3724 *Inorg. Chem.* **1992,** *31,* 3724–3727

Monomeric Uranyl Alkoxide and Amide Complexes

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Received March 26, 1992

Reaction of $UO_2Cl_2(Ph_3PO)_2$ with 2 equiv of KO-*t*-Bu or $NaN(SiMe_3)_2$ in THF results in the formation of $UO_2(O\text{-}t\text{-}Bu)_2(Ph_3PO)_2$ (**1**) or $UO_2[N(SiMe_3)_2]_2(Ph_3PO)_2$ (**2**); the yields are 84 (**1**) and 77% (**2**). The infrared spectra of these compounds exhibit strong U–O stretching bands at 861 (**1**) and 901 (**2**) cm^{-1}; these features shift to 822 and 854 cm^{-1}, respectively, upon ^{18}O substitution. The solid-state structure of **1** reveals that the alkoxide and phosphine oxide ligands are arranged in a cis geometry in the equatorial plane of the uranyl ion (U–O(1)(oxo) = 1.789 (5) Å, U–O(2)(oxo) = 1.795 (6) Å, O(1)–U–O(2) = 174.8 (2)°). NMR spectroscopy shows that both cis and trans isomers exist for **1** and **2**. Exchange with free phosphine and equilibration of the isomers occur at 80 °C for **1** and 55 °C for **2**. **1** and **2** luminesce (**1**, λ_{max} 571 nm; **2**, λ_{max} 555 nm); the 77 K excitation and emission spectra of **1** are highly structured, with the dominant vibronic progression assigned to the symmetric O–U–O stretch (excitation, 643 ± 16 cm^{-1}, with ^{18}O substitution 606 ± 10 cm^{-1}; emission, 770 ± 20 cm^{-1}, with ^{18}O substitution 737 ± 7 cm^{-1}).

Introduction

The coordination chemistry of the actinide elements in nonaqueous solvents has often made use of ligands such as amides and alkoxides.[1–6] These groups are strong σ donors and can solubilize the actinide cations in nonpolar media by providing the steric bulk necessary to prevent coordinative polymerization. There are few reported examples of amide or alkoxide complexes of the uranyl (UO_2^{2+}) ion,[7–14] because its low charge and large ionic radius lead to the formation of anionic "ate" species[11,15] or coordinatively unsaturated neutral complexes. Coordinatively unsaturated alkoxide complexes have been found to undergo ligand redistribution,[9,16] resulting in oxo–alkoxide clusters. These complications have led to a dearth of mononuclear species soluble in nonpolar media that are suitable for spectroscopic study or use as reagents in synthesis.

We report here the successful synthesis of monomeric uranyl alkoxides and amides stabilized by the coordination of phosphine oxides. Both spectroscopic and electrochemical data indicate that these six-coordinate uranium(VI) complexes are remarkably electron-rich species.

Experimental Section

General Procedures. All operations were carried out either by employing standard Schlenk techniques or in a helium-filled Vacuum Atmospheres drybox equipped with an MO-40-2 gas purification system. Solvents were purified by distillation from Na/K alloy under a nitrogen atmosphere. Anhydrous uranyl chloride and ^{18}O-labeled uranyl chloride were prepared according to the literature method[17] by reaction of UCl_4 under flowing oxygen at 300–350 °C. This was converted to $UO_2Cl_2(Ph_3PO)_2$ by reaction with triphenylphosphine oxide in anhydrous ethanol.[18] Potassium *tert*-butoxide was purchased (Aldrich) and sublimed prior to use. $NaN(SiMe_3)_2$ was prepared by a modification of the literature method, employing NaH instead of $NaNH_2$.[19]

^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AF-250 NMR spectrometer, with chemical shifts reported in parts per million relative to tetramethylsilane (δ 0.0). Infrared spectra were recorded on a Digilab 5DXB spectrometer as Nujols mulls between KBr plates. Elemental analyses were performed by V. Tashinian, Microanalytical Laboratory, Department of Chemistry, University of California, Berkeley. Cyclic voltammetry was conducted with a platinum working electrode and a silver wire quasi-reference electrode in a cell with anodic and cathodic compartments separated by a finely fritted glass disk. Ferrocene was used as an internal standard. Tetra-*n*-butylammonium tetrafluoroborate (0.1 M in THF) was used as a supporting electrolyte, and the potential was swept at 200 mV/s.

$UO_2(O\text{-}t\text{-}Bu)_2(Ph_3PO)_2$ (1). $UO_2Cl_2(Ph_3PO)_2$ (1.00 g, 1.11 mmol) and KO-*t*-Bu (0.25 g, 2.2 mmol) were slurried together in tetrahydrofuran (40 mL). The solids dissolved rapidly to give a light orange-yellow solution, which was stirred for 1–2 h. The solution was then filtered, and the solvent was removed under vacuum. The residue was extracted with toluene (20 mL), and the toluene solution was filtered again, concentrated to 10 mL, and cooled to −40 °C, producing yellow-orange prisms. A second crop was obtained from the mother liquor by additional concentration. The combined yield was 0.91 g (84%).

IR (Nujol): 3092 vw, 3076 w, 3054 w, 3027 vw, 1965 vw, 1899 vw, 1826 vw, 1778 vw, 1681 vw, 1587 w, 1485 w, 1480 w, 1436 s, 1348 m, 1335 vw, 1309 vw, 1217 m, 1185 s, 1157 vs, 1120 s, 1091 s, 1069 w, 1024 w, 995 m, 975 sh, 956 vs, 861 s, 763 m, 745 m, 724 s, 687 s, 539 s, 509 m cm^{-1}. Anal. Calcd for $UO_6P_2C_{44}H_{48}$: C, 54.3; H, 4.98. Found: C, 54.7; H, 4.96.

$UO_2[N(SiMe_3)_2]_2(Ph_3PO)_2$ (2). This complex was prepared in a manner similar to that employed for compound **1**, from $UO_2Cl_2(Ph_3PO)_2$ (1.00 g, 1.11 mmol) and $NaN(SiMe_3)_2$ (0.40, 2.2 mmol) in

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0020-1669/92/1331-3724$03.00/0

Table I. Crystallographic Parameters for $UO_2(O\text{-}t\text{-}Bu)_2(Ph_2PO)_2$

temp (°C)	25
space group	$P2_1/n$
a (Å)	10.802 (1)
b (Å)	21.758 (5)
c (Å)	18.386 (5)
β (deg)	97.98 (1)
V (Å^3)	4283 (3)
Z	4
chem formula	$UP_2O_6C_{44}H_{48}$
fw	972.89
d_{calcd} (g/cm^3)	1.509
μ (cm^{-1})	37.08
cryst size (mm)	0.18 × 0.25 × 0.28
radiation (λ (Å))	Mo Kα (0.709 26)
no. of reflns for $F_o^2 > 2\sigma(F_o^2)$	4339
I_{min}/I_{max}	0.80
no. of variables	479
R^a	0.035
R^{wa}	0.040
GOF	1.587
g (e^{-2})	1.6 (9) × 10^{-7}

[a] $R = \sum\|F_o| - |F_c\|/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$; $w = 4F^2/\sigma^2(I)$ where $\sigma(I) = \sigma_c(I) + (0.030I)^2$.

tetrahydrofuran (30 mL). The compound was recrystallized from hexane/THF (4:1). The total yield was 0.99 g (77%).

IR (Nujol): 3075 vw, 3055 w, 1963 vw, 1896 vw, 1812 vw, 1770 vw, 1673 vw, 1587 w, 1484 w, 1398 s, 1335 vw, 1310 vw, 1249 sh, 1237 m, 1185 vw, 1163 sh, 1141 vs, 1123 s, 1085 s, 1071 w, 1026 w, 996 w, 936 vs, 901 m, 869 m, 844 s, 776 sh, 752 w, 723 s, 693 s, 662 w, 613 w, 538 s cm^{-1}. Anal. Calcd for $UO_4N_2P_2Si_4C_{48}H_{66}$: C, 50.2; H, 8.51; N, 2.44. Found: C, 50.7; H, 5.76; N, 2.46.

X-ray Crystallography. Compound **1** was crystallized from hot toluene, yielding yellow-orange blocks that were wedged into 0.3-mm glass capillaries, which were then flame-sealed. The capillaries were mounted at room temperature on an Enraf-Nonius CAD-4 automated diffractometer and centered in the beam. Unit cell parameters were determined from a least-squares fit to the setting angles of the unresolved Mo Kα components of 25 reflections with 2θ near 30°. Cell constants and parameters for data collection and refinement are given in Table I.

Data were collected using variable-speed θ–2θ scans; no decay of intensity standards was observed. Systematic absences uniquely identified the space group as $P2_1/n$. The raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization effects. An empirical absorption correction was applied on the basis of the average relative intensity curve of azimuthal scan data. The structure was solved using standard Patterson and Fourier techniques, utilizing the Los Alamos Crystal Structure Codes.[20] Refinements were carried out by using the appropriate neutral-atom scattering factors[21] and a secondary extinction parameter.[22] All non-hydrogen atoms were refined anisotropically. Difference Fourier maps revealed the positions of some hydrogen atoms, but no attempt was made to include these in structure factor calculations. The function minimized was $R_f = \sum w(F_o - F_c)^2$, and weights were calculated as $w = 4F^2/\sigma^2(I)$ where $\sigma(I) = \sigma_c(i) + (0.030I)^2$. Positional and equivalent thermal parameters are given in Table II.

Table II. Atomic Coordinates and Isotropic Equivalent Thermal Parameters for $UO_2(O\text{-}t\text{-}Bu)_2(Ph_3PO)_2$

atom	x	y	z	$B_{eq}{}^a$ (Å^2)
U	−0.00152 (3)	0.13562 (2)	0.22717 (2)	3.29
P(1)	0.2642 (2)	0.0217 (1)	0.2050 (1)	3.8
P(2)	0.1262 (2)	0.2166 (1)	0.0635 (1)	4.4
O(1)	−0.1152 (5)	0.0985 (3)	0.1616 (3)	4.3
O(2)	0.1224 (5)	0.1719 (3)	0.2872 (3)	5.3
O(3)	−0.0598 (6)	0.0849 (3)	0.3164 (3)	5.5
O(4)	−0.1230 (5)	0.2144 (3)	0.2286 (3)	4.8
O(5)	0.1448 (5)	0.0567 (3)	0.2017 (3)	5.1
O(6)	0.0826 (5)	0.1824 (3)	0.1256 (3)	5.0
C(1)	−0.1476 (9)	0.0444 (5)	0.3416 (5)	5.6
C(2)	−0.2633 (10)	0.0803 (6)	0.3563 (6)	8.1
C(3)	−0.0854 (10)	0.0145 (6)	0.4134 (6)	8.4
C(4)	−0.1840 (12)	−0.0065 (6)	0.2832 (6)	8.2
C(5)	−0.1403 (9)	0.2663 (5)	0.2717 (6)	6.3
C(6)	−0.1589 (25)	0.2496 (7)	0.3437 (9)	23.0
C(7)	−0.0401 (13)	0.3110 (6)	0.2681 (9)	13.4
C(8)	−0.2591 (15)	0.2996 (8)	0.2338 (12)	16.6
C(9)	0.3194 (8)	−0.0107 (4)	0.2929 (4)	4.2
C(10)	0.4369 (10)	−0.0379 (5)	0.3080 (6)	6.7
C(11)	0.4789 (12)	−0.0609 (6)	0.3790 (6)	7.7
C(12)	0.4019 (13)	−0.0574 (6)	0.4331 (6)	7.9
C(13)	0.2873 (13)	−0.0309 (7)	0.4190 (6)	8.9
C(14)	0.2422 (9)	−0.0047 (5)	0.3477 (5)	6.6
C(15)	0.2429 (7)	−0.0367 (5)	0.1358 (5)	4.3
C(16)	0.2828 (9)	−0.0978 (5)	0.1465 (6)	6.0
C(17)	0.2699 (9)	−0.1378 (6)	0.0850 (6)	6.9
C(18)	0.2130 (11)	−0.1174 (6)	0.0167 (6)	7.3
C(19)	0.1708 (11)	−0.0574 (6)	0.0071 (6)	7.2
C(20)	0.1853 (9)	−0.0162 (5)	0.0652 (5)	5.7
C(21)	0.3888 (7)	0.0697 (4)	0.1830 (4)	3.7
C(22)	0.3950 (8)	0.1296 (5)	0.2098 (5)	4.5
C(23)	0.4976 (9)	0.1680 (5)	0.1980 (6)	5.9
C(24)	0.5905 (8)	0.1451 (5)	0.1601 (6)	5.7
C(25)	0.5820 (8)	0.0845 (5)	0.1328 (5)	5.5
C(26)	0.4815 (8)	0.0459 (5)	0.1431 (5)	4.9
C(27)	−0.0003 (10)	0.2611 (5)	0.0163 (5)	5.5
C(28)	−0.1703 (9)	0.2673 (5)	0.0497 (5)	6.0
C(29)	−0.2069 (12)	0.3036 (6)	0.0147 (7)	8.8
C(30)	−0.1960 (15)	0.3316 (8)	−0.0531 (8)	10.2
C(31)	−0.0870 (17)	0.3260 (7)	−0.0856 (7)	10.9
C(32)	0.0128 (12)	0.2893 (7)	−0.0516 (6)	8.9
C(33)	0.2532 (9)	0.2681 (5)	0.0950 (6)	5.5
C(34)	0.3278 (10)	0.2925 (5)	0.0456 (7)	7.6
C(35)	0.4246 (12)	0.3344 (6)	0.0782 (11)	10.2
C(36)	0.4389 (15)	0.3489 (6)	0.1543 (12)	10.6
C(37)	0.3652 (13)	0.3237 (7)	0.1988 (9)	9.2
C(38)	0.2680 (10)	0.2825 (6)	0.1712 (6)	6.6
C(39)	0.1802 (10)	0.1649 (5)	−0.0030 (5)	5.3
C(40)	0.0937 (10)	0.1405 (5)	−0.0585 (5)	6.8
C(41)	0.1336 (12)	0.0945 (6)	−0.1052 (6)	7.8
C(42)	0.2568 (14)	0.0763 (6)	−0.0959 (6)	8.3
C(43)	0.3412 (11)	0.1003 (6)	−0.0399 (6)	7.8
C(44)	0.3049 (9)	0.1457 (5)	0.0082 (5)	5.7

[a] $B_{eq} = 100(U_{11} + U_{22} + U_{33})/3$.

Absorption Spectroscopy. All solvents were dried and degassed by standard methods.[23,24] Absorption spectra were recorded with a Cary 17 spectrophotometer. Spectra were obtained for solutions prepared on a high-vacuum line in a cell consisting of a 10-mL Pyrex bulb, a 1 cm path length quartz cell, and a Teflon vacuum valve.

Electronic Emission and Excitation Spectroscopy. Electronic emission and excitation spectra were measured using a Perkin-Elmer MPF-66 fluorescence spectrophotometer. Spectra recorded at ambient temperatures and 77 K were obtained for solutions that were prepared on a high-vacuum line in a quartz NMR tube attached to a Teflon vacuum valve. Solvent was bulb-to-bulb distilled into the tube containing the compound from the appropriate solvent storage flask. For the 77 K emission measurements, the NMR tubes were held in a liquid-nitrogen-filled quartz finger dewar.

Emission Lifetime Measurements. Emission lifetime measurements were made with a Nd:YAG pulsed laser system (355-nm excitation).[25] Solutions were prepared by the procedures described above. Solid samples were placed in NMR tubes, which were then evacuated and flame-sealed. All emission intensity decays exhibited first-order kinetics over at least 3 half-lives. For the measurements at 77 K, the NMR tubes were held in a liquid-nitrogen-filled quartz finger dewar. The laser was operated at low power to minimize local sample heating.

Results and Discussion

Synthesis and Characterization. Reaction of $UO_2Cl_2(Ph_3PO)_2$ with 2 equiv of potassium *tert*-butoxide or sodium bis(trimeth-

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ylsilyl)amide in tetrahydrofuran results in the formation of the bis(alkoxide) (**1**) or bis(amide) (**2**) complex (eq 1: yields of 84%

$$UO_2Cl_2(Ph_3PO)_2 + 2MX \rightarrow \underset{\substack{\mathbf{1},\ MX = KO\text{-}t\text{-}Bu \\ \mathbf{2},\ MX = NaN(SiMe_3)_2}}{UO_2X_2(Ph_3PO)_2} + 2MCl \tag{1}$$

(**1**) and 77% (**2**)). The yellow-orange complexes are readily soluble in THF and are slightly soluble in aromatic hydrocarbons. The infrared spectra of the compounds reveal strong ν_3(U–O) stretching bands at 861 (**1**) and 901 (**2**) cm^{-1}; these features shift to 822 and 854 cm^{-1}, respectively, in the spectra of the ^{18}O-labeled uranyl compounds. These frequencies are lower than typically found for uranyl complexes (915–940 cm^{-1}),[26] suggesting that the alkoxide and amide ligands increase the basicity of the metal center. The complexity of the spectra of **1** and **2** in the 1000–1200-cm^{-1} region precludes firm identification of the ligand geometry in the equatorial plane.

NMR spectroscopy reveals that both cis and trans isomers of **1** are obtained in the reaction. The ^{1}H NMR spectrum at room temperature possesses *tert*-butoxide signals at δ 2.01 and 1.96 in a ratio of approximately 3:2, in addition to aryl multiplets at δ 7.75 and 7.00. Considering the ionic character inherent in the bonding of high-valent actinide complexes, it is likely that this equilibrium is dictated largely by steric factors. The ^{31}P{^{1}H} spectrum shows triphenylphosphine oxide resonances at δ 42.0 and 40.8; the complexes that give rise to these signals do not exchange with added phosphine oxide on the NMR time scale at room temperature. When the temperature is raised to 80 °C, the signals coalesce, and the phosphorus spectrum shows exchange with free ligand. Coalescence of the proton signals for the *t*-Bu groups cannot be accurately judged due to the appearance of additional decomposition peaks. In contrast, freshly prepared samples of **2** consist of predominantly one isomer, with a single amide resonance at δ 0.57 and aryl multiplets at δ 8.11 and 7.01. The ^{31}P{^{1}H} spectrum shows no exchange with added phosphine oxide at room temperature, with a single signal at δ 43.5. Warming the sample to 55 °C induces exchange between coordinated and free phosphine oxide. This exchange permits partial equilibration to a second isomer; cooling the sample to room temperature reveals a second amide resonance at δ 0.43 and a second phosphorus signal at δ 41.6. Prolonged heating of both **1** and **2** results in their decomposition.

The stability of **1** and **2** toward electrochemical reduction is indicative of the electron-rich nature of the uranyl group in these compounds. In 1 M perchloric acid solution, the uranyl ion exhibits a reversible one-electron reduction at a potential of +0.17 V vs SHE.[27] Compounds **1** and **2**, however, do not display an analogous metal-based reduction. Cyclic voltammograms of these complexes show identical reversible reduction waves at –3.0 V vs $FeCp_2^+/FeCp_2$; these waves are attributed to reduction of triphenylphosphine oxide by comparison with the observed reduction potential of the free ligand.

Structure of $UO_2(O\text{-}t\text{-}Bu)_2(Ph_3PO)_2$. An X-ray structure determination was undertaken on a crystal that proved to be the cis isomer of the *tert*-butoxide derivative, **1**. The solid-state structure of **1** consists of monomeric units in which the uranium atom is coordinated in a pseudooctahedral fashion by six oxygen atoms (Figure 1). Selected bond distances and angles are given in Tables III and IV. The oxo groups of the uranyl core lie trans to one another, with O(1)–U–O(2) = 174.8 (2)°. The U–O(oxo) distances are virtually identical at 1.789 (5) and 1.795 (6) Å for O(1) and O(2), respectively. These bonds are slightly longer than the 1.75–1.76-Å U–O distances commonly found in six-coordinate uranyl complexes,[28–31] consistent with the lower values of ν_3(U–O) modes extracted from the infrared spectra. The alkoxide and phosphine oxide ligands are arranged in a cis geometry in the equatorial plane of the uranyl ion, with O(3)–U–O(4) = 98.9 (2)° and O(5)–U–O(6) = 81.7 (2)°. The cis disposition of four monodentate ligands in the equatorial plane has no precedent in the structural chemistry of the uranyl ion.[32] Even the triphenylphosphine oxide chlorine complex from which

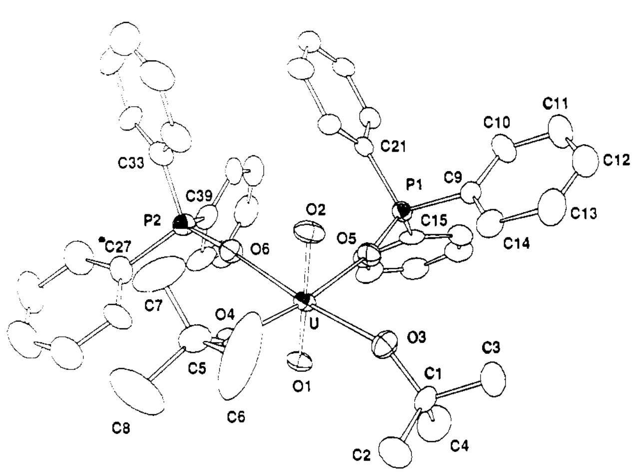

Figure 1. ORTEP drawing of $UO_2(O\text{-}t\text{-}Bu)_2(Ph_3PO)_2$ with the atomic numbering scheme. Thermal ellipsoids are at the 30% probability level.

Table III. Selected Bond Distances (Å) for $UO_2(O\text{-}t\text{-}Bu)_2(Ph_3PO)_2$

U–O(1)	1.789 (5)	U–O(2)	1.795 (6)
U–O(3)	2.143 (6)	U–O(4)	2.162 (6)
U–O(5)	2.398 (6)	U–O(6)	2.414 (5)
O(3)–C(1)	1.42 (1)	O(4)–C(5)	1.41 (1)
C(1)–C(2)	1.53 (1)	C(5)–C(6)	1.41 (2)
C(1)–C(3)	1.54 (1)	C(5)–C(7)	1.46 (1)
C(1)–C(4)	1.55 (1)	C(5)–C(8)	1.55 (2)
O(5)–P(1)	1.504 (6)	O(6)–P(2)	1.494 (6)
P(1)–C(9)	1.788 (8)	P(2)–C(27)	1.80 (1)
P(1)–C(15)	1.790 (9)	P(2)–C(33)	1.80 (1)
P(1)–C(21)	1.793 (9)	P(2)–C(39)	1.82 (1)

Table IV. Selected Interatomic Angles (deg) for $UO_2(O\text{-}t\text{-}Bu)_2(Ph_3PO)_2$

U(1)–U–O(2)	174.8 (2)	O(1)–U–O(3)	92.0 (2)
O(1)–U–O(4)	90.4 (2)	O(1)–U–O(5)	88.7 (2)
O(1)–U–O(6)	88.1 (2)	O(2)–U–O(3)	91.8 (3)
O(2)–U–O(4)	92.6 (3)	O(2)–U–O(5)	87.6 (2)
O(2)–U–O(6)	87.7 (2)	O(3)–U–O(4)	98.9 (2)
O(3)–U–O(5)	91.1 (2)	O(3)–U–O(6)	172.8 (2)
O(4)–U–O(5)	170.0 (2)	O(4)–U–O(6)	88.3 (2)
O(5)–U–O(6)	81.7 (2)		
O–O(3)–C(1)	148.3 (6)	U–O(4)–C(5)	140.6 (6)
O(3)–C(1)–C(2)	109.8 (9)	O(3)–C(1)–C(3)	108.1 (8)
O(3)–C(1)–C(4)	109.5 (8)	O(4)–C(5)–C(6)	111.5 (10)
O(4)–C(5)–C(7)	110.5 (8)	O(4)–C(5)–C(8)	110.6 (7)
U–O(5)–P(1)	162.5 (4)	U–O(6)–P(2)	174.3 (4)
O(5)–P(1)–C(9)	110.8 (4)	O(5)–P(1)–C(15)	110.7 (4)
O(5)–P(1)–C(21)	112.7 (4)	C(9)–P(1)–C(15)	110.7 (5)
C(9)–P(1)–C(21)	105.5 (4)	C(15)–P(1)–C(21)	106.3 (4)
O(6)–P(2)–C(27)	109.8 (4)	O(6)–P(2)–C(33)	111.8 (4)
O(6)–P(2)–C(39)	111.7 (4)	C(27)–P(2)–C(33)	108.2 (5)
C(27)–P(2)–C(39)	107.7 (5)	C(33)–P(2)–C(39)	107.4 (5)

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these species are prepared is reported to possess a trans geometry in the solid state.[30]

The uranium–phosphine oxide distances (U–O(5) = 2.398 (6) Å and U–O(6) = 2.414 (5) Å) are also somewhat longer than the corresponding U–O distance of 2.300 (8) Å in $UO_2Cl_2(Ph_3PO)_2$. The U–O(alkoxide) distances (U–O(3) = 2.143 (6) Å and U–O(4) = 2.162 (6) Å) lie within the range of uranium(VI)–terminal alkoxide bond lengths in other complexes.[3,16] While the U–O–P units in the monomer are nearly linear (U–O(5)–P(1) = 162.5 (4)° and U–O(6)–P(2) = 174.3 (4)°, the angles about the alkoxide oxygen atoms (U–O(3)–C(1) = 148.3 (6)° and U–O(4)–C(5) = 140.6 (6)°) are smaller than those generally found in uranium alkoxides.[3,4,16,33]

Electronic Spectra. The absorption spectrum of **1** in 2-MeTHF or benzene is red-shifted ~50 nm from that of aqueous UO_2^{2+},[34–36] thereby indicating that orbital interactions involving the equatorial ligands and UO_2^{2+} enhance electron density at the metal center, decreasing the HOMO–LUMO gap.[37] In contrast to **1**, **2** possesses a broad, featureless absorption spectrum.

Solid samples of **1** and **2** luminesce. The luminescences are red-shifted from those observed for similar UO_2^{2+} complexes.[35,38,39] and at room temperature they are broad and featureless (**1**, λ_{max} 571 nm; **2**, λ_{max} 555 nm). At 77 K, the luminescence of **1** is intense and highly structured; for **2**, the band remains broad and only weakly structured. The time-resolved emission of solid **2** is at least biexponential, even at low laser power. The luminescence of **1** is monophasic at low laser power with a room-temperature lifetime of 37 ± 2 μs; the lifetime increases to 114 ± 5 μs at 77 K (λ_{em} 575 nm). The emission lifetime of **1** in 2-MeTHF at room temperature is 5.0 ± 0.3 μs; it increases to 30 ± 1 μs in benzene solution.

The 77 K excitation and emission spectra of **1** in a 2-MeTHF glass are shown in Figure 2. Although uranyl spectra are notoriously difficult to interpret,[40] we can assign some of the structure in the spectrum of **1** to progressions in the symmetric O–U–O stretch. The progression of 643 ± 16 cm^{-1} is reduced from the more typical value of ~720 cm^{-1} for the symmetric O–U–O stretch in the excited state.[35] Noticeable shifts are observed in the excitation spectrum of **1** upon ^{18}O substitution ($1(^{18}O)$ = **1***); the vibronic spacing in the spectrum of **1*** is 606 ± 10 cm^{-1}.

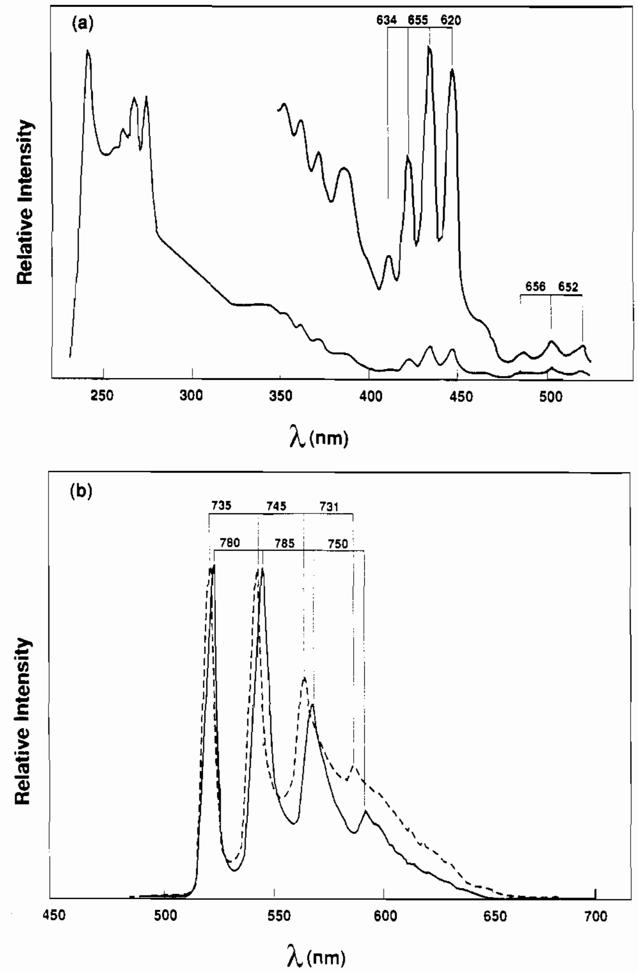

Figure 2. (a) 77 K excitation spectrum of **1** in a 2-MeTHF glass. (b) 77 K emission spectra of **1** (solid line) and **1*** (dashed line) in a 2-MeTHF glass. Vibronic spacings (in cm^{-1}) are indicated.

The emission spectrum of **1** (Figure 2b) shows one dominant vibrational progression of 770 ± 20 cm^{-1}. In the spectrum of **1***, a very slight shift of the 0–0 transition is observed, with a decrease in the spacing of the dominant vibronic progression to 737 ± 7 cm^{-1}. Close examination of the spectra of both **1** and **1*** reveals shoulders on the low-energy side of the dominant system that could be attributable to a second vibronic origin (or to another emissive species).

Acknowledgment. Work at Los Alamos National Laboratory was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Energy Sciences. Research of the California Institute of Technology was supported by the National Science Foundation (Contribution No. 8578 from the Arthur Amos Noyes Laboratory).

Supplementary Material Available: Full tables of crystallographic parameters and anisotropic thermal parameters (3 pages). Ordering information is given on any current masthead page.

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