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Actinide Alkoxide Chemistry

W. G. VAN DER SLUYS and A. P. SATTELBERGER*

Inorganic and Structural Chemistry Group (INC-4), Isotope and Nuclear Chemistry Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

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I. Introduction

Although some of the subject matter in this paper has been incorporated into several earlier reviews[1-3] and books,[4] there has not been a recent comprehensive review devoted entirely to the alkoxide chemistry of the 5f elements. Much new information on the synthesis, physiochemical properties, structures, and reactions of actinide alkoxide complexes has been published in the past decade, and in many instances, these new results have cleared up earlier misinterpretations on the nature of these compounds in the solid state and in solution. Recent developments in X-ray crystallographic characterization of metal alkoxides have shown that the older literature can be unreliable. In this context, the reader is warned that some of the early work on actinide alkoxides referenced herein may not be totally reliable.

Not every actinide element has known and/or well-developed alkoxide chemistry, some for obvious radiolytic considerations (i.e., americium, curium, and beyond). By far, the most research has been done on uranium alkoxides, much of which was pioneered by Henry Gilman and Don Bradley. In this paper we try to point out inconsistencies in previous work in the area, discuss some unresolved issues, and indicate areas where additional research is needed. We also describe some useful applications of actinide alkoxide complexes in the past, present, and possibly the future.

II. Actinide Elements

a. Synthesis

We begin this section by discussing the preparation of alkoxide complexes of thorium, protactinium, neptunium, and plutonium. Alkoxide complexes of the trans-plutonium elements have not been reported.

Thorium. The earliest work on thorium alkoxides was done by Bradley and co-workers. Thorium tetraisopropoxide, $[Th(O\text{-}i\text{-}Pr)_4]_n$, can be prepared[5] in excellent yield from thorium tetrachloride and sodium isopropoxide in refluxing 2-propanol followed by solvent

William G. Van Der Sluys was born in Gloversville, NY, in 1960. He received his B.S. degree from the State University of New York, College at Oneonta (1982), and his M.S. (1986) and Ph.D. (1987) degrees from Indiana University under the direction of Malcolm H. Chisholm. He is currently a postdoctoral fellow (with Alfred P. Sattelberger) at Los Alamos National Laboratory. In Sept 1990, he will join the faculty of the University of Montana as an Assistant Professor in the Chemistry Department. His research interests include both aqueous and nonaqueous actinide chemistry, the synthesis of new gold complexes for the treatment of rheumatoid arthritis, and early-transition-metal fluoroalkoxide complexes.

Alfred P. Sattelberger was born in Passaic, NJ, in 1949. He received his B.A. degree in chemistry from Rutgers University (1970) and his Ph.D. (with Ward B. Schaap) from Indiana University (1975). Following an NSF postdoctoral fellowship at Case Western Reserve University (with John P. Fackler, Jr.), he joined the faculty at The University of Michigan, Ann Arbor, as an Assistant Professor in 1977. In 1984, he moved to Los Alamos and joined the Inorganic and Structural Chemistry Group (INC-4). In 1988, he was promoted to his present position as the Inorganic Chemistry Section Leader of INC-4. He was recently appointed Adjunct Professor of Chemistry at Indiana University. His research interests include synthetic and mechanistic organometallic chemistry, actinide chemistry, multiple metal–metal bonding, technetium chemistry, and organometallic chemical vapor deposition.

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TABLE I. Solution (C_6H_6) Molecular Weight Data for Homoleptic Alkoxide Complexes of the Actinide Elements

compd	*n*	ref	compd	*n*	ref
$[Th(O\text{-}t\text{-}Bu)_4]_n$	3.4	7	$[U(OMe)_5]_n$	3.01	42a
$[Th(OCMe_2Et)_4]_n$	2.8	7	$[U(OEt)_5]_n$	1.90	42a
$[Th(OMeEt_2)_4]_n$	1.8	7	$[U(O\text{-}n\text{-}Pr)_5]_n$	1.95	42a
$[Th(OMe_2\text{-}n\text{-}Pr)_4]_n$	2.6	7	$[U(O\text{-}i\text{-}Pr)_5]_n$	1.93	42a
$[Th(OMe_2\text{-}i\text{-}Pr)_4]_n$	2.3	7	$[U(O\text{-}n\text{-}Bu)_5]_n$	1.94	42a
$[Th(OCEt_3)_4]_n$	1.0	7	$[U(O\text{-}i\text{-}Bu)_5]_n$	1.97	42a
$[Th(OCMeEt\text{-}n\text{-}Pr)_4]_n$	1.7	7	$[U(O\text{-}s\text{-}Bu)_5]_n$	1.85	42a
$[Th(OCMeEt\text{-}i\text{-}Pr)_4]_n$	1.0	7	$[U(O\text{-}t\text{-}Bu)_5]_n$	1.35	42a
$[Th(O\text{-}n\text{-}Bu)_4]_n$	6.44	6a	$[U(O\text{-}n\text{-}Am)_5]_n$	1.94	42a
$[Th(O\text{-}n\text{-}Pen)_4]_n$	6.20	6a	$[U(OMe\{CH_2\}_4)_5]_n$	1.94	42a
$[Th(O\text{-}neo\text{-}Pen)_4]_n$	4.01	6a	$[U(OCH_2CH_2\text{-}i\text{-}Pr)_5]_n$	1.76	42a
$[Th(O\text{-}i\text{-}Pr)_4]_n$	3.8	6b	$[U(OCH_2CHMeEt)_5]_n$	1.82	42a
$[Th(OCHMeEt)_4]_n$	4.2	6b	$[U(OCH_2\text{-}t\text{-}Bu)_5]_n$	1.61	42a
$[Th(OCHEt_2)_4]_n$	4.1	6b	$[U(OCHEt_2)_5]_n$	1.66	42a
$[Pa(OEt)_5]_n$	5.7	16	$[U(OCHMe\text{-}n\text{-}Pr)_5]_n$	1.70	42a
			$[U(OCHMe\text{-}i\text{-}Pr)_5]_n$	1.58	42a
			$[U(OCMe_2Et)_5]_n$	1.26	42a
			$[U(OCMe_2\text{-}n\text{-}Pr)_5]_n$	1.28	42a
			$[U(OCMeEt_2)_5]_n$	1.09	42a
			$[U(OCMeEt\text{-}i\text{-}Pr)_5]_n$	1.01	42a
			$[U(OCEt_3)_5]_n$	1.00	42a

removal and sublimation (200 °C, 0.05 mm) of the white residue (eqs 1 and 2). The compound is very soluble

$$ThCl_4 + 4NaO\text{-}i\text{-}Pr \xrightarrow{HO\text{-}i\text{-}Pr} Th(O\text{-}i\text{-}Pr)_4(HO\text{-}i\text{-}Pr)_x + 4NaCl \quad (1)$$

$$Th(O\text{-}i\text{-}Pr)_4(HO\text{-}i\text{-}Pr)_x \xrightarrow[\text{vacuum}]{\Delta} [Th(O\text{-}i\text{-}Pr)_4]_n + xHO\text{-}i\text{-}Pr \quad (2)$$

in 2-propanol and benzene and is instantly hydrolyed, even by trace amounts of water. Ebullioscopic molecular weight measurements indicate that it is a dimer in 2-propanol and a tetramer in benzene (Table I). Thorium methoxide and thorium ethoxide can be prepared from the isopropoxide by alcohol exchange.[5,6] A number of tertiary alkoxide complexes $Th(OCRR'R'')_4$ have also been prepared via alcoholysis of the isopropoxide. Most of these can be purified by sublimation in vacuo (0.05–0.30 mm) at temperatures in the range 140–200 °C.[7] With few exceptions, the primary, secondary, and tertiary thorium(IV) alkoxide complexes are oligomeric in solution (Table I) and in the solid state. In the presence of excess alcohol, it is likely that all of the coordinatively unsaturated derivatives form alcoholates $Th(OR)_4(HOR)_x$.

A number of heteroleptic and homoleptic (aryl oxide)thorium(IV) complexes have been reported by Lappert and co-workers.[8] The reaction of $ThCl_4$ with excess $[LiO\text{-}2,4,6\text{-}t\text{-}Bu_3C_6H_2(OEt_2)]_2$ in THF provides the white, hydrocarbon-soluble tris(phenoxide) complex $ThCl(O\text{-}2,4,6\text{-}t\text{-}Bu_3C_6H_2)_3$ in 60% yield.[9] Likewise, treatment of thorium tetrachloride with 2 equiv of $[LiO\text{-}2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2(OEt_2)]_2$ provides the cream-colored bis(phenoxide) $[ThCl_2(O\text{-}2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2)_2]_n$ in good yield. Reaction of $ThCl_4$ with excess $LiO\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3$ in THF provides the interesting lithium salt$[Li(THF)_4][Th(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_5]$. The anion is presumably isostructural with trigonal-bipyramidal $[U(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_5]^-$ (vide infra). Lappert et al. have also described the blue homoleptic aryl oxide $Th(O\text{-}2,6\text{-}Ph_2C_6H_3)_4$, obtained from the reaction of the tetrachloride with 4 equiv of $LiO\text{-}2,6\text{-}Ph_2C_6H_3$ in THF.

Marks and co-workers have developed the chemistry of mixed cyclopentadienyl(alkoxide)thorium(IV) complexes.[10–14] Bis(pentamethylcyclopentadienyl) complexes of the type $Cp^*_2Th(OR)_2$ or $Cp^*_2ThX(OR)$ ($Cp^* = \eta^5\text{-}C_5Me_5$; X = alkyl, hydride, halide) are typically prepared by alcoholysis of alkyl complexes, e.g., $Cp^*_2ThMe_2$, or reaction of $Cp^*_2ThCl_2$ with alkali metal alkoxides.[11] Alkoxide complexes of this type have also been obtained[12] via insertion of ketones into thorium–alkyl bonds (eq 3) and via hydrogenation of η^2-acyl complexes (eq 4).

$$Cp^*_2ThCl(CH_3) + (CH_3)_2CO \xrightarrow{PhCH_3} Cp^*_2ThCl[OC(CH_3)_3] \quad (3)$$

$$Cp^*_2ThCl(\eta^2\text{-}OCCH_2\text{-}t\text{-}Bu) + H_2 \xrightarrow{C_6D_6} Cp^*_2ThCl(OCH_2CH_2\text{-}t\text{-}Bu) \quad (4)$$

One novel route to methoxide derivatives involves the interaction of $[Cp^*_2MH_2]_2$ (M = Th, U) with trimethyl phosphite in pentane.[13] This reaction ultimately provides a mixture of $Cp^*_2M(OMe)_2$ and $[Cp^*_2M(OMe)]_2(\mu\text{-}PH)$ (eq 5). A number of intermediates in reaction 5 were detected by ^1H and ^{31}P NMR, and it was determined that cleavage of P–OMe bonds and formation of P–H groups occur during the initial stages of the reaction.

$$5[Cp^*_2ThH_2]_2 + 4P(OMe)_3 \xrightarrow{n\text{-}C_5H_{12}} 2Cp^*_2Th(OMe)_2 + 4[Cp^*_2Th(OMe)]_2(\mu\text{-}PH) + 8H_2 \quad (5)$$

A tris(cyclopentadienyl)(alkoxide)thorium(IV) complex, $(C_5H_5)_3ThOCH_2CF_3$ (eq 6), was prepared via alcoholysis of $Cp_3Th(alkyl)$ compounds.[14] No reaction was observed upon treatment of the same alkyls with 2-methyl-2-propanol. Alkoxide formation has also been observed in the reactions of the mono(pentamethylcyclopentadienyl) tris(benzyl) complex $Cp^*Th(CH_2Ph)_3$ with formaldehyde (eq 7) and alcohols.[15]

$$Cp_3Th\text{-}n\text{-}Bu + HOCH_2CF_3 \xrightarrow{n\text{-}C_5H_{12}} Cp_3ThOCH_2CF_3 + C_4H_{10} \quad (6)$$

$$Cp^*Th(CH_2Ph)_3 + H_2CO \xrightarrow{C_6D_6} Cp^*Th(OCH_2CH_2Ph)_3 \quad (7)$$

Protactinium. Only one alkoxide complex of this rare element has been described in the literature. The reaction of $PaCl_5$ with NaOEt in EtOH, followed by filtration and solvent removal, provides a benzene-soluble, pale yellow material formulated as $Pa(OEt)_5$ on the basis of a Pa elemental analysis and comparison of its infrared spectrum with those of $Ta(OEt)_5$ and $U(OEt)_5$.[16] This complex did not sublime up 250 °C in vacuo and decomposed above 300 °C. The molecular aggregation of $Pa(OEt)_5$ in benzene is reported as 5.7.

Neptunium. The preparation of brown $Np(OR)_4$ (R = Me, Et) by the reaction of $NpCl_4$ and 4 equiv of LiOR in the appropriate alcohol has been reported by Samulski and Karraker.[17] The methoxide is insoluble in common organic solvents, while the ethoxide is slightly soluble in ethanol and very soluble in carbon tetrachloride from which it can also be recrystallized. Attempts to sublime $Np(OEt)_4$ in a good vacuum (10^{-3}–10^{-4} mm) resulted in decomposition at ca. 200 °C. Molecular weight measurements have not been made on $Np(OEt)_4$, but it is probably safe to assume that this complex is oligomeric in solution. Oxidation of $Np(OEt)_4$ with bromine succeeded in producing only mixtures of the bromoethoxyneptunium(IV) compounds, $NpBr_x(OEt)_{4-x}$ ($x = 1, 2$). A green solid, formulated as the neptunium(V) complex $NpBr(OEt)_4$, was obtained when bromine *and* sodium ethoxide were added to a CCl_4 solution of $Np(OEt)_4$. Reaction of isolated $NpBr(OEt)_4$ with NaOEt in THF, a solvent where the Np(V) complex has appreciable solubility, causes a rapid color change from green to brown, indicative of reduction of Np(V) to Np(IV). On the basis of their results, the authors concluded that $Np(OR)_5$ compounds are much less stable than analogous $U(OR)_5$ complexes (vide infra) and suggested that neptunium(VI) alkoxides $Np(OR)_6$ may not be isolable. However, because these statements are based solely on work with primary alkoxide derivatives, it may be premature to generalize the findings to all types of alkoxide ligands. It is our view that the preparation of secondary and tertiary neptunium(IV), -(V), and -(VI) alkoxide complexes in aprotic solvents merits further study.

Neptunyl complexes of the type $NpO_2(OR)_x$ ($x = 1, 2$) have not been reported, but they may be isolable by synthetic methodologies similar to those employed in uranium chemistry (vide infra).

Plutonium. Because plutonium does not form a stable tetrachloride, Bradley and co-workers used the plutonium(IV) salt $[C_5H_6N]_2PuCl_6$ to develop the chemistry of plutonium(IV) alkoxides. Reaction of the pyridinium salt with excess ammonia in benzene/2-propanol followed by filtration and solvent removal, produces a mixture of chloride-free $Pu(O\text{-}i\text{-}Pr)_4$ and $Pu(O\text{-}i\text{-}Pr)_4(py)$. Recrystallization of this mixture from minimal hot 2-propanol provides emerald green $Pu(O\text{-}i\text{-}Pr)_4(HO\text{-}i\text{-}Pr)$.[18] Under vacuum (0.05 mm), alcohol is lost and pure $Pu(O\text{-}i\text{-}Pr)_4$ sublimes at 220 °C. Alcoholysis with a large excess of 2-methyl-2-propanol/benzene azeotrope provides $Pu(O\text{-}t\text{-}Bu)_4$, which is also volatile (112 °C, 0.05 mm). Molecular weight measurements have not been performed on either compound.

In recent work at Los Alamos, Zwick et al. have prepared (eq 8) the plutonium(III) complex $Pu(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_3$ by alcoholysis of $Pu[N(SiMe_3)_2]_3$.[19] We assume that this complex is monomeric like its uranium(III) analogue.

$$Pu[N(SiMe_3)_2]_3 + 3HO\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3 \xrightarrow{\text{hexane}} Pu(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_3 + 3HN(SiMe_3)_2 \quad (8)$$

No higher valent plutonium alkoxide complexes (nor attempts to prepare them) have been reported. The same is true of plutonyl alkoxide complexes, i.e., $PuO_2(OR)_2$.

Uranium. Because of the rather large number of alkoxide complexes, we have subdivided this section by oxidation state starting with the chemistry of uranium(III).

Uranium(III). The first reported attempt to prepare a homoleptic uranium(III) alkoxide complex was described in 1982.[20] Moody and co-workers reacted $UCl_3(THF)_x$ (prepared in situ from UCl_4 and NaH) with 3 equiv of sodium phenoxide in THF but were unable to isolate the desired product, viz., $U(OPh)_3$, from the resultant light red-brown reaction solution. Recently, Van Der Sluys and Sattelberger[21] reinvestigated the preparation of uranium(III) alkoxides and found that alcoholysis of the tris(silylamide) complex $U[N(SiMe_3)_2]_3$[22] with 2,6-disubstituted phenols $HO\text{-}2,6\text{-}R_2C_6H_3$ ($R = i\text{-Bu}$) provides the tris(phenoxides) in ≥50% yield (eq 9). These compounds were characterized by elemental analyses, ^1H NMR, mass spectroscopy ($R = t\text{-Bu}$; $x = 1$), and X-ray crystallography ($R = i\text{-Pr}$; $x = 2$). They react readily with Lewis bases (L) such as THF, $OPPh_3$, and CN-*t*-Bu in benzene to form 1:1 adducts $LU(OAr)_3$ which can be isolated from solution. For the sterically nondemanding CN-*t*-Bu ligand a 2:1 adduct was observed by proton NMR.[21b] Attempts to carry out reactions similar to eq 9 using aliphatic alcohols such as *t*-BuOH lead to oxidation of the metal and isolation of U(IV) products, some of which will be discussed in the next section.

$$U[N(SiMe_3)_2]_3 + 3HO\text{-}2,6\text{-}R_2C_6H_3 \xrightarrow{C_6H_{14}} [U(O\text{-}2,6\text{-}R_2C_6H_3)_3]_x + 3HN(SiMe_3)_2 \quad (9)$$

Lappert et al.[8,23] have reported the mixed cyclopentadienyl(aryl oxide)uranium(III) complexes $Cp''_2U(O\text{-}2,6\text{-}R_2C_6H_3)$ ($Cp'' = C_5H_3(SiMe_3)_2$; $R = Ph, i\text{-Pr}$), obtained via reaction of LiOAr with $[Cp''_2U(\mu\text{-Cl})]_2$ in hexane or sodium amalgam reduction of $Cp''_2UCl(O\text{-}2,6\text{-}R_2C_6H_3)$ in hexane. Both the dark green diphenyl phenoxide and dark blue diisopropyl phenoxide complexes readily form 1:1 adducts with THF.

Uranium(IV). Homoleptic uranium(IV) alkoxide complexes have been prepared via a number of synthetic routes. Gilman and co-workers reported[24] that the reaction of LiOR reagents (R = Me, Et) with UCl_4 in the appropriate alcohol provides green $U(OR)_4$ compounds, a result subsequently confirmed by Bradley et al.,[25] who also prepared $U(O\text{-}n\text{-}Pr)_4$ and $U(O\text{-}i\text{-}Pr)_4$ by a similar procedure in dimethylcellosolve. The latter authors also noted that the ethoxide, *n*-propoxide, and isopropoxide derivatives could be sublimed in vacuo (e.g., $U(O\text{-}i\text{-}Pr)_4$ sublimes at 160 °C, 0.01 mm). The reaction of excess alcohol with $U(NEt_2)_4$ was also reported by Gilman et al. as an excellent route to the tetramethoxide and tetraethoxide complexes. A novel electrochemical synthesis of $U(OEt)_4$ has been described by Pires de Matos and co-workers.[26] In an electrolysis run at 0 °C in ethanol with lithium chloride as the electrolyte, uranium metal as the anode, and platinum as the cathode, applied current in the range of 10–30 mA leads to evolution of hydrogen at the cathode and eventual precipitation of uranium(IV) ethoxide from the green electrolysis solution.

From the available molecular weight data (Table I) it appears that most of the primary, secondary, and tertiary uranium(IV) alkoxide complexes, like their thorium(IV) analogues, are oligomeric in solution (Table I).

Andersen has isolated the *monomeric* volatile alkoxides $U(OCH\text{-}t\text{-}Bu_2)_4$[27] (eq 10), $U[OC(CF_3)_3]_4(THF)_2$, $U[OCH(CF_3)_2]_4(THF)_2$, and $U[OCH(CF_3)_2]_4(TMEDA)$[28] (eq 11). Magnetic susceptibility data on these

$$UCl_4 + 4LiOCH\text{-}t\text{-}Bu_2 \xrightarrow{Et_2O} U(OCH\text{-}t\text{-}Bu_2)_4 + 4LiCl \quad (10)$$

$$UCl_4 + 4NaOR_f \xrightarrow{THF} U(OR_f)_4(THF)_2 \quad (11)$$

$$R_f = C(CF_3)_3,\ CH(CF_3)_2$$

monomers follow Curie–Weiss behavior over a wide temperature range and yield magnetic moments in the range 2.7–3.0 μ_B, consistent with uranium(IV). The pink di-*tert*-butylmethoxide complex reacts with 1 equiv of methyllithium in hexane to provide the purple addition compound $MeLi\cdot U(OCH\text{-}t\text{-}Bu_2)_4$.[27]

One reaction that has caused some controversy in the uranium(IV) alkoxide literature is that between "$U(NH_2)_4$" (prepared in situ from KNH_2 and UCl_4 in liquid ammonia) and 2-methyl-2-propanol (eq 12). Gil-

$$\text{"}U(NH_2)_4\text{"} + 4t\text{-}BuOH \rightarrow \text{"}U(O\text{-}t\text{-}Bu)_4\text{"} + 4NH_3 \tag{12}$$

man and co-workers claimed[24] that this reaction gave green hydrocarbon-soluble $U(O\text{-}t\text{-}Bu)_4$ in unspecified yield, while Bradley et al.[25] claimed that the reaction actually provides the hydrocarbon-soluble gray-brown uranium(V) complex $UO(O\text{-}t\text{-}Bu)_3\cdot HO\text{-}t\text{-}Bu$. Characterization of $U(O\text{-}t\text{-}Bu)_4$ in Gilman's laboratory was based on a uranium analysis; characterization of $UO(O\text{-}t\text{-}Bu)_3\cdot HO\text{-}t\text{-}Bu$ in Bradley's laboratory was based on a uranium analysis and an oxidation state determination.

A recent reinvestigation of reaction 12 by Cotton, Marler, and Schwotzer[29] led to the isolation and structural characterization of the green potassium salt $KU_2(O\text{-}t\text{-}Bu)_9$. These authors noted that the latter product was obtained in reasonable yield and purity only under rigorously dry and anaerobic conditions and when the temperature was kept below −10 °C throughout the course of the reaction. It would appear that the green products obtained in the Gilman and Cotton laboratories are identical. Prior to Cotton's report, Perego and co-workers isolated several $[U(C_3H_5)_2(OR)(\mu\text{-}OR)]_2$ and $U(OR)_4$ compounds,[30] *including* what was reported to be Gilman's green $U(O\text{-}t\text{-}Bu)_4$, via alcoholysis of $U(allyl)_4$ in diethyl ether at −30 °C. An X-ray structural investigation of this form of "$U(O\text{-}t\text{-}Bu)_4$" has not been reported.

In their studies of the chemistry of $KU_2(O\text{-}t\text{-}Bu)_9$, Cotton and co-workers[29] noted that hexane solutions of $KU_2(O\text{-}t\text{-}Bu)_9$ slowly (weeks) and "spontaneously" turn dark brown and that dichroic (black and light brown) crystals of the mixed-valence uranium(IV)–uranium(V) alkoxide $U_2(O\text{-}t\text{-}Bu)_9$ are obtained from the solution. On the basis of the colors reported by both groups, this complex could be "$UO(O\text{-}t\text{-}Bu)_3\cdot HO\text{-}t\text{-}Bu$".[25] A second green product was obtained, in unspecified yield, by Cotton, Marler, and Schwotzer during early work with the "$U(NH_2)_4$" plus t-BuOH reaction.[31] This complex, $U_3O(O\text{-}t\text{-}Bu)_{10}$, is reminiscent of molybdenum(IV) and tungsten(IV) complexes of similar stoichiometry, but there are important structural differences (vide infra).

Reaction of $[(Me_3Si)_2N]_2\overline{UN(SiMe_3)SiMe_2CH_2}$ with ≥4.5 equiv of t-BuOH in toluene (eq 13) results in complete substitution of amides for alkoxides, but the resulting green compound is not $U(O\text{-}t\text{-}Bu)_4$. The

$$[(Me_3Si)_2N]_2\overline{UN(SiMe_3)SiMe_2CH_2} + \geq 4.5t\text{-}BuOH \xrightarrow[25\ °C]{toluene} 0.5U_2(O\text{-}t\text{-}Bu)_8(HO\text{-}t\text{-}Bu) + 3(Me_3Si)_2NH \tag{13}$$

$$[U(NEt_2)_4]_2 + \geq 9.0t\text{-}BuOH \xrightarrow[25\ °C]{toluene} U_2(O\text{-}t\text{-}Bu)_8(HO\text{-}t\text{-}Bu) + 8Et_2NH \tag{14}$$

hydrocarbon-soluble product has been formulated as $U_2(O\text{-}t\text{-}Bu)_8(HO\text{-}t\text{-}Bu)$ on the basis of elemental analyses, proton NMR, IR, and UV–vis spectroscopies and chemical studies. The same compound can be prepared in an analogous fashion from $[U(NEt_2)_4]_2$ (eq 14).[32] The infrared spectrum of $U_2(O\text{-}t\text{-}Bu)_8(HO\text{-}t\text{-}Bu)$ is similar to, but not identical with, that reported by Perego et al.[30] for their sample of "$U(O\text{-}t\text{-}Bu)_4$".

$U_2(O\text{-}t\text{-}Bu)_8(HO\text{-}t\text{-}Bu)$ reacts readily with potassium *tert*-butoxide or potassium hydride in toluene or hexane to generate $KU_2(O\text{-}t\text{-}Bu)_9$ (eqs 15 and 16). Upon ex-

$$U_2(O\text{-}t\text{-}Bu)_8(HO\text{-}t\text{-}Bu) + KO\text{-}t\text{-}Bu \xrightarrow{toluene} KU_2(O\text{-}t\text{-}Bu)_9 + HO\text{-}t\text{-}Bu \tag{15}$$

$$U_2(O\text{-}t\text{-}Bu)_8(HO\text{-}t\text{-}Bu) + KH \xrightarrow{hexane} KU_2(O\text{-}t\text{-}Bu)_9 + 0.5H_2 \tag{16}$$

posure to dry air, green solutions of $U_2(O\text{-}t\text{-}Bu)_8(HO\text{-}t\text{-}Bu)$ rapidly turn orange-red. The UV–vis spectrum of the latter solution is essentially identical with that reported by Cotton and co-workers for a sample of the crystallographically characterized mixed-valence compound $U_2(O\text{-}t\text{-}Bu)_9$.[29] These results, coupled with the fact that the UV–vis spectra of $U_2(O\text{-}t\text{-}Bu)_8(HO\text{-}t\text{-}Bu)$ and $KU_2(O\text{-}t\text{-}Bu)_9$ are very similar, suggest that the compounds have similar structures. It has also been noted that when toluene solutions of $U_2(O\text{-}t\text{-}Bu)_8(HO\text{-}t\text{-}Bu)$ are treated with oxygen-free H_2O, $U_3O(O\text{-}t\text{-}Bu)_{10}$ is formed (eq 17). The 3:3:3:1 pattern of alkoxide

$$3U_2(O\text{-}t\text{-}Bu)_8(HO\text{-}t\text{-}Bu) + 2H_2O \xrightarrow{toluene} 2U_3O(O\text{-}t\text{-}Bu)_{10} + 7HO\text{-}t\text{-}Bu \tag{17}$$

groups in the ^1H NMR spectrum of $U_3O(O\text{-}t\text{-}Bu)_{10}$ is consistent with the solid-state C_{3v} structure (see section II.b), which reveals one triply bridging, three doubly bridging, and six terminal alkoxide ligands.[30,32]

$KU_2(O\text{-}t\text{-}Bu)_9$ can also be prepared in good yield directly from UCl_4 by the addition of 4.5 equiv of KO-t-Bu in THF (eq 18). This method is more convenient

$$UCl_4 + 4.5KO\text{-}t\text{-}Bu \xrightarrow{THF} 0.5KU_2(O\text{-}t\text{-}Bu)_9 + 4KCl \tag{18}$$

than the original liquid ammonia synthesis. $KU_2(O\text{-}t\text{-}Bu)_9$ prepared by this method is thermally stable at room temperature under *rigorously* dry and anaerobic conditions. When they are exposed to dry air, solutions of $KU_2(O\text{-}t\text{-}Bu)_9$ turn orange-red much more slowly (days) than do solutions of $U_2(O\text{-}t\text{-}Bu)_8(HO\text{-}t\text{-}Bu)$. This is consistent with Gilman's observations on the air sensitivity of "$U(O\text{-}t\text{-}Bu)_4$".[24] $KU_2(O\text{-}t\text{-}Bu)_9$, like $U_2(O\text{-}t\text{-}Bu)_8(HO\text{-}t\text{-}Bu)$, also reacts with H_2O to produce $U_3O(O\text{-}t\text{-}Bu)_{10}$.[31,32]

Lappert and co-workers[8] have synthesized a number of uranium(IV) analogues of the thorium 2,6-disubstituted phenoxide complexes described above, e.g., yellow $UCl(O\text{-}2,4,6\text{-}t\text{-}Bu_3C_6H_2)_3$ from UCl_4 plus excess LiOAr.

If the same reaction is carried out with the less sterically demanding 2,6-diisopropylphenoxide ligand, a complex of formula $[Li(THF)_4][U(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_5]$ can be isolated.[8] The same authors also prepared yellow-brown $U(NEt_2)_2(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_2$ and brown $U(NEt_2)(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_3$ from the reaction of $[U(NEt_2)_4]_2$ with 2 equiv and excess phenol, respectively.[9] None of the desired homoleptic $U(OAr)_4$ was obtained in the reaction with excess phenol. Dormond, E Bouadili, and Moïse[33] have prepared mixed (amide)(alkoxide)actinide(IV) complexes of the type $M(O\text{-}t\text{-}Bu)[N(SiMe_3)_2]_3$ and $M(O\text{-}2,6\text{-}Me_2C_6H_3)[N(SiMe_3)_2]_3$ (M = Th, U) from the reactions of $[(Me_3Si)_2N]_2\overline{UN(SiMe_3)SiMe_2CH_2}$[34] with the appropriate alcohol. They noted that further addition of either alcohol resulted in the production of other, uncharacterized products. Recently, it has been shown that the addition of 4 equiv of $HO\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3$ to $[(Me_3Si)_2N]_2\overline{UN(SiMe_3)SiMe_2CH_2}$ in refluxing toluene provides mononuclear $U(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_4$.[35] The synthesis of the first homoleptic uranium(IV) aryl oxide $U(O\text{-}2,6\text{-}Ph_2C_6H_3)_4$ (from UCl_4 and LiOAr in THF) was reported in 1987.[8]

Phosphine adducts of the type $M(OPh)_4(dmpe)_2$ (M = U, Th; dmpe = 1,2-bis(dimethylphosphino)ethane) complexes have been synthesized by Andersen, Edwards, and Zalkin[36] by two independent routes (eqs 19 and 20).

$$UCl_4 + 4LiOPh \xrightarrow[\text{toluene}]{\text{dmpe}} U(OPh)_4(dmpe)_2 + 4LiCl \qquad (19)$$

$$UMe_4(dmpe)_2 + 4HOPh \xrightarrow{\text{toluene}} U(OPh)_4(dmpe)_2 + 4CH_4 \qquad (20)$$

Alcoholysis of $Cp_2U(NEt_2)_2$ with ROH or ArOH provides mixed cyclopentadienyl alkoxide compounds. The yields of the $Cp_2U(OR)_2$ complexes are dependent upon the bulk of the alkoxide ligands.[37] With small alkoxide ligands (OEt, O-*i*-Pr), ligand redistribution follows metathesis and $Cp_3U(OR)$ compounds are isolated; HO-*t*-Bu provides a mixture of $Cp_2U(O\text{-}t\text{-}Bu)_2$ and $Cp_3U(O\text{-}t\text{-}Bu)$. With the sterically demanding 2,6-di-*tert*-butylphenol, only one amide group is replaced, giving $Cp_2U(NEt_2)(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)$; smaller 2,6-disubstituted phenols give $Cp_2U(OAr)_2$ complexes. $Cp_3U(O\text{-}n\text{-}Bu)$ has been obtained in a "one-pot" synthesis from UCl_4, NaO-*n*-Bu, and 3 equiv of NaCp or from UCl_3 and NaCp in THF.[38] In the latter reaction, the *n*-butoxide ligand results from ring opening of THF. The reaction of sodium fluoroalkoxides with Cp_3UCl cleanly provides the Cp_3UOR_f (R_f = C_6F_5, CH_2CF_3, $C(CF_3)_2CH_3$) compounds.[39] Marks and co-workers have prepared a number of $Cp^*_2UX(OR)$ (X = alkyl, hydride, halide), $Cp^*_2U(OR)_2$, and $Cp^*U(OR)_3$ complexes by routes analogous to those described above for thorium(IV).[10,11,37]

Uranium(V). Homoleptic $U(OR)_5$ compounds have been prepared by several techniques. Gilman[40,41] and Bradley[42] originally prepared these compounds via the routes shown in eqs 21–26. Of these, reactions 21 and 25 are the most important. Molar quantities of the brown pentaethoxide are easily synthesized via eq 21, and other $U(OR)_5$ compounds can be prepared from $U(OEt)_5$ by alcohol exchange (eq 25). These reactions proceed via $U(OEt)_{5-x}(OR)_x$ intermediates. Eller and Vergamini isolated the mixed uranium(V) alkoxide species $U[OC(CF_3)_3]_4(OEt)(HOEt)$ and $U[OCH(CF_3)_2]_4(OEt)(HOEt)$ from the direct room-temperature reactions of $U(OEt)_5$ with perfluoro-*tert*-butyl alcohol and hexafluoro-2-propanol, respectively.[43] Uranium pentaethoxide has also been obtained from the reaction of β-UF_5 with NaOEt in ethanol.[44] This method is less convenient than reaction 21 because β-UF_5 is not commercially available. An unusual route to $U(OEt)_5$ is photolysis of either $[pyH]_2UOCl_5$ or $UO_2Cl_2(py)_2$ in ethanol.[45] Mechanistic details of these photochemical transformations have not been established with certainty.

$$U(OEt)_4 + 0.5Br_2 \xrightarrow{\text{EtOH}} \text{“}U(OEt)_4Br\text{”} \xrightarrow{\text{EtOH, NaOEt}} U(OEt)_5 + NaBr \qquad (21)$$

$$UCl_5 + 5NaOEt \xrightarrow{\text{EtOH}} U(OEt)_5 + 5NaCl \qquad (22)$$

$$UCl_5 + 5EtOH + 5NH_3 \xrightarrow{\text{Et}_2\text{O}} U(OEt)_5 + 5NH_4Cl \qquad (23)$$

$$5U(OR)_4 + O_2 \xrightarrow{\text{ROH}} 4U(OR)_5 + UO_2 \qquad (24)$$

$$U(OR)_5 + 5R'OH \xrightarrow{\Delta} U(OR')_5 + 5ROH \qquad (25)$$

$$[pyH]_2UOCl_5 + ROH + NH_3 \xrightarrow{\text{C}_6\text{H}_6} UO(OR)_3 \xrightarrow{\Delta} U(OR)_5 \qquad (26)$$

The homoleptic $U(OR)_5$ compounds are distillable liquids (R = Et, *n*-Pr, *i*-Bu, *s*-Bu, *n*-Am) or sublimable solids (R = Me, *i*-Pr, *t*-Bu).[46] Ebullioscopic molecular weight determinations by Bradley and Chatterjee indicate that, with the exception of the pentamethoxide (possibly a trimer), the $U(OR)_5$ compounds, where R = Et, *n*-Pr, *n*-Bu, and *n*-Am, are dinuclear (Table I). The magnetic susceptibility of liquid $U_2(OEt)_{10}$ has been measured at 25 °C with the result $\mu_{eff} = 1.12\ \mu_B$. This low value may be a consequence of magnetic exchange between $5f^1$ metal centers, but variable-temperature susceptibility measurements are needed to confirm this. Low-temperature (−65 °C) ^1H[44] and ^{13}C NMR[47] data obtained for the pentaethoxide (fluxional above ca. −40 °C) in several solvents suggest that the molecule adopts an edge-sharing bioctahedral structure, the same geometry observed in the crystal structure of $U_2(O\text{-}i\text{-}Pr)_{10}$ (vide infra). The absorption spectrum (2800–300 nm) of $U_2(OEt)_{10}$ in CCl_4 has been recorded and the seven observed transitions assigned on the basis of a $5f^1$ ground-state electronic configuration.[29,48]

Several uranium(V) aryl oxide complexes have been described in the literature. Bagnall and co-workers reported that a 10:1 molar ratio of phenol to $U(OEt)_5$ in benzene (reflux, 9 h) provides the mixed alkoxide $U(OPh)_4(OEt)$.[49] In contrast, Eller and Vergamini report that stirring a 12:1 mixture of phenol and the pentaethoxide in pentane at room temperature for 2.5 h gives the fully substituted product $U(OPh)_5$ in quantitative yield.[43a] A mixed chloro phenoxide dimethylformamide complex, $U(OPh)_4Cl(DMF)_2$ (described as a viscous red-brown paste), has also been reported.[49]

The reactions of $U_2(OEt)_{10}$ with sodium, calcium, and aluminum ethoxides have been reported by Gilman and co-workers.[50] These give compounds of stoichiometry $NaU(OEt)_6$, $Ca[U(OEt)_6]_2$, and $Al[U(OEt)_6]_3$. $NaU(OR)_6$ compounds are useful intermediates in the preparation of uranium(VI) alkoxides.

Oxo(alkoxide)uranium(V) complexes of the type $UO(OR)_3$ have been mentioned briefly in the literature, but are not well characterized by today's standards. As already noted, Bradley and co-workers suggested, on the basis of a uranium analysis and a valency determination, that $UO(O\text{-}t\text{-}Bu)_3 \cdot t\text{-}BuOH$ was the gray-brown product they obtained from the reaction of "$U(NH_2)_4$" and HO-*t*-Bu in hexane.[25] Somewhat earlier, Bradley indicated that the brown products obtained upon treatment of $[pyH]_2UOCl_5$ with ammonia in ethanol or 2-propanol were $UO(OR)_3$ complexes.[51] These compounds definitely merit spectroscopic investigation and structural characterization.

Uranium pentaethoxide reacts with a variety of potentially bidentate ligands to produce complexes of formula $U(OEt)_{5-x}L_x$, e.g., L = acetylacetone,[52] carboxylate,[53] and thiocarboxylate.[54] The ethoxy groups may be exchanged for *tert*-butoxy groups without displacing the bidentate ligands. Reaction of $M(OEt)_5$ (M = Pa, U) with topolone (2-hydroxycyclohepta-2,4,6-trien-1-one) provides the $M(trop)_5$ complexes.[55]

Reaction of $M(OR)_n$ compounds (M = U,[50,56] $n = 5$; M = Th,[57] $n = 4$) with halogenating agents, such as HCl[50] and acetyl chloride,[56,57] effects chloride for alkoxide exchange. The esters produced in the acetyl chloride reactions may act as ligands, as in the $U(OR)Cl_4(MeCO_2R)$ (R = Et, *i*-Pr) complexes.

Uranium(VI). Monomeric homoleptic uranium(VI) alkoxides were first reported by Gilman in 1956.[58] A number of routes were investigated, but the synthetic method of choice for $U(OEt)_6$ (43% yield based on $U_2(OEt)_{10}$) is indicated in eq 27. Alcohol exchange

$$2NaU(OEt)_6 + (PhCO)_2O_2 \xrightarrow{EtOH} 2U(OEt)_6 + 2NaO_2CPh \quad (27)$$

reactions were then used to prepare the hexamethoxide, hexa-*n*-propoxide, and hexaisopropoxide from $U(OEt)_6$. Somewhat later, Bradley's group reported $U(O\text{-}t\text{-}Bu)_6$ and $U(O\text{-}s\text{-}Bu)_6$. These were obtained from the thermal decomposition of the red solids obtained after workup of the reactions of $UO_2(OMe)_2 \cdot HOMe$ (vide infra) with HO-*t*-Bu and HO-*s*-Bu, respectively.[59] The ethoxide and *n*-propoxide are distillable liquids, while the remaining compounds are sublimable solids. With the exception of sterically crowded $U(O\text{-}t\text{-}Bu)_6$, the hexaalkoxides are exceedingly moisture sensitive, ultimately decomposing to UO_3. As might be expected, uranium(VI) alkoxides are very good oxidizing agents. The hexaethoxide is easily reduced to $U_2(OEt)_{10}$ by ethyl mercaptan, diethylamine, or $U(OEt)_4$ (eq 28).[58]

$$U(OEt)_4 + U(OEt)_6 \xrightarrow{C_6H_{14}} U_2(OEt)_{10} \quad (28)$$

Marks and co-workers[60] have refined another of Gilman's routes to $U(OEt)_6$ and applied it to the synthesis of $U(OMe)_6$ (eqs 29 and 30). This two-step procedure provides the desired purple-red product in higher overall yield (51% based on UCl_4) and with less effort than the procedure described by Gilman.[58]

$$UCl_4 + 6LiOMe \xrightarrow{MeOH} \text{“}Li_2U(OMe)_6\text{”} + 4LiCl \quad (29)$$

$$\text{“}Li_2U(OMe)_6\text{”} + Pb(O_2CMe)_4 \xrightarrow{THF} U(OMe)_6 + 2LiO_2CMe + Pb(O_2CMe)_2 \quad (30)$$

Marks' group[61] has also described two additional routes to $U(OMe)_6$ starting with commercially available uranium hexafluoride (eqs 31 and 32). The first of

$$UF_6 + 6Me_3Si(OMe) \xrightarrow[-78\ °C]{CH_2Cl_2} U(OMe)_6 + 6Me_3SiF \quad (31)$$

$$UF_6 + 6NaOMe \xrightarrow[-78\ °C]{CH_2Cl_2} U(OMe)_6 + 6NaF \quad (32)$$

these (eq 31) provides the hexamethoxide in 72% yield versus 42% for reaction 32. Jacob has described a variation of reaction 31 using $Si(OMe)_4$ and has also observed $U(OMe)F_5$ at low temperature.[62a] Reaction of appropriate stoichiometric quantities of either $Me_3Si(OMe)$ or $U(OMe)_6$ with UF_6 produces a series of compounds of formula $U(OMe)_nF_{6-n}$ (n = 1–5).[61] $U(OMe)F_5$ can also be prepared from UF_6 and methanol at very low temperatures.[62b] Compound thermal stability progressively decreases as the number of fluorine atoms per $U(OMe)_nF_{6-n}$ molecule increases. Characterization by ^1H and ^{19}F NMR indicates that all of the $U(OMe)_nF_{6-n}$ species adopt a monomeric, six-coordinate geometry and that they undergo rapid *inter*molecular ligand exchange in solution.

There are several reports on the preparation of uranyl alkoxides and some controversy surrounding the exact composition of these compounds. Albers et al. reported the first uranyl alkoxide complex in 1952. They claimed ruby red, hydrocarbon-soluble uranyl diisoamyloxide from the reaction of uranyl chloride, UO_2Cl_2, and sodium isoamyloxide in isoamyl alcohol.[63] Five years later, Gilman and co-workers claimed yellow-brown $UO_2(OEt)_2 \cdot 3HOEt$ and red $UO_2(O\text{-}t\text{-}Bu)_2 \cdot 4HO\text{-}t\text{-}Bu$.[64] The former was prepared from uranyl chloride and sodium ethoxide in ethanol, while the latter was obtained by passage of dry dioxygen through a petroleum ether solution of "$U(O\text{-}t\text{-}Bu)_4$" (undoubtedly $KU_2(O\text{-}t\text{-}Bu)_9$) until the solution turned red. Bradley and coworkers challenged both of these reports in 1959.[59] Repeating Alber's work, they obtained a red solution from which a brown alcoholate $UO_2(O\text{-}i\text{-}Am)_2 \cdot HO\text{-}i\text{-}Am$ was isolated. Alcohol-free $UO_2(O\text{-}i\text{-}Am)_2$ was obtained by heating the solvate at 75 °C under 0.05-mm vacuum. The color of this material was not mentioned, but its insolubility in benzene was noted. Bradley's group could not reproduce the reported preparation of $UO_2(OEt)_2 \cdot 3HOEt$ and stated that, in their hands, *no* uranyl ethoxide was obtained.[59] A light brown uranyl ethoxide with a composition near $UO_2(OEt)_2 \cdot 2HOEt$ was obtained by treating an ethanolic solution of UO_2Cl_2 with LiOEt or by ethanolysis of uranyl methoxide. The latter, as bright yellow $UO_2(OMe)_2 \cdot HOMe$, was obtained from uranyl chloride and lithium methoxide in methanol. Bradley also reported when uranyl methoxide was treated with secondary or tertiary alcohols, alcohol interchange was accompanied by ligand redistribution; e.g., they obtained a red crystalline solid formulated as $UO(O\text{-}t\text{-}Bu)_4 \cdot HO\text{-}t\text{-}Bu$ when uranyl methoxide was treated with 2-methyl-2-propanol/benzene azeotrope. When $UO(O\text{-}t\text{-}Bu)_4 \cdot HO\text{-}t\text{-}Bu$ was heated at 110 °C and 0.05 mm in a molecular still, a small amount of U(O-

t-Bu)$_6$ was obtained.[59] It should be noted that all of the preceding stoichiometries were based solely on uranium elemental analyses. In 1979, Andersen described the preparation of $UO_2[OC(CF_3)_3]_2(THF)_2$ via reaction of $UO_2(NO_3)_2(THF)_2$ and sodium perfluoro-2-methyl-2-propanol in THF.[65] Proton and ^{19}F NMR and IR were reported. The asymmetric UO_2 stretching vibration was assigned as a band located at 928 cm^{-1}, and an all-trans geometry was proposed, analogous to that found in $UO_2Cl_2(OPPh_3)_2$.[66] Recently, Burns and Sattelberger have investigated the reactions of uranyl chloride with potassium *tert*-butoxide in THF.[67] In the presence of triphenylphosphine oxide, uranyl chloride reacts with KO-*t*-Bu according to eq 33. Orange $UO_2(O\text{-}t\text{-}Bu)_2(OPPh_3)_2$ was obtained in 70% yield. The complex was characterized by ^1H NMR, IR (918 cm^{-1}, UO_2 asymmetric stretch), and X-ray crystallography (vide infra). When the same reaction was carried out without $OPPh_3$, the anticipated product, viz., $UO_2(O\text{-}t\text{-}Bu)_2(THF)_2$, was not obtained. Red-orange, diamagnetic $UO_2(O\text{-}t\text{-}Bu)_2[OU(O\text{-}t\text{-}Bu)_4]_2$ was isolated in ca. 30% yield.[67a] The authors proposed that $UO_2(O\text{-}t\text{-}Bu)_2(THF)_2$ is the initial product of the reaction and that it subsequently decomposes to UO_3 and $UO(O\text{-}t\text{-}Bu)_4$. The latter then reacts with the primary product to give the observed trimeric species.

$$UO_2Cl_2 + 2KO\text{-}t\text{-}Bu + 2OPPh_3 \xrightarrow{THF} UO_2(O\text{-}t\text{-}Bu)_2(OPPh_3)_2 + 2KCl \quad (33)$$

Uranyl phenoxides of stoichiometry $UO_2(OAr)_2$ (Ar = Ph, *o*-$NO_2C_6H_5$, *o*-ClC_6H_5) have been reported by Malhotra et al. from the reaction of either uranyl chloride or uranyl acetate with an excess of phenol in refluxing xylene.[68] $UO_2(OPh)_2$ forms Lewis base adducts, $UO_2(OPh)_2L$, with nitrogenous bases such as pyridine and bipyridine and the salts $M_2[UO_2(OPh)_4]$ (M = Na, K) upon treatment with MOPh in refluxing xylene. Burns and Sattelberger have prepared and structurally characterized a THF-soluble phenoxide, $[Na(THF)_3]_2[UO_2(O\text{-}2,6\text{-}Me_2C_6H_3)_4]$, by reacting $\{[Na(THF)_3]_2\}\{UO_2[N(SiMe_3)_2]_4\}$ with HOAr in THF.[67b]

An unusual mixed-valence oxo phenoxide complex was obtained by Moody and co-workers[20] from the reaction of "$U(OPh)_3$" and dry dioxygen in THF. Red-brown, tetranuclear $[U(OPh)_3(THF)]_2[UO_2(THF)_2]_2(\mu\text{-}OPh)_4(\mu_3\text{-}O)_2$, whose structure is discussed below, is one of two known uranium mixed-valence alkoxide complexes (see $U_2(O\text{-}t\text{-}Bu)_9$ above).

Air-stable uranyl monoalkoxide complexes supported by monothiocarbamate ligands have been prepared by Perry according to eq 34 and characterized by IR, X-ray photoelectron spectroscopy, and X-ray crystallography.[69]

$$UO_2Cl_2 + 2[R'_2NH_2](R'_2NCOS) \xrightarrow{HOR} [R'_2NH_2][UO_2(OSCNR'_2)_2(OR)] + HCl + R'_2NH_2Cl \ (R = Et, n\text{-}Pr) \quad (34)$$

b. Molecular Structures

As with homoleptic alkoxide compounds of the lanthanide and early transition elements, the nuclearity, *n*, of homoleptic actinide(IV) and actinide(V) complexes in benzene solution is dependent on the size of the alkoxide ligand. Table I summarizes the available molecular weight data for a number of thorium(IV), protactinum(V), uranium(IV), and uranium(V) alkoxide complexes. Of these, only $[U(O\text{-}i\text{-}Pr)_5]_2$ has been characterized by single-crystal X-ray diffraction. In fact, there are no examples of crystallographically characterized actinide alkoxide complexes other than those of uranium. A number of representative examples are described below. In some uranium alkoxide publications, NMR spectroscopy has been used as a structural tool and these are indicated where appropriate. Other spectroscopic techniques are noted where they contribute to the discussion.

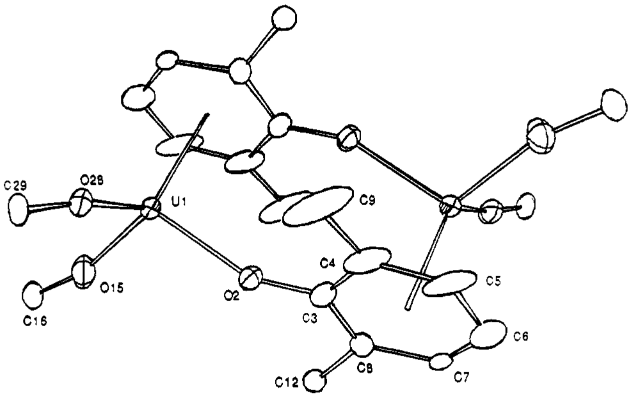


Figure 1. ORTEP view of $[U(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_3]_2$. The figure shows the dimeric unit with the π-arene bridging interaction. For clarity, the isopropyl methyl groups of the bridging phenoxides have been omitted and only the ipso carbons of the terminal phenoxides are shown (reprinted from ref 21a; copyright 1988 American Chemical Society).

Uranium(III). Only one homoleptic uranium(III) alkoxide complex, viz., $[U(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_3]_2$, has been structurally characterized.[21] An ORTEP view of the molecule is shown in Figure 1. In the solid state, this molecule adopts an unprecedented structure, that of a bis(π-arene)-bridged centrosymmetric dimer. The U–U separation is 5.34 (1) Å, and the average U–C distance is 2.92 (2) Å. The Nujol mull infrared spectrum of $[U(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_3]_2$ shows two aromatic C=C stretching vibrations at 1588 cm^{-1} (terminal OAr) and 1553 cm^{-1} (bridging OAr) in an approximately 2:1 ratio. In contrast, the ^1H NMR spectrum of $[U(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_3]_2$, recorded in benzene-$d_6$, shows only one type of phenoxide ligand, which suggests that the complex either is mononuclear in solution or is undergoing a rapid fluxional process that equilibrates all of the aryl oxide ligands.

Uranium(IV). $K[U_2(O\text{-}t\text{-}Bu)_9]$, the product of the reaction between "$U(NH_2)_4$" and HO-*t*-Bu isolated by Cotton et al.,[29] has been structurally characterized (Figure 2). The anion adopts a confacial bioctahedral geometry with a U–U distance of 3.631 (2) Å. The potassium ion in this complex is four-coordinate, ligated by two bridging and two terminal alkoxide oxygen atoms. The one-electron oxidation product of the potassium salt, $U_2(O\text{-}t\text{-}Bu)_9$, was also structurally characterized by the Cotton group, and an ORTEP drawing is shown in Figure 3.[29] This mixed-valence U(IV)–U(V) dimer has a U–U separation slightly shorter (3.549 (1) Å) than that found in $K[U_2(O\text{-}t\text{-}Bu)_9]$. UV–vis spectroscopy was particularly useful in assigning the mixed-valence formulation. According to the authors, the spectrum of $U_2(O\text{-}t\text{-}Bu)_9$ roughly approximates the sum of the $K[U_2(O\text{-}t\text{-}Bu)_9]$ and $U_2(O\text{-}i\text{-}Pr)_{10}$ spectra (Figure 4).

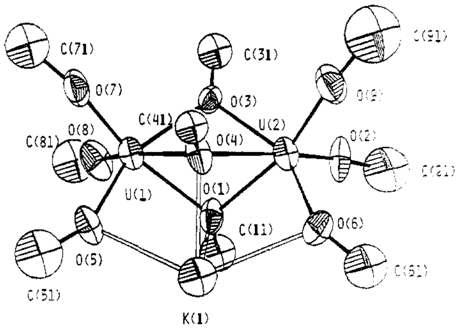


Figure 2. ORTEP view of $KU_2(O\text{-}t\text{-}Bu)_9$ (reprinted from ref 29; copyright 1979 The Chemical Society).

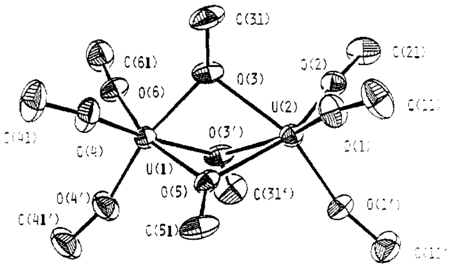


Figure 3. ORTEP view of $U_2(O\text{-}t\text{-}Bu)_9$ (reprinted from ref 29; copyright 1984 American Chemical Society).

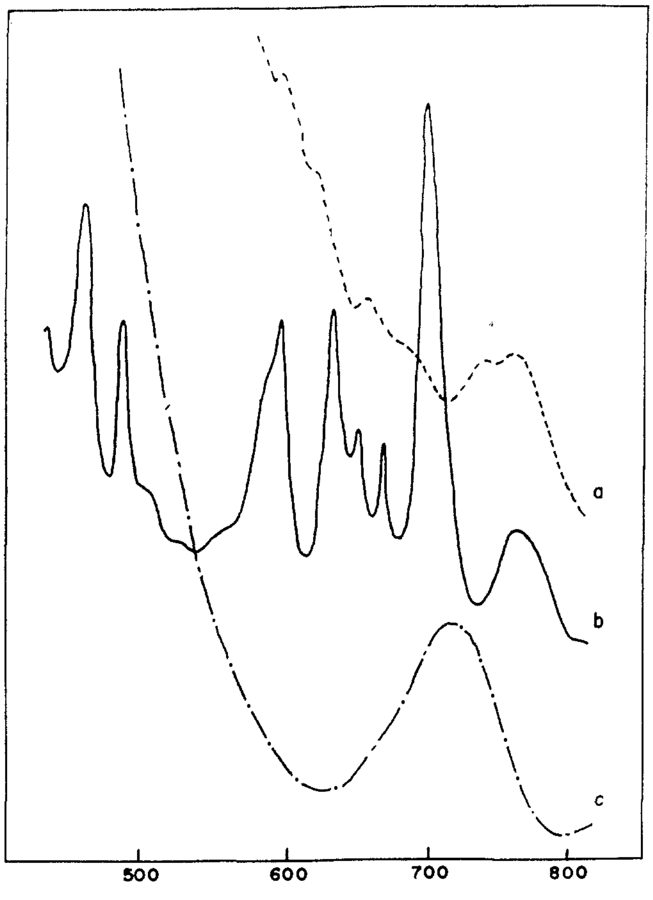


Figure 4. Electronic absorption spectra of (a) $U_2(O\text{-}t\text{-}Bu)_9$, (b) $KU_2(O\text{-}t\text{-}Bu)_9$, and (c) $U_2(O\text{-}i\text{-}Pr)_{10}$ (reprinted from ref 29; copyright 1984 American Chemical Society).

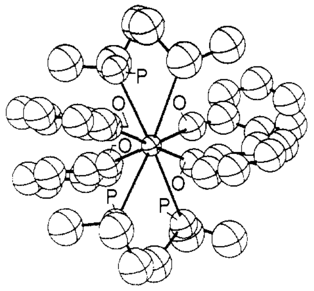


Figure 5. ORTEP view of $U(OPh)_4(dmpe)_2$ (reprinted from ref 36; copyright 1981 American Chemical Society).

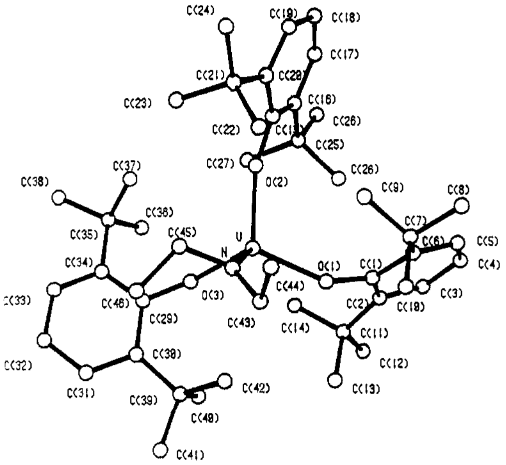


Figure 6. ORTEP view of $U(NEt_2)(O\text{-}2{,}6\text{-}t\text{-}Bu_2C_6H_3)_3$ (reprinted from ref 9; copyright 1983 The Chemical Society).

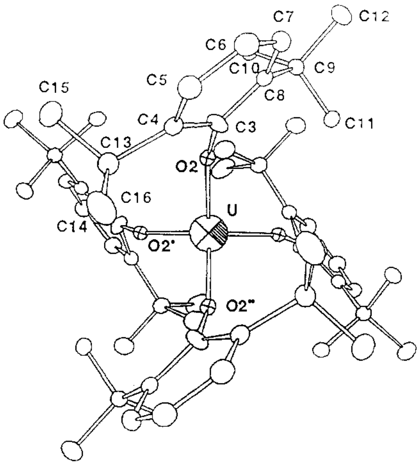


Figure 7. ORTEP view of $U(O\text{-}2{,}6\text{-}t\text{-}Bu_2C_6H_3)_4$ looking down the molecular S_4 axis of symmetry (reprinted from ref 35a; copyright 1989 Pergamon).

There are several examples of crystallographically characterized uranium(IV) phenoxide complexes. Andersen et al. used the chelating phosphine, 1,2-bis(dimethylphosphino)ethane (dmpe), to prevent oligomerization of $U(OPh)_4$. An ORTEP view of $U(OPh)_4(dmpe)_2$ is shown in Figure 5.[36] The uranium atom is coordinated to eight donor atoms in a dodecahedral coordination environment, with each phosphorous atom trans to an oxygen. Another example of a monomeric uranium(IV) phenoxide complex is $U(NEt_2)(O\text{-}2{,}6\text{-}t\text{-}Bu_2C_6H_3)_3$.[9] Here the uranium atom is ligated by three phenoxides and one amide in a roughly tetrahedral arrangement. The amido nitrogen atom is in an essentially planar environment (U–N = 2.162 (5) Å), and the U–O–C angles average 154° (Figure 6). The coordination geometry about uranium in $[Li(THF)_4][U(O\text{-}2{,}6\text{-}i\text{-}Pr_2C_6H_3)_5]$ is that of a trigonal bipyramid.[8] The U–O distances range from 2.15 (1) to 2.10 (1) Å. A final example is $U(O\text{-}2{,}6\text{-}t\text{-}Bu_2C_6H_3)_4$, the only structurally characterized neutral $U(OAr)_4$ complex.[35] The molecule

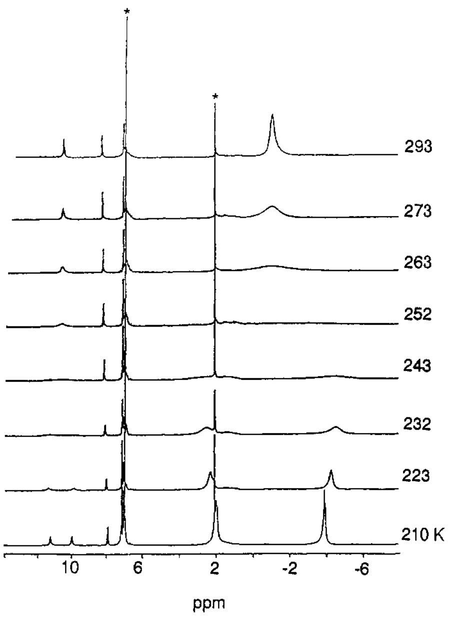
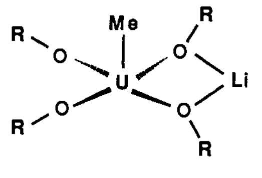


Figure 8. Variable-temperature ^1H NMR spectra of $U(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_4$ at 250 MHz. The ^1H impurities in toluene-d_8 are denoted with an asterisk.

has crystallographically imposed S_4 symmetry, and the coordination geometry about uranium is nearly tetrahedral (Figure 7). The 210 K solution ^1H NMR spectrum (Figure 8) is consistent with the solid-state structure, showing chemically inequivalent *t*-Bu and meta proton resonances.[35] The room-temperature spectrum shows one *t*-Bu and one meta proton environment consistent with rapid rotation about the U–O and/or O–C bonds.

Reaction of uranium alkoxides with organolithium or other main-group metal alkyls may give either substitution or addition products. $U(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_3$, for example, reacts with 3 equiv of $LiCH(SiMe_3)_2$ in hexane to provide the royal blue homoleptic uranium(III) alkyl compound $U[CH(SiMe_3)_2]_3$.[70] In contrast, and as noted above, $U[OCH(CMe_3)_2]_4$ reacts with 1 equiv of methyllithium in hexane to give a pale green solution from which purple crystals of the uranium(IV) addition compound $MeLi\cdot U[OCH(CMe_3)_2]_4$ may be isolated in ca. 35% yield. The complex is based upon two-coordinate lithium and five-coordinate uranium (structure I), with the geometry of the uranium being near that of a square pyramid with an apical methyl group (U–C = 2.465 (7) Å). The oxygens occupy the basal sites with an averaged U–O (terminal) distance of 2.103 (2) Å and a U–O (bridging) distance of 2.262 (4) Å. The U–O and U–C distances are normal for tetravalent uranium compounds.



(I)

The interesting mixed allyl(alkoxide)uranium(IV) dimer $U_2(\eta^3\text{-}C_3H_5)_4(\mu\text{-}O\text{-}i\text{-}Pr)_2(O\text{-}i\text{-}Pr)_2$ has been characterized by IR, ^1H NMR, and X-ray crystallography (Figure 9).[30] Proton NMR data are consistent with the observed solid-state structure. The allyl groups are coordinated in an η^3 fashion, and the dimer is held together by two bridging isopropoxide ligands. The coordination environment of the uranium atoms is roughly pentagonal bipyramidal; the pentagonal plane is defined by the terminal carbons of the allyl ligands and a bridging oxygen. The U–O–C angle of the terminal isopropoxides is 178.0 (10)°.

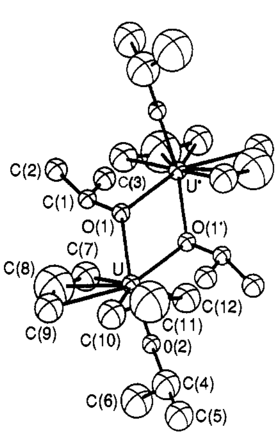


Figure 9. ORTEP view of $U_2(C_3H_5)_4(\mu\text{-}O\text{-}i\text{-}Pr)_2(O\text{-}i\text{-}Pr)_2$ (reprinted from ref 30; copyright 1979 The Chemical Society).

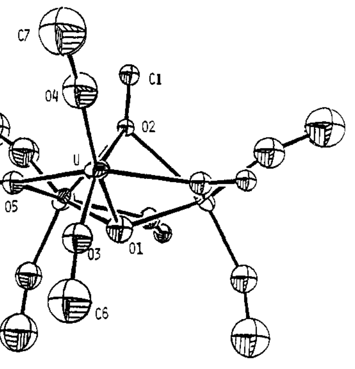


Figure 10. ORTEP view of $U_3O(O\text{-}t\text{-}Bu)_{10}$ (reprinted from ref 31; copyright 1984 Elsevier).

The $Cp_2M(OR)_2$ (M = U, Th) molecules have been characterized by a number of spectroscopic methods and have been extensively studied.[37] The crystal structure of a representative example, $Cp''_2UCl(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)$, has been determined by Atwood et al.[8] The U–O distance is 2.061 (8) Å, and the U–O–C angle is 169.2 (8)°. The crystal structure of a tris(cyclopentadienyl) derivative $Cp_3U(OC(CF_3)_2CCl_3)$ has also been reported.[39a] A comparison of the bonding of uranium to N- and O-donors in Cp_3UX complexes, including Cp_3UOCH_3, has been reported.[39b]

The structure of the mixed oxo(alkoxide)uranium(IV) trimer $U_3O(O\text{-}t\text{-}Bu)_{10}$ has been determined by Cotton et al. and is shown in Figure 10.[31] This complex adopts a structure similar to those of the metal–metal-bonded $M_3O(OR)_{10}$ clusters (M = Mo, W) reported by Chisholm and co-workers.[72] However, the U–U distance of 3.574 (1) Å suggests that 5f–5f overlap is insufficient to support U–U bonds, a conclusion supported by recent variable-temperature magnetic susceptibility measurements on the complex.[32]

Uranium(V). Several studies of $U_2(OR)_{10}$ compounds (R = Me,[46], Et,[46–48] Ph,[49] and *n*-Bu[46]) have been described in the literature. On the basis of ^{13}C NMR, ^1H NMR, and magnetic susceptibility measurements,[47] it has been proposed that the ethoxide and phenoxide derivatives adopt edge-shared bioctahedral geometries

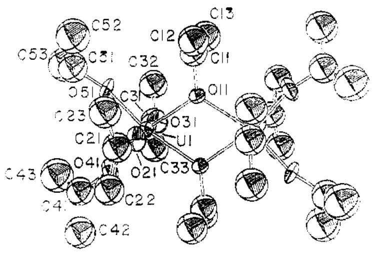


Figure 11. ORTEP view of $U_2(O\text{-}i\text{-}Pr)_{10}$ (reprinted from ref 29; copyright 1984 American Chemical Society).

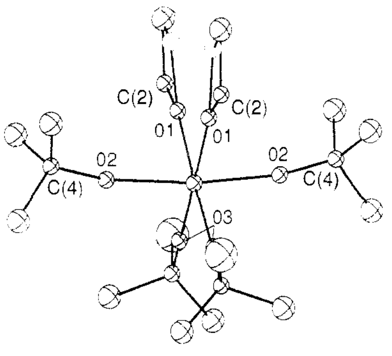


Figure 12. ORTEP view of $U[OC(CF_3)_3]_4(OEt)(HOEt)$. The ethoxy and ethanol ligands are disordered (reprinted from ref 43b; copyright 1987 VCH Publishers).

in solution. The NMR spectra of the isopropoxide derivative suggest a monomer–dimer equilibrium in solution.[47] The X-ray crystal structure of $U_2(O\text{-}i\text{-}Pr)_{10}$ confirmed the edge-shared bioctahedral geometry in the solid state (Figure 11) with a U–U separation of 3.789 (1) Å and a U–O–U angle of 111.4 (5)°. The authors suggest that the large U–O–C angles of the terminal alkoxides (160–176°) in $U_2(O\text{-}i\text{-}Pr)_{10}$, $KU_2(O\text{-}t\text{-}Bu)_9$, and $U_2(O\text{-}t\text{-}Bu)_9$ are indicative of substantial π bonding from oxygen lone-pair orbitals to uranium.[29] The current data base of uranium alkoxide structures does not lend itself to meaningful correlations between U–O–C angles, U–O distances, and the extent of U–O π bonding.

Treatment of $U_2(OEt)_{10}$ with $HOC(CF_3)_3$ has lead to the isolation of crystalline $U[OC(CF_3)_3]_4(OEt)(HOEt)$, which was characterized by X-ray crystallography and NMR techniques.[43] The uranium is octahedrally coordinated (Figure 12), with U–O distances of 2.08–2.09 Å for the fluoroalkoxides and 2.16 Å for the disordered ethoxy/ethanol ligands, which are in a cis arrangement. The ethanol proton is probably located between the ethanol and the ethoxy group (hydrogen bonding). The U–O–C angles of the fluoroalkoxides average 173°.

Uranium(VI). Moody et al. have reported the crystal structure of an interesting tetranuclear mixed-valence oxo phenoxide cluster[20] obtained by the air oxidation of uranium(III) phenoxide solutions. The molecular structure (Figure 13) is reminiscent of that of $Ti_4(OEt)_{16}$.[73] There are two U(V) atoms (U(2)) and two U(VI) atoms (U(1)) connected by four bridging phenoxides and two triply-bridging oxygen atoms. Each uranium is ligated to a single THF molecule. The uranium(V) atoms are also bonded to three terminal phenoxide ligands, while the uranium(VI) atoms are each multiply bonded to two terminal oxo ligands (uranyl groups).

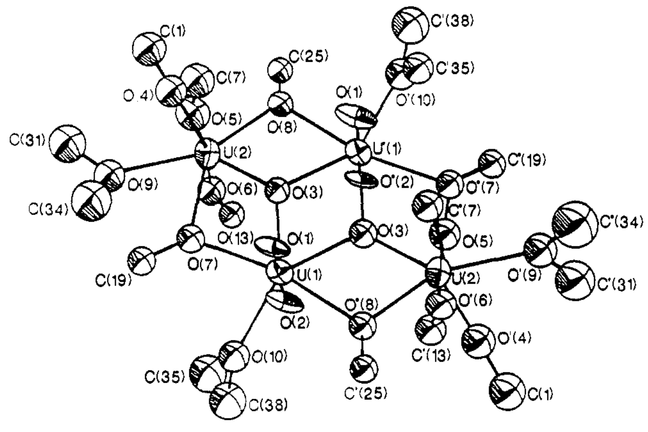


Figure 13. ORTEP view of $U_4(\mu_3\text{-}O)_2(O)_4(\mu_2\text{-}OPh)_4(OPh)_6(THF)_4$ (reprinted from ref 20; copyright 1982 American Chemical Society).

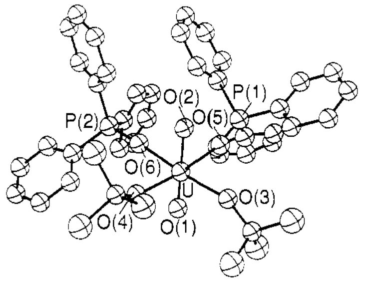


Figure 14. ORTEP view of $UO_2(O\text{-}t\text{-}Bu)_2(OPPh_3)_2$.

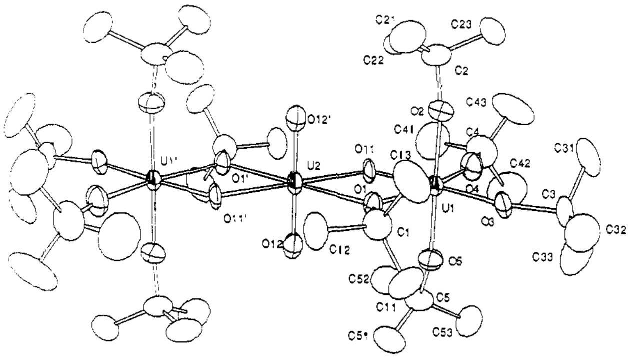


Figure 15. ORTEP view of $UO_2(O\text{-}t\text{-}Bu)_2[UO(O\text{-}t\text{-}Bu)_4]_2$ (reprinted from 67a; copyright 1988 American Chemical Society).

Three mononuclear uranyl alkoxide complexes have been structurally characterized. In the $(R_2NH_2)[UO_2(SOCNR_2)_2(OEt)]$ complexes (R = n-Pr, Et), the anion adopts a pentagonal-bipyramidal geometry, with the two monothiocarbamates and the ethoxide in the pentagonal plane.[74] Orange $UO_2(O\text{-}t\text{-}Bu)_2(OPPh_3)_2$ adopts an octahedral structure with a cis,cis disposition of alkoxide and phosphine oxide ligands (Figure 14).[67] All other structurally characterized $UO_2X_2L_2$ complexes adopt an all-trans octahedral geometry.[4b] The U=O, U—OR, and U—OPPh$_3$ bond distances average 1.792 (6), 2.153 (7), and 2.406 (6) Å, respectively. In contrast to the obtuse U–O–C angles normally observed in uranium alkoxide complexes, the U–O–C angles in $UO_2(O\text{-}t\text{-}Bu)_2(OPPh_3)_2$ average 141.0 (7)°.

The trinuclear complex $UO_2(O\text{-}t\text{-}Bu)_2[UO(O\text{-}t\text{-}Bu)_4]_2$, which was isolated from the reaction of UO_2Cl_2 with 2 equiv of KO-t-Bu in THF, adopts the structure shown in Figure 15. Here each uranium atom is coordinated by six oxygen atoms in a nearly octahedral arrangement. The trimer has approximate C_{2h} symmetry, and the central $UO_2(O\text{-}t\text{-}Bu)_2$ unit is symmetrically ligated by two $UO(O\text{-}t\text{-}Bu)_4$ units.[67] The U=O (uranyl) distance of the central fragment is 1.753 (6) Å. The U–O dis-

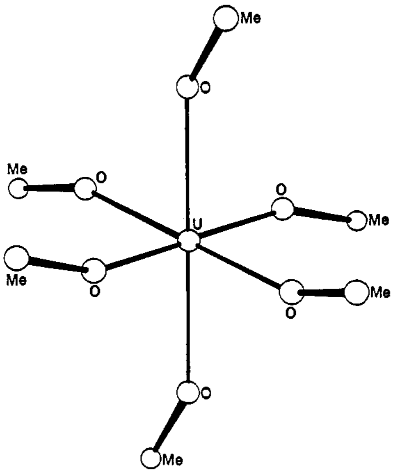


Figure 16. ORTEP view of $U(OMe)_6$ (reprinted from ref 60; copyright 1983 American Chemical Society).

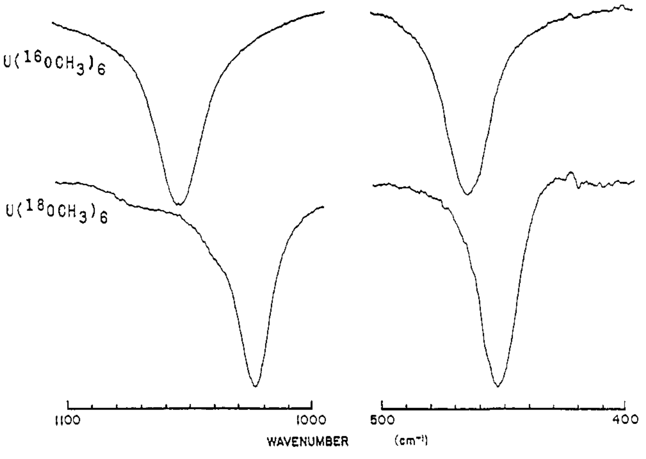


Figure 17. Infrared spectra of $U(^{18}OMe)_6$ and $U(^{18}OMe)_6$ showing the effect of isotopic labeling on the C–O (1000–1100 cm^{-1}) and U–O (400–500 cm^{-1}) stretches (reprinted from ref 60; copyright 1983 American Chemical Society).

tance associated with the $UO(O\text{-}t\text{-}Bu)_4$ fragment (U(1)–O(11) = 1.923 (6) Å) is, according to the authors, indicative of some degree of multiple bond character.

$U(OMe)_6$ has been characterized by several techniques[60,75] including X-ray crystallography (Figure 16). The UO_6 framework is essentially octahedral, but the presence and orientation of the methyl groups cause a reduction in the overall molecular symmetry to C_i. The mean U–O and C–O bond lengths are 2.10 and 1.35 Å, respectively, and the mean U–O–C bond angle is 153.7°. The IR and Raman spectra of both $U(^{16}OMe)_6$ and $U(^{18}OMe)_6$ have been studied.[60] Figure 17 shows the dependence of both the C–O (1000–1100 cm^{-1}) and U–O (T_{1u}, 400–500 cm^{-1}) infrared stretches on isotopic oxygen substitution. Discrete variational Xα molecular orbital calculations have been used to assign the He I and He II gas-phase photoelectron spectra of this complex.[75] The results of the calculated and experimental values for the energies of the highest lying filled MOs are presented in Figure 18. These molecular orbitals consist primarily of lone-pair orbitals on the methoxide ligands. They are split due to the interaction with empty orbitals (5f, 6d, 6p) on the uranium atom (ligand → uranium π bonding) and by ligand–ligand repulsions. The detailed discussion of the bonding in $U(OMe)_6$ by Bursten et al. is an important contribution to actinide alkoxide chemistry. As more data on actinide alkoxides become available, additional theoretical work will be required to interpret the bonding, magnetic, and spectroscopic properties of this important class of inorganic molecules.

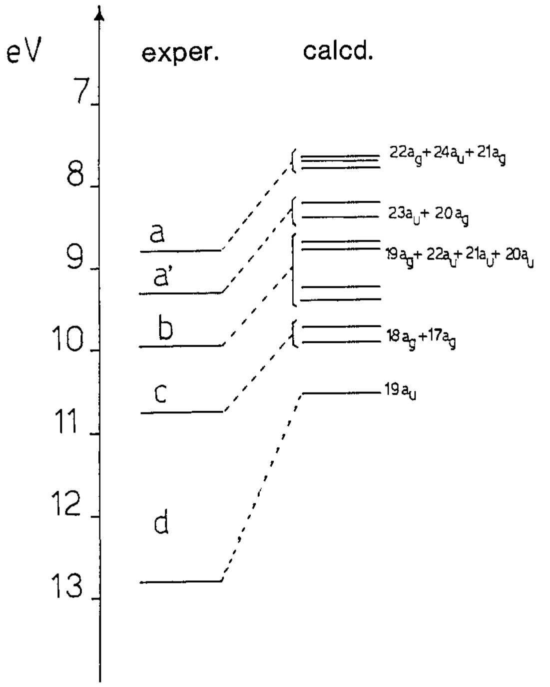


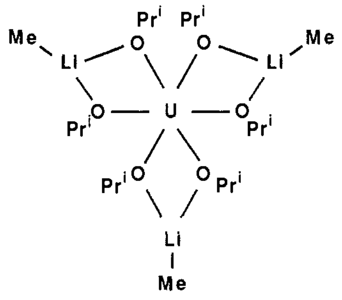
Figure 18. Comparison of the calculated and observed (PES) energies of the molecular orbitals of $U(OMe)_6$ (reprinted from ref 74; copyright American Chemical Society).

Wilkinson and Sigurdson have investigated the reactions of uranium(VI) isopropoxide with a number of main-group metal alkyls.[76] Solid, ether-free methyllithium readily dissolves in a light petroleum ether solution of $U(O\text{-}i\text{-}Pr)_6$ and forms a 3:1 addition complex, $(MeLi)_3{\cdot}U(O\text{-}i\text{-}Pr)_6$. Similarly, dimethyl-, dineopentyl- and bis[(trimethylsilyl)methyl]magnesium react with uranium hexaisopropoxide to form $(R_2Mg)_3{\cdot}U(O\text{-}i\text{-}Pr)_6$. Trimethylaluminum forms a 6:1 adduct $(Me_3Al)_6{\cdot}U(O\text{-}i\text{-}Pr)_6$. All of these addition compounds are thermally stable oils that cannot be chromatographed or sublimed. They are very soluble in common organic solvents, e.g., diethyl ether, benzene, or hexane, and do not react with Lewis bases. The authors have proposed structures II–IV for the compounds.

c. Applications

Uranium Isotope Separation. The use of volatile $U(OMe)_6$ for uranium isotope separation/enrichment via IR laser-induced multiphoton excitations has received much attention.[77-82] The key molecular requirements for *any* efficient laser-induced isotope separation process employing polyatomic molecules include (i) volatility, (ii) the existence of an infrared-active normal vibrational mode that exhibits a nonzero isotope shift and absorbs in a spectral region corresponding to the output of an efficient laser system, (iii) the absence of interfering ligand absorptions, (iv) the ready synthesis of large quantities of the target molecule, (v) the facile separation and recycling of enriched and depleted material, and (vi) the absence of undesirable photochemical side reactions.

Detailed spectroscopic studies of UF_6, arguably the most attractive candidate for a molecular process, indicate that this molecule does possess suitable vibra-



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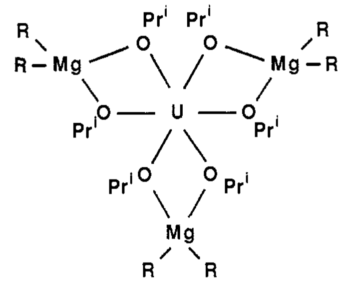

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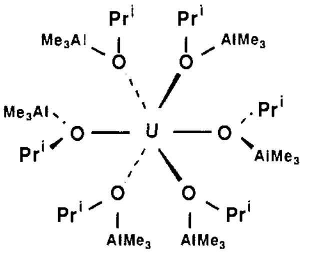

(IV)

tional transitions in the 16-μm region, a region outside the range of the CO_2 gas laser. Intense effort was directed toward the development of efficient and reliable 16-μm sources for UF_6 infrared photochemistry, but to the best of our knowledge, the UF_6-based laser isotope separation process has now been abandoned.

A challenging alternative *molecular* approach, and the one advanced by the Marks' group, is to "tailor" volatile uranium complexes for isotope-sensitive absorption in the 10-μm region. The basis of the Marks' isotope separation process is the selective irradiation of $U(OMe)_6$ using a CO_2 laser. Under idealized O_h symmetry, the $U(^{16}OMe)_6$ U–O stretching fundamentals (in a Nujol solution) are assigned at 505.0 (A_{1g}), 464.8 (T_{1u}), and 414.0 cm^{-1} (E_g). Weak bands (possibly combination modes) are also observed in the infrared spectrum of $U(^{16}OMe)_6$ at 937 and 925 cm^{-1}; these shift to 910 and 898 cm^{-1} in the IR spectrum of $U(^{18}OCH_3)_6$. Isotopically selective reactions were observed for five CO_2 laser lines between 919 and 935 cm^{-1}, with the largest separation factor being observed for the P(38) laser line of the 10.6-μm branch at 927 cm^{-1}. The maximum enrichment, β, observed was $\beta \sim 1.034$ (10) at a laser fluence of ca. 3.2 J/cm^2, where β is defined in eq 35.

$$\beta = (^{235}U/^{238}U)_{final}/(^{235}U/^{238}U)_{initial} \qquad (35)$$

The prediminant $U(OMe)_6$ photoproducts are $U(OMe)_5$, methanol, and formaldehyde. These are suggestive of multiphoton U–O bond homolysis to produce uranium pentamethoxide and methoxy radicals (eqs 36 and 37).

$$U(OMe)_6 \xrightarrow{h\nu} U(OMe)_5 + MeO^\bullet \qquad (36)$$

$$2MeO^\bullet \rightarrow MeOH + CH_2O \qquad (37)$$

Thermochemistry. Alcoholysis of Cp'_xThR_{4-x} (x = 3, 2) complexes[14,37b] has been used to estimate M–C bond strengths with an anaerobic batch titration isoperibol reaction calorimeter to determine heats of solution and reaction in toluene. The desired data can be obtained from eq 38.

$$D(Th{-}O)_{soln} + D(R{-}H)_{soln} - D(Th{-}R)_{soln} - D(O{-}H)_{soln} = -\Delta H_{alcoholysis\ rxn} \qquad (38)$$

Values of D(R–H) and D(O–H) are available from the literature. The authors assumed that $D(R{-}H) \sim D(R{-}H)_{soln}$ and $D(O{-}H) \sim D(O{-}H)_{soln}$. Another important assumption made is that D(Th–O) can be approximated from the mean bond disruption enthalpy data for $M(O\text{-}i\text{-}Pr)_4$ complexes (M = Ti, Zr, Hf). Full details of the calorimeter and the derivation of eq 38 can be found in ref 37b. These thermochemical studies have expanded our understanding of organoactinide reaction chemistry and the difference in reactivity between analogous organoactinide and organo-transition-metal systems.

Environmental Chemistry. There is a growing interest in actinide alkoxide complexes as model compounds for environmentally important species that are responsible for transporting actinide elements in ground waters. The metal-bound ligands thought to be responsible for the mobility of the actinides in aqueous solution include oxo, hydroxide, and water.[4b] In many cases, the true identity of the complexes is not known and the fact that a number of formulations are possible depending on the identity and makeup of the ground water and soil in question makes this problem a very difficult one. A major impediment to these efforts is the scarcity of baseline spectroscopic data in complexing solutions relating specific spectral features to fundamental structural information such as stoichiometry and complex geometry. The lack of data is predominantly attributable to experimental difficulties associated with the separation and isolation of aqueous phase species.

The historically implemented approach is to obtain spectroscopic data for complicated, multicomponent systems. These measurements are usually made under environmentally irrelevant conditions so that the actinide concentrations are at a sufficiently high level to obtain good signal to noise. Attempts are then made to deconvolute the spectral data, which requires mathematical modeling of the system based on *estimates* of the chemical and spectroscopic properties of the species.

Alkoxide ligands can serve as models for hydroxide ligands and have many advantages when preparing well-characterized complexes that may contain other environmentally relevant ligands, e.g., sulfate and carbonate. The emerging cluster chemistry of actinide alkoxides may also mimic cluster compounds likely to be present in aqueous solution. The spectroscopic signatures of alkoxide complexes with provide a first-order approximation of the spectroscopic properties of the analogous hydroxide species. In addition, structurally characterized mononuclear and polynuclear actinide alkoxide complexes can provide accurate baseline structural data for EXAFS measurements on environmental samples.

III. Conclusions

Research on the chemistry of actinide alkoxide complexes has grown steadily since the 1950s. Early synthetic efforts were devoted to the preparation of volatile uranium complexes suitable for isotope separation, and the characterization of products was limited by the available analytical techniques of the time. Reinvestigations of these reactions and their products, utilizing modern spectroscopic and structural techniques, are shedding new light on the stoichiometries and structures of actinide alkoxides and the mechanisms of their formation. However, much work remains to be done on the synthesis, characterization, and especially the reaction chemistry of these compounds. The dearth of structural information on thorium, protactinium, neptunium, and plutonium alkoxide complexes needs to be addressed, and more structural data are needed on uranium compounds. The present situation is like the early days of group 4, 5, and 6 transition metal alkoxide chemistry. A wealth of data on these early transition metal systems has emerged over the past two decades and has led, inter alia, to exciting new cluster compounds, to some enlightened thinking on the relationship between metal alkoxides and metal oxides, and to a seemingly endless array of interesting reactions involving inorganic and organic substrates.

We see actinide alkoxide chemistry as a growth area in inorganic chemistry. It is our hope that the present coverage will encourage future activity in this field.

Acknowledgments. This work was performed under the auspices of the Division of Chemical Energy Sciences, Office of Energy Research, U.S. Department of Energy. Financial support for our actinide chemistry program at Los Alamos is gratefully acknowledged. We thank our colleagues at Los Alamos and Professors T. J. Marks (Northwestern University), R. A. Andersen (University of California—Berkeley), and B. E. Bursten (The Ohio State University) for helpful discussions. We also thank those authors who supplied figures from their original publications.

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