calvin, *J. Inorg. Nucl. Chem.*, **14**, 169 (1969).
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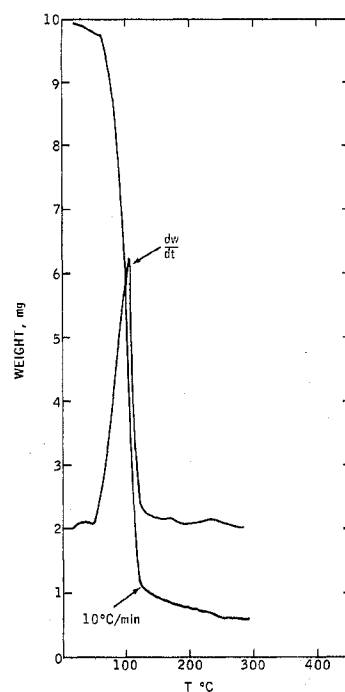


Figure 1. Thermogravimetric behavior of 1 (in flowing argon).

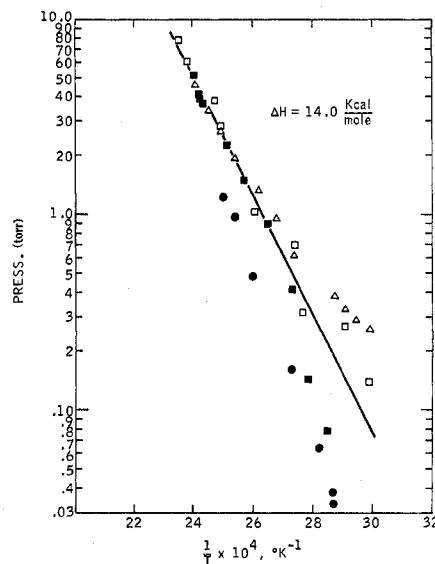


Figure 2. Vapor pressure vs. temperature for $\text{UO}_2(\text{FAA})_2\cdot\text{THF}$.

Experimental Section

$\text{UO}_2[(\text{CF}_3\text{CO})_2\text{CH}]_2\cdot\text{THF}$ (1). Method A. Anhydrous uranyl chloride (3.4 g, 10 mmol) is dissolved in 25 mL of THF, and to this solution is added 25 mL of another THF solution containing 4.6 g (20 mmol), of the sodium salt of hexafluoroacetylacetonate. The mixture is refluxed 1 h, sodium chloride removed by filtration, and the filtrate evaporated to yield 7.5 g of a yellow solid, mp $85\text{--}86^\circ\text{C}$ (crude 1).

Method B. Uranyl nitrate (5.0 g, 10 mmol) is dissolved in 100 mL of aqueous HCl at pH 3. In a separating funnel this solution is added to 100 mL of a benzene solution containing 4.2 g of hexafluoroacetylacetonate and 5 mL of tetrahydrofuran. Upon shaking of the mixture, a yellow compound rapidly forms and is extracted into the benzene layer which is separated, dried over Na_2SO_4 , and evaporated leaving 3.0 g of yellow solid, mp 90°C .

The product from either of these procedures may be purified by sublimation at about 0.1 torr at $50\text{--}70^\circ\text{C}$ or by recrystallization from benzene or hexane. These procedures yield yellow crystals with melting points of $91.5 \pm 1^\circ\text{C}$. Anal. Calcd: C, 22.2; H, 1.3; F, 30.1. Found: C, 22.5; H, 1.5; F, 28.6.

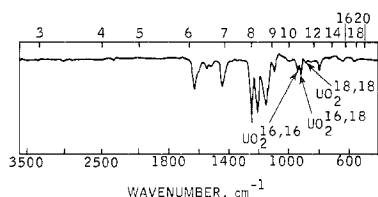


Figure 3. IR spectrum of $\text{UO}_2[(\text{CF}_3\text{CO})_2\text{CH}]_2\cdot\text{THF}$.

Table I. Isotope Shifts (cm^{-1}) in $\text{UO}_2(\text{FAA})_2\cdot\text{THF}$

	exptl ^a	theory ^{b,2}
$^{16}\text{O}-^{18}\text{O}$	16	14.9
$^{18}\text{O}-^{18}\text{O}$	46	47.3
^{235}U	0.7	0.71

^a ν_3 is at 945.4 cm^{-1} in $\text{UO}_2(\text{FAA})_2\cdot\text{THF}$ in benzene. ^b Assuming UO_2^{2+} has its asymmetric stretch at 940 cm^{-1} .

Discussion

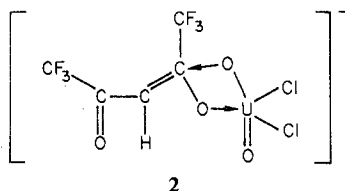
The tetrahydrofuran complex may be repeatedly sublimed below 100°C without decomposition and has been characterized by IR, UV, and ^1H , ^{13}C and F NMR and elemental analyses. It has also been probed by vapor pressure measurements, by its gas-phase IR and UV spectra, by the ^{18}O and ^{235}U isotope shifts of appropriately labeled molecules, and by liquid-, solid-, and gas-phase fluorescence measurements as well as temperature-dependent NMR studies.¹⁴ In addition its structure has been determined by an X-ray analysis.

Volatility. Thermal gravimetric analyses in flowing argon indicate that over 90% of the compound may be volatilized below 120°C without decomposition (Figure 1). Sublimations can in fact easily be conducted at about 70°C .

The equilibrium vapor pressure of compound **1** was measured by using a monel capacitance manometer in a constant-temperature oven. A plot of $\ln(\text{vapor pressure})$ vs. $(\text{temperature})^{-1}$ indicates a heat of vaporization of 14.0 kcal/mol and a vapor pressure of about 0.7 torr at 100°C , Figure 2.

Infrared and Isotope Shifts. The infrared spectra of an ^{18}O -labeled compound in benzene is shown in Figure 3. The sample was prepared by reacting $\text{U}^{18,18}\text{O}_2\text{Cl}_2$ with the sodium salt of hexafluoroacetylacetonate in tetrahydrofuran. The product shows three peaks characteristic of (18, 18), (18, 16), and (16, 16) labeled uranyl ions.

The oxygen exchange mechanism has not been established, but it is plausible that it occurs through an intermediate like **2**. A similar



intermediate might also form during the displacement of the second chloride. Another possibility is that the exchange is catalyzed by the presence of a small amount of UO_2^{2+} which Taube and Gordon²⁷ have proposed as a catalyst for oxygen exchange between UO_2^{2+} and H_2O . If UO_2^{2+} was present in significant quantity, however, it would be reasonable to expect the formation of some U^{IV} compounds, but these have not been detected during this reaction.

The exchange normally proceeds more than halfway toward the statistical redistribution of the two uranyl oxygens with the four carbonyl oxygens. The exchange can be impeded by preparing $\text{U}^{18,18}\text{O}_2\text{Cl}_2$ with a four- or fivefold excess of H_2^{18}O . If this complex is added to a mixture of benzene, tetrahydrofuran, hexafluoroacetylacetonate, and H_2^{16}O , compound **1** can be synthesized with more than 75% ^{18}O retained in the uranyl ion. Once formed, the isotopically labeled compound is stable and has been found to undergo essentially no further oxygen exchange during three repeated sublimations.

The ν_3 asymmetric stretch of the uranyl ion in **1** occurs at 945.4 cm^{-1} . In the $\text{U}^{16}\text{O}^{18}\text{O}$ and $\text{U}^{18}\text{O}^{18}\text{O}$ compounds it is shifted by 16 and 46 cm^{-1} to lower frequencies, Table I. The position of the ν_3

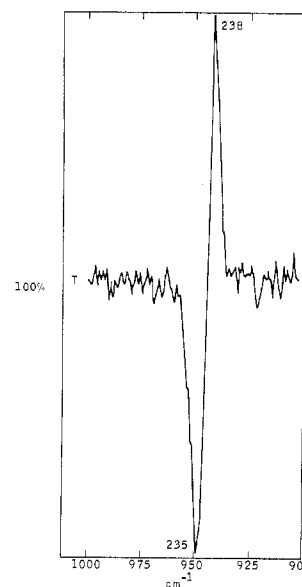


Figure 4. Difference spectra between 50/50 mixture of $^{235}\text{UO}_2$ and $^{238}\text{UO}_2$ in **1**.

Table II. UV Spectra of $\text{UO}_2[(\text{CF}_3\text{CO})_2\text{CH}]_2\cdot\text{THF}$

τ , nm	ϵ , cm^2/mol	τ , nm	ϵ , cm^2/mol
286 ± 2.0	8137	441	237
307	7669	456	147
362	6055	482	39
414	293	499	30
428	294	513	3

band is dependent on the medium and has been found to shift to 956.1 cm^{-1} in vapor-phase studies above 100°C .

Table I also shows the uranium isotope shifts to be 0.7 cm^{-1} . This is in excellent agreement with Dieck and Duncan's theoretical estimates.² These isotope shifts provide convincing evidence that the 945.4 cm^{-1} band is that of the ν_3 stretch.

An illustration of the difference spectrum of a 50/50 mixture of the ^{235}U and ^{238}U compounds obtained by calculation from the spectra of the individual components on a Fourier transform IR is shown in Figure 4. The two peaks represent the points at which the relative absorbances of these compounds are most different.

Numerous other IR bands characterize this molecule. Among the major features are intense bands at 1630 and 1440 cm^{-1} which are probably associated with $\text{C}=\text{O}$ stretching vibrations, but the $\text{C}=\text{C}$ bond of the FAA^- anion may also be involved.

Assignment to $\text{C}=\text{O}$ stretching modes is consistent with detailed assignments for the analogous $[(\text{CH}_3\text{CO})_2\text{CH}]_2\text{Cu}^{\text{II}}$ molecule made by Jung and Musso¹⁵ after extensive isotopic substitution studies. However, the possibility of the intrusion of $\text{C}-\text{C}=\text{C}$ skeletal vibrations in this region is raised by both these authors and several others.^{16,17}

The bands from 1252 to 1098 cm^{-1} are generally characteristic of the FAA^- anion. Of more interest are three peaks at 1010 , 876 , and 846 cm^{-1} as these are associated with the complexed THF ligand. The spectra of **1** in C_6D_6 are also occasionally found to contain a band at 800 cm^{-1} , but this is attributed to a benzene vibration observed because of incomplete cancellation by C_6D_6 in the reference cell.

UV Spectrum. The UV spectrum of **1** in benzene differs from typical spectra of uranyl ions by the presence of an intense band at 362 nm . This feature is probably a charge-transfer band involving the transfer of an electron from FAA^- to an empty $5f$ orbital of uranium. Similar ligand to metal ($\text{L} \rightarrow \text{M}$) transitions involving hexafluoroacetylacetonate, trifluoroacetylacetonate (TFA), and acetylacetonate (AA), anions have been proposed to explain the spectra of their chelates of various inorganic ions such as Na^+ and Cr^{3+} .¹⁸

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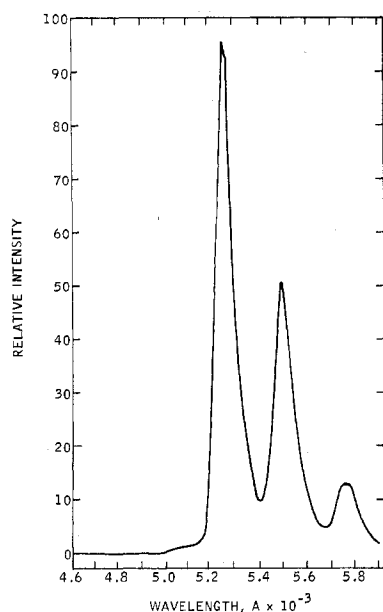


Figure 5. Fluorescence of $\text{UO}_2[(\text{CF}_3\text{CO})_2\text{CH}]_2\cdot\text{THF}$ in 20/80 $i\text{C}_5/\text{MCH}$, 77 K.

The strong bands at 286 and 307 nm probably contain significant contributions from both $\pi \rightarrow \pi^*$ transitions in the anion and absorption of the uranyl ion. The relatively weak band system detected from 414 to 513 nm is characteristic of the uranyl ion, the low values indicating an apparently "forbidden absorption process". The extinction coefficients are significantly stronger for **1** however than for the aqueous UO_2^{2+} ion ($\epsilon = 13 \text{ cm}^2/\text{mol}$ at 415 nm in dilute H_2SO_4), which may partly reflect the tail of the 326-nm charge-transfer band. The exact process leading to the characteristic uranyl absorption band is uncertain but may be hypothesized as one in which an electron is excited from a bonding molecular orbital extending over the UO_2^{2+} ion to a vacant 5f orbital on uranium. The electronically excited state therefore partakes the character of a diradical. A good review of the older literature has been given by Burrows and Kemp,^{12b} but the subject is under constant study.^{19,20}

In the region from 340 to 700 nm, the gas-phase absorption spectrum of compound **1** at 125 °C is similar to that observed in solution. No significant differences were observed between 100 and 160 °C. Excitation spectra at wavelengths above 440 nm, obtained by measuring the total fluorescence yield as a function of either CW or pulsed laser excitation wavelength, show identical features within the wavelength resolution of the experiments ($\sim \pm 2.5 \text{ nm}$). In all cases, the observed gas-phase peaks were 200 cm^{-1} to the red of those observed in solution. Absorption cross sections were measured at 450 and 353.3 nm, assuming Beer's law attenuation of the transmitted laser beam with increasing pressure. The values obtained were $\sigma_{353.3 \text{ nm}} = 3 \times 10^{-18} \text{ cm}^2$ and $\sigma_{450 \text{ nm}} = 3 \times 10^{-19} \text{ cm}^2$.

Fluorescence. Fluorescence studies have been made in the gas as well as in solution and in frozen matrix. Compound **1** has essentially no detectable fluorescence in hydrocarbon solution at 20 °C. Its fluorescence lifetime when frozen at liquid-nitrogen temperatures in a methylcyclohexane glass is about 300 μs , but it decreases rapidly on warming. From the decay rate between 77 and 120 K, one can estimate its lifetime as several orders of magnitude shorter than for UO_2^{2+} in H_2O at ambient conditions.²¹

The fluorescence spectrum of **1** in a mixture of isopentane (0.2) and methylcyclohexane (0.8) at 77 K was measured on a Spex spectrometer. The spectrum consists of three bands at 19059, 18189, and 17731 cm^{-1} with decreasing intensity, Figure 5. The highest energy band (525 nm) should represent emission from the ground vibrational level of the excited state to the ground state of the system, i.e., the 0-0 transition.

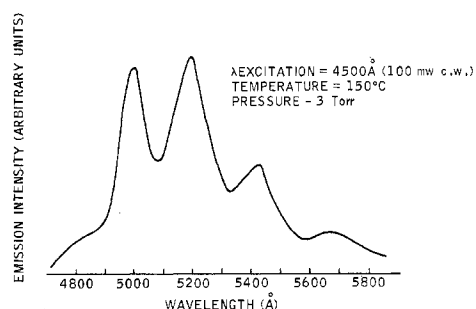


Figure 6. $\text{UO}_2\text{L}_2\cdot\text{THF}$ gas-phase emission spectrum.

The exact placement of the (0-0) transition was found by McClure by high-resolution studies of **1** as a crystalline solid.²³ At 2 K absorption at 19225 cm^{-1} and emission at 19215 cm^{-1} was detected. At 4 K net absorption at both these bands and emission at slightly longer wavelengths were served. The data have been interpreted as indicating that the excited state is a doublet with an energy level spacing of 10 cm^{-1} . Upon irradiation (with a 366-nm source), the electronically excited state of the uranyl system is populated, and relaxation processes rapidly quench vibrationally excited molecules to the $v = 0$ state. At 2 K these molecules emit at 19215 cm^{-1} , but at the slightly higher temperature of 4 K, the molecules appear to transfer energy to "traps" in the frozen lattice which subsequently emit at longer wavelengths. The nature of the traps is uncertain, but they are thought to be other uranyl-containing impurity molecules present in low concentration. One conjecture is that they may be photoproducts produced during the experiments themselves.

The emission spectrum in the gas phase has been measured under a variety of excitation conditions: (i) 365, 355.1 nm (300 mW, CW) from the Ar^+ laser; (ii) 450 nm (15 mW, CW) from the Ar^+ pumped dye; (iii) 450 nm ($\sim < 100 \text{ J/pulse}$, 5 Hz, 15 ns FWHM) from the N_2 pumped dye system. Uranyl pressures ranged from 2 to 5 torr for the CW excitation experiments and about 1 torr for the ones with pulsed excitation. In all cases, the observed spectra were identical within the experimental resolution ($\pm 5 \text{ nm}$). As shown in Figure 6, the gas-phase emission spectrum consists of the same progression to the red of 521.1 nm (the assumed 0-0 transition) that is observed in solution and the low-temperature solid. In addition, however, there is at least one feature to the blue of 521.1 nm. This feature at $\sim 500 \text{ nm}$ is postulated as due to emission from excited vibrational levels of the upper electronic state and is not observed in solution or solid because vibrational relaxation times are in those cases usually very much faster than emission times. If true, the lack of a pressure dependence of the relative intensities implies that, in the gas phase, the collisional quenching of the electronic energy occurs on a much faster time scale than vibrational energy relaxation. A more direct indication of this is to observe in real time the fluorescence lifetimes of each of these features separately. Such experiments are described below.

Fluorescence Lifetimes. For information on lifetimes and collisional quenching efficiencies, fluorescence lifetimes in the gas phase have been obtained at two excitation wavelengths, 353.3 nm (which excites into an electronic state above the emitting state thereby requiring an interconversion before fluorescence can occur) and 450 nm (which excites vibrational levels $\sim > 3$ in the emitting state itself). The dependence of the lifetime of the total fluorescence signal on pressure of uranyl and the effects of added gas moderators, Ar and N_2 , were studied (all $\lambda < 480.0 \text{ nm}$). In addition, spectrally resolved lifetime data were obtained with 450-nm excitation.

A Chromatix Model 1000 Nd:YAG system was used to produce pulsed 353.3-nm radiation. The measurement of fluorescence lifetimes in unmoderated uranyl gas was complicated by the fact that in the accessible pressure range of 0.5-5 torr, the signal obtained was temporally indistinguishable from the system response time (a combination of laser pulse shape—30 nm rise, 50 ns fall, 60 ns FWHM—and phototube response—50 ns). The lifetimes at these pressure could, however, be greater than 100 ns as the system acts as an integrator over its response time and signal levels at longer times show up only if sufficiently intense. In fact, significant enhancements ($\times 10$) in fluorescence quantum yields were observed on addition of $\sim 100 \text{ torr}$

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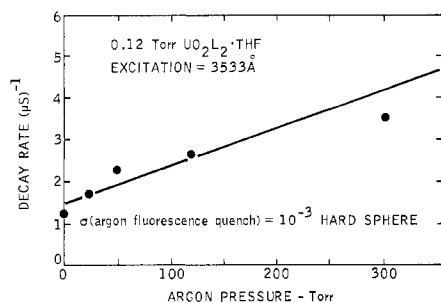
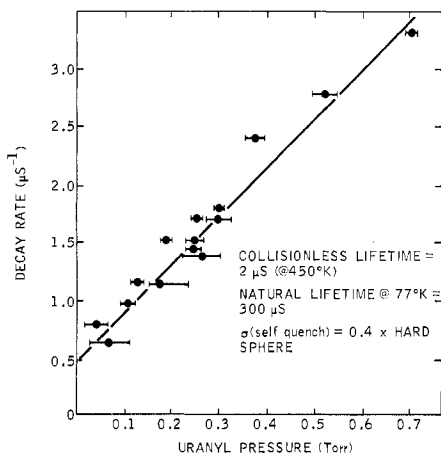


Figure 7. Fluorescence quenching by argon.

Figure 8. $\text{UO}_2^{16}\text{O}_2\text{L}_2\cdot\text{THF}$ fluorescence lifetimes (gas phase, 450 K).

of either argon or nitrogen moderator gas. Under these conditions a signal with an exponential fall off was observed for times very much longer than the system response time. At 500 torr of moderator, the maximum in the fluorescence signal shifted 50–100 ns beyond the system response limit and the shape was considerably broadened. We postulate that the shape of the observed signal may be the result of two competing effects: first, the collision-induced interconversion of the upper electronic state excited to the lower emitting state and, second, the collision-induced interconversion to a still lower, non-fluorescing state (i.e., collisional quenching). On the basis of the rate of increase of the peak fluorescence intensity and the reduction in lifetime (see Figure 7) with moderator pressure, it is concluded that the cross section for collisional interconversion into the emitting state is on the order of 10 uranyl-moderator hard-sphere collisions and that the cross section for collisional quenching is approximately 1000 hard-sphere collisions. Estimates based on the observed fluorescence intensities, which are proportional to uranyl pressure with or without added moderator gas, indicate that the quantum efficiency of 353.3-nm excitation is on the order of 10^{-4} . The apparent quantum yield at 450 nm is $\sim 10^{-3}$.

Better temporal resolution was obtained by using a nitrogen-pumped dye laser that produced 15-ns FWHM pulses at 450 nm. In addition, an increased signal to noise ratio in this experiment permitted investigations at pressures down to 0.1 torr. The fluorescence lifetimes derived from the exponential decay of the fluorescence signal in time are shown in Figure 8 as a function of uranyl pressure. On extrapolation to zero pressure, the value for the natural lifetime in the gas phase from these data is $\sim 2 \mu\text{s}$. Although the uncertainty in this measurement is quite large, this value represents a good lower limit. The slope of this plot gives a cross section for self-quenching equal to half the hard-sphere collision cross section. The fluorescence quenching induced by argon is illustrated in Figure 9. The argon quenching rate is on the order of 1500 hard-sphere collisions. This is slower than that estimated from the 353-nm excitation data, but as mentioned, these data result from a combination of collisional population of the fluorescing level and collisional quenching. The value obtained at 450 nm does not have this added complication and is the preferred value.

As a test of the postulate that the emission feature at 497 nm (blue shifted from the assigned (0,0) band at 52 nm) originates from the same electronic band as the remaining features, the emission lifetimes

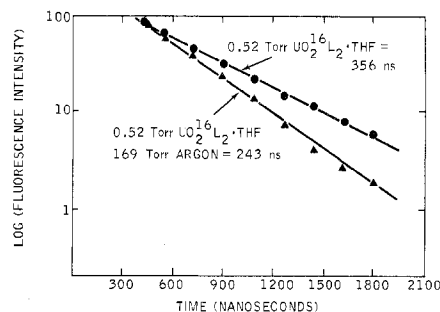
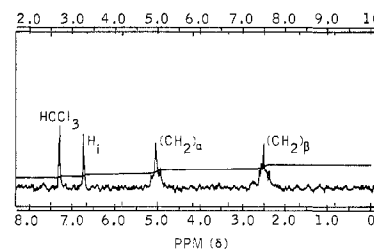


Figure 9. Fluorescence quenching by argon lifetime effects.

Figure 10. ^1H NMR spectrum of $\text{UO}_2[(\text{CF}_3\text{CO})_2\text{CH}]_2\cdot\text{THF}$ in DCCl_3 , ppm (τ).

of each feature were measured individually. This was done by tuning a Spex 0.25-m monochromator with a bandwidth of 2.5 nm to the center of each band and measuring the emission lifetime. For sufficient signal, roughly 1 torr of the uranyl compound was required. The observed lifetime for each feature is about 200 ns, implying that the feature at 497.5 nm originates either from the same electronic state as the remaining features or from another electronic state with the same lifetime. The latter seems unlikely. As each feature exhibits the same time dependence, it is not surprising that a plot of the peak emission intensity, taken under the above conditions at 5.0-nm intervals, mirrors the fluorescence spectra observed under CW excitation. These observations are consistent with the postulate that the emission originates from a single electronic state with the 497.5-nm emission coming from the vibrational hot band of this state.

NMR Behavior. Proton NMR in DCCl_3 reveals three bands at δ 6.72, 5.03, and 2.48 ppm vs. Me_4Si (Figure 10). These have relative areas of 1:2:2, consistent with the formula $\text{UO}_2[(\text{CF}_3\text{CO})_2\text{CH}]_2\cdot\text{C}_4\text{H}_8\text{O}$. The hydrogen on the anion is a sharp singlet at 6.72 ppm and the α - and β - CH_2 groups of $\text{C}_4\text{H}_8\text{O}$ are multiplets resembling a triplet and quintet. The α group is deshielded by 1.43 ppm and the β group by 0.89 ppm from their respective positions in neat THF of 3.60 and 1.79 ppm. The shifts are indicative of strong complexing of THF to the uranyl ion which results in a net transfer of electron density away from the ether. Similar spectra are obtained in C_6D_6 as in DCCl_3 , but with slight differences in chemical shifts which are attributed to normal solvent shielding effects.

The proton spectrum of the complex changes markedly on irradiation with UV or visible light. These phenomena will be discussed in a separate report. They are, however, believed to be related to the displacement of THF and the formation of U^{4+} compounds upon illumination.

The ^{13}C NMR spectra are not as easy to rationalize on the basis of structure 1. This is because 1 contains pairs of CF_3 groups, as well as carbonyl carbons which are in slightly different molecular environments. This should result in the appearance of distinct ^{13}C shifts for each pair of groups. However, the spectra show only one peak for all the CF_3 groups and another for all the carbonyls. The chemical shifts, δ , of the α and β carbons of THF measured from internal CD_2Cl_2 but referenced to Me_4Si are 31 and 77 ppm. The anion shows three bands, a singlet at 96.7 ppm for the $-\text{CH}$ carbons, a quartet at $\delta = 120$, $J = 245$ Hz, for the trifluoromethyl groups, and a quartet for the carbonyl carbons at $\delta = 183$, $J = 40$ Hz.

At room temperature the ^{19}F NMR shows a single sharp resonance 74 ppm upfield of FCCl_3 . This band and the ^{13}C spectra suggest that 1 may be fluxional because in a static configuration the fluorines near the tetrahydrofuran molecule should be in a different magnetic environment than those more remote and hence two bands would be anticipated. As indicated above, the investigation of this process will

Table III. Mass Spectra of $\text{UO}_2[(\text{CF}_3\text{CO})_2\text{CH}]_2\cdot\text{THF}$

m/e	rel intens		assignment ^b
	100 °C ^a	135 °C ^a	
756	25	47	$\text{UO}_2[(\text{CF}_3\text{CO})_2\text{CH}]_2\cdot\text{THF}$
687	6	6	P - CF_3
684	2	3	P - THF
621	2	102	$\text{UO}_2(\text{CF}_3\text{CO})_2\text{CH}\cdot 2\text{THF}$
549	99	sat.	$\text{UO}_2(\text{CF}_3\text{CO})_2\text{CH}\cdot\text{THF}$
477	42	129	$\text{UO}_2(\text{CF}_3\text{CO})_2\text{CH}$
427	18	69	$\text{UO}_2(\text{CF}_3\text{CO})\text{CHCOF}$
361	13	51	427 - COF_2
289	16	65	UO_2F
270	21	44	UO_2

^a Probe temperature. ^b P = $\text{UO}_2[(\text{CF}_3\text{CO})_2\text{CH}]_2\cdot\text{THF}$.

be the subject of a future publication.

Mass Spectra. Electron impact mass spectra of **1** have been obtained at 70 eV on a DuPont 21-491 spectrometer. Table III lists the major cracking components.

For this analysis the sample was placed in a holder and heated to 100 °C at which point there is a liquid melt in equilibrium with vapor. In addition to the indicated components the spectra contain small amounts of heavier peaks indicating that dimerization or condensation reactions of some type may be occurring.

The remarkable stability of the molecule under electron impact conditions is suggested by the relative intensities of the parent peak, P, and the P - 72 and P - 207 fragments of 684 and 549. The 549 signal appears to be the strongest peak in this spectrum. It saturated the detector and is much larger than the 684 peak, indicating that the $(\text{CF}_3\text{CO})_2\text{CH}$ group is significantly easier to detach than tetrahydrofuran from the parent ion.

Other major peaks are at 477 ($\text{UO}_2[(\text{CF}_3\text{CO})_2\text{CH}]$), 427 ($[\text{UO}_2\text{OCFCHCOF}_3]$), 289 (UO_2F), 270 (UO_2), and 361. The 361 species is an unknown ion that can be formed by the elimination of COF_2 from the 427 compound.

When the sample probe is heated, the cracking pattern remains relatively constant except for the growth of a 621 peak. The 621 species is intriguing since it might be $[\text{UO}_2\text{FAA}(\text{THF})_2]^+$. If it is, it would suggest that THF can be vaporized in addition to **1** from the melt and that there may be a $\text{UO}_2(\text{FAA})_2(\text{THF})_2$ (828) species in the vapor phase. This forms 621 upon elimination of FAA (207).

Reactivity. The THF complex undergoes reversible displacement reactions when contacted with solutions of nucleophiles in hydrocarbons or relatively nonpolar solvents. These reactions have been used to synthesize many other complexes. Typical products have been 1:1 complexes with dimethyl sulfoxide, pyridine, methanol, dimethylformamide, pyridine *N*-oxide, and trimethyl phosphate. All of these appear to be less volatile than that of the THF adduct.

Crystal Structure Determination

Preliminary Investigation. A batch of crystals were examined optically and a small well-developed crystal selected for a precession camera study. The crystal was sealed in a quartz capillary. A preliminary survey located two orthogonal planes at close to 90° which were tentatively assumed to be $hk0$ and $0kl$. Upper level photographs out to $l = 3$ as well as an $l = 1/2$ were taken to check for extinctions. Additional skew orientations around b were examined to confirm the absences.

Systematic extinctions $h0l$ ($l = 2n$) and $0k0$ ($k = 2n$) indicated that $P2_1/c$ was the likely space group. However, weak reflections at $l = 1/2$ indicated that the c axis might be doubled or alternatively that the crystal was twinned. Approximate lattice parameters $a = 8.5 \text{ \AA}$, $b = 9.1 \text{ \AA}$, $c = 28.4 \text{ \AA}$, and $\beta = 92.2^\circ$ were obtained from the precession photographs. At this stage a batch of crystals was sent to the Molecular Structure Corp. for further examination. A preliminary analysis confirmed our unit cell and space group and indicated that the apparently doubled c axis was a result of twinning. The three best crystals from this first batch were all twinned. Examination of a second batch of crystals eventually yielded an untwinned crystal which was, however, small with no well-defined faces. The results below were obtained with this crystal.

Data Collection and Reduction. The X-ray intensity data were collected on an Enraf-Nonius CAD 4 diffractometer with a random

crystal orientation. The crystal was sealed in a glass capillary and was approximately $0.35 \times 0.35 \times 0.32 \text{ mm}$ though irregular in shape with no well-defined faces. The radiation was $\text{Mo K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) filtered by a graphite-crystal incident-beam monochromator. The cell constants were determined by computer centering of 25 reflections followed by least-squares refinement of the setting angles. The intensities of 3439 reflections were measured by the θ - 2θ scan method with variable scan rates between 4 and $20^\circ/\text{min}$; the reflection half-widths from ω scans were 0.3° . The range of data collected corresponds to $0^\circ < 2\theta < 45^\circ$, and the scan range was from $2\theta(\text{Mo K}\alpha_1) - 0.7^\circ$ to $2\theta(\text{Mo K}\alpha_2) + 0.7^\circ$. As a check on crystal and electronic stability three standard reflections were measured periodically, and a total linear decrease in intensity of 8% was observed. The absorption correction was applied by using the empirical ψ scan technique, and the correction factors ranged from 0.58 to 1.0 with an average of 0.8. Intensities and standard deviations on the intensities were calculated by using the following relations

$$I = S(C - RB)$$

$$\sigma(I) = [S^2(C + R^2B) + (\rho I)^2]^{1/2}$$

S is the scan rate, C is the total integrated intensity, R is the ratio of scan time to background counting time, and B is the total background count. $\rho (=0.07)$ is used to downweight intense reflections. A correction was applied to compensate for the small linear decrease in intensity with time. After averaging equivalent reflections there were 3359 independent reflections. A complete list of observed and calculated structure factors is given as supplementary material, Table S-1. Crystal data: $\text{C}_{14}\text{H}_8\text{F}_{12}\text{O}_7\text{U}$, $M = 754.23$, monoclinic $a = 8.540$ (3) \AA , $b = 9.110$ (4) \AA , $c = 28.884$ (11) \AA , $\beta = 94.26$ (3)°, $Z = 4$, $D(\text{calcd}) = 2.238 \text{ g/cm}^3$, $F(000) = 1392$, space group $P2_1/c$ with $h0l$, $l \neq 2n$, and $0k0$, $k \neq 2n$. $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$), $\mu(\text{Mo K}\alpha) = 70.99 \text{ cm}^{-1}$. An absorption correction was applied (see above).

Structure Solution and Refinement. The structure was solved by using the Patterson method. The Patterson map showed the position of the uranium. Least-squares refinement of the uranium position gave agreement factors of $R_1 = 0.232$ and $R_2 = 0.303$. The remaining atoms (excluding the hydrogens) were located by successive difference Fourier syntheses. Anomalous dispersion effects were included in F_o^{24} with values for the scattering factors taken from ref 25. A total of 1716 reflections with $F_o^2 > 3\sigma F_o^2$ were included in the final refinement which gave

$$R_1 = \sum(|F_o| - |F_c|) / \sum|F_o| = 0.118$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2} = 0.143$$

The refinement was terminated when all parameter shifts were less than 0.5σ . A total of 34 atoms and 142 variable parameters were included in the refinement. The final atom positions are shown in the supplementary material, Table S-2. The final difference Fourier synthesis was not completely featureless but showed peaks in the vicinity of the uranium atom. This residual electron density is probably associated with errors in the absorption correction applied using the empirical and approximate ψ -scan correction method. A more sophisticated numerical absorption correction was not possible because the crystal was very irregular with no well-defined faces. All other crystals examined (with better faces) were found to be twinned. Because of this problem it was thought not worthwhile to carry out a complete anisotropic refinement on all atoms. Consequently, only the uranium atom anisotropic thermal parameters were refined, and all other atoms were treated isotropically. Consideration of the data shows that the fluorine thermal parameters were large, 10 – 18 \AA^2 , indicating possible positional disorder of these atoms. In the closely related molecule $[\text{UO}_2(\text{FAA})_2][\text{PO}(\text{OMe})_3]$,¹¹ a similar effect was observed, and an attempt was made to introduce this into the refinement by giving each fluorine two positions with unequal fraction occupancies. In our system this was not done because of the absorption correction problem and also the lower symmetry. $\text{UO}_2(\text{hfacac})_2\cdot\text{THF}$ already has twice as many inequivalent fluorines as the $\text{PO}(\text{OMe})_3$ derivative. Figure 11 shows an ORTEP drawing of the molecular unit.

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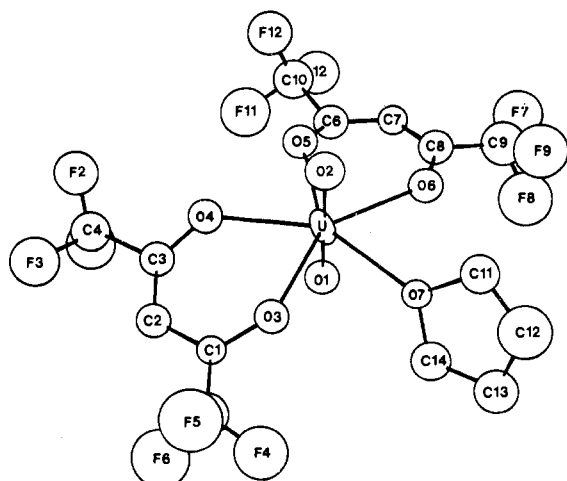


Figure 11. Structure of $\text{UO}_2[(\text{CF}_3\text{CO})_2\text{CH}]_2 \cdot \text{THF}$.

Table IV. Bond Distances in the Uranium Pentagonal Bipyramid (Å)^a

U-O(1)	1.66 (2)	U-O(5)	2.37 (2)
U-O(2)	1.66 (2)	U-O(6)	2.41 (2)
U-O(3)	2.42 (2)	U-O(7)	2.347 (14)
U-O(4)	2.33 (2)		

^a Average U-O distance in the pentagon is 2.375 Å.

Table V. O-U-O Angles in the Pentagonal Bipyramid (Deg)

O(1)-U-O(2)		179.4 (9)	
O(1)-U-O(3)	89.3 (8)	O(2)-U-O(3)	90.8 (8)
O(1)-U-O(4)	92.2 (8)	O(2)-U-O(4)	87.2 (8)
O(1)-U-O(5)	90.6 (8)	O(2)-U-O(5)	89.0 (8)
O(1)-U-O(6)	87.0 (8)	O(2)-U-O(6)	93.3 (8)
O(1)-U-O(7)	85.5 (7)	O(2)-U-O(7)	95.1 (7)
O(7)-U-O(3) ^a	72.9 (5)	O(5)-U-O(6) ^a	70.5 (6)
O(3)-U-O(4) ^a	70.4 (6)	O(6)-U-O(7) ^a	71.6 (6)
O(4)-U-O(5) ^a	74.5 (6)		

^a Average value 72°.

Table VI. Planarity of the Pentagonal Ring

Equation of the Plane Containing \bar{U} , O(3), O(4), O(5), O(6), and O(7) $-0.4655x - 0.3711y - 0.8035z = 8.3630$			
atom	dev from plane, Å	atom	dev from plane, Å
U	0.001 (1)	O(5)	-0.059 (32)
O(3)	-0.031 (27)	O(6)	-0.037 (30)
O(4)	-0.049 (30)	O(7)	-0.041 (25)

Results and Discussion

The Pentagonal-Bipyramidal Uranium Polyhedron. The general dimensions of the uranium pentagonal bipyramid are as expected (see Tables IV and V). The U(1)-U-O(2) angle, 179.4 (9)°, is linear and the uranyl oxygen distances at 1.66 (2) are close to but a little shorter than the usual value of 1.71 Å. The remaining oxygens U(3) to U(7) form the pentagonal ring with U-O bond distances in the range 2.42-2.33 Å. There is nothing unusual about the oxygen from the THF molecule, O(7), which has a bond distance of 2.35 Å, close to the average value. The O-U-O angles in the plane are all very close to the ideal value of 72° for a regular pentagon. The ring is very nearly planar (see Table VI). A least-squares plane through the disk atoms shows that no atom deviates by more than 0.06 (3) Å. The uranyl group is almost normal to the plane but the O(1)-U-O(7) and O(2)-U-O(7) angles of 85.5 (7) and 95.1 (7)° suggest a possible small tilting relative to the THF molecule. The tilting is less noticeable in the other angles.

The Hexafluoroacetylacetonate Ligands. The hfacac molecule has itself been investigated by electron diffraction

Table VII. Bond Distances in the FAA Ligands (Å)^a

C(3)-O(4)	1.27 (3)	C(4)-F(1)	1.12 (4)
C(1)-O(3)	1.30 (3)	C(4)-F(2)	1.29 (3)
C(2)-C(3)	1.35 (4)	C(4)-F(3)	1.35 (4)
C(1)-C(2)	1.36 (3)	C(5)-F(4)	1.23 (4)
C(1)-C(5)	1.43 (4)	C(5)-F(5)	1.06 (4)
C(3)-C(4)	1.67 (4)	C(5)-F(6)	1.42 (5)
C(6)-O(5)	1.29 (3)	C(10)-F(10)	1.24 (4)
C(8)-C(7)	1.37 (4)	C(10)-F(11)	1.33 (5)
C(6)-C(7)	1.37 (4)	C(10)-F(12)	1.27 (4)
C(7)-C(8)	1.33 (3)	C(9)-F(8)	1.66 (5)
C(6)-C(10)	1.57 (4)	C(9)-F(9)	1.34 (5)

^a Average values: C-O = 1.295 Å; C-C(ring) = 1.35 Å; C-C(CF₃) = 1.54 Å; C-F = 1.30 Å.

Table VIII. Bond Angles (Deg) in the FAA Ligands

O(4)-C(3)-C(2)	132 (3)	O(6)-C(8)-C(7)	127 (3)
C(3)-C(2)-C(1)	122 (3)	C(8)-C(7)-C(6)	122 (3)
C(2)-C(1)-O(3)	123 (2)	C(7)-C(6)-O(5)	128 (3)
O(4)-C(3)-C(4)	108 (2)	O(5)-C(6)-C(10)	115 (3)
C(2)-C(3)-C(4)	120 (3)	C(7)-C(6)-C(10)	114 (3)
C(2)-C(1)-C(5)	122 (3)	O(6)-C(8)-C(9)	111 (3)
C(5)-C(1)-O(3)	113 (3)	C(9)-C(8)-C(7)	121 (4)
C(1)-O(3)-U	133 (2)	C(6)-O(5)-U	132 (2)
C(3)-O(4)-U	132 (2)	C(8)-O(6)-U	135 (2)

Table IX. Planarity of the FAA Rings

Equation of the Plane through O(3), O(4), C(1), C(2), C(3), C(4), and C(5) $-0.6831x - 0.4530y - 0.5728z = 5.2802$			
atom	dev from the plane, Å	atom	dev from the plane, Å
O(3)	-0.005 (26)	C(3)	0.040 (47)
O(4)	0.017 (24)	C(4)	-0.020 (53)
C(1)	-0.079 (38)	C(5)	0.149 (58)
C(2)	-0.022 (44)		
		U	-0.581 (1)
Equation of the Plane through O(5), O(6), C(6), C(7), C(8), C(9), and C(10) $-0.2634x - 0.4718y - 0.8414z = 8.4759$			
atom	dev from the plane, Å	atom	dev from the plane, Å
O(5)	0.060 (31)	C(8)	0.053 (44)
O(6)	-0.044 (30)	C(9)	0.175 (73)
C(6)	-0.122 (46)	C(10)	0.037 (62)
C(7)	-0.041 (43)		
		U	-0.378 (1)

and the following values have been obtained for the bond distances:^{11b} C-O = 1.259 (6) Å, C-C (ring) = 1.407 (10) Å, C-C(CF₃) = 1.546 (3) Å, and C-F = 1.337 (2) Å. The bond distances for the hfacac rings are given in Table VII and although there are some variations particularly in C-F distances (see below) the average values are in agreement with those of the parent molecule within the errors. The bond angles are given in Table VIII. Least-squares planes through the two FAA planes were calculated and the deviations of the atoms from these planes are shown in Table IX. Within 3σ both FAA rings are planar. However, the uranium atom lies below both planes by 0.58 and 0.38 Å indicating that the FAA planes are tilted relative to the UO₅ pentagon. The angles between the UO₅ plane and the FAA planes containing O(3) and O(4) and O(5) and O(6) are 18.9 and 13.2°, respectively.

The CF₃ Groups. The CF₃ groups are difficult to define precisely because of the high fluorine thermal motion. The isotropic Debye-Waller factors are in the range 10-18 Å² which correspond to large root-mean-square vibration amplitudes. Some of this thermal motion may be associated with errors in the absorption correction, but the values are not

Table X. Bond Distances (Å) and Bond Angles (Deg) in the THF Ligand

O(7)-C(11)	1.49 (3)	C(11)-C(12)	1.37 (5)
O(7)-C(14)	1.42 (3)	C(12)-C(13)	1.44 (5)
		C(13)-C(14)	1.45 (4)
C(11)-O(7)-C(14)	105 (2)	C(12)-C(11)-O(7)	105 (3)
O(7)-C(14)-C(13)	113 (2)	U-O(7)-C(11)	128 (1)
C(14)-C(13)-C(12)	101 (3)	U-O(7)-C(14)	127 (2)
C(13)-C(12)-C(11)	116 (4)		

Table XI. Comparison of $\text{UO}_2(\text{FAA})_2\text{THF}$ and $\text{UO}_2(\text{FAA})_2\text{OP}(\text{OMe})_3$, Bond Distances (Å)

	$\text{UO}_2(\text{FAA})_2\text{-THF}$	$\text{UO}_2(\text{FAA})_2\text{-OP}(\text{OMe})_3$
U-O(uranyl)	1.66	1.74
U-O(carbonyl)	2.38	2.40
U-O(THF or OP(OMe) ₃)	2.35	2.31
C-O(carbonyl)	1.30	1.25
C-C(ring)	1.35	1.36
C-C(CF ₃)	1.54	1.62
C-F	1.30	1.34

unusually large when compared with those in $\text{UO}_2(\text{FAA})_2\text{OP}(\text{OMe})_3$. The high thermal motions may be a consequence of some positional disorder. The main structural consequence is that there is uncertainty in the C-F distances which show a wide range of values from 1.06 to 1.66 Å although the average distance is reasonable.

The THF Ligand. Bond distances and bond angles for the THF ligand are given in Table X. The distances are similar to those in $\text{Li}_4[\text{Mo}_2(\text{CH}_3)_8]\cdot 4\text{THF}$ ²⁶ (average C-O = 1.44 Å, average C-C = 1.47 Å) although C(1)-C(12) is perhaps a little short. A least-squares plane through O(7), C(11), and C(14) was calculated as $0.9894x + 0.050y - 0.1324z = 1.8538$, and the angles between this plane and the UO_5 pentagon were

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calculated as 67.9° indicating that the THF ligand is tilted with C(11) toward O(6) and C(14) toward O(3).

Comparison with $\text{UO}_2(\text{FAA})_2\text{OP}(\text{OMe})_3$.^{11b} Some points of comparison with $\text{UO}_2(\text{FAA})_2\text{OP}(\text{OMe})_3$ have been noted above. In general the two molecules are very similar as can be seen from a comparison of average bond distances (Table XI). Most of the differences are within the experimental errors although the uranyl oxygen distances are somewhat short which probably reflects absorption errors. Residual peaks were found in the final difference Fourier in the vicinity of the uranium atom. The hfacac rings in both molecules are planar indicating delocalization and tilted in the same direction with respect to the UO_5 pentagon. In the $\text{OP}(\text{OMe})_3$ derivative both planes are equivalent and tilted by 22.5° compared with 18.9 and 13.2° in the THF compound. This tilting is not an unusual feature of chelated uranyl compounds, and tilting angles in the range 3-42° have been observed in other systems.²⁴ Both compounds show high thermal motion and disorder of the peripheral CF_3 groups and consequently variations and uncertainties in the C-F distances.

Summary

A THF adduct of $\text{UO}_2(\text{FAA})_2$ with an unobstructed IR absorption band near 950 cm^{-1} and vapor pressures of about 1 torr at 100 °C has been prepared. The compound sublimes as a unit and has considerable thermal stability as evidenced by its mass spectroscopic cracking pattern in which the FAA^- anions are lost more easily than THF. Its crystal structure has been determined and the compound has been further characterized by its UV-visible spectrum, NMR spectrum, and other physical tools which are generally consistent with the formulation $\text{UO}_2(\text{FAA})_2\cdot\text{THF}$. The excited-state lifetimes obtained are indicative of the suitability of compound 1 for isotope separations with a CO_2 laser.

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Supplementary Material Available: Positional and thermal parameters (Table S-2) and calculated and observed structure factors (Table S-1) (10 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Iowa State University, Ames, Iowa 50011

Preparations and Spectral Characterizations of the β -(2-Pyridyl)- α -alanine Complexes: Trans-Amino $\text{Co}(\text{D-Pyala})_2^+$, Racemic *all-cis*- $\text{Co}(\text{D-Pyala})(\text{L-Pyala})^+$, and Trans-Carboxylate $\text{Cr}(\text{D-Pyala})_2^+$

STEPHEN R. EBNER and ROBERT J. ANGELICI*

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The trans-amino complex $[\text{Co}(\text{D-Pyala})_2]\text{NO}_3\cdot 1\frac{1}{2}\text{H}_2\text{O}$ was prepared by reaction of $\text{Co}(\text{II})$ with $\text{D-H}_2\text{NCH}(\text{CH}_2\text{C}_5\text{H}_4\text{N})\text{CO}_2^-$, D-Pyala^- , and subsequent oxidation to form the $\text{Co}(\text{III})$ complex. Isomerization of this complex to the more stable trans-carboxylate structure occurred in aqueous solution at room temperature. From the reaction of D,L-Pyala^- with $\text{Co}(\text{III})$, racemic *all-cis*- $[\text{Co}(\text{D-Pyala})(\text{L-Pyala})]\text{NO}_3\cdot\text{H}_2\text{O}$ was isolated. The greater stability of certain $\text{Co}(\text{Pyala})_2^+$ isomers suggests that (1) amino groups avoid being trans to each other and (2) pyridyl groups avoid being trans to each other and prefer to be trans to an amino group. The reaction of $\text{Cr}(\text{III})$ with D-Pyala^- produced a tris(amino acid) complex, Δ -*fac*- $[\text{Cr}(\text{D-Pyala})_3]\cdot\text{H}_2\text{O}$, and a bis complex, trans-carboxylate $[\text{Cr}(\text{D-Pyala})_2]\text{Cl}$. Structural assignments of the $\text{Co}(\text{III})$ and $\text{Cr}(\text{III})$ complexes were based on their infrared, ¹H NMR, visible, ORD, and CD spectra.

Introduction

This study is part of an investigation into the origins of the stereoselectivity observed in the chelation of β -(2-pyridyl)- α -alanine, $^+\text{H}_3\text{NCH}(\text{CH}_2\text{C}_5\text{H}_4\text{N})\text{CO}_2^-$, PyalaH , to transition-metal ions.¹ When the Pyala^- ligands are allowed to have either the D or L configuration, five different geometrical

isomers of the $\text{M}(\text{Pyala})_2^+$ complexes are possible as indicated in Figure 1. Four of these, a-d, are optically active, and the fifth, e, is a meso complex.

Recently, the trans-carboxylate $\text{Co}(\text{D-Pyala})_2^+$ complex (Figure 1a) was isolated and characterized.² It was suggested

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