

a dihedral angle of $2.7(20)^\circ$. The Fe atom lies $1.641(1) \text{ \AA}$ from the plane of Cp1 (C1–C5) and $1.647(1) \text{ \AA}$ from the plane of Cp2 (C14–C18). Fe–C distances range from $2.030(3)$ – $2.042(3) \text{ \AA}$. The two Cp rings are nearly eclipsed, forming a twist angle of $10.4(3)^\circ$ (average of five C–Cp–Cp–C torsion-angle magnitudes, where Cp are ring centroids). The Cp1–Fe–Cp2 angle is 177.8° . Bulky substituents directly bound to the ferrocene moiety have been reported with larger distortions from ideal geometry. The crystal structure of 1-(1-hydroxy-1-phenylpropyl)-2,1'-trimethyleneferrocene (Lecomte, Dusaosoy, Protas, Moïse & Tirouflet, 1973) shows a Cp1–Fe–Cp2 angle of 170° . Similarly, 1,1',3,3'-tetra-*tert*-butylferrocene (Kaluski, Gusev, Kalinin & Struchkov, 1972) has a Cp1–Fe–Cp2 angle of 173° .

The two fused oxacyclohexane rings which comprise the lactol exhibit typical chair conformations. There is probably a favorable dipolar interaction which accounts for close interaction [$3.515(2) \text{ \AA}$] between O1 and the positively charged Fe atom. The Fe–C1–C6–O1 torsion angle of the title compound is $54.5(4)^\circ$, whereas 1-(1-hydroxy-1-phenylpropyl)-2,1'-trimethyleneferrocene contains an analogous torsion angle of $42.5(14)^\circ$ (Lecomte *et al.*, 1973).

The hydroxy group O2 forms two independent hydrogen-bonding contacts about point-symmetry elements with O2 of other molecules, $2.804(4) \text{ \AA}$ to that at $1-x, 1-y, 1-z$ and $2.838(4) \text{ \AA}$ to that at $1-x, y, \frac{1}{2}-z$, with the H atom half-populated in each. O–H...O angles are *ca* 153° for the hydrogen bond disordered

about the center, and *ca* 170° for that disordered about the twofold axis.

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Structure of Di[bis(1,4,7,10-tetraoxacyclododecane)sodium] Tetrachlorodioxouranate(VI)–Methanol (1/2), $[\text{Na}(\text{12-crown-4})_2]_2[\text{UO}_2\text{Cl}_4] \cdot 2\text{MeOH}^*$

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Abstract. $[\text{Na}(\text{C}_8\text{H}_{16}\text{O}_4)_2]_2[\text{UCl}_4\text{O}_2] \cdot 2\text{CH}_3\text{O}$, $M_r = 1147$, orthorhombic, *Pbca*, $a = 14.393(3)$, $b = 23.223(5)$, $c = 14.909(3) \text{ \AA}$, $V = 4983.0 \text{ \AA}^3$, $Z = 4$, $D_x = 1.53 \text{ g cm}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71073 \text{ \AA}$, $\mu = 33.8 \text{ cm}^{-1}$, $F(000) = 2472$, $T = 293 \text{ K}$, final $R = 0.030$ for 2097 observed [$F_o \geq 5\sigma(F_o)$] reflections. The cations have no crystallographically imposed symmetry and consist of Na ions coordinated to all four O atoms of two unique crown ethers in a square antiprismatic

geometry. The Na–O separations average $2.49(2) \text{ \AA}$. The tetrachlorodioxouranate(VI) dianions are pseudo-octahedral and reside on crystallographic centers of inversion. The bonding parameters are normal. The solvent molecules are hydrogen bonded to the Cl atoms of the anions and are disordered.

Introduction. In the presence of benzo-15-crown-5, the slow aerial oxidation of a solution of UCl_3 in tetrahydrofuran (THF) and incorporation of Na^+ from the glass container resulted in the crystallization of $[\text{Na}(\text{benzo-15-crown-5})]_2[\text{UO}_2\text{Cl}_4]$, which has been

* *f*-Element/Crown Ether Complexes 18. Part 17: Rogers, Voss & Etzenhouser (1987).

structurally characterized (Moody & Ryan, 1979). A similar oxidation reaction occurs with UCl_4 and we have studied this reaction in 3:1 mixtures of acetonitrile and methanol in the presence of crown ethers such as 18-crown-6, dibenzo-18-crown-6, 15-crown-5, benzo-15-crown-5, and 12-crown-4 (Rogers, Kurihara & Benning, 1987). In each case, crystallization resulted from the production or abstraction of a suitable counterion: either the ammonium ion in $[(\text{NH}_4)(15\text{-crown-5})_2]_2[\text{UO}_2\text{Cl}_4] \cdot 2\text{CH}_3\text{CN}$, $[(\text{NH}_4)(\text{benzo-15-crown-5})_2]_2[\text{UCl}_6] \cdot 4\text{CH}_3\text{CN}$ and $[(\text{NH}_4)(\text{dibenzo-18-crown-6})_2]_2[\text{UO}_2\text{Cl}_4] \cdot 2\text{CH}_3\text{CN}$ or an Na ion as found in the title complex. This latter complex is quite different from $[\text{Na}(\text{benzo-15-crown-5})_2]_2[\text{UO}_2\text{Cl}_4]$ and this difference is the subject of this report.

Experimental. The synthesis of the title complex has been reported (Rogers, Kurihara & Benning, 1987). Greenish-yellow plates grown from acetonitrile:methanol (3:1). D_m not determined. Crystal $0.13 \times 0.33 \times 0.38$ mm. Enraf-Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$. Cell constants from setting angles of 25 reflections ($\theta > 20^\circ$). Three standard reflections, no intensity variation. Corrections for Lorentz-polarization effects and for absorption (empirical), range of relative transmission factors 53/100%. $\theta_{\text{max}} = 25^\circ$; h 0 to 12, k 0 to 20, l 0 to 12. 4871 reflections measured, 2097 independent observed reflections [$F_o \geq 5\sigma(F_o)$]. Structure solved via Patterson function and subsequent difference Fourier techniques. Crown-ether H atoms placed 0.95 Å from the bonded C atom with a fixed isotropic thermal parameter $B = 5.5 \text{ \AA}^2$ and allowed to ride with the C-H distance fixed. Two disordered orientations were observed for the unique solvent molecule. The two orientations were refined in alternate least-squares cycles at 50% occupancy with isotropic temperature factors only. Solvent H atoms were not included. Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974); structure refined with *SHELX76* (Sheldrick, 1976). $\sum w(|F_o| - |F_c|)^2$ minimized, weights = $[\sigma(F_o)^2 + 0.00003 F_o^2]^{-1}$, 275 parameters varied. $R = 0.030$, $wR = 0.030$, $S = 1.7$. Δ/σ in final least-squares refinement cycle < 0.01 , $\Delta\rho < 0.9 \text{ e \AA}^{-3}$ in final difference map.*

Discussion. Fractional coordinates and U_{eq} values are given in Table 1, distances and angles in Table 2, and an *ORTEP* illustration (Johnson, 1976) of the formula

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, torsion angles and least-squares-planes results have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44637 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final fractional coordinates for* $[\text{Na}(12\text{-crown-4})_2]_2[\text{UO}_2\text{Cl}_4] \cdot 2\text{MeOH}$

U	x	y	z	U_{eq} (Å ²)
U	0.5000	0.5000	0.5000	0.035
Cl(1)	0.5084 (2)	0.45462 (9)	0.3350 (1)	0.065
Cl(2)	0.6729 (1)	0.4628 (1)	0.5291 (2)	0.062
Na	0.5596 (2)	0.1966 (1)	0.4014 (2)	0.040
O(1)	0.4557 (3)	0.4347 (2)	0.5424 (3)	0.049
O(2)	0.6762 (3)	0.2666 (2)	0.3429 (4)	0.047
O(3)	0.4947 (4)	0.2576 (2)	0.2773 (3)	0.046
O(4)	0.4299 (3)	0.2563 (2)	0.4558 (4)	0.044
O(5)	0.6121 (3)	0.2639 (2)	0.5208 (3)	0.047
O(6)	0.4410 (3)	0.1249 (2)	0.3476 (4)	0.047
O(7)	0.6216 (3)	0.1379 (2)	0.2797 (3)	0.044
O(8)	0.6963 (4)	0.1376 (2)	0.4514 (4)	0.052
O(9)	0.5178 (4)	0.1258 (2)	0.5207 (3)	0.057
C(1)	0.6518 (5)	0.2851 (3)	0.2546 (5)	0.053
C(2)	0.5517 (5)	0.3046 (3)	0.2504 (5)	0.052
C(3)	0.4031 (5)	0.2744 (4)	0.3028 (5)	0.054
C(4)	0.3999 (5)	0.3000 (4)	0.3946 (5)	0.056
C(5)	0.4514 (6)	0.2777 (4)	0.5430 (6)	0.056
C(6)	0.5441 (5)	0.3052 (4)	0.5477 (6)	0.058
C(7)	0.6992 (5)	0.2886 (3)	0.4948 (5)	0.053
C(8)	0.6982 (5)	0.3126 (3)	0.4017 (5)	0.054
C(9)	0.4682 (5)	0.1059 (4)	0.2598 (6)	0.054
C(10)	0.5687 (5)	0.0895 (4)	0.2530 (5)	0.054
C(11)	0.7161 (5)	0.1240 (4)	0.2983 (6)	0.060
C(12)	0.7290 (5)	0.0979 (4)	0.3884 (6)	0.062
C(13)	0.6791 (6)	0.1127 (4)	0.5383 (6)	0.067
C(14)	0.5864 (6)	0.0848 (4)	0.5426 (6)	0.066
C(15)	0.4274 (6)	0.1026 (4)	0.5012 (6)	0.072
C(16)	0.4215 (6)	0.0796 (4)	0.4075 (6)	0.068
O(10) <i>a</i> †	0.2494 (9)	0.5483 (5)	0.7454 (9)	(iso)
C(17) <i>a</i>	0.161 (2)	0.583 (1)	0.715 (2)	(iso)
O(10) <i>b</i>	0.1921 (8)	0.5956 (6)	0.7659 (8)	(iso)
C(17) <i>b</i>	0.222 (2)	0.547 (1)	0.697 (2)	(iso)

* $U_{\text{eq}} = (U_{11} + U_{22} + U_{33})/3$.

† Designations *a* and *b* refer to the two orientations of the disordered methanol moiety. Each was refined at 50% occupancy.

Table 2. *Bond distances (Å) and angles (°) for* $[\text{Na}(12\text{-crown-4})_2]_2[\text{UO}_2\text{Cl}_4] \cdot 2\text{MeOH}$

U-Cl(1)	2.678 (2)	U-Cl(2)	2.670 (2)
U-O(1)	1.763 (5)	O(2)-C(8)	1.418 (9)
O(2)-C(1)	1.429 (9)	O(3)-C(3)	1.427 (9)
O(3)-C(2)	1.425 (9)	O(4)-C(5)	1.43 (1)
O(4)-C(4)	1.43 (1)	O(5)-C(7)	1.434 (9)
O(5)-C(6)	1.428 (9)	O(6)-C(16)	1.41 (1)
O(6)-C(9)	1.44 (1)	O(7)-C(11)	1.426 (9)
O(7)-C(10)	1.414 (9)	O(8)-C(13)	1.44 (1)
O(8)-C(12)	1.40 (1)	O(9)-C(15)	1.44 (1)
O(9)-C(14)	1.41 (1)	C(3)-C(4)	1.49 (1)
C(1)-C(2)	1.51 (1)	C(7)-C(8)	1.49 (1)
C(5)-C(6)	1.48 (1)	C(11)-C(12)	1.49 (1)
C(9)-C(10)	1.50 (1)	C(15)-C(16)	1.50 (1)
C(13)-C(14)	1.49 (1)	O(10) <i>b</i> -C(17) <i>b</i>	1.58 (3)
O(10) <i>a</i> -C(17) <i>a</i>	1.58 (3)	Na-O(6)	2.515 (6)
Na-O(2)	2.494 (6)	Na-O(7)	2.438 (6)
Na-O(3)	2.510 (5)	Na-O(8)	2.510 (6)
Na-O(4)	2.462 (6)	Na-O(9)	2.496 (6)
Na-O(5)	2.487 (6)		
Cl(1)-U-Cl(2)	88.86 (7)	Cl(1)-U-O(1)	90.4 (2)
Cl(1)-U-Cl(1')*	180.0	Cl(1)-U-Cl(2')	91.14 (7)
Cl(1)-U-O(1')	89.6 (2)	Cl(2)-U-O(1)	90.0 (2)
Cl(2)-U-Cl(2')	180.0	Cl(2)-U-O(1')	90.0 (2)
O(1)-U-O(1')	180.0		
C(1)-O(2)-C(8)	113.5 (6)	C(2)-O(3)-C(3)	113.4 (6)
C(4)-O(4)-C(5)	113.5 (6)	C(6)-O(5)-C(7)	114.0 (6)
C(9)-O(6)-C(16)	113.7 (6)	C(10)-O(7)-C(11)	112.9 (6)
C(12)-O(8)-C(13)	113.4 (6)	C(14)-O(9)-C(15)	115.3 (6)
O(2)-C(1)-C(2)	111.2 (6)	O(3)-C(2)-C(1)	107.9 (6)
O(3)-C(3)-C(4)	112.4 (6)	O(4)-C(4)-C(3)	107.0 (6)
O(4)-C(5)-C(6)	112.9 (7)	O(5)-C(6)-C(5)	108.4 (6)
O(5)-C(7)-C(8)	113.1 (6)	O(2)-C(8)-C(7)	107.2 (6)
O(6)-C(9)-C(10)	113.8 (6)	O(7)-C(10)-C(9)	107.4 (6)
O(7)-C(11)-C(12)	112.8 (6)	O(8)-C(12)-C(11)	107.2 (7)
O(8)-C(13)-C(14)	111.7 (7)	O(9)-C(14)-C(13)	109.0 (7)
O(9)-C(15)-C(16)	111.9 (7)	O(6)-C(16)-C(15)	108.3 (7)

* Primed atoms are related to those in Table 1 by a crystallographic center of inversion.

unit and atom labeling in Fig. 1. Crown-ether coordination of the Na ions in the title complex results in complete charge separation. As seen in the cell-packing diagram (Fig. 2), the [Na(12-crown-4)]⁺ ions form essentially organic layers with the [UO₂Cl₄]²⁻ and hydrogen-bonded solvent molecules forming inorganic layers throughout the crystal. Similar charge separation was observed in [(NH₄)(15-crown-5)]₂[UO₂Cl₄].2CH₃CN and [(NH₄)(benzo-15-crown-5)]₂[UCl₆].4CH₃CN, but not in [(NH₄)(dibenzo-18-crown-6)]₂[UO₂Cl₄].2CH₃CN, or in [Na(benzo-15-crown-5)]₂[UO₂Cl₄]. In the latter two complexes, the cation interacts with a crown ether on one side and the uranyl tetrachloride anion on the other, either *via* electrostatic or a combination of electrostatic and hydrogen-bonding interactions. In the former two

complexes, acetonitrile molecules interact weakly with the Cl atoms of the dianions. If we assume that dibenzo-18-crown-6 is simply too large and too inflexible to form a simple 2:1 adduct with NH₄⁺, the differences in the title complex and the closely related [Na(benzo-15-crown-5)]₂[UO₂Cl₄] may reflect the crystallization of the latter from a solvent (THF) which is not a hydrogen-bond donor.

The [Na(12-crown-4)]⁺ cation is square antiprismatic with all eight O atoms coordinated to the metal and an average Na—O separation of 2.49 (2) Å. The O...O contacts forming the square planes (*s*) average 2.80 (1) Å, while those between planes (*l*) average 3.38 (8) Å. The *s/l* ratio is 0.83 and the Na⁺ ion is 1.50 and 1.52 Å from the mean plane of O(2)—O(5) (planar to within 0.009 Å) and O(6)—O(9) (planar to within 0.006 Å), respectively. These values are almost identical to those found in four other structures containing this ion: [Na(12-crown-4)]₂Cl.5H₂O (van Remoortere & Boer, 1974), [Na(12-crown-4)]₂OH.8H₂O (Boer, Neuman, van Remoortere & Steiner, 1974), [Na(12-crown-4)]₂[ClO₄] (Mason & Eick, 1982) and [Lu(OH₂)₈][Na(12-crown-4)]₂Cl₄.2H₂O (Rogers & Voss, 1987).

As expected, the two unique crown-ether molecules exhibit approximate C₄ symmetry as shown by the sequence of torsion angles starting with O—C—O of: *g*⁻(-60°) *a* (180°) *g*⁻*g*⁻ *a* *g*⁻*g*⁻ *a* *g*⁻*g*⁻ *a* *g*⁻. As expected from steric repulsions when C—O—C—C angles are forced *gauche* in crown ethers, these angles are all greater than 70° (average ~80°). The average internal-bonding parameters of the crown molecules are normal: C—O = 1.43 (1), C—C = 1.49 (1) Å and C—O—C = 113.7 (7)°. In the C₄ conformation of 12-crown-4, there are two types of C atoms. In the title complex, the angles at these positions average O—Cα—Cβ = 107.8 (7), O—Cβ—Cα = 112.5 (8)°.

The linear uranyl moiety and four Cl atoms give the U atoms in the anions an octahedral geometry. The U=O separation is 1.763 (5) Å and the two unique U—Cl distances average 2.674 (4) Å. The two U—Cl separations are slightly different at the 3σ level [U—Cl (1) = 2.678 (2), U—Cl (2) = 2.670 (2) Å] and may be a manifestation of slightly different hydrogen-bonding environments. The anion parameters fall within the range found for other uranyl tetrachloride compounds (Rogers, Kurihara & Benning, 1987, and references therein).

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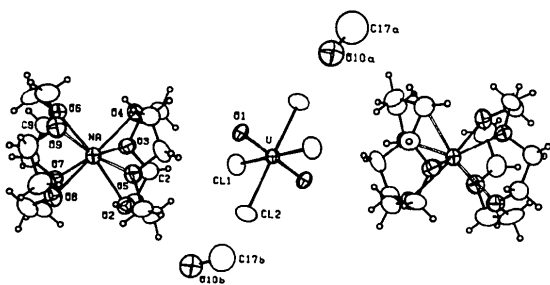


Fig. 1. [Na(12-crown-4)]₂[UO₂Cl₄].2MeOH. 50% probability ellipsoids for thermal motion. H atoms arbitrarily reduced.

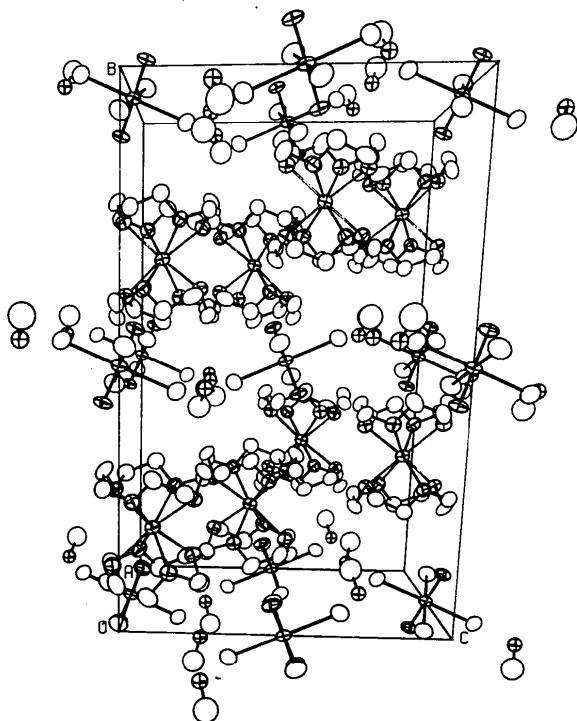


Fig. 2. Cell packing revealing the overall layer-like structure.

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Synthesis and Structure of Thorium Chloride–1,4,7,10,13-Pentaoxacyclopentadecane–Water–Methanol–Acetonitrile (1/1/2/2/1), [ThCl₄(OHMe)₂(OH₂)₂].15-Crown-5.CH₃CN*

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Abstract. Diaquatetrachlorobis(methanol)thorium(IV)–15-crown-5–acetonitrile, [ThCl₄(CH₄O)₂(OH₂)₂].C₁₀H₂₀O₅.C₂H₃N, $M_r = 735.3$, monoclinic, $P2_1/n$, $a = 8.686$ (1), $b = 18.620$ (2), $c = 16.043$ (3) Å, $\beta = 99.56$ (1)°, $V = 2558$ Å³, $Z = 4$, $D_x = 1.91$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 59.9$ cm⁻¹, $F(000) = 1424$, $T = 123$ K, $R = 0.045$ for 3387 independent observed [$F_o \geq 5\sigma(F_o)$] reflections. The Th^{IV} ion is eight-coordinate with approximate dodecahedral geometry. The four Cl atoms occupy *A* sites [Th–Cl average = 2.710 (7) Å] with the remaining *B* sites occupied by two water molecules [Th–O average = 2.527 (4) Å] and two methanol groups [Th–O average = 2.562 (3) Å]. The water and methanol groups are hydrogen-bonded to symmetry-related crown-ether molecules forming polymeric chains. One O atom of the crown molecule accepts two hydrogen bonds which has an interesting effect on this molecule's conformation. The acetonitrile molecule has close contacts suggesting hydrogen bonds with two of the Cl atoms from different asymmetric units, thus bridging the polymeric chains.

Introduction. In our investigation into *f*-element/crown-ether complexation we have tried to find clues to the effects of such variables as metal-ion size, crown-

ether-cavity size, crown-ether conformation, anion, solvent, conditions of reaction, and method of crystallization on the actual complexation of the crown ether directly to the metal ion. Since a study of various metal-ion sizes in the actinide series is difficult for us to accomplish limited to thorium and uranium, we have concentrated on investigations of changing the anion and solvent for these metals. Although examples of crown ethers coordinated directly to uranium have been reported (see, for example, de Villardi, Charpin, Costes, Folcher, Plurien, Rigny & de Rango, 1978; Navaza, Villain & Charpin, 1984; Dejean, Charpin, Folcher, Rigny, Navaza & Tsoucaris, 1987), we have only managed to crystallize second-sphere hydrogen-bonded complexes such as [Th(NO₃)₄(OH₂)₃].18-crown-6 (Rogers, Kurihara & Benning, 1987*a*), [ThCl₄(OH₂)₃(OH₂)].18-crown-6.H₂O (Rogers, Kurihara & Benning, 1988), [UO₂(OH₂)₅](ClO₄)₂.2(18-crown-6).H₂O.CH₃CN, and [UO₂(OH₂)₃](ClO₄)₂.3(15-crown-5).CH₃CN (Rogers, Kurihara & Benning, 1987*b*). The isolation and structural characterization of the title complex gives us this opportunity to compare the effects of methanol *versus* ethanol in the primary coordination sphere of similar complexes – [ThCl₄(OHMe)₂(OH₂)₂].15-crown-5.CH₃CN and [ThCl₄(OH₂)₃(OH₂)].18-crown-6.H₂O.

Experimental. Under Ar, 10 mmol of 15-crown-5 in 25 mL of a 3:1 mixture of acetonitrile:methanol was added to a stirring solution of 10 mmol of ThCl₄.*n*H₂O

* *f*-Element/Crown Ether Complexes. 19. Part 18: Rogers (1988).

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