metal-organic compounds

Dihydro[2.2.2]cryptand di-μ-hydroxo-bis[bis(nitrato-$\kappa^2 O,O'$)-dioxouranium(VI)] monohydrate

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In the title dinuclear uranyl complex, $(C_{18}H_{38}N_2O_6)[(UO_2)_2(NO_3)_4(OH)_2]\cdot H_2O$, each pair of uranyl ions in the two independent centrosymmetric dianionic dimers is bridged by the two hydroxide ions, with the nitrate ions ensuring equatorial hexagonal coordination. The dihydro[2.2.2]cryptand (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) dication presents an 'in–in' conformation (*endo* protonation) and it is hydrogen bonded to the hydroxide ions, either directly or *via* a water molecule, resulting in the formation of linear hydrogen-bonded polymers.

Comment

[2.2.2]Cryptand has recently been used as a basic agent in the synthesis of uranyl ion complexes of hexahomotrioxacalix[3]arenes (Masci *et al.*, 2002). In some of the resulting supramolecular assemblies, the dihydro[2.2.2]cryptand dication is encapsulated between two complex molecules and held by feeble forces (cation–π and C—H···π interactions). Compound (I) was obtained as a by-product during the investigation of a similar reaction with another calixarene. A search of the Cambridge Structural Database (Version 5.23; Allen & Kennard, 1993) gives few compounds closely related to (I). The di-μ-hydroxo-bis[bis(nitrato-$\kappa^2 O,O'$)dioxouranium(VI)] complex has been described previously, in association with choline (Viossat *et al.*, 1983) or 4,4′-bipyridinium (Alcock & Flanders, 1987), as well as the related di-μ-aqua-bis[bis(nitrato-$\kappa^2 O,O'$)dioxouranium(VI)] complex (Perry *et al.*, 1980; Hämäläinen *et al.*, 1996). The *cis* positioning of two nitrate ions bound to a dihydroxouranyl group was first observed in the related compound triaquadioxouranium(VI)-di-μ-hydroxo-[bis(nitrato-$\kappa^2 O,O'$)dioxouranium(VI)] monohydrate (Perrin, 1976).

The asymmetric unit in (I) comprises two half complex molecules, a complete dihydro[2.2.2]cryptand dication and a water molecule. The two complex molecules have similar geometries. The U atoms are in distorted hexagonal–bipyramidal environments, with a common edge defined by the

double hydroxide bridge. The six O atoms of the nitrate and hydroxide ions around each U atom define a plane with r.m.s. deviations of 0.077 (3) and 0.081 (3) Å and distances to U of 0.009 (1) and 0.028 (1) Å in the two molecules. The O_{ax}—U—O_{eq} angles are in the range 85.82 (17)–92.94 (18)° in the first molecule and 86.63 (16)–94.33 (17)° in the second, indicating some puckering of the equatorial donor atoms.

(I)
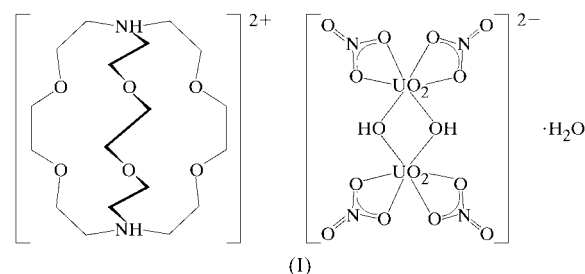
The U—$O_{nitrate}$ bond lengths are in the range 2.515 (4)–2.561 (4) Å, in agreement with values in analogous complexes. The U—O_{OH} bond lengths are shorter, in the range 2.313 (4)–2.342 (4) Å, and the U—O_{OH}—U angles are 112.77 (16) and 113.60 (15)°; all these values are in agreement with those in the previous compounds. The U···U distances are 3.8556 (5) and 3.9156 (5) Å in the two molecules, close to the range of 3.896–3.944 Å in the examples cited above.

The dihydro[2.2.2]cryptand dication is in the 'in–in' conformation, the two H atoms bound to the N atoms being directed inwards as a result of *endo* protonation. This is the most common geometry for this cation, although it has been shown that *exo* protonation, associated with the 'out–out' conformation, could be stabilized in the solid state when the H atoms are involved in hydrogen bonding with an external acceptor (MacGillivray & Atwood, 1997*a*). However, even when such acceptors are available, the 'in–in' conformation may be observed, as in the present case or in the assemblies involving uranyl complexes of hexahomotrioxacalix[3]arenes (Masci *et al.*, 2002).

The ammonium H atoms in (I) are involved in loose trifurcated hydrogen bonds with the ether O atoms (MacGillivray & Atwood, 1997*b*), some of the latter being themselves also hydrogen bonded to external donors. Atom O22 is thus hydrogen bonded to the hydroxide ion of the second complex molecule, whereas atoms O19 and O23, which pertain to different ether chains, are bonded to the two H atoms of the water molecule. This peculiar involvement of three ether O atoms, one in each 'arm', in external hydrogen bonds, results in a rather distorted cryptand geometry. All N—C—C—O and O—C—C—O torsion angles are *gauche* [in the range 50.3 (6)–70.0 (6)°], but two C—O—C—C angles are *gauche* instead of *anti*, with values of 77.8 (6) and 75.3 (6)°.

The N···N separation is 5.710 (7) Å, much shorter than in the neutral ligand (6.87 Å; Metz *et al.*, 1976) due to the internal hydrogen bonds, and in agreement with those in other diprotonated species (Masci *et al.*, 2002). The O···O separations in each half-molecule are in the range 3.881 (6)–4.303 (6) Å.
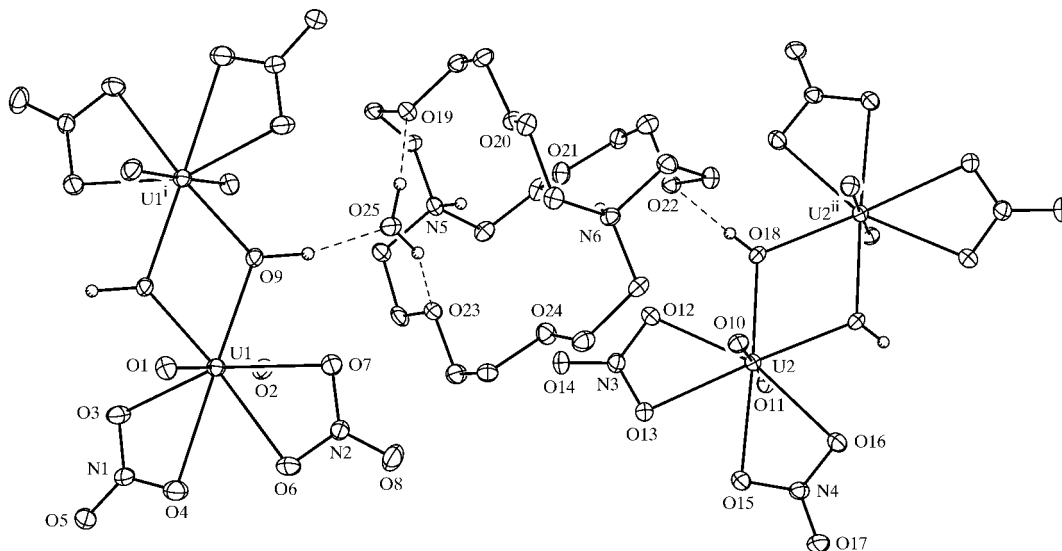
Figure 1
A view showing the two centrosymmetric complex molecules surrounding the hydrogen-bonded dication and water molecule in (I), with a partial atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms involved in hydrogen bonding are drawn as small spheres of arbitrary radii and other H atoms have been omitted for clarity. Intermolecular hydrogen bonds are shown as dashed lines and intramolecular hydrogen bonds are not represented [symmetry codes: (i) $-x, 1 - y, 2 - z$; (ii) $2 - x, 1 - y, 1 - z$.]

The water molecule acts as a hydrogen-bond acceptor towards the hydroxide ion of the first molecule (this bond being seemingly the strongest of all hydrogen bonds in this compound). The cryptand cations are thus held between successive complex molecules, either directly or *via* the water molecules. Both cryptand and water molecules can be considered as second-sphere ligands with respect to the uranyl ions. This arrangement results in the formation of linear polymers along the (20$\bar{1}$) direction. A similar arrangement has been described in the complex 4,4′-bipyridinium di-μ-hydroxo-bis[dinitratodioxouranium(VI)] monohydrate (Alcock & Flanders, 1987), in which chains of alternating uranyl complexes and 4,4′-bipyridinium ions are held together by hydrogen bonds, either directly between ammonium and hydroxide ions or *via* a water molecule.

Experimental

The reaction of uranyl nitrate hexahydrate with a stoichiometric amount of [2.2.2]cryptand in a boiling CH$_3$CN–CHCl$_3$ (1:1) mixture in the presence of *p-tert*-butylcalix[5]arene gave a light-yellow solution, which indicated the absence of complexation of uranyl ions by the calixarene (the characteristic colour of such complexes is dark orange), and yielded crystals of (I) suitable for X-ray crystallographic analysis.

Crystal data

$(C_{18}H_{38}N_2O_6)[U_2O_4(NO_3)_4$
$(OH)_2]\cdot H_2O$
$M_r = 1218.64$
Triclinic, $P\bar{1}$
$a = 9.0595 (5)$ Å
$b = 9.8517 (5)$ Å
$c = 20.8019 (12)$ Å
$\alpha = 86.528 (3)°$
$\beta = 82.042 (3)°$
$\gamma = 74.826 (3)°$
$V = 1774.04 (17)$ Å^3

$Z = 2$
$D_x = 2.281$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12 164
reflections
$\theta = 2.8$–$25.7°$
$\mu = 9.22$ mm^{-1}
$T = 100 (2)$ K
Needle, light yellow
$0.3 \times 0.1 \times 0.1$ mm

Data collection

Nonius KappaCCD area-detector
diffractometer
φ scans
Absorption correction: empirical
(*DELABS* in *PLATON*;
Spek, 2000)
$T_{min} = 0.201$, $T_{max} = 0.398$
12 164 measured reflections

6199 independent reflections
5014 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$
$\theta_{max} = 25.7°$
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.068$
$S = 1.04$
6199 reflections
460 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2)]$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.92$ e Å^{-3}
$\Delta\rho_{min} = -0.90$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

U1—O1	1.789 (4)	U2—O10	1.785 (4)
U1—O2	1.786 (4)	U2—O11	1.784 (4)
U1—O3	2.531 (4)	U2—O12	2.515 (4)
U1—O4	2.561 (4)	U2—O13	2.534 (4)
U1—O6	2.529 (4)	U2—O15	2.560 (4)
U1—O7	2.559 (4)	U2—O16	2.539 (4)
U1—O9	2.313 (4)	U2—O18	2.338 (4)
U1—O9^i	2.317 (4)	U2—O18^{ii}	2.341 (4)
U1···U1^i	3.8556 (5)	U2···U2^{ii}	3.9156 (5)
O1—U1—O2	178.51 (18)	O10—U2—O11	177.80 (17)
O3—U1—O4	49.89 (14)	O12—U2—O13	50.52 (13)
O4—U1—O6	59.24 (14)	O13—U2—O15	61.18 (13)
O6—U1—O7	50.29 (14)	O15—U2—O16	50.02 (13)
O7—U1—O9	67.56 (14)	O12—U2—O18	66.28 (13)
O9—U1—O9^i	67.23 (16)	O18—U2—O18^{ii}	66.40 (15)
O9^i—U1—O3	66.26 (13)	O18^{ii}—U2—O16	66.15 (13)
U1—O9—U1^i	112.77 (16)	U2—O18—U2^{ii}	113.60 (15)

Symmetry codes: (i) $-x, 1 - y, 2 - z$; (ii) $2 - x, 1 - y, 1 - z$.

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Table 2
Hydrogen-bonding and short-contact geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N5—H5$\cdots$O19	0.87	2.56	2.837 (6)	100
N5—H5$\cdots$O21	0.87	2.28	2.805 (6)	119
N5—H5$\cdots$O23	0.87	2.57	2.824 (6)	98
N6—H6$\cdots$O20	0.91	2.47	2.777 (6)	100
N6—H6$\cdots$O22	0.91	2.23	2.858 (6)	126
N6—H6$\cdots$O24	0.91	2.72	2.806 (6)	86
O9—H9$\cdots$O25	1.04	1.73	2.746 (6)	165
O18—H18$\cdots$O22	0.84	2.14	2.961 (6)	165
O25—H25$B\cdots$O19	0.91	2.22	3.035 (6)	150
O25—H25$A\cdots$O23	0.96	1.95	2.849 (6)	155

H atoms bound to N and O atoms were found in a difference Fourier map and introduced as riding atoms, with $U_{iso}(H) = 1.2U_{eq}(N, O)$. All other H atoms were introduced at calculated positions as riding atoms, with C—H distances of 0.97 Å and $U_{iso}(H)$ values of $1.2U_{eq}(C)$.

Data collection: *KappaCCD Server Software* (Nonius, 1997); 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*.

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