

Articles

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Lanthanide Complexes of Ionophores. Laser-Excited Luminescence Spectroscopy of Bis(4,5-dimethyl-*N,N,N',N'*-tetrapropyl-3,6-dioxaoctanediamide)europium(III) Tetrafluoroborate

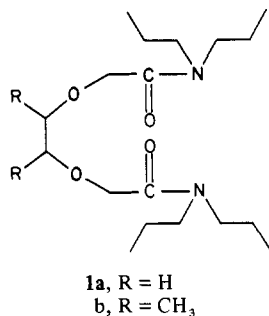
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The title complex has been synthesized by using a novel precursor species designed for the nonaqueous synthesis of lanthanide complexes of weakly coordinating ligands without anion coordination. Europium metal reacts with NOBF_4 or NOPF_6 in anhydrous acetonitrile to form the solvated species $\text{Eu}(\text{CH}_3\text{CN})_x(\text{BF}_4)_3$ or $\text{Eu}(\text{CH}_3\text{CN})_x(\text{PF}_6)_3$. These compounds react with 2 equiv of neutral ionophoric ligands to yield bis(ligand) complexes. The title europium(III) ionophoric complex was characterized by laser excitation and emission spectroscopy showing it to have a structure consistent with that known for an analogous calcium(II) complex. The metal ion site symmetry is D_{2h} or less. Excited-state lifetime measurements demonstrate that in aqueous acetone solution one water molecule is coordinated to the Eu(III) in the complex.

The use of trivalent lanthanide ions, Ln(III), to probe the calcium ion binding sites of macromolecules is well established.¹ Of the various spectroscopic and magnetic properties that render Ln(III) ions useful as probe species, the ability of several ions in this series (most notably Eu(III) and Tb(III)) to luminesce in solution at room temperature is particularly important.²⁻⁴ The present report represents the initial stages of a program designed to exploit laser luminescence techniques developed in this laboratory⁴⁻⁶ to probe metal ion-ionophore complexes. Ionophores are organic sequestering agents that facilitate the transport of metal ions across lipid membranes. Among the molecules classified as ionophores are antibiotics of both the neutral (e.g. valinomycin) and carboxylic (e.g. lasalocid) varieties and synthetic models such as the crown ethers and cryptands. Most ionophores possess a specificity for complexation of particular metal ions owing to steric constraints and the size of the cavity available to accommodate the ion.⁷

An example of a synthetic neutral ionophore that exhibits a high specificity for calcium(II) is a ligand of type 1.⁸ The



structure of $[\text{Ca}(\mathbf{1a})_2]\text{Cl}_2$ has been determined by X-ray crystallography.⁹ The Ca(II) ion is sequestered by two mutually perpendicular, roughly planar, ligands with a total coordination number of 8 (two ether and two carbonyl oxygen atoms from each ligand). The chloride ions are not in the first coordination sphere. Using a synthetic technique developed by us designed to prevent coordination of the central ion by both water and anions, we have synthesized $[\text{Eu}(\mathbf{1b})_2](\text{BF}_4)_3$ using $\text{Eu}(\text{CH}_3\text{CN})_x(\text{BF}_4)_3$ in CH_3CN as a starting material. The latter substance, made by reacting europium metal with NOBF_4 in anhydrous acetonitrile, provides a highly reactive (toward even weakly coordinating ligands) anhydrous reagent that involves an anion not known to coordinate to metals. An analogous compound with PF_6^- as the anion has also been synthesized.

As part of our effort to assess the structural similarities between Ca(II) and Ln(III) ionophore complexes, we report the characterization via laser luminescence and lifetime spectroscopy of $[\text{Eu}(\mathbf{1b})_2](\text{BF}_4)_3$ both in the solid state and in solution.

Experimental Section

Infrared spectra were recorded with a Perkin-Elmer Model 580 grating infrared spectrometer. ¹H NMR spectra were obtained on a Varian A-60A spectrometer employing D₂O or CDCl₃ as solvent (99.8% D, Aldrich Chemical Co.). Emission and excitation spectra and lifetime data were obtained by using a previously described pulsed dye laser system.^{4,10} Single-crystal excitation spectra were obtained by modifying the cell holder so as to allow the crystal to be placed in the laser beam while mounted on a goniometer head. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Materials. Acetonitrile was refluxed over P₂O₅ (24 h) and freshly distilled prior to use. Toluene and methylene chloride were distilled from CaSO₄ and stored over Linde 4-Å molecular sieves. Dipropylamine was freshly distilled prior to use. NOBF_4 and NOPF_6 were obtained from Aldrich Chemical Co. and were stored under dry nitrogen. Eu chips (99.9 REO) were from Sharpe Chemical Co. All other reagents used in the preparation of the ionophore were obtained

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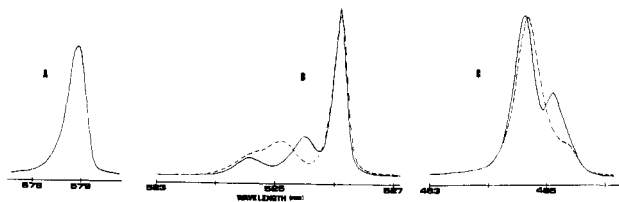


Figure 1. Excitation spectra of $[\text{Eu}(\mathbf{1b})_2](\text{BF}_4)_3$, $\lambda_{\text{em}} = 616 \text{ nm}$, for (A) ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$, (B) ${}^7\text{F}_0 \rightarrow {}^5\text{D}_1$, and (C) ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ transitions: (—) solid; (---) acetone-water solution ($\sim 10:1$).

from Aldrich Chemical Co. and used without further purification.

4,5-Dimethyl-*N,N,N',N'*-tetrapropyl-3,6-dioxaoctanediamide (1b). This ionophore was prepared by the method of Ammann et al.⁸ IR and NMR spectra matched those of Ammann et al.⁸ at each step in the synthesis.

$\text{Eu}(\text{CH}_3\text{CN})_x(\text{Y})_3$, $\text{Y} = \text{BF}_4, \text{PF}_6$. These complexes were prepared by reacting 1 equiv of europium metal with 3 equiv of NOY in acetonitrile and using vacuum and Schlenk techniques. In a typical experiment, 0.50 g of Eu and 1.65 g of NOPF_6 were stirred under N_2 at room temperature for 24 h in 30 mL of acetonitrile. $\text{NO}(\text{g})$ was evolved, and a bright orange solution resulted. The solution was filtered under nitrogen, and solvent was removed to yield an orange, gummy solid. Addition of benzene followed by removal of all solvent under vacuum yielded an orange powder. IR (Nujol/NaCl plates): $\nu(\text{CN})$ 2312, 2342 cm^{-1} (m); $\nu(\text{PF}_6)$ 835 cm^{-1} (s); $\nu(\text{BF}_4)$ $\sim 1050 \text{ cm}^{-1}$. Alternatively, one can use the filtered solution directly in further synthetic steps. The Eu(III) concentration is determined by titration with EDTA using arsenazo indicator.

$\text{Eu}(\mathbf{1b})_2(\text{BF}_4)_3$. Two equivalents of **1b** and 1 equiv of $\text{Eu}(\text{CH}_3\text{CN})_x(\text{BF}_4)_3$ were stirred for 1 h at room temperature in acetonitrile. The solvent was then removed under vacuum, yielding a pale yellow oil. The oil was dissolved in a minimum volume of acetone, and hexane was added until the onset of precipitation. The mixture was diluted tenfold with ethyl acetate and allowed to evaporate slowly in air. White needles resulted after 1–2 weeks. Anal. Calcd for $\text{EuC}_{40}\text{H}_{80}\text{N}_4\text{O}_8\text{B}_3\text{F}_{12}$: C, 41.49; H, 6.92; N, 4.84. Found: C, 41.41; H, 6.87; N, 4.82.

Results and Discussion

The reaction of europium metal with NO^+Y^- ($\text{Y} = \text{BF}_4, \text{PF}_6$) yields $\text{Eu}(\text{CH}_3\text{CN})_x(\text{Y})_3$, a useful precursor to other europium(III) complexes. This complex, analogous to that obtained by Wayland¹¹ using palladium metal, contains only weakly coordinating solvent molecule ligands and "noncoordinating" anions. This complex may prove to be extremely useful in preparing europium complexes of ligands for which Eu(III) has little natural affinity (e.g. sulfur, nitrogen, and phosphorus donor molecules). The presence of anions not known to coordinate directly to metal ions enables whatever neutral ligand is present to achieve maximal coordination.

The coordination of acetonitrile is characterized in the IR spectrum of a complex by an increase in C–N stretching frequency. Two C–N stretching bands are observed for $\text{Eu}(\text{CH}_3\text{CN})_x(\text{Y})_3$ at 2312 and 2342 cm^{-1} compared to 2266 cm^{-1} for free solvent. The fluorine stretching modes of PF_6^- and BF_4^- are very broad and occur at ~ 835 and 1050 cm^{-1} , respectively. These are consistent with uncoordinated anion¹² (although the large peak width makes small shifts difficult to measure).

The excitation spectrum (${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$) of $\text{Eu}(\text{CH}_3\text{CN})_x(\text{BF}_4)_3$ in acetonitrile consists of a broad peak ($\text{fwhm} = 28 \text{ cm}^{-1}$) centered at 17290 cm^{-1} . The excited-state lifetime, τ , is 1.83 ms. Similar results are obtained for the solid complex, the hexafluorophosphate salt, and a nitromethane solution of the complex. The long lifetime is expected, as no O–H or N–H

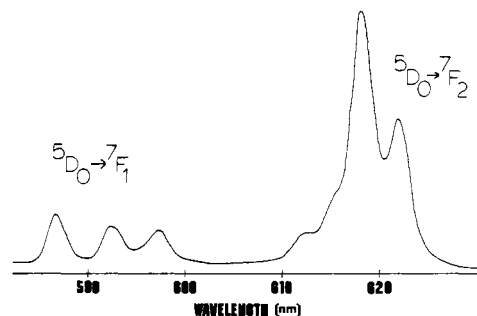


Figure 2. Emission spectrum of $[\text{Eu}(\mathbf{1b})_2](\text{BF}_4)_3$, solid, $\lambda_{\text{ex}} = 578.9 \text{ nm}$.

Table I. Frequencies of $[\text{Eu}(\text{ionophore})_2](\text{BF}_4)_3$ Excitation and Emission Transitions (Solid)

transition	freq, cm^{-1}	transition	freq, cm^{-1}
${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$	17 273	${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$	16 330
${}^7\text{F}_0 \rightarrow {}^5\text{D}_1$	19 060		16 190
	19 031		16 080
	19 007	${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$	14 570
${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$	21 525		14 420
	21 503		14 350
${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$	17 060		14 220
	16 890		
	16 750		

oscillators are coordinated to Eu(III) to provide an efficient pathway for radiationless deexcitation.⁶ The large width of the excitation peak is suggestive of the weakness of the metal–ligand bonding. The ${}^7\text{F}_0 \rightarrow {}^5\text{D}_1$ excitation spectrum consists of two broad peaks at 19065 and 19050 cm^{-1} . Again, the spectra are similar for the solid and for CH_3CN or CH_3NO_2 solutions of the complex, indicating that the inner coordination sphere of the Eu(III) is unperturbed in either solvent.

Laser excitation and emission spectra for the solid complex, $[\text{Eu}(\mathbf{1b})_2](\text{BF}_4)_3$, are shown in Figures 1 and 2, respectively. Spectra obtained on single crystals or on chloroform and acetone solutions of the complex appear identical. The transition frequencies are given in Table I. The measured τ for the complex is 1.56 ms.

The ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$ excitation spectrum consists of a single, Lorentzian peak indicating the presence of a single species since neither level can be split by a ligand field (this result is confirmed by obtaining the identical spectrum from single crystals of the complex).

The ${}^7\text{F}_0 \rightarrow {}^5\text{D}_1$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transitions each consist of three peaks. This finding requires that the symmetry about the Eu(III) ion be less than tetragonal (D_{2h} or lower symmetry).¹³

Further insight into the coordination at the metal center was gained by dissolving the complex in acetone and adding H_2O or D_2O . The spectrum of the complex dissolved in anhydrous acetone is identical with that of the solid. When water is added, changes in the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_1$, ${}^5\text{D}_2$ excitation spectra are observed (Figure 1). This implies that the inner coordination sphere has been altered. Measurement of excited-state lifetimes separately in the presence of H_2O and D_2O allowed the determination of the number of water molecules that coordinate to the Eu(III) in complex.⁶ The limiting value, obtained at high mole fractions of H_2O or D_2O , is 0.90 ± 0.4 water molecules ($\tau_{\text{H}_2\text{O}}^{-1} = 1.40 \text{ ms}^{-1}$, $\tau_{\text{D}_2\text{O}}^{-1} = 0.54 \text{ ms}^{-1}$). The fact that the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$ spectrum does not change as water is added and that one can only get one water molecule to coordinate suggests that the Eu(III) coordination sphere has not been drastically altered but that the coordination number has simply

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

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

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

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

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

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

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

Introduction

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

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

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

Experimental Section

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

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