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Uranium Alkoxide Chemistry. 1. Synthesis and the Novel Dimeric Structure of the First Homoleptic Uranium(III) Aryloxide Complex

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A number of homoleptic uranium alkoxide complexes have been reported, and the structurally characterized examples include $[U(O\text{-}2,6\text{-}Pr^i_2C_6H_3)_5]^-$, $[U_2(OBu^t)_9]^-$, $U_2(OBu^t)_9$, $U_2(OPr^i)_{10}$, and $U(OMe)_6$.[2-7] Conspicuous in their absence are any examples of homoleptic uranium(III) alkoxide complexes.[8] These would be valuable starting materials for further investigations of nonaqueous uranium(III) chemistry and for uranium alkoxide cluster syntheses via comproportionation reactions with higher oxidation state uranium alkoxides[2,3] and oxo-alkoxides.[9] In addition, there is also a possibility that alkoxide-ligated uranium(III) centers might be coaxed into homodinuclear relationships.[5b] Here we describe the successful syntheses of two uranium(III) aryloxide complexes.

Addition of 3.1 equiv of $HO\text{-}2,6\text{-}R_2C_6H_3$ (R = Bu^t or Pr^i) to concentrated hexane solutions of $U[N(SiMe_3)_2]_3$[10] at room temperature causes a rapid color change from bright red to dark brown and precipitation of a dark green (R = Bu^t, **1**) or dark purple (R = Pr^i, **2**) solid. After 4 h, the $U(O\text{-}2,6\text{-}R_2C_6H_3)_3$ complexes are isolated (50% yield) by filtration, washed with cold hexane, and dried in vacuo (eq 1). Both compounds are ether- and hydrocarbon-soluble and very air-sensitive.[11] The ^1H NMR spectra of **1** and **2**, recorded at 25 °C in benzene-d_6, show only one type of phenoxide R group.[12]

$$U[N(SiMe_3)_2]_3 + 3HO\text{-}2,6\text{-}R_2C_6H_3 \xrightarrow{C_6H_{14}} U(O\text{-}2,6\text{-}R_2C_6H_3)_3 + 3HN(SiMe_3)_2 \qquad (1)$$

1, R = Bu^t
2, R = Pr^i

Single crystals of **2** were grown from a concentrated hexane solution at −40 °C, and the structure was determined from X-ray diffraction data collected at −155 °C.[13] In the solid state, **2** adopts an unprecedented structure, that of a bis π-arene-bridged centrosymmetric dimer, $[U(O\text{-}2,6\text{-}Pr^i_2C_6H_3)_3]_2$. The coordination environment (Figure 1) of each uranium approximates a three-legged piano stool, i.e., each uranium is ligated by three terminal phenoxide oxygens and an arene ring of a phenoxide bound to its symmetry-related actinide partner. The O(2)–U–O(15) and O(2)–U–O(28) bond angles are 106.3 (3)° and 103.5 (3)°, respectively, while the angle between terminal phenoxide ligands, O(15)–U–O(28), is 99.0 (3)°. Two η^6-arene bridges [U–C(range) = 2.82 (1) Å–3.02 (1) Å; U–C(av) = 2.92 (2) Å] hold the dinuclear unit together, and the U–U separation is 5.34 Å. The uranium–oxygen bond lengths are 2.214 (7) Å (bridging phenoxides) and 2.132 (8) Å (terminal phenoxides), and the U–O–C bond angles are 156.8 (7)° (bridging phenoxide) and 164.5 (8)° and 166.8 (9)° (terminal phenoxides). Short U–O distances and large U–O–C angles, especially in the case of the terminal phenoxides, may be taken as an indication of π-bonding between the oxygen lone pairs and empty metal-based orbitals.[5,6] We note that the terminal U–O bonds in **2** are actually shorter than the aryloxide U–O bonds of the uranium(IV) complexes $[U(O\text{-}2,6\text{-}Pr^i_2C_6H_3)_5]^-$ and $U(NEt_2)(O\text{-}2,6\text{-}Bu^t_2C_6H_3)_3$.[4,14]

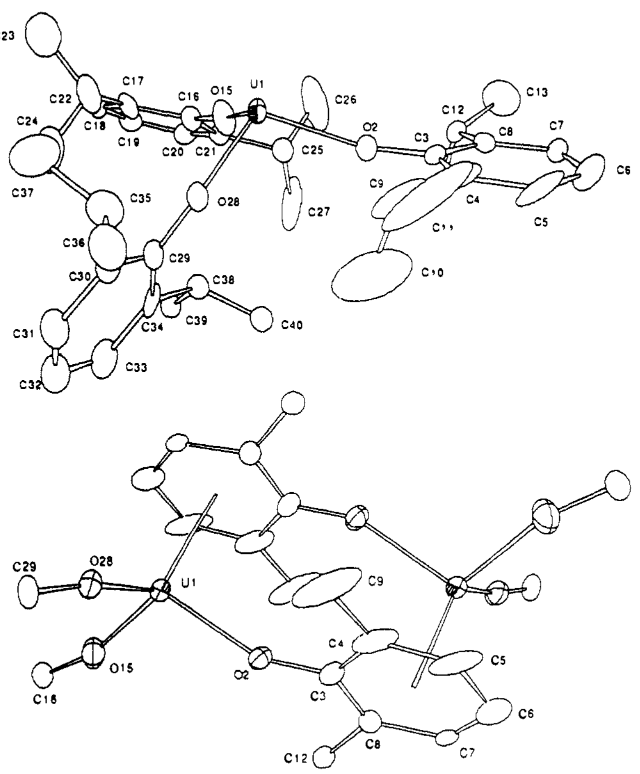

Figure 1. Two ORTEP views of **2**. The top figure is an isolated $U(O\text{-}2,6\text{-}Pr^i_2C_6H_3)_3$ unit with complete atom numbering scheme. The lower figure shows the π-arene bridging interaction. For viewing clarity, we have deleted the isopropyl methyl groups from the bridging phenoxides and show only the ipso carbons of the terminal phenoxides.

Coordination of an arene ring to a uranium(III) center has been observed previously in the complex $(\eta^6\text{-}C_6H_6)U(AlCl_4)_3$,[15] and the average U–C bond distance in the latter is essentially identical with that found in $[U(O\text{-}2,6\text{-}Pr^i_2C_6H_3)_3]_2$. However, it is not entirely obvious why $U(O\text{-}2,6\text{-}Pr^i_2C_6H_3)_3$ dimerizes via arene

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[1] (a) Los Alamos National Laboratory. (b) Indiana University.

[2] Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*; Academic Press: London, 1978.

[3] Mehrotra, R. C.; Kapoor, P. N.; Batwara, J. M. *Coord. Chem. Rev.* **1980**, *31*, 67.

[4] Blake, P. C.; Lappert, M. F.; Taylor, R. G.; Atwood, J. L.; Zhang, H. *Inorg. Chim. Acta* **1987**, *139*, 13.

[5] (a) Cotton, F. A.; Marler, D. O.; Schwotzer, W. *Inorg. Chem.* **1984**, *23*, 4211. (b) Cotton, F. A.; Marler, D. O.; Schwotzer, W. *Inorg. Chim. Acta* **1984**, *85*, L31.

[6] Bursten, B. E.; Casarin, M.; Ellis, D. E.; Fragala, I.; Marks, T. J. *Inorg. Chem.* **1986**, *25*, 1257 and references therein.

[7] Van Der Sluys, W. G.; Sattelberger, A. P., in preparation (a review of lanthanide and actinide alkoxide chemistry).

[8] Zozulin, A. J.; Moody, D. C.; Ryan, R. R. *Inorg. Chem.* **1982**, *21*, 3083. This paper describes an unsuccessful attempt to prepare $U(OC_6H_5)_3$.

[9] New uranium(VI) oxo-alkoxide complexes, $UO_2(OCMe_3)_2(OPPh_3)_2$ and $UO_2(OCMe_3)_2[OU(OCMe_3)_4]_2$, have been synthesized and structurally characterized at Los Alamos. Burns, C. J.; Sattelberger, A. P., submitted for publication.

[10] Andersen, R. A. *Inorg. Chem.* **1979**, *18*, 1507.

[11] Anal. Calcd (Found) for $UO_3C_{42}H_{63}$: C, 59.06 (58.43); H, 7.45 (7.48); N, 0.00 (<0.02). For $UO_3C_{36}H_{51}$: C, 56.16 (56.23); H, 6.69 (6.74).

[12] ^1H NMR (25 °C, benzene-d_6, 300 MHz) $U[O\text{-}2,6\text{-}(Me_3C)_2C_6H_3]_3$ δ 16.7 (d, $^3J_{HH}$ = 7.2 Hz, meta), δ 13.7 (t, $^3J_{HH}$ = 7.2 Hz, para), δ −6.1 (br s, Me_3C); $U[O\text{-}2,6\text{-}i\text{-}C_3H_7)_2C_6H_3]_3$ δ 10.9 (d, $^3J_{HH}$ = 7.2 Hz, meta), δ 9.2 (t, $^3J_{HH}$ = 7.2 Hz, para), δ 2.0 (br s, $CHMe_2$), δ −1.6 (br s, $CHMe_2$).

[13] Crystal data for $[U(O\text{-}2,6\text{-}Pr^i_2C_6H_3)_3]_2$ at −155 °C: monoclinic space group $P2_1/a$, a = 9.616 (2) Å, b = 21.260 (7) Å, c = 17.236 (5) Å, β = 107.31 (1)°, Z = 2, d_{calcd} = 1.520 g cm^{-3}. Diffraction data were corrected for absorption, and the structure was solved by a combination of direct methods and Fourier techniques and refined by full-matrix least-squares. Final discrepancy indices were R_F = 0.051 and R_{wF} = 0.043 for those 3271 reflections with $F_o \geq 2.33\sigma(F_o)$. The limits of data collection were $6° \leq 2\theta \leq 45°$ (Mo Kα).

[14] Hitchcock, P. B.; Lappert, M. F.; Singh, A.; Taylor, R. G.; Brown, D. *J. Chem. Soc., Chem. Commun.* **1983**, 561.

[15] Cesari, M.; Pedretti, U.; Zazetta, A.; Lugli, G.; Marconi, W. *Inorg. Chim. Acta* **1971**, *5*, 439.

0002-7863/88/1510-5924$01.50/0

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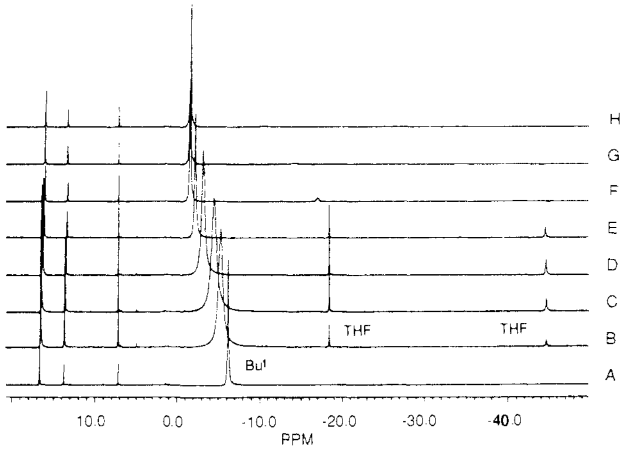

Figure 2. A series of ^{1}H NMR spectra (300 MHz, 22 °C) in which (A) 0 equiv; (B) 0.208 equiv; (C) 0.417 equiv; (D) 0.625 equiv; (E) 0.833 equiv; (F) 1.04 equiv; (G) 1.25 equiv; (H) 1.77 equiv of THF were added to 50.0 mg of $\mathrm{U(O\text{-}2,6\text{-}Bu^t{}_2C_6H_3)_3}$ in ca. 2 mL of benzene-d_6. The ^{1}H impurity signal of the benzene-d_6 solvent is indicated with an asterisk.

bridges rather than phenoxide oxygens. If we assume that it does so for steric reasons, then replacement of the diisopropylphenoxide with less bulky aryloxides or alkoxides may well lead to other interesting geometries. We are currently investigating this possibility. The phenoxide π-arene–uranium(III) interaction in $\mathrm{[U(O\text{-}2,6\text{-}Pr^i{}_2C_6H_3)_3]_2}$ is weak, and the dimer is cleaved in benzene-d_6. Only one broad isopropyl methyl resonance is observed in the proton NMR spectrum, consistent with either mononuclear $\mathrm{U(O\text{-}2,6\text{-}Pr^i{}_2C_6H_3)_3}$ or $\mathrm{(C_6D_6)U(O\text{-}2,6\text{-}Pr^i{}_2C_6H_3)_3}$.

Thus far, we have not been able to grow X-ray quality crystals of **1**, but a comparison of the Nujol mull infrared spectra of **1** and **2** indicates that they have different solid-state structures. Most important is the observation of two aromatic C=C stretching vibrations at 1588 cm^{-1} (terminal OAr) and 1553 cm^{-1} (bridging OAr) in the IR spectrum of **2** and only one, at 1583 cm^{-1}, in the IR spectrum of **1**. We propose, therefore, that **1** is monomeric in the solid state. It is reasonable to suggest that intermolecular aryloxide ring coordination does not occur in **1** because of the increased steric requirements of the *tert*-butyl groups.

Unlike $\mathrm{U[N(SiMe_3)_2]_3}$, which has a very limited coordination chemistry,[10] the uranium(III) tris-aryloxides readily coordinate a number of Lewis bases (e.g., THF, EtCN, and $\mathrm{OPPh_3}$) in solution *and* form isolable, presumably pseudotetrahedral, adducts.[16] For example, recrystallization of **1** from THF provides a brown crystalline complex, which by elemental analysis and proton NMR[17] is $\mathrm{(THF)U(O\text{-}2,6\text{-}Bu^t{}_2C_6H_3)_3}$, **3** (eq 2). Adduct

$$\underset{\mathbf{1}}{\mathrm{U(O\text{-}2,6\text{-}Bu^t{}_2C_6H_3)_3}} + \mathrm{THF} \rightarrow \underset{\mathbf{3}}{\mathrm{(THF)U(O\text{-}2,6\text{-}Bu^t{}_2C_6H_3)_3}} \qquad (2)$$

3 is stable at room temperature and does not lose THF under dynamic vacuum (10^{-6} Torr). We have monitored the course of reaction 2 by ^{1}H NMR spectroscopy at ambient temperature, and the results are shown in Figure 2. At THF:**1** ratios less than 1.0, the NMR resonances of THF (at δ −18.4 and δ −44.6) correspond to those for coordinated THF, and the *tert*-butyl resonance is the weighted average of the *tert*-butyl resonances of $\mathrm{U(O\text{-}2,6\text{-}Bu^t{}_2C_6H_3)_3}$ and $\mathrm{(THF)U(O\text{-}2,6\text{-}Bu^t{}_2C_6H_3)_3}$. At THF:**1** ratios greater than 1.0, chemical exchange of free and coordinated THF begins. The broad THF resonances (now barely visible in spectra F→H) are the weighted average of free and coordinated THF, and the *tert*-butyl resonance corresponds to $\mathrm{(THF)U(O\text{-}2,6\text{-}Bu^t{}_2C_6H_3)_3}$.

Further studies of the reactivity, electronic structure, and magnetic properties of the $\mathrm{U(OAr)_3}$ molecules described herein are in progress.

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Supplementary Material Available: Tables of atomic positional and isotropic equivalent thermal parameters (S1), anisotropic thermal parameters (S2), and selected bond distances and angles (S3) for **2** (6 pages). Ordering information is given on any current masthead page.

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(16) Van Der Sluys, W. G.; Burns, C. J.; Sattelberger, A. P., work in progress.

(17) ^{1}H NMR (25 °C, benzene-d_6, 300 MHz) $\mathrm{(THF)U[O\text{-}2,6\text{-}(Me_3C)_2C_6H_3]_3}$ δ 16.0 (br s, meta), δ 13.4 (br s, para), δ −1.5 (br s, Me_3C), δ −18.4 (s, THF-β), δ −44.6 (br s, THF-α). Anal. Calcd (Found) for $\mathrm{UO_4C_{46}H_{71}}$: C, 59.59 (59.57); H, 7.73 (7.58).

A Concise Strategy for the Syntheses of Indole Alkaloids of the Heteroyohimboid and Corynantheioid Families. Total Syntheses of (±)-Tetrahydroalstonine, (±)-Cathenamine, and (±)-Geissoschizine

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For a number of years, we have been engaged in the design of general strategies for the total syntheses of structurally complex alkaloids of the indole family.[2] Within this context we have recently developed an effective approach to the yohimboid[3] and heteroyohimboid classes[4] utilizing a strategy that features an intramolecular Diels–Alder reaction as a key step for the construction of the D/E ring subunit. In order to expand further the scope of these initial results in the indole alkaloid arena, we focused upon some of the unresolved challenges posed by the syntheses of tetrahydroalstonine (**1**)[5] and its biogenetic precursor cathenamine (**2**),[6] which are members of the heteroyohimboid group,

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[1] Recipient of a National Institutes of Health (National Cancer Institute) Research Career Development Award, 1980–1985.

[2] For leading references and reviews of the monoterpenoid alkaloids of the indole family, see: (a) *The Alkaloids, Chemistry and Physiology*; Manske, R. H. F., Ed.; Academic Press: New York, 1981; Vol. XX. (b) Saxton, J. E. In *Specialist Periodical Reports, The Alkaloids*; The Royal Society of Chemistry, Burlington House: London, 1983; Vol. 13, pp 221–237. See also In Vol, 1–12. (c) Cordell, G. A. *Introduction to Alkaloids, a Biogenetic Approach*; Wiley-Interscience: New York, 1981; pp 574–832.

[3] (a) Martin, S. F.; Rüeger, H.; Williamson, S. A.; Grzejszczak, S. *J. Am. Chem. Soc.* **1987**, *109*, 6124. (b) Martin, S. F.; Geraci, L. S., unpublished results.

[4] Martin, S. F.; Benage, B.; Williamson, S. A.; Brown, S. P. *Tetrahedron* **1986**, *42*, 2903.

[5] For previous syntheses of tetrahydroalstonine, see: (a) Winterfeldt, E.; Radunz, H.; Korth, T. *Chem. Ber.* **1968**, *101*, 3172. (b) Brown, R. T.; Leonard, J.; Sleigh, S. K. *J. Chem. Soc., Chem. Commun.* **1977**, 636. (c) Sakai, S.-I.; Aimi, N.; Endo, J.; Shimizu, M.; Yamanaka, E.; Katano, K.; Kashiwazaki (nee Matsubara), M.; Fujiu, M.; Yamamoto, Y. *Yakugaku Zasshi* **1978**, *98*, 850. (d) Uskoković, M. R.; Lewis, R. L.; Partridge, J. J.; Despreaux, C. W.; Pruess, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 6742. (e) Takano, S.; Satoh, S.; Ogasawara, K. *J. Chem. Soc., Chem. Commun.* **1988**, 59. (f) Reference 4.

[6] Although there have been no reports of the total synthesis of cathenamine, for leading references to work involving the isolation, characterization, and biosynthesis of cathenamine, see: (a) Stöckigt, J.; Husson, H. P.; Kan-Fan, C.; Zenk, M. H. *J. Chem. Soc., Chem. Commun.* **1977**, 164. (b) Stöckigt, J. *Phytochemistry* **1979**, *18*, 965. (c) Brown, R. T.; Leonard, J. *J. Chem. Soc., Chem. Commun.* **1979**, 877. (d) Heinstein, P.; Stöckigt, J.; Zenk, M. H. *Tetrahedron Lett.* **1980**, *21*, 141. (e) Kan-Fan, C.; Husson, H.-P. *Ibid.* **1980**, *21*, 1463. (f) Kan, C.; Kan, S.-K.; Lounasmaa, M.; Husson, H.-P. *Acta Chim. Scand. B* **1981**, *35*, 269.

0002-7863/88/1510-5925$01.50/0