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First- and second-sphere coordination of the uranyl ion by bis[2-(2-hydroxyphenoxy)ethoxy]ethane

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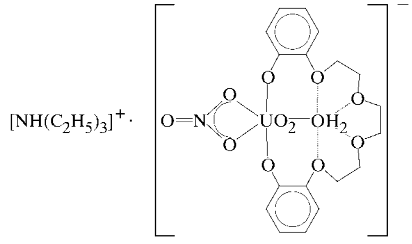
Uranyl nitrate hexahydrate reacts with bis[2-(2-hydroxyphenoxy)ethoxy]ethane ($C_{18}H_{22}O_6$), denoted LH_2 hereafter, in the presence of triethylamine to give triethylammonium aqua[2,2′-(3,6-dioxaoctane-1,8-diyldioxy)diphenolato-κ^2O,O']-(nitrato-κ^2O,O')dioxouranium(VI), $(Et_3NH)[UO_2(H_2O)L(NO_3)]$, which possesses a symmetry plane. The uranyl ion is coordinated to the two phenoxide O atoms, a nitrate ion and a water molecule (first sphere); the water molecule is itself held in the crown ether chain by hydrogen-bonding interactions, thus ensuring second-sphere coordination by the ligand *L*.

Comment

Bis[2-(2-hydroxyphenoxy)ethoxy]ethane, LH_2, which is analogous to dibenzo-24-crown-8 less one of the $–[O(CH_2)_2]_3O–$ ether chains, is a frequently encountered unit. Linked further in the 6-position of both aromatic rings, it can be included in macrocycles designed for metal-ion complexation (Casellato *et al.*, 1997). The ligands thus obtained have been used in the synthesis of heterobinuclear species [see *e.g.* Reetz *et al.* (1995) and Arion *et al.* (1998)]. We report herein the crystal structure of the uranyl ion complex, (I), of the dianionic ligand *L*, which presents some interesting features. Up to now, the only structure reported for this molecule is that of its hydrate (Suh *et al.*, 1985). The structure of the sodium isothiocyanate complex of the related dimethoxy ligand has also been described (Suh *et al.*, 1978). We reported previously the structure of a compound with a shorter ether chain, namely bis[2-(2-hydroxyphenoxy)ethyl] ether methanol solvate (Thuéry *et al.*, 2002), in which the methanol molecule, similar to the water molecule in the hydrate cited above, is hydrogen bonded to phenolic and ether O atoms.

The asymmetric unit of (I) comprises half the complex unit and its counter-ion, the whole molecular assembly being given by a mirror plane containing the uranyl ion. The uranyl ion is bound in its equatorial plane to the doubly deprotonated ligand *L* by the two equivalent phenoxide O atoms, with a U—O bond length of 2.180 (6) Å, slightly shorter than the U—O(phenoxide) bond length in uranyl calixarene complexes (Thuéry *et al.*, 2001). The metal atom is also bound to two equivalent nitrate O atoms with a usual U—O bond length of 2.521 (7) Å, and to a water molecule with a U—O distance of 2.478 (11) Å. Together with the two oxo atoms, these five donor O atoms constitute the uranium first coordination sphere, which displays the common pentagonal bipyramidal geometry, distorted mainly as a result of the small 'bite' of the chelating nitrate ion. The five equatorial donor O atoms define a plane with an r.m.s. deviation of 0.024 Å, the U atom being at 0.007 (5) Å from this plane. The two aromatic rings are nearly orthogonal, with a dihedral angle of 89.6 (3)°. This coordination geometry is quite different from the wrapping annular structure observed in the sodium complex of the dimethoxy derivative (Suh *et al.*, 1978).



(I)

The coordinated water molecule is located near the centre of the O2···O2^i (Fig. 1) diameter of the semicircle defined by the ether chain, which, if the phenolic rings are neglected, is analogous to half an 18-crown-6 moiety. Atoms O2 and O3 are

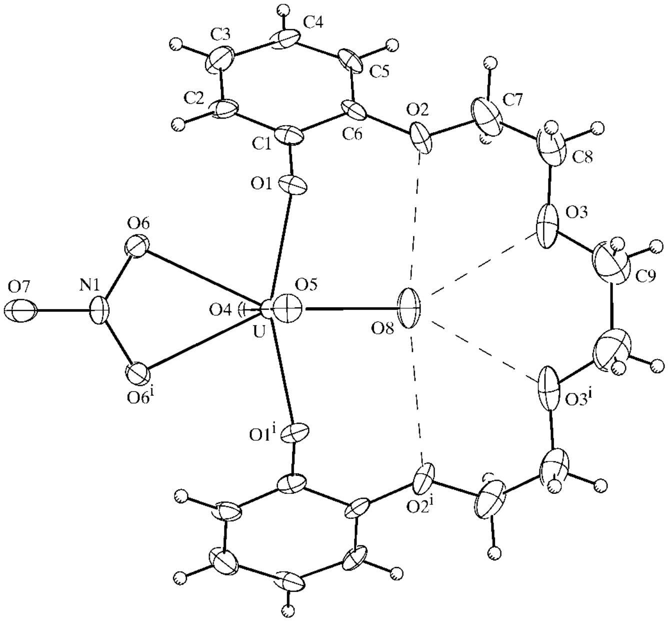


Figure 1
The title molecule with the atomic numbering scheme. H atoms are drawn as small spheres of arbitrary radii. Possible hydrogen bonds are shown as dashed lines. Displacement ellipsoids are drawn at the 30% probability level. The triethylammonium counter-ion has been omitted for clarity. [Symmetry code: (i) 1 $-x$, y, z.]

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located at distances of −0.50 (1) and 0.07 (2) Å from the mean O_5 plane defined above. The distances between O8 and the ether O atoms are indicative of loose hydrogen bonds [O8···O2 3.095 (11) Å and O8···O3 2.942 (14) Å; the O2···O8···O3(1 − *x*, *y*, *z*) angle of 111.7 (4)° is also compatible with a bonding of both water H atoms to these two ether O atoms]. However, as the water H atoms have not been found, it appears impossible to describe more precisely the nature, possibly bifurcated, of the hydrogen bonding in this case. It may be noted that, in the hydrate of LH_2 (Suh *et al.*, 1985), in which the H atoms have been located, the O(water)···O(ether) distances corresponding to possible hydrogen bonds are comparable to the present distances (2.916–3.039 Å). The situation is however somewhat different in the hydrate since hydrogen bonds involving the phenolic groups are also present. The conformation of the ether chain is characterized by C—O—C—C torsion angles near 180° (*anti* angles), an O2—C7—C8—O3 *gauche* torsion angle of 65 (2)° and a more unusual O3—C9—C9^{i}—O3^{i} angle (0° by symmetry). The ligand *L* in (I) appears as a ditopic ligand; only the phenoxide groups are involved in first-sphere coordination of the uranyl ion, whereas the ether coordination site is involved in second-sphere non-covalent bonding *via* the first-sphere water ligand. Second-sphere coordination is a well documented feature (Alston *et al.*, 1989; Atwood *et al.*, 1991; Steed, 2001). The present case is reminiscent of second-sphere coordination *via* intramolecular hydrogen bonding of hydrated alkali metal cations by crown ethers (Steed, 2001, and references therein).

The triethylammonium ion in (I) is located 'above' the complex anion and is likely involved in a hydrogen bond with oxo atom O5, with an N2···O5 distance of 3.22 (6) Å (this bond may result in the U—O5 bond length being slightly longer than the U—O4 bond). Such hydrogen bonds between ammonium counter-ions and oxo atoms are very common in uranyl complexes (Thuéry *et al.*, 2001, and references therein). The ammonium ion is further 'capped' by the cavity formed by the aromatic rings of the neighbouring molecule along the *c* axis. C—H···π interactions may be present, the shortest H···C(aromatic) distance being 2.74 Å.

Experimental

The LH_2 ligand was prepared as reported previously (Bartsch *et al.*, 1983). LH_2 was reacted with $UO_2(NO_3)_2{\cdot}6H_2O$ in boiling $CHCl_3$–CH_3CN (3:1) in the presence of a large excess of NEt_3. On slow evaporation, the resulting orange solution deposited crystals suitable for X-ray crystallographic analysis.

Crystal data

$(C_6H_{16}N)[UO_2(H_2O)(C_{18}H_{20}O_6)(NO_3)]$
$M_r = 784.59$
Orthorhombic, $Pmn2_1$
$a = 15.6688\ (10)$ Å
$b = 9.6025\ (5)$ Å
$c = 9.5303\ (7)$ Å
$V = 1433.93\ (16)$ Å^3
$Z = 2$
$D_x = 1.817$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9425 reflections
$\theta = 2.6$–25.7°
$\mu = 5.72$ mm^{-1}
$T = 100\ (2)$ K
Needle, dark red (translucent)
$0.20 \times 0.08 \times 0.05$ mm

Table 1
Selected geometric parameters (Å, °).

U—O1	2.180 (6)	U—O6	2.521 (7)
U—O4	1.779 (9)	U—O8	2.478 (11)
U—O5	1.819 (9)		
O1—U—O6	76.4 (2)	O1^{i}—U—O1	156.7 (4)
O6^{i}—U—O6	50.4 (3)	O4—U—O5	177.3 (5)
O1—U—O8	78.40 (18)		

Symmetry code: (i) 1 − *x*, *y*, *z*.

Data collection

Nonius KappaCCD diffractometer
φ scans
Absorption correction: empirical (*DELABS* from *PLATON*; Spek, 2000)
$T_{min} = 0.326$, $T_{max} = 0.756$
9425 measured reflections
2768 independent reflections
2546 reflections with $I > 2\sigma(I)$
$R_{int} = 0.061$
$\theta_{max} = 25.7°$
$h = -19 \rightarrow 17$
$k = -11 \rightarrow 11$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.091$
$S = 1.20$
2768 reflections
191 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0249P)^2 + 4.7737P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.46$ e Å^{-3}
$\Delta\rho_{min} = -0.60$ e Å^{-3}
Absolute structure: Flack (1983), 1382 Friedel pairs
Flack parameter = −0.024 (16)

The water H atoms, likely disordered over the four positions compatible with hydrogen bonding with the ether O atoms, together with the H atom bound to the ammonium N atom, were not found on the difference Fourier map. All other H atoms were introduced at calculated positions, with C—H bond lengths of 0.93 (CH), 0.97 (CH_2) or 0.96 Å (CH_3), and were treated as riding atoms with a displacement parameter equal to 1.2 (CH, CH_2) or 1.5 (CH_3) times that of the parent atom. The cation lies on a mirror plane and the methyl group in a general position was refined as a rotating rigid group, whereas the methyl group located on the symmetry plane was not allowed to rotate.

Data collection: *KappaCCD Software* (Nonius, 1998); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL* and *PARST*97 (Nardelli, 1995).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1095). Services for accessing these data are described at the back of the journal.

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