Novel Unidentate Co-ordination of a Crown Ether and of a Polyethylene Glycol to Uranium(VI)[1]

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The syntheses and structural characterizations of $[UO_2Cl_2(OH_2)_2$(1,4,7,10-tetraoxacyclododecane)]·1,4,7,10-tetraoxacyclododecane and $UO_2Cl_2(OH_2)_2$(3,6,9,12,15-pentaoxaheptadecane-1,17-diol) have revealed that individual 12-crown-4 and hexaethylene glycol (EO6) molecules can behave as both unidentate donors and hydrogen bond acceptors.

The complexation chemistry of uranium with macrocyclic crown ethers has been of interest in recent years,[2—10] yet structural confirmation of uranium insertion into the crown ether cavity has been limited to $[U(BH_4)_2$(dicyclohexyl-18-crown-6)$]_2[UCl_5(BH_4)]$,[4] $[UO_2$(dicyclohexyl-18-crown-6)]$(ClO_4)_2$,[5] and $[UCl_3$(dicyclohexyl-18-crown-6)$]_2[UCl_6]$.[6] It is more common to find that reactions of uranium salts with crown ethers lead to hydrogen bonded systems (*via* metal co-ordinated water molecules)[5,8—10] or crown complexation of suitable counterions.[2,3] We recently observed the latter in our studies of the oxidation of UCl_4 to $[UO_2Cl_4]^{2-}$ in the presence of crown ethers.[2,3] We isolated Na^+ and NH_4^+ complexes of crown ethers with $[UO_2Cl_4]^{2-}$ counterions.

In another attack on this same problem we decided to utilize UO_2Cl_2 as a starting material to avoid unwanted oxidation products from interfering with the complexation chemistry. We have isolated novel unidentate 12-crown-4 and hexaethylene glycol (EO6)† complexes of UO_2Cl_2 in this fashion. Since the number of structurally characterized crown ether complexes of uranium is limited and since variably dentate co-ordination of the hard donor crown ethers or polyethylene glycols is rare for any metal‡ we report here the structural characterization of the title complexes.

The complex $[UO_2Cl_2(OH_2)_2$(12-crown-4)]·(12-crown-4) was crystallized from the equimolar reaction of anhydrous UO_2Cl_2 and 12-crown-4 in tetrahydrofuran (THF) containing traces of water.§ An ORTEP illustration of this complex is

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† 1,4,7,10-tetraoxyacyclododecane = 12-crown-4. 3,6,9,12,15-pentaoxaheptadecane-1,17-diol = hexaethylene glycol and is abbreviated here as EO6.

‡ Atwood has observed monodentate crown ether complexes of trimethylaluminum: $[AlMe_3]_2$[dibenzo-18-crown-6],[11] $[AlMe_3]_3$[dibenzo-18-crown-6],[12] $[AlMe_3]_4$[15-crown-5],[11] $[AlMe_3]_4$[18-crown-6];[12] and bidentate complexes of Ti^{III}, Ti^{IV}, V^{III}, V^{IV}, and Sn^{IV}: $[TiCl_3(OH_2)$(18-crown-6)$]\cdot CH_2Cl_2$,[13] $[MCl_4$(18-crown-6)] (M = Ti, Sn),[14] $VCl_3(OH_2)$(18-crown-6),[15] $[PPh_4]_2$(18-crown-6)].[15]

§ 1.5 mmol of 12-crown-4 was added to a stirred solution of 1.5 mmol of anhydrous UO_2Cl_2 in 5 ml of THF. The water content of the THF was <2.56%. The reaction mixture was heated to 60 °C for 1 h, cooled to 20 °C, and the volume reduced by 1/3. Yellow crystals formed overnight by slowly evaporating the solution at 20 °C. Satisfactory analytical data were obtained.

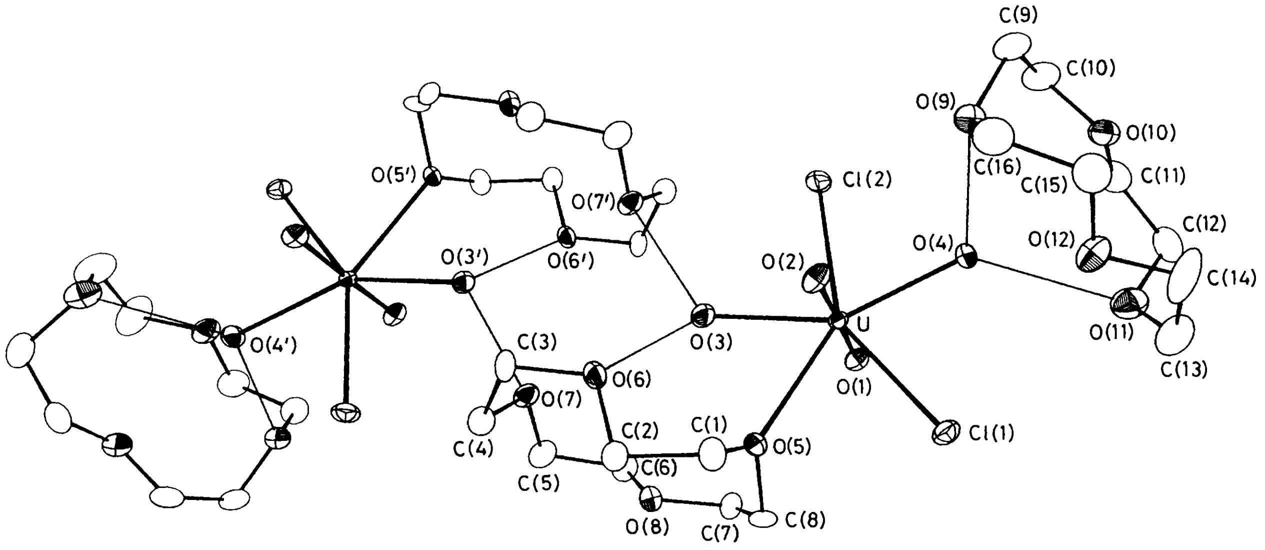

Figure 1. $[UO_2Cl_2(OH_2)_2(12\text{-crown-}4)]\cdot 12\text{-crown-}4$.

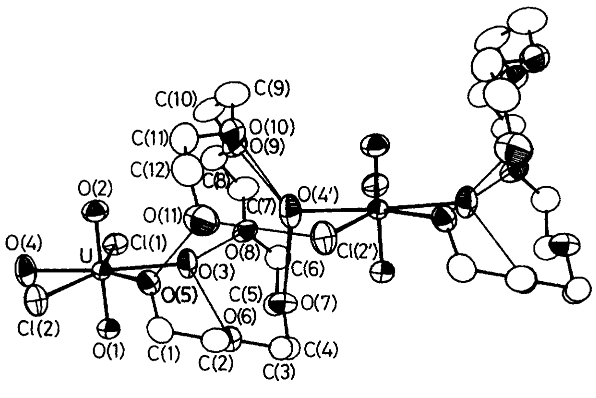

Figure 2. $UO_2Cl_2(OH_2)_2(EO6)$.

presented in Figure 1.¶ The uranyl fragment, two chlorine atoms, two water molecules, and one crown oxygen atom describe the metal ion's pentagonal bipyramidal geometry. The formula unit is completed by a 12-crown-4 moiety which is hydrogen bonded to one of the two water molecules [O(4)] co-ordinated to the metal. The other water molecule [O(3)] is hydrogen bonded to the crown ether directly co-ordinated to the metal ion and to its symmetry-related equivalent (crystallographic centre of inversion) forming a dimer.

The uranyl moiety is linear, with an average U=O separation of 1.758(5) Å and an average U–Cl distance of 2.69(2) Å; both distances are normal. It is interesting to note that the U–O separation for the water molecule which is hydrogen bonded to only one crown ether is shorter [U–O(4) = 2.410(3) Å] than that for the water molecule that interacts with two different crown ethers [U–O(3) = 2.443(4)]. The longest U–O distance, 2.546(4) Å, involves the ethereal oxygen. The long separation is probably due to the fact that the crown ether is less basic than the water molecules and sterically more demanding.

The two crown ether molecules exhibit neither of the common conformations found for these molecules (C_4 in most|| metal complexes[18] and C_i in the free ether[19]).[20] In addition both have different conformations. The co-ordinated ether is very close to the normal C_4 conformation. Distortions occur around O(6) which has no complexation or hydrogen bonding interactions and is thus turned out away from the metal hydrogen bond donors. The terminal ether approximates the C_i conformation with O(9) and O(11) severely distorted up toward O(4) to accept hydrogen bonds. It is noted that 12-crown-4 is not flexible enough to provide maximum overlap in this conformation and the O(4)···O(9) and O(11) contacts are quite long, averaging 2.76(9) Å.

The complex $UO_2Cl_2(OH_2)_2(EO6)$ was prepared in an analogous manner to the 12-crown-4 complex. An ORTEP illustration of the formula unit and a portion of the polymeric chain are presented in Figure 2.¶ The pentagonal bipyramidal geometry of the uranium ion consists of the uranyl oxygen atoms, two chloride ions, two water molecules, and a terminal (alcoholic) oxygen atom of the EO6 molecule. Two of the oxygens within the glycol, O(6) and O(8), accept hydrogen bonds from one of the co-ordinated water molecules [O(3)]. The Cl(2) atom accepts a hydrogen bond from the terminal alcoholic oxygen atom [unco-ordinated, O(11)] of a symmetry-related (unit translation along *b*) EO6 molecule. Co-ordinated water molecule O(4) donates hydrogen bonds to this same symmetry related glycol and the overall structure is polymeric.

The uranyl fragment is linear and has an average U=O separation of 1.750(4) Å. The U–Cl(1) and U–Cl(2) separa-

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¶ *Crystal data* for $[UO_2Cl_2(OH_2)_2(12\text{-crown-}4)]\cdot 12\text{-crown-}4$: monoclinic, $P2_1/c$ with (at −150 °C) a = 17.512(8), b = 9.413(4), c = 16.723(9) Å, β = 115.25(6)°, U = 2493 Å^3 and D_c = 1.94 g cm^{-3} for Z = 4 formula units. 3680 independent observed reflections [$F_o \geqslant 5\sigma(F_o)$] were measured on a CAD4 diffractometer using Mo-K_α radiation and used in the least squares refinement leading to the current R value of 0.028. *Crystal data* for $UO_2Cl_2(OH_2)_2(EO6)$: monoclinic, $P2_1/n$ with (at 20 °C) a = 16.761(8), b = 7.897(5), c = 16.975(6) Å, β = 107.85(4)°, U = 2139 Å^3, and D_c = 2.05 g cm^{-3} for Z = 4 formula units. Utilization of 2708 independent observed [$F_o \geqslant 5\sigma(F_o)$] reflections led to the current R value of 0.032. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

|| Exceptions include a C_i conformation in $[Mg(OH_2)_6]Cl_2\cdot 12\text{-crown-}4$[16] and a C_s conformation in $[CuCl_2(12\text{-crown-}4)]$.[17]

tions are 2.683(2) and 2.731(2) Å, the difference in the U–Cl distances, probably due to the fact that Cl(2) is involved in a hydrogen bond. The alcoholic U–O(5) separation of 2.433(5) Å is actually shorter than the average U–OH_2 distance of 2.47(1) Å.

One of the more interesting aspects of this structure is the behaviour of the EO6 molecule. The O(5) atom donates a hydrogen bond to terminal O(11) actually cyclizing the molecule. The resulting glycol conformation is very similar to the D_{3d} form of 18-crown-6.[20]††

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†† Yellow crystals were isolated by addition of an equal volume of MeCl. Satisfactory analytical data were obtained.

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