Synthesis and crystal structure of 1:2 mixed uranyl/alkali metal ions (Li⁺, Na⁺, K⁺, Cs⁺) complexes of *p-tert*-butyltetrahomodioxacalix[4]arene

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p-tert-Butyltetrahomodioxacalix[4]arene LH₄ reacts with uranyl nitrate hexahydrate in the presence of alkali metal hydroxides to give mixed complexes containing the same $[UO_2(L)]^{2-}$ central core. All alkali metal ions are bound to the basic uranyl oxo groups, which act as mono- (Li⁺, Na⁺) or bidentate (K⁺, Cs⁺) ligands. The resulting structures largely depend on the size and predominantly "hard" or "soft" character of the alkali metal ion. Li⁺ and Na⁺ are coordinated in both "endo" and "exo" modes, Li⁺ giving a monomer with one cation bound to each oxo group and Na⁺ a dimer with a bridging, oxo-coordinated, Na₂(CH₃OH)₈ moiety. Both K⁺ and Cs⁺ give polymeric chains, with two cations in the macrocycle cavity, involved in cation-π interactions with the aromatic rings and bound to the oxo groups from two neighbouring molecules in the chain, with differences in further coordination to the calixarenes which are related to the softer nature of Cs⁺. Unprecedented supramolecular architectures based on coordination bonds are thus obtained.

Complexation of alkali metal ions by calixarenes and their various derivatives is a subject of wide interest which has been an impulse for much work in the past few years. The efficiency of *p-tert*-butylcalix[4,6,8]arenes for the selective transportation of caesium ions through liquid membranes has been demonstrated in the early 1980s,[1] which evidenced the richness of these macrocycles for ion separation purposes. From the structural point of view, one of the landmarks of the investigation of such complexes has been the demonstration of the occurrence of polyhapto cation-π interactions in the case of the largest caesium ion coordinated in an "endo" fashion (within the macrocycle cavity).[2] This phenomenon has found a practical application in the design of selective caesium extractants in the "1,3-alternate" calix[4]crown family, intended for use in nuclear fuel reprocessing.[3] Recently, detailed structural investigations of the complexes formed by alkali metal ions with *p-tert*-butyl-tetrathiacalix[4]arene[4] or *p*-sulfonatocalix[6]arene,[5] evidencing the different possible bonding modes, have been published. In both cases, additional bonding, to sulfur bridges or sulfonato groups, occurs. Complexes including both transition and alkali metal ions are also known,[6] which have been described in the context of metal reactivity studies. In the case of the uranyl ion, which we have studied in the last few years, in association with calixarenes and homooxa- or homoazacalixarenes,[7] the only case of a binuclear "exo" uranyl complex of *p-tert*-butylcalix[6]arene including a caesium ion bound to two phenolic groups, two oxo groups from uranyl ions and two aromatic rings has been reported.[8] As an extension of our previous work, we decided to study the formation of uranyl ion complexes in the presence of alkali metal ion hydroxides, in order to obtain mixed complexes for different alkali cations. We report herein on the synthesis and crystal structures of the uranyl complexes including Li⁺, Na⁺, K⁺ and Cs⁺ cations, with *p-tert*-butyltetrahomodioxacalix[4]arene, denoted LH₄ hereafter (Scheme 1), as a ligand. Several uranyl complexes of this macrocycle have previously been reported, obtained with different amines as deprotonating agents.[9] In all the cases, the central mononuclear uranyl complex core, with tetra-phenoxide coordination, is identical, with no significant changes in metal location or macrocycle conformation, the different counter-ions resulting in
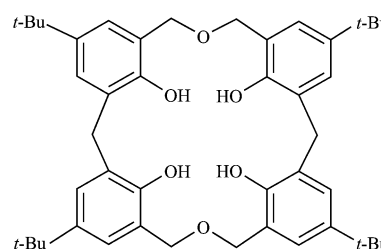
Scheme 1 *p-tert*-Butyltetrahomodioxacalix[4]arene, LH₄.

various supramolecular assemblages owing to differing hydrogen bonding, cation-π and/or CH-π interactions. It can thus be assumed that, with various alkali metal ions as deprotonating agents, the differences in crystal structures will also be primarily dependent on the alkali metal and that different cation sizes and bonding behaviour will result in new arrangements.

Experimental

Synthesis

p-tert-Butyltetrahomodioxacalix[4]arene LH₄ was synthesized as reported in the literature.[10]

[UO₂Li₂(L)(H₂O)₅(CH₃OH)]·2H₂O·2CH₃OH 1. LH₄ (34 mg, 0.048 mmol) was dissolved in CHCl₃ (70 ml). An excess of LiOH·H₂O (17 mg, 0.405 mmol) in CH₃OH (25 ml) was then added. Further addition of UO₂(NO₃)₂·6H₂O (27 mg, 0.054 mmol) in CH₃OH (20 ml) resulted in an orange solution which was stirred for half-an-hour at ambient temperature. Orange single crystals suitable for X-ray crystallography deposited upon standing overnight. Anal. calc. for C₄₉H₈₂Li₂O₁₈U: C, 48.60; H, 6.82. Found: C, 48.02; H, 6.50.

[UO₂Na₂(L)(H₂O)(CH₃OH)₆]·2CH₃OH 2. LH₄ (30 mg, 0.042 mmol) was dissolved in CHCl₃ (70 ml). NaOH (7 mg, 0.175 mmol) in CH₃OH (7 ml) was then added. Further addition of UO₂(NO₃)₂·6H₂O (21 mg, 0.041 mmol) in CH₃OH (20 ml) resulted in an orange solution which was refluxed for

15 min. Orange single crystals suitable for X-ray crystallography were obtained together with a brown powder upon slow evaporation. Anal. calc. for $C_{54}H_{90}Na_2O_{17}U$: C, 50.07; H, 7.00. Found: C, 53.12; H, 7.28.

[UO₂K₂(L)(H₂O)₂(py)]·0.5H₂O·0.5py 3. LH_4 (44 mg, 0.062 mmol) was dissolved in CH_2Cl_2 (70 ml). An excess of KOH (20 mg, 0.357 mmol) in CH_3OH (15 ml) was then added. Further addition of $UO_2(NO_3)_2$·6H₂O (30 mg, 0.060 mmol) in CH_3OH (15 ml) resulted in a bright orange solution which was stirred for half-an-hour at ambient temperature. The powder obtained after evaporation to dryness was dissolved in pyridine. Orange single crystals suitable for X-ray crystallography were obtained upon slow evaporation in few days. Anal. calc. for $C_{53.5}H_{68.5}$-$K_2N_{1.5}O_{10.5}U$: C, 52.81; H, 5.67; N, 1.73. Found: C, 51.61; H, 5.28; N, 1.61%.

[UO₂Cs₂(L)(H₂O)₀.₅(CH₃OH)₃.₅]·0.5CHCl₃ 4. LH_4 (29 mg, 0.041 mmol) was dissolved in $CHCl_3$ (60 ml). CsOH·H₂O (36 mg, 0.214 mmol) in CH_3OH (20 ml) was then added. Further addition of $UO_2(NO_3)_2$·6H₂O (25 mg, 0.050 mmol) in CH_3OH (20 ml) resulted in an orange solution which was refluxed for 5 min. Orange single crystals suitable for X-ray crystallography were obtained upon standing overnight. Anal. calc. for $C_{50}H_{71.5}Cl_{1.5}Cs_2O_{12}U$: C, 42.24; H, 5.07. Found: C, 41.52; H, 4.59%.

Loss of included organic solvents can partly account for unsatisfactory elemental analysis of **1**, **3** and **4**. On the other hand the larger deviations observed in the case of **2** are possibly due to the presence of powdered side-products mixed with the crystals.

Crystallography

The data were collected on a Nonius Kappa-CCD area detector diffractometer[11] using graphite-monochromated Mo Kα radiation (λ 0.71073 Å). The crystals were introduced in glass capillaries with a protecting "Paratone-N" oil (Hampton Research) coating. The unit cell parameters were determined from ten frames, then refined on all data. A 180° φ-range was scanned with 2° steps during data collection, with a crystal-to-detector distance fixed to 28 mm. The data were processed with DENZO-SMN.[12] The structures were solved by direct methods (**1**, **3** and **4**) or by Patterson map interpretation (**2**) with SHELXS-97[13] and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on F^2 with SHELXL-97.[13] Absorption effects were corrected empirically with the program DELABS from PLATON.[14] Two *tert*-butyl groups and the carbon atom of a methanol molecule were found disordered over two positions in compound **2**. In compound **3**, one pyridine molecule is disordered over two positions and the other one is located around a symmetry centre; the water molecule which is not bound to the potassium atom is located too close to one of the positions of the first pyridine molecule and has been affected with a partial occupancy factor in consequence. These disordered positions in **2** and **3** were refined with occupancy parameters constrained to sum to unity [refined to 0.500(12) in **3**]. In compound **4**, the carbon atom of one of the methanol molecules is located close to a chlorine atom of the very badly resolved and likely partially occupied chloroform molecule; both have been affected with an occupancy factor of 0.5, which implies that the caesium atom is bound to half a water and half a methanol molecules. All non-hydrogen atoms were refined with anisotropic displacement parameters, except the disordered ones when present. Some restraints on bond lengths and/or displacement parameters were applied for some badly behaving atoms, particularly in the disordered parts. Hydrogen atoms bound to oxygen atoms were not found, nor introduced. The other hydrogen atoms were introduced at calculated positions, except in the disordered parts when present,

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 highest residual electron density peak in compound **4** is located near the badly resolved chloroform molecule. Crystal data and structure refinement parameters are given in Table 1. The molecular plots were drawn with SHELXTL.[15] All calculations were performed on a Silicon Graphics R5000 workstation. CCDC reference numbers 204860–204863. See http://www.rsc.org/suppdata/dt/b3/b302233a/ for crystallographic data in .cif or other electronic format.

NMR measurements

^{1}H NMR spectra at 298 K were taken on either a Bruker AC 300 or a Bruker 200 AC spectrometers in CD_3CN, the residual non deuterated solvent being used for calibration ($\delta = 1.95$).

Solution of **1**: $\delta = 1.27$ (s, 36H, *t*-Bu), 3.58 (d, $J = 11.8$ Hz, 2H, ArCH₂Ar), 4.47 (d, $J = 8.8$ Hz, 4H, ArCH₂OCH₂Ar), 5.04 (d, $J = 8.8$ Hz, 4H, ArCH₂OCH₂Ar), 5.68 (d, $J = 11.8$ Hz, 2H, ArCH₂Ar), 7.01 (d, $J = 2.6$ Hz, 2H, Ar), 7.66 (d, $J = 2.6$ Hz, 2H, Ar).

Solution of **3**: $\delta = 1.27$ (s, 36H, *t*-Bu), 3.34 (d, $J = 11.4$ Hz, 2H, ArCH₂Ar), 4.23 (d, $J = 8.2$ Hz, 4H, ArCH₂OCH₂Ar), 5.16 (d, $J = 8.2$ Hz, 4H, ArCH₂OCH₂Ar), 5.74 (d, $J = 11.4$ Hz, 2H, ArCH₂Ar), 7.00 (d, $J = 2.6$ Hz, 2H, Ar), 7.57 (d, $J = 2.6$ Hz, 2H, Ar).

Solution of **4**: $\delta = 1.26$ (s, 36H, *t*-Bu), 3.43 (d, $J = 11.7$ Hz, 2H, ArCH₂Ar), 4.27 (d, $J = 8.5$ Hz, 4H, ArCH₂OCH₂Ar), 5.14 (d, $J = 8.5$ Hz, 4H, ArCH₂OCH₂Ar), 5.72 (d, $J = 11.7$ Hz, 2H, ArCH₂Ar), 7.01 (d, $J = 2.6$ Hz, 2H, Ar), 7.61 (d, $J = 2.6$ Hz, 2H, Ar).

Results and discussion

Complexes in the solid state

The four complexes [UO₂Li₂(L)(H₂O)₅(CH₃OH)]·2H₂O·2CH₃OH **1**, [UO₂Na₂(L)(H₂O)(CH₃OH)₆]·2CH₃OH **2**, [UO₂K₂(L)(H₂O)₂(py)]·0.5H₂O·0.5py **3** and [UO₂Cs₂(L)(H₂O)₀.₅(CH₃OH)₃.₅]·0.5CHCl₃ **4** possess the same anionic complex core [UO₂(L)]²⁻, which was previously described with various ammonium ions, primary, secondary or tertiary, as counterions.[9] By contrast with some other calixarenes, homooxa- or homoazacalixarenes which can accomodate uranyl ions with different coordination geometries or stoichiometries depending upon the experimental conditions, LH_4 probably always gives this arrangement due to its size being perfectly adapted to the complexation of a central uranyl ion bound to all four phenoxide groups, thus giving a more stable species. The geometric parameters of the anion [UO₂(L)]²⁻ are nearly identical in compounds **1**–**4** (Table 2). The uranyl ion is in a distorted square planar equatorial environment, with a mean U–O-(phenoxide) bond length of 2.28(1) Å, as usual (value including the four compounds; standard deviation in parentheses, as for all other mean values below). The O(phenoxide)–U–O(phenoxide) angles are larger for phenoxide groups separated by the ether bridges [mean value 95(2)°] than for those separated by methylene bridges [mean value 85(2)°]. The four phenoxide oxygen atoms define a mean plane with rms deviations of 0.001–0.005 Å, the uranium atoms being at distances of 0.054(3)–0.083(3) Å from this plane. The dihedral angles between the four phenolic rings and this plane are 46.3(2), 40.8(2), 52.0(2) and 45.5(2)° in **1**, 48.1(3), 40.2(3), 47.0(3) and 42.3(3)° in **2**, 37.2(3), 46.2(2), 48.6(2) and 42.6(3)° in **3** and 43.5(4), 42.2(3), 42.6(3) and 46.7(3)° in **4**, the differences being likely due to the species present in the cavity (*vide infra*). The ether oxygen atoms are not bound to the uranium atom (such bonds have been observed with other homooxacalixarenes[16]), the U · · · O(ether) distances being in the range 3.724(8)–4.017(6) Å. The fragments C(arom)–C–O–C–C(arom) define *anti* torsion angles in all cases (162.3–173.1°). All these

Table 1 Crystal data and structure refinement details

	1	2	3	4
Chemical formula	$C_{49}H_{82}Li_2O_{18}U$	$C_{54}H_{90}Na_2O_{17}U$	$C_{53.5}H_{68.5}K_2N_{1.5}O_{10.5}U$	$C_{50}H_{71.5}Cl_{1.5}Cs_2O_{12}U$
M/g mol^{-1}	1211.06	1295.27	1216.83	1421.60
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$C2/c$
a/Å	12.5382(11)	12.5111(12)	15.6461(9)	36.118(2)
b/Å	19.656(2)	15.2227(15)	24.2868(15)	16.2137(9)
c/Å	23.1000(19)	16.7853(11)	14.9430(6)	23.4909(14)
α/°	90	97.961(6)	90	90
β/°	98.597(6)	106.010(6)	100.979(3)	121.606(4)
γ/°	90	93.142(4)	90	90
V/Å^3	5629.2(9)	3028.6(5)	5574.3(5)	11716.1(12)
Z	4	2	4	8
D_{calc}/g cm^{-3}	1.429	1.420	1.450	1.612
μ(Mo Kα)/mm^{-1}	2.949	2.758	3.116	4.117
Crystal size/mm	$0.35 \times 0.25 \times 0.10$	$0.30 \times 0.20 \times 0.05$	$0.22 \times 0.22 \times 0.05$	$0.45 \times 0.10 \times 0.05$
$F(000)$	2472	1328	2456	5560
θ range/°	2.7–25.7	2.9–25.7	2.8–25.7	2.9–25.7
T/K	100(2)	100(2)	100(2)	100(2)
Number of data collected	32084	19838	37294	33693
Number of unique data	10526	10421	10366	10927
Number of "observed" data [$I > 2\sigma(I)$]	6449	8180	6966	6583
R_{int}	0.073	0.083	0.077	0.113
Number of parameters	646	700	660	634
$R_1{}^a$	0.061	0.071	0.064	0.070
$wR_2{}^b$	0.135	0.176	0.120	0.144
S	1.015	0.990	1.034	1.018
$\Delta\rho_{min}$/e Å^{-3}	-0.91	-1.38	-1.13	-1.18
$\Delta\rho_{max}$/e Å^{-3}	1.06	1.24	1.22	1.93

^{a} $R_1 = \Sigma||F_o| - |F_c||/|F_o|$ ("observed" reflections). ^{b} $wR_2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$ ("observed" reflections).

parameters agree with those in the previous complexes and will not be discussed further. In compounds **1**–**3**, more or less extended hydrogen bonding links phenoxide, water and methanol molecules, including solvents, as frequently observed in this family of compounds.

In compounds **1**–**4**, the anion $[UO_2(L)]^{2-}$ is associated to its two alkali metal counter-ions to give different association types, depending on the size and coordination preferences of the alkali metal ion. In compound **1**, the two lithium ions are bound to the two oxo groups, with a mean Li–O(oxo) bond length of 1.98(4) Å, one of them being located out of the cavity and the other inside (Fig. 1). They are further bound either to three water molecules (Li1), or two water and one methanol molecules (Li2), with a mean Li–O bond length of 1.94(5) Å, thus giving discrete $[UO_2Li_2(L)(H_2O)_5(CH_3OH)]$ molecules with distorted tetrahedral environments around Li$^+$ ions. Such U=O–X bonds, where X is an alkali metal ion, are rather
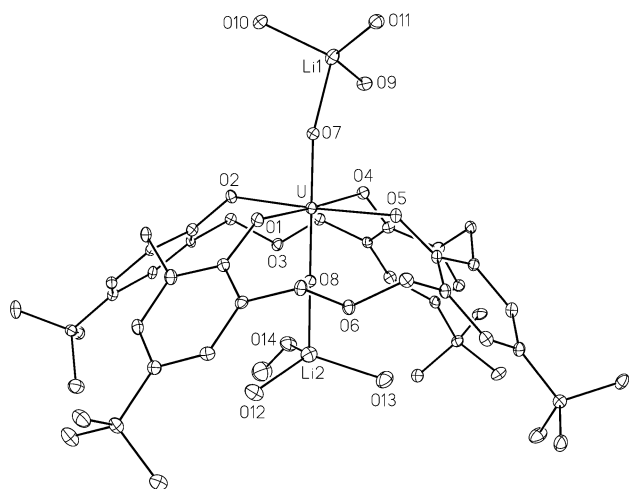

Fig. 1 View of the complex $[UO_2Li_2(L)(H_2O)_5(CH_3OH)]$ in **1**. Hydrogen atoms and solvent molecules omitted for clarity. Displacement ellipsoids drawn at the 10% probability level.

rare occurrences in molecular compounds: a search of the Cambridge Structural Database [17] and a survey of recent literature gives few examples, three of them with X = Li$^+$,[18,19] three other ones with X = Na$^+$,[19–21] and only one with Cs$^+$.[18] However, these bonds will be encountered in all the present compounds. In the examples of U=O–Li bonds present in the literature, the Li–O bond lengths are 1.89(2) and 2.04(3) Å, in agreement with that in the present case. The U=O bond lengths in compound **1**, close to 1.80 Å, are somewhat larger than in non-oxo-coordinated uranyl ions [mean value 1.76(4) Å from the structures contained in the Cambridge Structural Database], whereas they are in the range 1.767(9)–1.79(1) in the structures from the literature cited above. Such a lengthening of the U=O bond length is likely due to the transfer of part of the electronic density of the basic oxo group to the alkali-metal ion. The U=O–Li angles are 151.6(6)° for Li1 and 171.4(7)° for Li2, showing no influence of the more or less pronounced linearity on the Li–O bond length.

The situation in $[UO_2Na_2(L)(H_2O)(CH_3OH)_6]\cdot 2CH_3OH$ **2** is quite different. As represented in Fig. 2, the two sodium ions are also bound to the oxo groups, with a mean Na–O bond length of 2.42(5) Å, in agreement with most of the values in the papers previously cited [2.456(3),[19] 2.357(6) and 2.392(6),[20] the value 2.201(6) Å in a uranyl tris(amido) complex[21] is out of the range defined by all other compounds]. The present value is also consistent with that in hydrated $Na_2Ca[UO_2(CO_3)_3]$, i.e. 2.47(2) Å.[22] Both U=O bond lengths in compound **2** are larger than usual, at about 1.80 Å. The sodium ion located in the macrocycle cavity (Na2) completes its coordination sphere with the ether oxygen atom O3, one water and two methanol molecules [mean Na–O(water, methanol) bond length 2.4(1) Å], whereas the cation located outside (Na1) is bound to five methanol molecules, of which two are bridging towards the centrosymmetrically related sodium ion [mean Na–O(methanol) distance 2.35(4) Å for terminal and 2.42(2) Å for bridging molecules; Na1 $\cdots$ Na1$'$ 3.516(9) Å]. This bridging results in the formation of dimers built from two slightly offset $[UO_2-Na(L)(H_2O)(CH_3OH)_2]^-$ species facing each other with a central oxo-bound $Na_2(CH_3OH)_8$ dication. The U=O–Na angles

Table 2 Environment of the uranium and alkali metal atoms in compounds **1**–**4**: selected distances (Å) and angles (°)[a]

1

U–O1	2.265(5)	Li1–O7	2.002(19)
U–O2	2.285(6)	Li1–O9	1.985(17)
U–O4	2.275(6)	Li1–O10	1.951(18)
U–O5	2.286(6)	Li1–O11	1.894(19)
U–O7	1.798(6)	Li2–O8	1.95(2)
U–O8	1.797(6)	Li2–O12	1.97(2)
O1–U–O2	86.7(2)	Li2–O13	1.99(2)
O2–U–O4	95.0(2)	Li2–O14	1.859(19)
O4–U–O5	85.3(2)		
O5–U–O1	92.9(2)		
O7–U–O8	179.6(3)		

2

U–O1	2.294(6)	Na1–O7	2.460(8)
U–O2	2.282(6)	Na1–O9	2.403(9)
U–O4	2.281(6)	Na1–O10	2.307(9)
U–O5	2.273(6)	Na1–O11	2.351(11)
U–O7	1.813(6)	Na1–O12	2.390(9)
U–O8	1.803(6)	Na1–O9′	2.433(9)
O1–U–O2	83.7(2)	Na2–O3	2.456(8)
O2–U–O4	95.2(2)	Na2–O8	2.383(8)
O4–U–O5	85.9(2)	Na2–O13	2.451(11)
O5–U–O1	94.9(2)	Na2–O14	2.251(11)
O7–U–O8	179.0(3)	Na2–O15	2.503(13)

3

U–O1	2.249(6)	K1–O3	2.811(6)
U–O2	2.292(6)	K1–O7″	2.708(6)
U–O4	2.294(6)	K1–O8	2.658(6)
U–O5	2.269(6)	K1–O9	2.801(7)
U–O7	1.799(5)	K1–O10	2.886(8)
U–O8	1.800(5)	K1–N	2.773(8)
O1–U–O2	86.8(2)	K2–O4″	2.731(6)
O2–U–O4	93.6(2)	K2–O6	2.804(6)
O4–U–O5	86.3(2)	K2–O7″	3.230(6)
O5–U–O1	93.2(2)	K2–O8	2.732(6)
O7–U–O8	178.8(3)	K2–O9	2.842(8)
		K2–O10	2.685(7)

4

U–O1	2.299(8)	Cs1–O4‴	3.549(8)
U–O2	2.291(7)	Cs1–O5‴	3.740(8)
U–O4	2.257(8)	Cs1–O7‴	3.085(8)
U–O5	2.287(7)	Cs1–O8	3.140(8)
U–O7	1.805(8)	Cs1–O9	3.028(9)
U–O8	1.799(8)	Cs1–O10	2.993(9)
O1–U–O2	82.1(3)	Cs2–O7‴	3.201(8)
O2–U–O4	97.7(3)	Cs2–O8	3.269(8)
O4–U–O5	82.3(3)	Cs2–O9	3.075(9)
O5–U–O1	97.6(3)	Cs2–O10	3.076(8)
O7–U–O8	178.8(3)	Cs2–O11	3.309(10)
		Cs2–O12	3.189(12)

[a] Symmetry codes: ′ = 1 − x, 1 − y, 1 − z; ″ = x, 1.5 − y, z − 0.5; ‴ = 0.5 − x, y − 0.5, 0.5 − z.

Fig. 2 View of the dimer formed by the complex $[UO_2Na_2(L)$-$(H_2O)(CH_3OH)_6]$ in **2**. Hydrogen atoms and solvent molecules omitted for clarity. Displacement ellipsoids drawn at the 10% probability level. Only one position of the disordered parts is represented. Symmetry code: ′ = 1 − x, 1 − y, 1 − z.

Fig. 3 Partial view of the polymeric chain formed by the complex $[UO_2K_2(L)(H_2O)_2(py)]$ in **3**. Hydrogen atoms and solvent molecules omitted for clarity. Cation–π interactions represented as dashed lines. Displacement ellipsoids drawn at the 10% probability level. Only one position of the disordered parts is represented. Symmetry codes: ′ = x, 1.5 − y, z + 0.5; ″ = x, 1.5 − y, z − 0.5.

are 147.1(4)° for Na1 and 133.9(3)° for Na2, both values being lower than their counterparts in **1**. The angle corresponding to Na2 in particular is very low due to the off-center position of this ion resulting from its bonding to the ether atom O3. The coordination geometry around Na1 is distorted octahedral (the two centrosymmetrically related octahedra sharing a common edge) and that around Na2 can best be viewed as much distorted square pyramidal, with the water atom O15 at the apex.

Compound **3**, $[UO_2K_2(L)(H_2O)_2(py)]·0.5H_2O·0.5py$, presents a much different arrangement (Fig. 3). The two potassium ions are located in the cavity of the $[UO_2(L)]^{2−}$ species, and are both bound to the same inwardly directed oxo atom O8, with not much different bond lengths [mean value 2.70(5) Å]. The U=O8–K angles are nearly equal, 138.7(3)° for K1 and 137.4(3)° for K2, the K1–O8–K2 angle being 83.8(2)° and the K1 ⋯ K2 distance 3.599(3) Å. Both potassium ions are also bound to the second, out-of-cavity, oxo atom O7 of a neighbouring complex, albeit in a dissymmetrical way, K1 being involved in a much
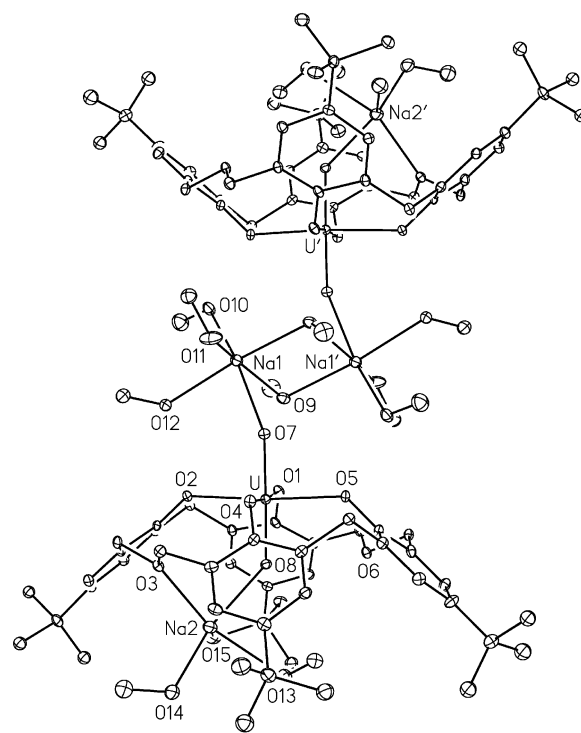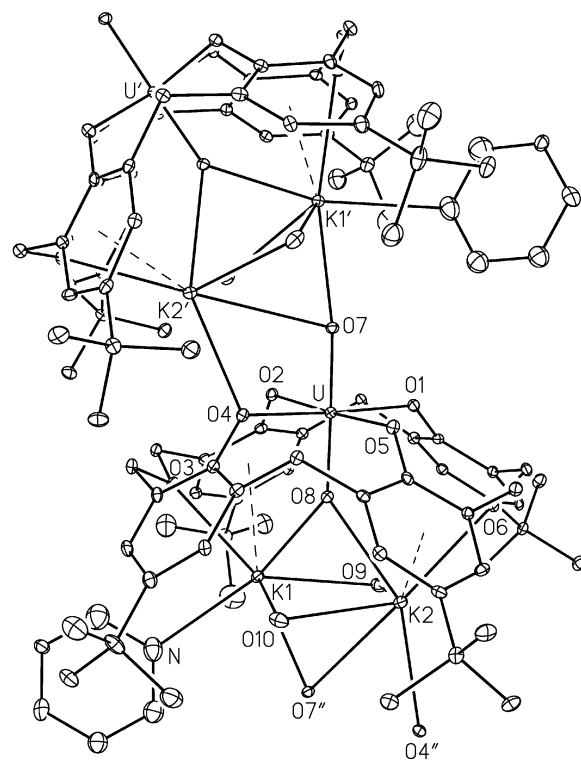
shorter bond [2.708(6) Å, close to the K–O8 bond lengths] than K2 [3.230(6) Å], the angle around O7 being 74.0(1)°. The U=O7–K′ angles are also much different, with a nearly linear bond for K1 [164.3(3)°] and a very bent one for K2 [104.3(2)°].

This could at first be considered as indicative of a relation between degree of linearity and bond strength, but further results with caesium ions will not support this view. The U=O bond lengths are identical to those in compounds **1** and **2**, at about 1.80 Å. The two potassium ions complete their coordination sphere differently. Both are bound to two bridging water molecules [mean K–O(water) bond length 2.80(9) Å, each of the water molecules being closer to one cation than to the other one]. Each potassium atom is also bound to an ether oxygen atom (O3 or O6) [mean K–O(ether) bond length 2.808(5) Å]. K1 is further bound to the nitrogen atom of a pyridine molecule and K2 to a phenoxide group of the neighbouring complex. Some cation-π interactions are also seemingly present between each potassium ion and one aromatic ring [K1 ··· centroid 3.495 Å, shortest K1 ··· C contact 3.180(8) Å; K2 ··· centroid 3.647 Å, shortest K2 ··· C contact 3.255(9) Å]. If this polyhapto–aromatic interaction is counted as one bond, both cations are hepta-coordinated, the geometry being that of a distorted capped trigonal prism.[23] The overall arrangement is made of columns of tilted $[UO_2(L)]^{2-}$ anions bridged by the potassium ions and related one to the other by the axial glide plane parallel to the *ac* plane, the polymeric chain being directed along the *c* axis. The dihedral angle between successive O_4(phenoxide) planes is 38.4(1)°, which enables the pyridine molecule to come in the vicinity of K1 and brings K2 closer to the neighbouring molecule than K1, with formation of a bond with the phenoxide atom O4. It can be noted that the $K_2(H_2O)_2$ fragment, which is a distorted parallelogram, has none of its pseudo-symmetry planes in common with the macrocycle, but is tilted so as to bring each potassium ion as close as possible to both one ether group and one of the aromatic rings bound to it (Fig. 4). To the best of our knowledge, this is the first example of a complex with bifurcated U=O–X bonds (where X is an alkali metal ion) and also containing the ··· (O=U=O)K_2(O=U=O) ··· polymeric arrangement.
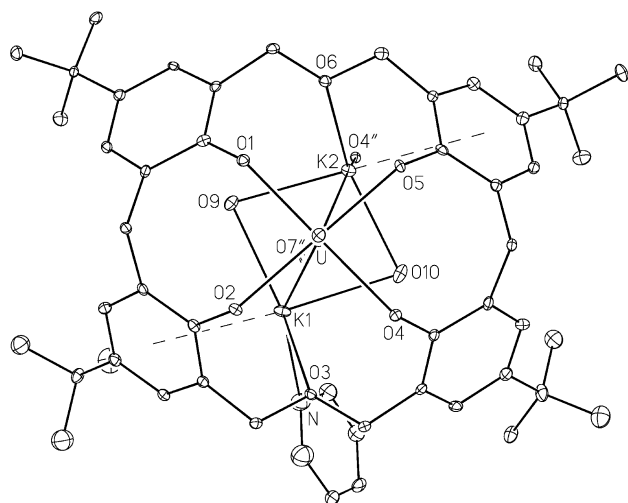

Fig. 4 View of the complex $[UO_2K_2(L)(H_2O)_2(py)]$ in **3** down the uranyl ion axis. Hydrogen atoms and solvent molecules omitted for clarity. Cation–π interactions represented as dashed lines. Displacement ellipsoids drawn at the 10% probability level. Only one position of the disordered parts is represented. Symmetry code: ″ = *x*, 1.5 − *y*, *z* − 0.5.

Compound **4**, $[UO_2Cs_2(L)(H_2O)_{0.5}(CH_3OH)_{3.5}]\cdot0.5CHCl_3$, presents some common features with compound **3**, but also some noteworthy differences (Fig. 5). The two caesium ions are located in the macrocycle cavity, with bonding to the oxo group pointing inwards [Cs–O bond length and U=O8–Cs angle: 3.140(8) Å and 134.3(4)° for Cs1, 3.269(8) Å and 140.8(4)° for Cs2, mean Cs–O8 bond length 3.20(9) Å, Cs1–O8–Cs2 84.9(2)°]. Both caesium ions are also bound to the oxo group pointing outwards from the neighbouring molecule [Cs–O bond length and U=O7–Cs angle: 3.085(8) Å and 117.1(4)° for
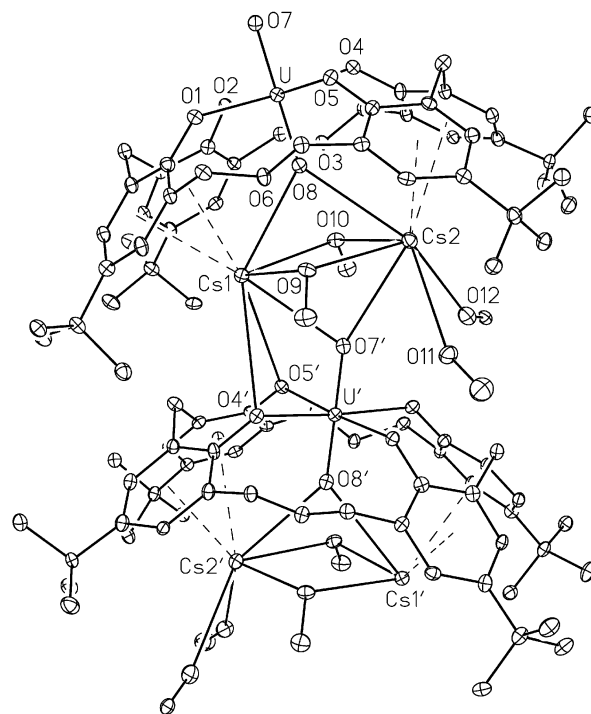

Fig. 5 Partial view of the polymeric chain formed by the complex $[UO_2Cs_2(L)(H_2O)_{0.5}(CH_3OH)_{3.5}]$ in **4**. Hydrogen atoms and solvent molecules omitted for clarity. Cation–π interactions represented as dashed lines. Displacement ellipsoids drawn at the 10% probability level. Only one position of the disordered parts is represented. Symmetry code: ′ = 0.5 − *x*, *y* − 0.5, 0.5 − *z*.

Cs1, 3.201(8) Å and 155.9(4)° for Cs2, mean Cs–O7 bond length 3.14(8) Å, Cs1–O7–Cs2 87.0(2)°]. The difference between the latter distances and angles is less pronounced than in compound **3**, in agreement with a lower dihedral angle between the reference O_4(phenoxide) planes of successive molecules along the *b* axis [23.5(1)°]. By contrast with compound **3**, the longer distances are associated with the more linear bonds, hence no clear relation is obvious. These Cs–O(oxo) bond lengths are shorter than those in the *p-tert*-butylcalix[6]arene complex previously cited (3.39 and 3.45 Å).[8] In a manner analogous to the potassium ions in **3**, the caesium ions are bridged by two methanol molecules [mean Cs–O bond length 3.04(4) Å], Cs2 being further bound to 1.5 methanol and half a water molecule located where the separation between successive macrocycles is largest [mean Cs–O bond length 3.25(8) Å]. The $Cs_2[O(oxo)]_2$-[O(bridging methanol)]$_2$ fragment defines a slightly distorted octahedron, more regular than its counterpart in **3**. Cs1 is bound to two phenoxide groups of the neighbouring complex [mean Cs–O bond length 3.6(1) Å], being closer to it than Cs2. Both cations are also involved in polyhapto bonding with two aromatic rings each [Cs1 ··· centroid 3.582 and 3.706 Å, shortest Cs1 ··· C contact 3.60(1) and 3.66(1) Å; Cs2 ··· centroid 3.785 and 3.727 Å, shortest Cs2 ··· C contact 3.75(1) and 3.79(1) Å; these values are larger than those in caesium complexes of calixcrowns:[3e] shortest Cs ··· C contact 3.09, mean value 3.54(16) Å]. The assemblage resulting from this bonding pattern is a polymeric chain directed along the *b* axis, with tilted successive units related by the screw axis parallel to the *b* axis and having as a skeleton the ··· (O=U=O)Cs_2(O=U=O) ··· polymer analogous to that in **3**. As can be seen in Fig. 6, the distorted parallelogram defined by the $Cs_2(CH_3OH)_2$ fragment shares the same pseudo-symmetry planes as the $[UO_2(L)]^{2-}$ anion. Instead of being located halfway between an ether oxygen atom and an aromatic ring as are the potassium ions in **3**, the caesium ions are located on the methylene-bridged side of the homooxacalixarene and are equally separated from the two proximal aromatic rings. This arrangement permits also the
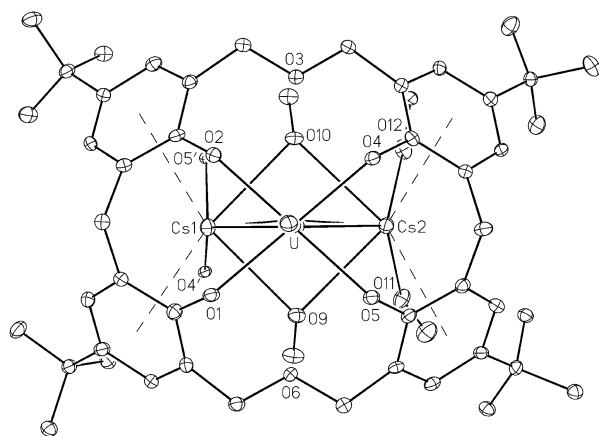
Fig. 6 View of the complex $[UO_2Cs_2(L)(H_2O)_{0.5}(CH_3OH)_{3.5}]$ in **4** down the uranyl ion axis. Hydrogen atoms and solvent molecules omitted for clarity. Cation–π interactions represented as dashed lines. Displacement ellipsoids drawn at the 10% probability level. Only one position of the disordered parts is represented. Symmetry code: $' = 0.5 - x$, $y - 0.5$, $0.5 - z$.

Fig. 7 X–O(oxo) bond length (X = Li^+, Na^+, K^+, Cs^+) *versus* ionic radius. Empty symbols: individual values, full symbols: mean values. The best fit line through mean values is represented.

bonding of Cs1 to two phenoxide groups of the neighbouring molecule, and not one only as for potassium. If the polyhapto interactions are considered as a single bond, both caesium ions are octa-coordinated, with a much distorted square antiprism geometry.

Investigation of calixarene complexes is often hampered by the difficulty of growing single crystals of suitable size and quality and, unfortunately, we did not manage to grow single crystals of the complex obtained in the presence of rubidium hydroxide. The similarities between the potassium and caesium cases permits one to make the hypothesis that, with rubidium also, a polymeric chain would have been obtained with an analogous ··· (O=U=O)Rb₂(O=U=O) ··· central "backbone" and tilted macrocycles, but the fine details of bonding to the macrocycles could have been different and possibly intermediate between those in **3** and **4**. Nonetheless, the present series permits some general trends to be discussed. Complexes **1**, **2** and **4** were obtained with the same solvents (CHCl₃, CH₃OH). This is not the case for the potassium complex **3**, which could only be isolated in single crystal form from a pyridine solution, but this point does not seem to matter much since comparison of **3** and **4** shows that the coordinated methanol and water in the latter are replaced by water and pyridine in the former, as bridging or terminal ligands, with seemingly little effect on the overall structure. A particular interest of the present series is the regular occurrence of alkali metal ion bonding to both oxo groups of uranyl ions, with bridging oxo atoms in the case of **3** and **4**, in which each uranyl ion is bound to four alkali metal ions. Such bonds are possible due to the basic nature of the oxo groups,[24] which enables also the dissymmetrical O=U=O–U bonds sometimes observed.[24,25] The involvement of the oxo group in alkali metal complexation results in a lengthening of the U=O bond by about 0.04 Å, but no significant deviation from linearity of the uranyl ion is observed. It has been shown that such bonds have little effect on the U–O bond order and U–O vibrations.[20] The X–O(oxo) bond lengths (X = Li^+, Na^+, K^+, Cs^+) are plotted in Fig. 7, *versus* ionic radii (taking into account the coordination numbers).[26] In spite of the large dispersion in the values for potassium, the mean values follow nicely a linear law (notwithstanding the bridging character of the bonds with K^+ and Cs^+). The bond length exactly follows the increase in ionic radius, which indicates the ionic nature of such bonds (a search of the Cambridge Structural Database for bonds between alkali metal ions and transition metal oxo groups gives a similar linear plot, with however only one caesium complex).

The differences in the structures of **1**–**4**, all containing the same uranyl complex core, are to be ascribed primarily to the
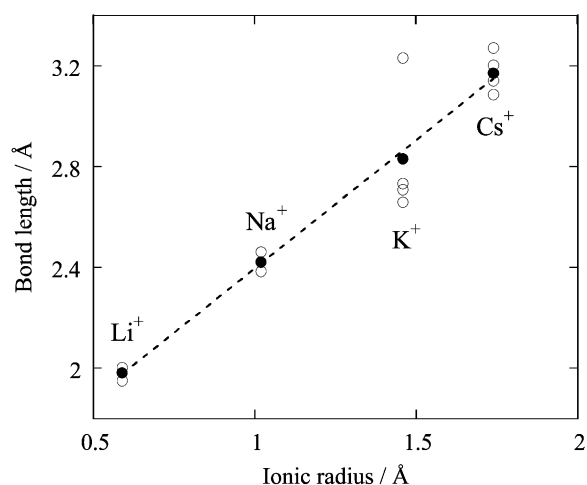
nature of the alkali metal ions, and particularly to their size and "hard" or "soft" character, which increase in the series [structural variations dependent on the latter character were also found in the alkali metal ions/uranyl halides complexes: the hard lithium ion bonds only to the oxo groups whereas halide bonding is preferred in the case of the softer potassium ion, intermediate cases being observed with sodium ions[19]]. There is a clear trend for the largest and softer ions K^+ and Cs^+ to prefer "endo" coordination (inside the cavity) with polyhapto–aromatic bonding, whereas the harder ions are located either in "exo" or in "endo" mode, but devoid of cation–π interactions in the latter case. This may explain why, as a consequence of this location, a bidentate oxo bonding is present with K^+ and Cs^+, further *bis*(bidentate) oxo bonding resulting in polymerization by column-packing of conical units. The differences between Li^+ and Na^+ are essentially due to the larger coordination number of the latter, which results in bonding to the macrocycle, and to dimerization due to bridging ligands. Some differences between **3** and **4**, in what concerns the interactions between the alkali metal ion and the macrocycle, can be accounted for by the softer nature of Cs^+. K^+ adopts a position which permits bonding to one ether oxygen atom and to one aromatic ring, whereas Cs^+ is located so as to maximize the interactions with the aromatic rings and is no more bound to the ether groups.

Complexes in solution

Complexes **1**–**4** could not be dissolved in chloroform and other poorly coordinating solvents. ¹H NMR spectra were taken of dilute (0.1–0.4 mmol dm⁻³) CD₃CN solutions of complexes **1**, **3** and **4**. Geminal coupling for the methylene protons of the ligand indicates that the "cone" conformation is frozen due to the coordination with uranyl ion. The signals of included organic solvents are found in the same position as in the case of unbound molecules but their intensity largely depends on exposition of the crystals to the atmosphere. The tight involvement of the alkali metal ions in solution is supported by the different chemical shifts for the macrocyclic ligand moiety in the three cases. Moreover, small but significant shifts were observed on addition of 10 mmol dm⁻³ 18-crown-6, namely up to 0.15 ppm in the spectrum of complex **3** and up to 0.07 ppm in the case of complex **4**.

Conclusion

We have reported recently an investigation of the crystal structures of Na^+ and Cs^+ complexes of calix[4]arene, in which two acetone-bridged Na^+ were sandwiched in "exo" fashion

between two facing calixarenes, with only phenol/phenoxide bonding, in a way similar to that observed for Na1 in compound **2**, whereas Cs^+ was involved in polymer-building through "endo" coordination in a calixarene cavity and phenol/phenoxide bonding to a neighbouring macrocycle.[27] This confirms a tendency to monomer or small oligomer formation with the smaller cations and of polymerization by stacking of alternate π-bonded calixarene-containing anions and cations with the largest ones. It has been noted, in relation to complexation of alkali metal ions by *p-tert*-butyltetrathiacalix[4]arene, that in these calixarene-like macrocycles in the "cone" conformation, a segregation of polar and lipophilic groups occur,[4] however, in the present cases, the oxo group of uranyl directed inwards constitutes a polar site in the lipophilic cavity, which permits "endo" complexation through O-coordination possibly associated with cation–π interactions, and not solely or predominantly through the latter. We have described previously some supramolecular assemblies obtained with the same $[UO_2(L)]^{2-}$ complex core, which were dependent on various interactions, among which hydrogen bonding of primary or secondary ammonium ions to the oxo group of uranyl. In compounds **3** and **4**, replacement of ammonium by alkali metal ions results in the formation of infinite architectures based on stronger, ionic bonds, in which the uranyl and alkali metal ions play an unprecedented structural role.

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