Inorg. Chem. **1982**, *21*, 3083–3086

Contribution from Los Alamos National Laboratory,
University of California, Los Alamos, New Mexico 87545

Synthesis and Structure of a Mixed-Valent Uranium Complex: Tetra-μ-phenoxy-di-μ_3-oxo-[bis(triphenoxy(tetrahydrofuran)uranium(V))bis((tetrahydrofuran)dioxouranium(VI))][1]

A. J. ZOZULIN, D. C. MOODY,* and R. R. RYAN

Received October 6, 1981

The synthesis and structure of the title compound are reported. The complex crystallizes in the space group $R\bar{3}$ with hexagonal lattice parameters of $a = 35.30$ (4) Å and $c = 16.40$ (1) Å with $Z = 9$. Refinements, carried out with anisotropic thermal parameters for the uranium atoms and the uranyl oxygen atoms, converged to an unweighted R value of 7.4% and a weighted R value of 7.2%. The compound consists of a tetrameric unit composed of two uranium(V) atoms and two uranium(VI) atoms connected by four bridging phenoxides and two triply bridging oxygens. The coordination polyhedron around each uranium atom can be regarded as a distorted pentagonal bipyramid with the four uranium atoms, the triply bridging oxygens and the oxygen atoms of the bridging phenoxides forming a nearly planar configuration. The uranium atoms are 3.818 (4) and 3.854 (4) Å apart. The U–O bond lengths for the bridging oxygens are 2.25 (2) and 2.08 (2) Å. The uranyl groups show an average U–O bond distance of 1.77 (2) Å.

Introduction

The alkoxides of uranium(IV), -(V), and -(VI) have received considerable attention. Early synthetic work was performed by Gilman and co-workers during a search for volatile uranium compounds suitable for the separation of uranium isotopes.[2-7] These reports consisted of syntheses, chemical analyses, and relative volatilities. In these studies it was found that uranium(IV) tetraalkoxides are extremely susceptible to oxidation and can be readily converted to uranium(V) pentaalkoxides, while more powerful oxidizing agents produce the uranium(VI) hexaalkoxides. Subsequent work by Bradley et al. showed the uranium(V) alkoxides to be oligomeric. The methoxide, for example, is trimeric, $U_3(OMe)_{15}$, while other alkoxides are dimeric, $U_2(OR)_{10}$.[8,9] The effect of steric hindrance of the alkyl groups on the degree of polymerization and volatility of uranium(IV) alkoxides has also been studied,[9,10] while others have shown the uranium alkoxides undergo derivative chemistry.[11-13] Finally, other studies have reported infrared, electronic, and ^1H, ^{19}F, and ^{13}C NMR data.[14-16]

In contrast, there are no reports of an uranium(III) alkoxide. Since the preparation of a soluble form of uranium(III) chloride, $UCl_3(THF)_x$ (THF = tetrahydrofuran), by Moody and Odom,[17] we have been interested in the coordination and reaction chemistry of U(III).[18] Recently, we have begun a study to synthesize uranium(III) alkoxides, and during the course of this investigation we have prepared a unique mixed-oxidation-state uranium phenoxide. The synthesis, characterization, and crystal structure of this compound are reported herein.

Experimental Section

Materials. All preparative work was accomplished with inert-atmosphere techniques in all-glass Schlenkware equipped with greaseless stopcocks.[19] UCl_4 was prepared from literature procedures with UO_3 and hexachloropropene (Aldrich).[20] Sodium hydride (Apache Chemicals) was obtained commercially as an oil dispersion. The oil was removed by successive washing with heptane. The oil-free NaH was dried under vacuum and then stored in an inert-atmosphere glovebox. $UCl_3(THF)_x$ was synthesized from UCl_4 with excess NaH in THF.[17] Sodium phenoxide was prepared from phenol (Eastman) and excess NaH in THF. The resulting THF solution was filtered to remove the unreacted NaH, and the filtrate was vacuum distilled to dryness to yield $NaOC_6H_5$. All solvents were reagent grade and were thoroughly dried and then distilled prior to use.

Synthesis. In a typical reaction a THF solution containing 0.8–0.95 mmol of UCl_3 $(THF)_x$ was added to 0.35 g (3.02 mmol) of $NaOC_6H_5$ contained in a 100-mL reaction vessel equipped with a greaseless stopcock. An immediate color change was apparent, converting the dark purple color of $UCl_3(THF)_x$ to a light red-brown color. A precipitate was also present at this time. The solution was stirred at ambient temperature for 1 day. The volume of the solution was reduced to 5 mL of THF and diethyl ether added (75–100 mL). The solid which was present was isolated by filtration, and analysis of this solid indicated chloride present. The filtrate was then exposed to dry O_2 with which it reacts rapidly to produce a very dark red-brown solution. This solution after standing for several days yielded a dark red-brown crystalline product. Anal. Calcd for $U_4O_{20}C_{76}H_{82}$: C, 40.26; H, 3.64; U, 41.99; O, 14.11. Found: C, 39.83; H, 3.78; U, 43.6; O, 12.54. A hydropyrolysis analysis was performed on the crystalline solid in which a 3.6090-mg sample was converted to 1.7735 mg of U_3O_8 or 41.66% of U (calcd 41.99%). A portion of uranium phenoxide was hydrolyzed with a mixture of DCl/D_2O and acetone-d_6, and the ^1H NMR spectrum was recorded. The spectrum consisted of three major resonances. A complex resonance in the aromatic region for a monosubstituted benzene and two other resonances each a triplet

---

(1) This work performed under the auspices of the U.S. Department of Energy.

(2) Gilman, H.; Jones, R. G.; Karmas, G.; Martin, G. A. *J. Am. Chem. Soc.* **1956**, *78*, 4285.

(3) Gilman, H.; Jones, R. G.; Bindschadler, E.; Karmas, G.; Yoeman, F. A. *J. Am. Chem. Soc.* **1956**, *78*, 4287.

(4) Jones, R. G.; Bindschadler, E.; Karmas, G.; Martin, G. A., Jr.; Thirtle, J. R.; Yoeman, F. A.; Gilman, H. *J. Am. Chem. Soc.* **1956**, *78*, 4289.

(5) Jones, R. G.; Bindschadler, E.; Blume, D.; Karmas, G.; Martin, G. A., Jr.; Thirtle, J. R.; Gilman, H. *J. Am. Chem. Soc.* **1956**, *78*, 6027.

(6) Jones, R. G.; Bindschadler, E.; Blume, D.; Karmas, G.; Martin, G. A., Jr.; Thirtle, J. R.; Yoeman, F. A.; Gilman, H. *J. Am. Chem. Soc.* **1956**, *78*, 6030.

(7) Jones, R. G.; Bindschadler, E.; Blume, D.; Karmas, G.; Martin, G. A.; Thirtle, J. R.; Yoeman, F. A.; Gilman, H. *J. Am. Chem. Soc.* **1956**, *78*, 7030.

(8) Bradley, D. C.; Chakravarti, B. N.; Chatterjee, A. K. *J. Inorg. Nucl. Chem.* **1957**, *3*, 367.

(9) Bradley, D. C.; Chatterjee, A. K. *J. Inorg. Nucl. Chem.* **1957**, *4*, 279.

(10) Bradley, D. C.; Kapoor, R. N.; Smith, B. C. *J. Inorg. Nucl. Chem.* **1962**, *24*, 863.

(11) Bhandari, A. M.; Kapoor, R. N. *J. Chem. Soc. A* **1967**, 1618.

(12) Dubey, S.; Bhandari, A. M.; Misra, S. N.; Kapoor, R. N. *Ind. J. Chem.* **1970**, *8*, 97.

(13) Bagnall, K. W.; Bhandari, A. M.; Brown, D. *J. Inorg. Nucl. Chem.* **1975**, *37*, 1815.

(14) Bradley, D. C. *Adv. Inorg. Chem. Radiochem.* **1972**, *15*, 259.

(15) Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. "Metal Alkoxides"; Academic Press: New York, 1978, and references therein.

(16) Eller, P. G.; Vergamini, P. J. *Inorg. Chem.*, in press.

(17) Moody, D. C.; Odom, J. D. *J. Inorg. Nucl. Chem.* **1979**, *41*, 533.

(18) Moody, D. C.; Penneman, R. A.; Salazar, K. V. *Inorg. Chem.* **1979**, *18*, 208.

(19) Shriver, D. F. "The Manipulation of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969.

(20) Hermann, J. A.; Suttle, J. F. *Inorg. Synth.* **1957**, *5*, 143.

(21) Lenhert, P. G. *J. Appl. Crystallogr.* **1975**, *8*, 568.

(22) Cromer, D. T.; Waber, J. T. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A. Cromer, D. T. *Ibid.*, Table 2.3.1.

0020-1669/82/1321-3083$01.25/0

Table I. Crystal Data and Collection Methods

compd	$C_{76}H_{82}O_{20}U_4$
mol wt	2266
space group	$R\bar{3}$
cell parameters	$a = b = 35.30$ (4), $c = 16.40$ (1) Å, $V =$ 17 698 Å^3
Z	9 (for tetramer unit)
cell refinement	12 high-order reflections
diffractometer and counting technique	Picker FACS-I, P. G. Lenhert's disk operating system,[21] Wang encoders, graphite monochromator, 3.5° takeoff angle, (1.5° + dispersion) continuous scans, 20-s symmetric bkgd counts, Mo Kα radiation (λ 0.709 30 Å), ω scan (2°/min)
2θ limits, deg	1.0–45.0
ω scans	$\leqslant$0.3° at half-height on all three axes, slightly asymmetric
intensities	5174 after averaging equiv reflctn; 3286 for which $I \geqslant 2\sigma(I)$
crystal morphology	irregular shape (~radius 0.08 mm)
abs coeff, cm^{-1}	101
transmission (min, max)	0.24, 0.33 by ψ scans superimposed on spherical abs cor
scattering factors	neutral-atom scattering factors for all atoms[22]

at higher field for THF. Integration of these resonances gave an area ratio of 2.1:1 (phenyl:THF) with the calculated ratio being 1.6:1. The infrared spectrum of the complex in Nujol gave the following absorptions: 1585.4 (s), 1271.2 (m), 1236.9 (s), 1158.3 (m), 917.5 (m), 859.1 (m), 757.3 (s), 723.2 (s), 689.9 (m), 609.3 (m), 602.5 (sh), 509.6 (s) and 493.7 (s) cm^{-1}. Pyrolysis of the compound indicated it does not sublime but decomposes to produce a colorless liquid, identified as a mixture of phenol and THF by their mass spectra and ^{1}H NMR, and an unidentified black residue. The uranium phenoxide complex was found to be soluble in pyridine and acetonitrile and insoluble in THF and ether.

Physical Measurements. Nuclear magnetic resonance spectra (^{1}H) were obtained by hydrolyzing the compound in a mixture of DCl/D_2O and acetone-d_6. Measurements were made on a Varian EM-360 spectrometer. Infrared spectra were measured on Nujol mulls with a Perkin-Elmer Model 683 infrared spectrophotometer. All samples were prepared in an argon atmosphere with KBr plates used to support the samples. Magnetic susceptibility measurements were obtained with a Princeton Applied Research Corp. vibrating-sample magnetometer used with a superconducting magnet capable of a maximum field strength of 54 kG. Temperatures were controlled with a Janis Research Corp. Vari-Temp system with sample temperatures in the range of 1.4–80 K. Elemental analysis was performed by Galbraith Laboratories, Inc., Knoxville, TN. Uranium analysis as U_3O_8 was determined by hydropyrolysis at 1000 °C on a Perkin-Elmer TGS-2 thermogravimetric system.

X-ray Measurement and Refinement. Due to the decomposition of the unprotected compound in the X-ray beam, a single crystal was mounted in a capillary tube and sealed under vacuum. Pertinent information concerning the cell, crystal morphology, and intensity measurements are given in Table I. Two standard reflections, measured after every 100 measurements, were stable during the period of data collection. The structure was determined by standard MULTAN, difference Fourier, and least-squares methods with use of the Los Alamos system of crystal structure programs. Refinements, carried out with anisotropic thermal parameters for the uranium atoms and the uranyl oxygen atoms, converged to an unweighted R value of 7.4% and a weighted R value of 7.2%. A final difference Fourier map contained no peaks whose positions could be interpreted in terms of additional structural features. Hydrogen atoms were not located nor were they used in the structural refinements. The final structural parameters are given in Table II (anisotropic thermal parameters included in supplementary data as Table V), and selected distances and angles are shown in Tables III and IV. Selected angles and distances involving carbon atoms are included as supplementary data in Table VI.

Discussion

The addition of 3 equiv of sodium phenoxide to a THF solution of $UCl_3(THF)_x$ leads to an immediate color change (purple to red-brown) and the precipitation of NaCl. When a quantitative chloride analysis is performed on the NaCl byproduct, only 50–60% of the theoretical yield is obtained while analyses of the uranium product consistently showed the presence of chloride. The addition of ether, however, results in a quantitative precipitation of sodium chloride. In view of the insolubility of sodium chloride in THF, these facts suggest a possible initial uranium salt formation which is disrupted upon addition of diethyl ether. We have thus far been unsuccessful at characterizing the products of this reaction, and no uranium(III) phenoxide, the desired product, has been isolated. However, during these studies the above ethereal solution was exposed to molecular oxygen and an interesting reaction was observed which resulted in a dark red-brown solution, from which the title complex (I) was isolated.

Table II. Fractional Coordinates and Thermal Parameters

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
U(1)	0.55960 (4)	0.01213 (4)	−0.00299 (8)	a	C(35)	0.6631 (13)	0.0581 (12)	−0.0845 (23)	6.2 (10)
O(1)	0.55901 (55)	−0.00846 (63)	0.09533 (111)	a	C(37)	0.7060 (16)	0.0402 (15)	0.0077 (30)	9.2 (14)
O(2)	0.56548 (60)	0.03467 (71)	−0.10167 (114)	a	O(4)	0.5849 (8)	0.1548 (8)	0.1177 (14)	5.6 (6)
U(2)	0.53327 (4)	0.09716 (4)	0.08130 (8)	a	C(2)	0.6371 (14)	0.2289 (15)	0.0854 (26)	7.5 (12)
O(3)	0.5113 (6)	0.0360 (6)	0.0290 (11)	3.5 (4)	C(4)	0.6821 (15)	0.2805 (15)	0.1855 (32)	8.8 (13)
C(1)	0.6187 (14)	0.1956 (14)	0.1347 (27)	6.6 (11)	C(6)	0.6316 (16)	0.2026 (16)	0.2183 (31)	9.2 (14)
C(3)	0.6711 (14)	0.2742 (14)	0.1078 (29)	7.7 (12)	C(7)	0.5485 (12)	0.1403 (12)	−0.1122 (23)	5.0 (9)
C(5)	0.6649 (16)	0.2487 (17)	−0.2466 (29)	9.0 (13)	C(9)	0.5776 (13)	0.1419 (14)	−0.2444 (25)	6.9 (11)
O(5)	0.5379 (7)	0.1261 (7)	−0.0318 (14)	5.3 (6)	C(11)	0.5520 (15)	0.1937 (16)	−0.2145 (32)	9.4 (14)
C(8)	0.5664 (14)	0.1228 (13)	−0.1625 (27)	7.1 (11)	O(6)	0.5262 (7)	0.0730 (7)	0.2019 (13)	4.4 (5)
C(10)	0.5705 (15)	0.1777 (15)	−0.2650 (27)	7.9 (12)	C(14)	0.5055 (11)	0.0009 (11)	0.2548 (20)	4.3 (8)
C(12)	0.5417 (13)	0.1780 (14)	−0.1269 (26)	7.2 (11)	C(16)	0.5224 (11)	−0.0023 (12)	0.3975 (22)	5.0 (9)
C(13)	0.5231 (11)	0.0452 (11)	0.2650 (20)	4.2 (8)	C(18)	0.5411 (11)	0.0691 (12)	0.3369 (23)	5.2 (9)
C(15)	0.5049 (12)	−0.0232 (12)	0.3204 (24)	5.8 (10)	C(19)	0.6307 (11)	0.1061 (11)	0.0971 (20)	3.8 (8)
C(17)	0.5390 (12)	0.0406 (13)	0.4028 (23)	5.7 (9)	C(21)	0.7061 (12)	0.1611 (12)	0.1026 (23)	5.7 (9)
O(7)	0.5916 (6)	0.0850 (6)	0.0599 (12)	3.2 (4)	C(23)	0.6768 (14)	0.1152 (14)	0.2210 (24)	6.7 (11)
C(20)	0.6654 (13)	0.1417 (12)	0.0632 (22)	5.5 (9)	O(8)	0.5450 (6)	−0.0563 (6)	−0.0618 (12)	3.6 (5)
C(22)	0.7104 (13)	0.1467 (13)	0.1825 (26)	6.8 (11)	C(26)	0.6056 (10)	−0.0616 (10)	−0.1154 (19)	3.5 (7)
C(24)	0.6313 (12)	0.0881 (11)	0.1775 (22)	5.0 (9)	C(28)	0.6380 (12)	−0.0952 (12)	−0.0306 (23)	5.6 (9)
C(25)	0.5769 (10)	−0.0702 (10)	−0.0524 (20)	3.7 (7)	C(30)	0.5742 (11)	−0.0915 (11)	0.0215 (21)	4.3 (8)
C(27)	0.6359 (12)	−0.0755 (12)	−0.1058 (23)	5.7 (9)	C(31)	0.5068 (14)	0.1806 (14)	0.1022 (26)	7.4 (11)
C(29)	0.6071 (11)	−0.1036 (11)	0.0295 (21)	4.7 (8)	C(33)	0.4933 (21)	0.1829 (22)	0.2347 (42)	14.8 (21)
O(9)	0.4995 (7)	0.1400 (7)	0.1392 (14)	5.0 (6)	O(10)	0.6360 (7)	0.0337 (7)	−0.0149 (14)	4.8 (5)
C(32)	0.4857 (23)	0.1958 (22)	0.1594 (46)	16.0 (23)	C(36)	0.7050 (16)	0.0615 (15)	−0.0672 (29)	9.1 (13)
C(34)	0.4894 (15)	0.1373 (16)	0.2308 (28)	8.9 (13)	C(38)	0.6624 (13)	0.0254 (12)	0.0436 (23)	5.8 (10)

[a] Anisotropic.

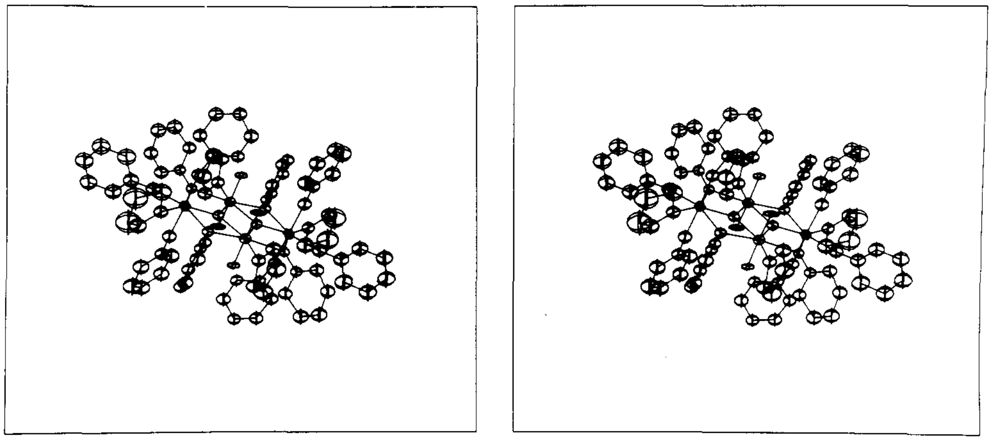


Figure 1. Stereoview of complex I.

Table III. Interatomic Distances (Å)

U(1)-U'(1)	3.854 (4)	U(2)-O(3)	2.08 (2)
U(1)-O(1)	1.76 (2)	U(2)-O(7)	2.33 (2)
U(1)-O(2)	1.77 (2)	U(2)-O(8)	2.42 (2)
U(1)-O(3)	2.25 (2)	U(2)-O(4)	2.03 (2)
U(1)-O'(3)	2.31 (2)	U(2)-O(5)	2.08 (2)
U(1)-U(2)	3.826 (5)	U(2)-O(6)	2.12 (2)
U(1)-U'(2)	3.818 (4)	U(2)-O(9)	2.53 (2)
U(1)-O(7)	2.46 (2)		
U(1)-O(8)	2.40 (2)		
U(1)-O(10)	2.42 (2)		

Table IV. Angles (Deg)

O(1)-U(1)-O(2)	174.7 (8)	O(4)-U(2)-O(8)	145.6 (8)
O(1)-U(1)-O(3)	94.7 (7)	O(5)-U(2)-O(7)	95.5 (8)
O(1)-U(1)-O(10)	89.1 (8)	O(5)-U(2)-O(8)	87.8 (8)
O(3)-U(2)-O(4)	147.6 (8)	O(6)-U(2)-O(7)	90.2 (8)
O(3)-U(2)-O(5)	92.2 (8)	O(6)-U(2)-O(8)	90.8 (7)
O(3)-U(2)-O(6)	93.4 (8)	O(7)-U(2)-O(9)	152.9 (7)
O(3)-U(2)-O(9)	137.1 (7)	O(8)-U(2)-O(9)	70.6 (7)
O(4)-U(2)-O(7)	78.2 (8)	U(1)-O(3)-U(2)	123.8 (9)
		U(1)-O(3)-U'(1)	115.3 (8)
U(2)-O(4)-C(1)	174 (3)	U(1)-O(8)-C(25)	119 (2)
U(2)-O(5)-C(7)	164 (2)	U(2)-O(9)-C(31)	122 (2)
U(2)-O(6)-C(13)	158 (2)	U(2)-O(9)-C(34)	120 (2)
U(1)-O(7)-U(2)	105.7 (7)	C(31)-O(9)-C(34)	113 (3)
U(1)-O(7)-C(19)	125 (2)	U(1)-O(10)-C(35)	123 (2)
U(1)-O(8)-U(2)	105.1 (7)	C(35)-O(10)-C(38)	110 (3)

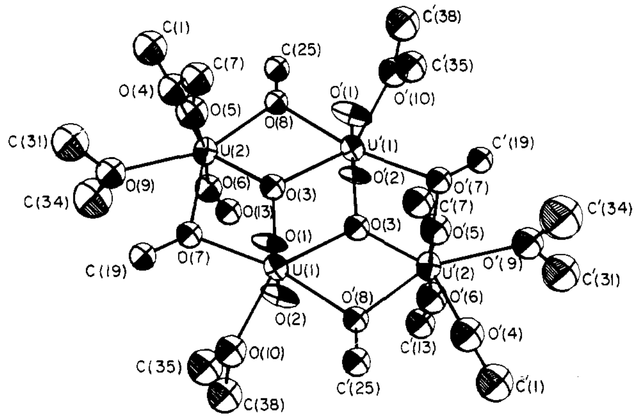


Figure 2. ORTEP drawing of coordination around the uranium atoms.

Air oxidation was previously employed by Gilman and coworkers to synthesize uranium(V) alkoxides from the uranium(IV) alkoxides.[3] In these reactions it was believed that part of the uranium was converted to the oxide, either as UO_2 or U_3O_8. In contrast, we have not observed the uranium oxide products but have isolated a complex incorporating a bridging oxygen between a uranium(V) alkoxide and a uranyl alkoxide (vide infra).

The molecular structure of I is shown in the stereoview (Figure 1). The compound exists as a tetrameric unit, with crystallographically imposed $\bar{1}$ symmetry, composed of two uranium(V) atoms, U(2), and two uranium(VI) atoms, U(1), connected via four bridging phenoxides and two triply bridging oxygens. Each uranium atom has a single coordinated THF molecule. The U(V) atoms are also bonded to three terminal phenoxides while the U(VI) atoms exist as a uranyl moiety. The coordination polyhedron around each uranium atom can be regarded as a distorted pentagonal bypyramid with O(1), O(2), O(5), and O(6) in the axial positions (Figure 2). The four uranium atoms plus O(7), O(8), and O(3) form a nearly planar configuration. Atoms U(1) and U(2) are 3.818 (4) Å apart while U(1)-U'(1) and U(2)-U'(2) are 3.854 (4) Å apart. The uranyl groups show an average U—O bond length of 1.77 (2) Å, which is normal for a terminal U═O group.[23] The uranyl angle is nearly linear at 174.7 (8)°. The THF oxygen–uranium distance for the uranyl group is 2.42 (2) Å and is similar to bond distances found for coordinated THF in other uranyl complexes.[24,25] A considerably longer distance [2.53 (2) Å] is observed for the THF oxygen–uranium(V). The bridging phenoxides show an average U–O bond length of 2.42 (2) Å as compared to 2.07 (2) Å for the terminal phenoxides. This trend is consistent with bond lengths for bridging and nonbridging alkoxides found in other metal alkoxides.[15,26] Finally, the triply bridging oxygens which occur in I are commonly observed in the uranium oxides and are found in the structures of UO_3 and U_3O_8.[27-30] For I the distances are 2.08 (2) Å for the unique U(2)–O(3), suggesting a bond order of 1 by comparison with the terminal alkoxide distances, and 2.28 (2) Å for the average U(1)–O(3).

From the crystal structure it can be seen that this complex contains uranium in both the +5 and +6 oxidation states. This represents the first structure determination of a uranium alkoxide containing uranium in two oxidation states. With summation of the formal charges of the ligands around each uranium atom, U(1) would represent uranium in the +6 oxidation state while U(2) exists as U(V). The magnetic sus-

---

(23) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, 1962; Vol. 3.
(24) Reynolds, J. G.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1977**, *16*, 3357.
(25) Kramer, G. M.; Dines, M. B.; Hall, R. B.; Kaldor, A.; Jacobsen, A. J.; Scanlon, J. C. *Inorg. Chem.* **1980**, *19*, 1340.
(26) Caughlan, C. N.; Smith, H. M.; Watenpaugh, K. *Inorg. Chem.* **1966**, *5*, 2131.
(27) Andresen, A. F. *Acta Crystallogr.* **1958**, *11*, 612.
(28) Loopstra, B. O. *Acta Crystallogr.* **1964**, *17*, 651.
(29) Siegel, S.; Hoekstra, H.; Sherry, E. *Acta Crystallogr.* **1966**, *20*, 292.
(30) Loopstra, B. O. *Acta Crystallogr., Sect. B* **1970**, *B26*, 656.

ceptibility of the complex also suggests the presence of a uranium(V) ion. The compound obeys a Curie–Weiss plot at low temperatures with a calculated moment of 1.10 μ_B. With the assumption that there is little or no contribution to the moment from +6, this value is then consistent with moments reported for other uranium(V) complexes.[31,32] The oxidation states may also be calculated from Zachariasen's bond length–bond strength relationships.[33,34] In the present structure the oxidation states of each uranium atom were calculated to be +6.09 and +5.51 for U(1) and U(2), respectively. Abnormally high values for the +5 oxidation state have been obtained in calculations performed in this laboratory on U(V) compounds containing U–O–U bonds. This suggests a better correlation of Zachariasen's formalism to U^{6+} complexes than U^{5+} and may be due in part to more abundant crystallographic data available on bond lengths in U^{6+} compounds as compared to U^{5+} compounds.

In conclusion, the attempted synthesis of uranium(III) phenoxide complexes and subsequent air oxidation has led to the isolation and characterization of a unique mixed-valent alkoxide complex, I. An earlier report of an unusual red uranyl alkoxide, $UO_2(OC_4H_9)_2 \cdot 4C_4H_9OH$, isolated from the air oxidation of $U(OC_4H_9)_4$, was characterized only by chemical analysis.[35] In light of the data presented herein, it appears likely that the previously reported red uranyl alkoxide also exists as a mixed-valent complex and not as a pure uranyl alkoxide.

Acknowledgment. The authors wish to thank E. Duesler, University of New Mexico, for the preliminary crystallographic data and J. Smith for the magnetic susceptibility measurements. We also thank R. A. Penneman and P. G. Eller for helpful discussions.

Supplementary Material Available: Listings of structure factors, anisotropic thermal parameters (Table V), and selected carbon distances and angles (Table VI) (19 pages). Ordering information is given on any current masthead page.

---

(31) Bagnall, K. W.; Brown, D.; DuPreez, J. G. H. *J. Chem. Soc.* **1964**, 2603.
(32) Soulie, E. Doctoral Thesis, University of Paris, 1977.
(33) Zachariasen, W. H. *J. Less-Common Met.* **1978**, *62*, 1.
(34) Zachariasen, W. H.; Penneman, R. A. *J. Less-Common Met.* **1980**, *69*, 369.
(35) Jones, R. G.; Bindschadler, E.; Martin, G. A., Jr.; Thirtle, J. R.; Gilman, H. *J. Am. Chem. Soc.* **1957**, *79*, 4921.

Contribution from the Lehrstuhl für Anorganische Chemie I der Ruhr-Universität, D-4630 Bochum 1, West Germany, and the Anorganisch Chemisches Institut der Universität Heidelberg, D-6900 Heidelberg, West Germany

New Triply Hydroxo-Bridged Complexes of Chromium(III), Cobalt(III), and Rhodium(III): Crystal Structure of Tris(μ-hydroxo)bis[(1,4,7-trimethyl-1,4,7-triazacyclononane)chromium(III)] Triiodide Trihydrate

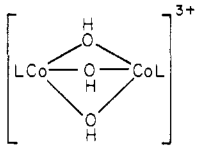
KARL WIEGHARDT,*[1a] PHALGUNI CHAUDHURI,[1a] BERNHARD NUBER,[1b] and JOHANNES WEISS*[1b]

Received October 7, 1981

The synthesis of the cyclic amine 1,4,7-trimethyl-1,4,7-triazacyclononane ($Me_3[9]aneN_3$) is reported, and its ligating properties toward chromium(III), cobalt(III), and rhodium(III) are described. Triply OH-bridged binuclear cations have been prepared, $[(Me_3[9]aneN_3)M(OH)_3M(Me_3[9]aneN_3)]^{3+}$ (M = Cr(III), Co(III), Rh(III)). In contrast to their analogues containing the nonmethylated ligand 1,4,7-triazacyclononane the binuclear cations are stable in 2 M perchloric acid—no acid-catalyzed OH-bridge cleavage has been detected. The complex $[(Me_3[9]aneN_3)_2Cr_2(OH)_3]^{3+}$ represents the first genuine tris(μ-hydroxo) complex of chromium(III). The iodide salt, $[(Me_3[9]aneN_3)_2Cr_2(OH)]I_3 \cdot 3H_2O$, has been characterized by a three-dimensional X-ray diffraction study. The complex crystallizes in the hexagonal space group C_{6h}^2-$P6_3/m$ with a = 9.698 (1) Å, c = 20.621 (4) Å, and V = 1680 Å^3; Z = 2. Diffraction data were collected on a Syntex R3 diffractometer with θ–2θ scan and Mo Kα radiation, and the structure was solved by conventional methods, resulting in a final R factor of 0.046 for 1405 independent reflections. The structure consists of binuclear cations of Cr(III) (face-sharing distorted octahedra), iodide ions, and waters of crystallization, which are bound to the hydroxo bridges via a short hydrogen bond (O···O = 2.787 (4) Å). The Cr–Cr separation is the shortest known to date for binuclear complexes of chromium(III) (2.642 (2) Å).

Introduction

Binuclear complexes of cobalt(III) with three hydroxo bridges and amine ligands (two face-sharing octahedra) have been described by Werner[2] and since then by many other groups:[3–6]



L = 3 NH_3,[2] 3 py$_3$,[3] *cis,cis*-1,3,5-triaminocyclohexane,[4] diethylenetriamine,[5] 1,4,7-triazacyclononane[6]

The chemistry of these tris(μ-hydroxo) complexes has attracted much interest because in acidic solution one hydroxo bridge is cleaved rapidly and the resulting bis(μ-hydroxo) species (edge-sharing octahedra) are very stable.[2,4,6,7] Thus the kinetics of this OH-bridge cleavage (eq 1) have been studied in detail[5–9] and were mechanistically interpreted in

---

(1) (a) Ruhr-Universität. (b) Universität Heidelberg.
(2) Werner, A. *Ber. Dtsch. Chem. Ges.* **1907**, *40*, 4834; **1908**, *41*, 3879.
(3) Laier, T.; Springborg, J. *Acta Chem. Scand., Ser. A* **1981**, *A35*, 145.
(4) Schwarzenbach, G.; Boessch, J.; Egli, H. *J. Inorg. Nucl. Chem.* **1971**, *33*, 2141.
(5) Kähler, H. C.; Geier, G.; Schwarzenbach, G. *Helv. Chim. Acta* **1974**, *57*, 802.
(6) Wieghardt, K.; Schmidt, W.; Nuber, B.; Weiss, J. *Chem. Ber.* **1979**, *112*, 2220.
(7) Linhard, M.; Siebert, H. *Z. Anorg. Allg. Chem.* **1969**, *364*, 24.
(8) Edwards, J. D.; Wieghardt, K.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1974**, 2198.
(9) Jentsch, W.; Schmidt, W.; Sykes, A. G.; Wieghardt, K. *Inorg. Chem.* **1977**, *16*, 1935.