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A uranyl ion complex of *N*-methyl-*p*-*tert*-butyldihomoammoniocalix[4]-arene with diaquadipyridinelithium as counter-ion[1]

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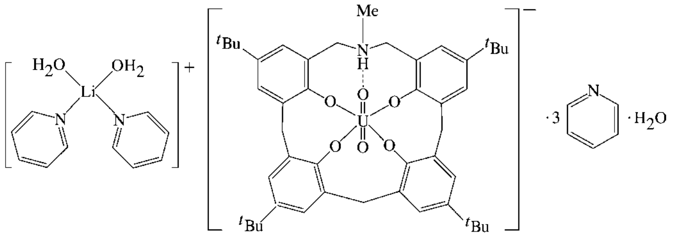
The title complex, diaquadipyridinelithium (*N*-methyl-*p*-*tert*-butyldihomoammoniocalix[4]arene-κ^4O)dioxouranium(VI) tripyridine solvate monohydrate, $[Li(C_5H_5N)_2(H_2O)_2][UO_2(C_{46}H_{58}NO_4)]\cdot 3C_5H_5N\cdot H_2O$, contains an 'internal' tetraphenoxide-coordinated uranyl complex of the macrocycle, in which the protonated N atom is involved in an intramolecular hydrogen bond with the uranyl oxo group located in the cavity. The Li^+ ion is in a tetrahedral environment and its two water ligands are involved in hydrogen bonds with two phenoxide O atoms, two pyridine molecules and one water molecule. This arrangement is compared with those obtained previously for other homoazacalixarenes and also for homooxacalixarenes in the presence of alkali metal hydroxides.

Comment

Homoazacalixarenes (Takemura, 2002) and homooxacalixarenes (Masci, 2001) are macrocycles that differ from usual calixarenes by the lengthening of at least one methylene bridge, as a result of its replacement by a 2-oxa- or 2-aza-1,3-propylene bridge. Such modifications of the calixarene skeleton provide the molecule with increased flexibility, novel donor atoms and, in the case of homoazacalixarenes, new sites for functionalization. We reported some years ago the syntheses and crystal structures of rare earth (Thuéry *et al.*, 2000*a*,*b*; Thuéry, Nierlich, Vicens & Takemura, 2001) and uranyl ion (Thuéry, Nierlich, Harrowfield & Ogden, 2001; Thuéry, Nierlich, Vicens, Masci & Takemura, 2001) complexes of homoazacalixarenes. A peculiarity of these ligands is their ability to complex these metal ions without addition of a base, since H atoms can be transferred from the phenol to the amine groups, resulting in the formation of zwitterionic species. In the case of the uranyl ion and the *p*-chloro-*N*-benzylhexahomotriazacalix[3]arene and *p*-methyl-*N*-benzyltetrahomodiazacalix[4]arene ligands, 'external' complexation results because of the repulsion between the metal cation and the ammonium groups in the complex. By contrast, in the presence of an extra base (triethylamine), a different 'internal' coordination mode is observed in the case of *p*-methyl-*N*-benzyltetrahomodiazacalix[4]arene; this mode results from an enlargement of the cavity due to the higher deprotonation degree and the removal of intramolecular phenol–phenoxide hydrogen bonds (Thuéry, Nierlich, Vicens & Takemura, 2001). We report here the crystal structure of the uranyl complex, (I), with another ligand comprising only one amine link, obtained in the presence of lithium hydroxide as a base. This work is part of an investigation of mixed uranyl/alkali metal ion complexes, which was first carried out for homooxacalixarenes (Thuéry & Masci, 2003).



(I)

The asymmetric unit in (I) contains the uranyl complex itself, which is a monoanion, one water and three pyridine solvent molecules, and the lithium counter-ion bound to two pyridine and two water molecules (Fig. 1 and Table 1). As in the uranyl complex with *p*-methyl-*N*-benzyltetrahomodiazacalix[4]arene obtained in the presence of triethylamine, the cation is complexed in an 'internal' mode and is bound to the four phenoxide groups in its equatorial plane; the mean U—O distance of 2.27 (2) Å is typical of such complexes. The four donor atoms are coplanar, the maximum deviation from the plane being 0.008 (3) Å, and the U atom lies 0.106 (3) Å from this plane, on the same side as oxo atom O5. The coordination geometry of the U atom would thus be square-planar-bipyramidal but for the distortion in the plane resulting from the presence of the longer N-containing bridge. The O1—U—O4 angle is about 15° larger than the O1—U—O2 and O3—U—O4 angles, whereas the O2—U—O3 angle is about 6° smaller than O1—U—O2 and O3—U—O4. The N atom is protonated and is involved in a hydrogen bond (Table 2) with the uranyl oxo group located in the macrocycle cavity. Such hydrogen bonds with uranyl oxo groups are extremely common because of the basicity of the O atom, but this case presents the unusual feature of the U=O6···N1 angle being particularly far from linearity, having a value of 99.2 (2)°. A search of the Cambridge Structural Database (CSD; Version 5.24; Allen, 2002) for hydrogen-bonding contacts between uranyl ions and O- or N-containing donors shows that the largest number of cases correspond to U=O···(O,N) angles of about 110–160° and O···(O,N) distances larger than 2.80 Å (with no

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[1] Systematic name: diaquadipyridinelithium dioxo[$1^5,3^5,5^5,7^5$-tetra-*tert*-butyl-$1^2,3^2,5^2,7^2$-tetraoxido-9-methyl-9-azonia-1,3,5,7(1,3)-tetrabenzenanonacyclophane-κ^4O]uranium(VI) tripyridine solvate monohydrate.

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straightforward correlation between angle and distance). The N1$\cdots$O6 and H1$\cdots$O6 distances in (I) are 3.083 (8) and 2.17 Å, respectively, which indicate a weak hydrogen bond; the U=O6$\cdots$N1 angle is probably small because of geometric constraints resulting from the macrocyclic nature of the ligand. In the previously reported 'internal' uranyl complex of a homoazacalixarene, the two diametrically located ammonium groups were involved in hydrogen bonds with the closest phenoxide groups and not with the uranyl ion. The two torsion angles defined by the ammonium-containing bridge are both *anti* angles [C44—N1—C45—C1 = 165.3 (6)° and C45—N1—C44—C36 = −167.2 (6)°], the resulting conformation bringing the ammonium H atom as close as possible to atom O6. Atom N1 is located 1.895 (9) Å from the mean O_4 plane and 3.808 (6) Å from the U atom. The latter distance is slightly smaller than those observed in other uranyl complexes of homoazacalixarenes (3.93–4.30 Å), probably because of the different macrocycle geometry and the presence of the uranyl–ammonium hydrogen bond. In the uranyl ion complex of the related ligand *p-tert*-butyldihomooxacalix[4]arene, which differs from (I) in the replacement of the ammonium by an ether group, the U$\cdots$O$_{\rm ether}$ distance is shorter [3.534 (8) Å; Harrowfield *et al.*, 1991], and even shorter U$\cdots$O$_{\rm ether}$ distances, some of them indicating bonding interactions [2.609 (8)–2.950 (4) Å], have been observed in complexes with other homooxacalixarenes (Thuéry, Nierlich, Vicens & Masci, 2001; Masci *et al.*, 2002*a*,*b*). The larger distance for the ammonium N atom in (I) probably arises from a subtle balance between cation–cation repulsion, hydrogen-bonding interaction and macrocycle geometric requirements.

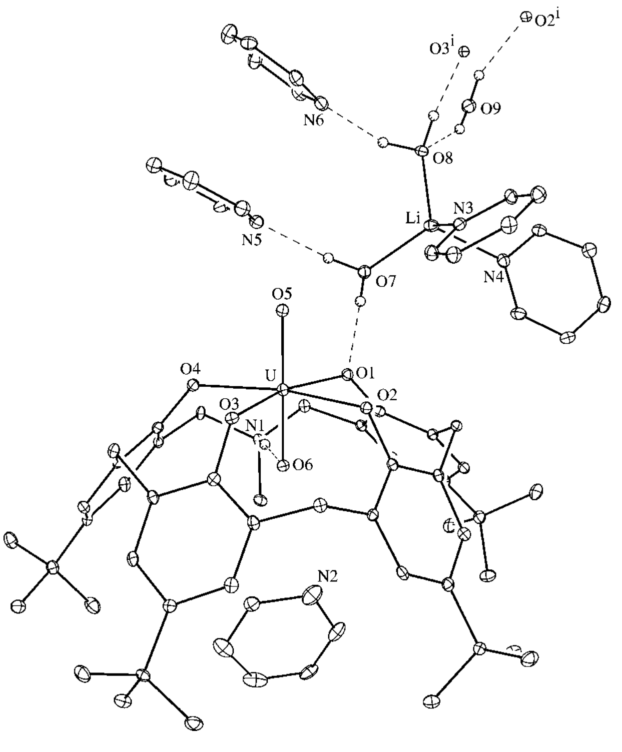

Figure 1
A view of complex (I). Ammonium and water H atoms are drawn as small spheres of arbitrary radii and hydrogen bonds are shown as dashed lines. The other H atoms have been omitted. Displacement ellipsoids are drawn at the 10% probability level. [Symmetry code: (i) $1-x, y+\frac{1}{2}, \frac{1}{2}-z$.]

The macrocycle in (I) has the usual cone conformation. With respect to the O_4 reference plane, the four aromatic rings subtend dihedral angles of 46.5 (2), 64.6 (2), 58.2 (2) and 52.0 (2)°. The resulting bowl shape accommodates a pyridine molecule, as is often observed. The O1$\cdots$O2, O2$\cdots$O3, O3$\cdots$O4 and O1$\cdots$O4 distances are 3.157 (7), 2.935 (7), 3.129 (7) and 3.576 (7) Å, respectively. A similar geometry is encountered in the uranyl complex of *p-tert*-butyldihomooxacalix[4]arene, in which, however, the included pyridine molecule is replaced by a triethylammonium counter-ion (Harrowfield *et al.*, 1991).

The lithium ion is surrounded by two water and two pyridine molecules, with mean Li—O and Li—N bond lengths of 1.910 (6) and 2.08 (2) Å, respectively. The angles around the Li atom are in the range 98.6 (7)–113.9 (8)° and the coordination geometry is that of a slightly distorted tetrahedron. The two metal complexes are linked by hydrogen bonds between water atom O7 and phenoxide atom O1, and also between atom O8 and phenoxide atom O3 of a neighbouring molecule at ($1-x, y+\frac{1}{2}, \frac{1}{2}-z$). The two water molecules bound to the Li atom are also hydrogen bonded to two pyridine molecules, and the solvent water molecule (containing atom O9) is hydrogen bonded to atom O8 and to a phenoxide O atom of the same neighbouring molecule at ($1-x$, $y+\frac{1}{2}$, $\frac{1}{2}-z$). Polymeric zigzag chains, in which successive macrocycles are turned upside down with respect to one another, are thus formed along the *b* axis.

The only feeble, but significant, π–π stacking interaction in (I) is that between the two solvent pyridine rings containing atoms N5 and N6 [centroid–centroid distance = 3.80 Å, interplanar spacing = 3.44 Å, centroid offset = 1.62 Å, shortest interatomic contact = N6$\cdots$C66 = 3.41 (1) Å and dihedral angle between the two rings = 9.6 (5)°].

We have recently reported the syntheses and crystal structures of complexes uniting uranyl and alkali metal ions in a 1:2 ratio with *p-tert*-butyltetrahomodioxacalix[4]arene (Thuéry & Masci, 2003). This work has evidenced different arrangements depending on the alkali ion, *viz*. monomeric with Li^+, dimeric with Na^+, and polymeric with K^+ and Cs^+. The uranyl–lithium stoichiometry in (I) is obviously different because of the cationic nature of the ammonium bridge, but the monomeric nature of the complex is once more encountered (considering coordination bonds only, and not hydrogen-bonding interactions). However, the uranyl–alkali metal interactions differ from those found previously. In the series of homooxacalixarene complexes, the presence of U=O—*M* bonds ($M = Li^+$, Na^+, K^+ and Cs^+) is a general trend, whereas the interactions between the two moieties in (I) are indirect and are mediated through hydrogen-bonded lithium-coordinated water molecules and phenoxide groups. The U=O bond lengths in (I) are larger than is usual for non-oxo-coordinated ions [the mean value is 1.76 (4) Å for the structures contained in the CSD] and are comparable to those in uranyl ions bound to alkali metal ions.

Experimental

N-Methyl-*p*-*tert*-butyldihomoammoniocalix[4]arene (LH$_4$) was prepared as reported previously (Takemura, 2002). For the synthesis of complex (I), LH$_4$ (22 mg, 0.032 mmol) was dissolved in CHCl$_3$/CH$_3$OH (2:1, 100 ml) in the presence of a large excess of LiOH·H$_2$O (15 mg, 0.357 mmol). UO$_2$(NO$_3$)$_2$·6H$_2$O (20 mg, 0.040 mmol) in pyridine (10 ml) was then added and the resulting orange solution was refluxed for 15 min. Crystals of (I) were obtained by slow evaporation of the solution.

Crystal data

[Li(C$_5$H$_5$N)$_2$(H$_2$O)$_2$][UO$_2$(C$_{46}$H$_{58}$NO$_4$)]·3C$_5$H$_5$N·H$_2$O
M_r = 1415.45
Monoclinic, $P2_1/c$
a = 20.8644 (16) Å
b = 16.6147 (13) Å
c = 19.7150 (14) Å
β = 96.321 (5)°
V = 6792.8 (9) Å^3
Z = 4
D_x = 1.384 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 45 959 reflections
θ = 2.7–25.7°
μ = 2.45 mm^{-1}
T = 100 (2) K
Platelet, translucent dark orange
0.38 × 0.12 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
φ scans
Absorption correction: refined from ΔF (*DELABS* in *PLATON*; Spek, 2003)
$T_{\min}$ = 0.698, $T_{\max}$ = 0.872
45 959 measured reflections
12 756 independent reflections
7934 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.096
$\theta_{\max}$ = 25.7°
$h = -25 \rightarrow 25$
$k = -20 \rightarrow 20$
$l = -23 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.126
S = 1.03
12 756 reflections
806 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0088P)^2 + 25.0468P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.82 e Å^{-3}
$\Delta\rho_{\min}$ = −1.03 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

U—O1	2.301 (5)	U—O6	1.796 (5)
U—O2	2.262 (5)	Li—O7	1.914 (15)
U—O3	2.243 (5)	Li—O8	1.906 (15)
U—O4	2.272 (5)	Li—N3	2.064 (16)
U—O5	1.805 (5)	Li—N4	2.089 (16)
O1—U—O2	87.56 (17)	O7—Li—O8	113.2 (8)
O2—U—O3	81.30 (17)	O7—Li—N3	110.4 (7)
O3—U—O4	87.73 (17)	O7—Li—N4	113.9 (8)
O4—U—O1	102.91 (17)	O8—Li—N3	111.6 (8)
O1—U—N1	55.79 (15)	O8—Li—N4	108.4 (7)
O4—U—N1	57.05 (15)	N3—Li—N4	98.6 (7)
O5—U—O6	176.8 (2)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O6	0.92	2.17	3.083 (8)	173
O7—H7A···O1	0.90	1.92	2.799 (7)	168
O7—H7B···N5	0.91	1.89	2.793 (9)	169
O8—H8A···N6	0.95	1.82	2.732 (9)	159
O8—H8B···O3$^{\rm i}$	0.91	1.84	2.735 (7)	166
O9—H9A···O8	0.87	2.12	2.922 (8)	153
O9—H9B···O2$^{\rm i}$	0.89	1.95	2.808 (8)	161

Symmetry code: (i) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$.

The ammonium and hydroxy H atoms were found in difference Fourier maps and were introduced as riding atoms, with isotropic displacement parameters equal to 1.2$U_{\rm eq}$ of the parent atom. All other H atoms were introduced at calculated positions as riding atoms, with C—H bond lengths of 0.93 (CH), 0.97 (CH$_2$) or 0.96 Å (CH$_3$), and isotropic displacement parameters equal to 1.2$U_{\rm eq}$ (CH and CH$_2$) or 1.5$U_{\rm eq}$ (CH$_3$) of the parent atom. After refinement of the pyridine molecule included in the cavity with six C atoms, the N atom was assigned to the position with the lowest displacement factor. However, atom N2 exhibits a high displacement parameter with respect to those of its neighbours, which may indicate some rotational disorder of this pyridine molecule. The minimum and maximum residual electron-density peaks were located 0.97 Å from the U atom and 1.16 Å from the solvent pyridine atom C66, respectively, which may indicate an imperfect absorption correction in the first case and some unresolved disorder in the second.

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* and *PLATON* (Spek, 2003).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1134). Services for accessing these data are described at the back of the journal.

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