



Ditopic Calixcrowns with Inequivalent Crown Loops: Synthesis and Structural Characterisation of an Unsymmetrical Calix[4]arene**biscrown**-6

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Abstract. Consecutive base-catalysed reactions of calix[4]arene with the ditosylates of two different polyetherdiols result in the relatively efficient production of an unsymmetrical calix**biscrown**-6 which, after reduction of an ethoxycarbonyl substituent to an hydroxymethyl group, has been characterised structurally by a room-temperature, single crystal X-ray study of its chloroform solvate. Crystals of (**4**), $C_{53}H_{62}O_{13} \cdot \sim 0.57CHCl_3$, are triclinic, $P\bar{1}$, a 18.95(3), b 12.394(9), c 11.756(7) Å, α 106.93(5), β 101.77(8), γ 94.63(8)°, $Z = 2$; R was 0.088 for 2231 'observed' ($I > 3\sigma(I)$) diffractometer data.

Key words: unsymmetrical ditopic calixcrown, synthesis, crystal structure.

1. Introduction

Calix[4]arenes fixed in the 1,3-alternate conformation by the linkage of rings 1,3 and 2,4 with separate polyether chains, "doubly-crowned calices" or "calix**biscrowns**" (Figure 1), have recently been shown to be highly selective caesium ion carriers when the polyether chains contain six oxygen donor atoms and the polyether links are ethylene or 1,2-phenylene groups [1–4]. Very similar properties are found for "singly-crowned" calixarenes conformationally locked by the attachment of sufficiently large simple alkyl groups to the two phenolic oxygen atoms not involved in the crown loop [5]. The practical interest in such materials arises from their possible use in the selective extraction of ^{137}Cs from nuclear

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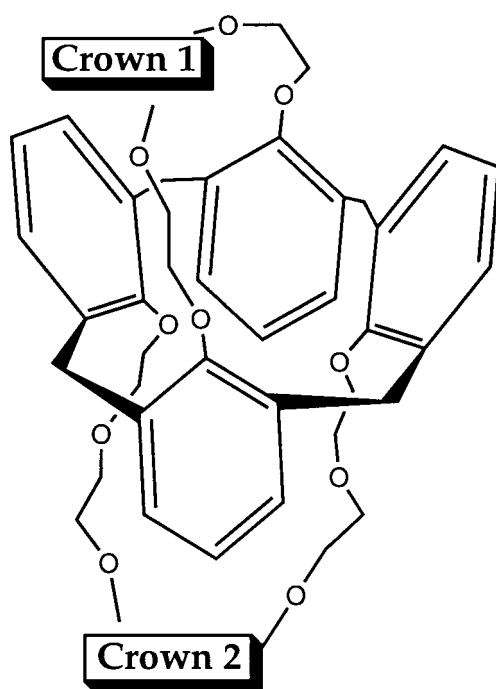


Figure 1. General representation of a calixbiscrown derived by linkage of the 1,3 and 2,4 rings of a calix[4]arene in the 1,3-alternate conformation. The “Crown 1” and “Crown 2” loops may contain various links other than CH_2CH_2 between pairs of oxygen atoms.

wastes [6, 7]. Although Cs^+ transport phenomena for both ligand systems could be rationalised simply in terms of the formation of 1 : 1 complexes [1–5, 7, 8], other spectroscopic [9–11] and X-ray structural studies [12] have all shown that dicaesium complexes may also be readily formed by the doubly-crowned ligands. In both 1 : 1 and 2 : 1 complexes of calixcrown-6 ligands characterised structurally [5, 7, 12, 13], Cs^+ is bound to all six (except in one instance of five [13]) oxygen atoms of a polyether loop and to one or two atoms of a counteranion. There is also evidence of some degree of coordinative interaction of the caesium with the π -electrons of the calixarene phenyl rings. [5, 7, 12–14] In this regard it is of interest that our recent structural study of a symmetrical calixbiscrown-6 in which a single 1,3-phenylene ‘spacer’ group was introduced between one pair of oxygen atoms in each arm has shown that the tilt of the phenyl rings towards the potential cation binding cavities is opposite to that in other known analogues and unfavourable for cation interaction [15]. This may partly explain why the ligand appears to be a relatively poor caesium binder and forms a complex of 1 : 2 (metal : ligand) stoichiometry. We have previously observed with calixcrown-5 ligands that weak and presumably exocyclic cation binding can still occur even when entry to the ligand cavity is inhibited (there, by *t*-butyl substituents on the calixarene) [15, 16].

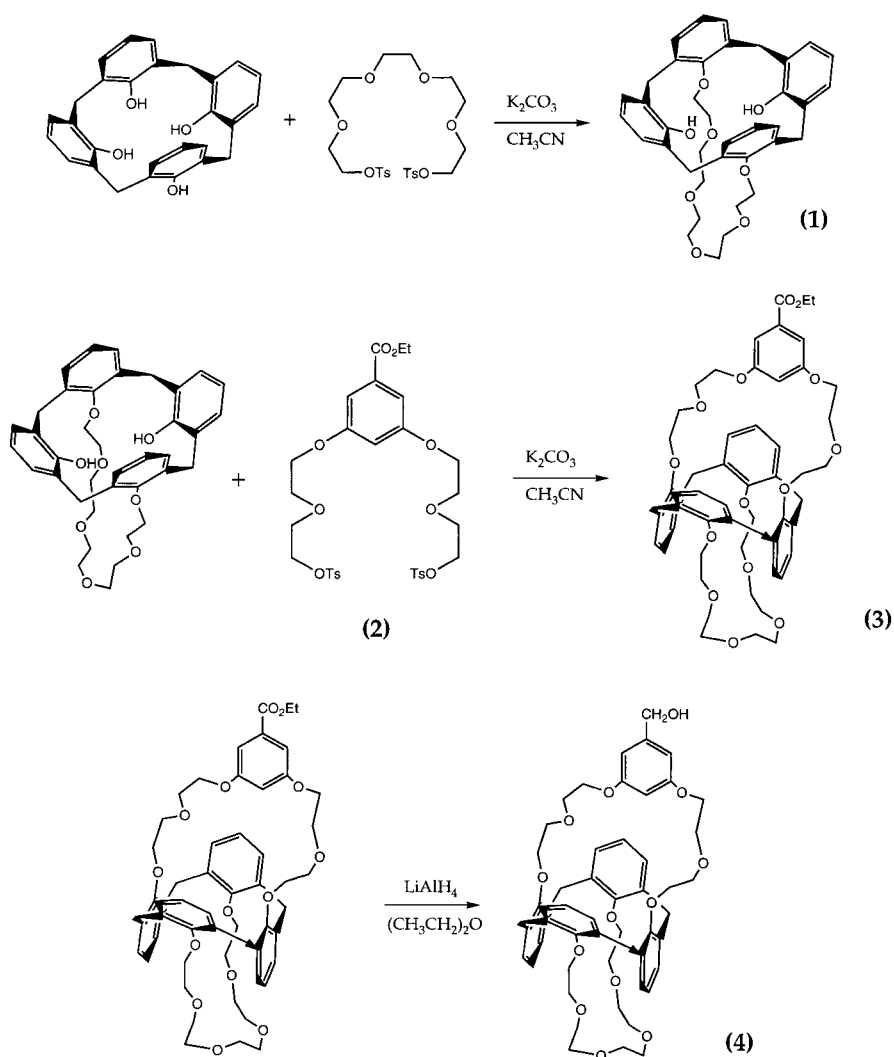


Figure 2. Reaction scheme for the synthesis of the unsymmetrical calixbiscrown-6, (4).

Thus, to further explore the factors controlling selectivity in metal ion binding by calixcrowns, we have been interested in the properties of unsymmetrical species (including aza-crown derivatives [18–20], which certainly appear to have some unusual properties [21]), and report herein the synthesis and structural characterisation of such a compound, 1,3-alternate calix[4]arene-1,3-crown-6;2,4-[(5-hydroxymethyl)-1,3-phenylene]crown-6, (4) (Figure 2). The significance of the hydroxymethyl substituent in this molecule is its possible use as a site for tethering the calixcrown to an immobilising support.

2. Experimental

2.1. INSTRUMENTATION AND ANALYSIS

Melting points were measured with a Büchi 500 apparatus in sealed capillaries under nitrogen. Chromatography columns were prepared from Merck Kieselgel No. 11567. $^1\text{H-NMR}$ spectra were recorded on Bruker SY200 or AM300 spectrometers and FAB mass spectra on a VG-Analytical ZAB HF instrument. Elemental analyses were provided by the Service de Microanalyse of the Institut de Chimie de Strasbourg.

2.2. SYNTHESIS

All commercial solvents and basic reagents were used without purification. Calix[4]arene [22, 23] and the ditosylate (**2**) [15] were prepared as described in the literature. Pentaethyleneglycol di-*p*-toluenesulfonate (tosylate) (Aldrich) was used as received.

2.2.1. Calix[4]crown-6, (**1**) was prepared as described previously.[5]

$^1\text{H NMR}$ (200 MHz, CDCl_3): δ 3.37 (d, 4H, $J = 13.1$ Hz, ArCH_2Ar); 3.71 (s, 4H, $-\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{Ar}$); 3.85 (t, 4H, $J = 4.0$ Hz, $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OAr}$); 3.92 (t, 4H, $J = 4.0$ Hz, $-\text{CH}_2\text{OCH}_2\text{CH}_2\text{OAr}$); 4.00 (t, 4H, $J = 4.0$ Hz, $-\text{OCH}_2\text{CH}_2\text{OAr}$); 4.16 (t, 4H, $J = 4.0$ Hz, $-\text{CH}_2\text{OAr}$); 4.41 (d, 4H, $J = 13.1$ Hz, ArCH_2Ar); 6.70–6.75 (m, 4H, *p*-ArH (calix)); 6.84 (d, 4H, $J = 7.4$ Hz, *m*-ArH (calix)); 7.07 (d, 4H, $J = 7.4$ Hz, *m*-Ar'H (calix)); 7.50 (s, 2H, ArOH). Analysis calculated for $\text{C}_{38}\text{H}_{42}\text{O}_8$: C, 72.82; H, 6.75. Found: C, 72.76; H, 6.68.

2.2.2. Unsymmetrical calix[4]biscrown-6, (**3**)

A slurry of (**1**) (9.44 g, 15 mmol) and K_2CO_3 (20.7 g, 150 mmol) in CH_3CN (1.7 L) was stirred at room temperature for 3 h. Ditosylate (**2**) (10.1 g, 15 mmol) was added and the mixture then heated at reflux for 1 week. On cooling, the solvent was removed under reduced pressure and the residue neutralised by the addition of dilute HCl. The resultant mixture was extracted with CH_2Cl_2 and the extract dried over Na_2SO_4 , filtered and evaporated to dryness. Column chromatography (silica; 80/20 dichloromethane/acetone) provided the pure doubly crowned calix[4]arene, (**3**) (5.9 g, 41%) as a transparent liquid. $^1\text{H NMR}$ (200 MHz, CDCl_3): δ 1.42 (t, 3H, $J = 7.1$ Hz, $-\text{CH}_2\text{CH}_3$); 3.69–3.85 (m, 28H, glycolic CH_2); 3.76 (s, 8H, ArCH_2Ar (calix)); 3.94 (t, 4H, $J = 4.7$ Hz, $-\text{CH}_2\text{OAr}$ (calix)); 4.33 (t, 4H, $J = 4.7$ Hz, $-\text{CH}_2\text{OAr}'$ (calix)); 4.38 (q, 2H, $J = 7.1$ Hz, $-\text{CH}_2\text{CH}_3$); 6.53 (t, 2H, $J = 7.5$ Hz, *p*-ArH (calix)); 6.82 (t, 2H, $J = 7.5$ Hz, *p*-Ar'H (calix)); 6.96 (t, 1H, $J = 1.9$ Hz, ArH on C2); 7.08 (d, 4H, $J = 7.5$ Hz, *m*-ArH (calix)); 7.14 (d, 4H, $J = 7.5$ Hz, *m*-Ar'H (calix)); 7.29 (d, 2H, $J = 1.9$ Hz, ArH on C4,6). Analysis calculated for $\text{C}_{55}\text{H}_{64}\text{O}_{14}$: C, 69.60; H, 6.80. Found: C, 69.71; H, 6.72.

2.2.3. *Unsymmetrical calix[4]biscrown-6*, (**4**)

Under a nitrogen atmosphere, a solution of (**3**) (2.87 g, 3 mmol) in diethylether (30 mL) was added to a suspension of LiAlH₄ (2.01 g, 53 mmol) in ether (50 mL). The mixture was heated at reflux for 96 h. The excess LiAlH₄ was destroyed by gradual addition of methanol and then water. The precipitated Al(OH)₃ was dissolved by the addition of dilute H₂SO₄, the aqueous phase extracted with CH₂Cl₂, and the ether and CH₂Cl₂ phases combined, dried over Na₂SO₄ and evaporated to dryness. Crystallisation of the beige residue from 80/20 dichloromethane/acetone provided pure (**4**) (1.3 g, 50%). m.p. 134–5 °C. ¹H NMR (200 MHz, CDCl₃): δ 3.68–3.79 (m, 28H, glycolic CH₂); 3.73 (s, 8H, ArCH₂Ar (calix)); 3.85 (t, 4H, J = 5.0 Hz, —CH₂OAr (calix)); 4.26 (t, 4H, J = 4.7 Hz, —CH₂OAr' (calix)); 4.65 (s, 1H, —OH); 4.68 (s, 2H, —CH₂OH); 6.57 (t, 2H, J = 7.6 Hz, *p*-ArH (calix)); 6.63 (d, 2H, J = 2.0 Hz, ArH on C4,6); 6.70 (t, 1H, J = 2.0 Hz, ArH on C2); 6.82 (t, 2H, J = 7.6 Hz, *p*-Ar'H (calix)); 7.10 (d, 4H, J = 7.6 Hz, *m*-ArH (calix)); 7.12 (d, 4H, J = 7.5 Hz, *m*-Ar'H (calix)). Analysis calculated for C₅₃H₆₂O₁₃: C, 70.18; H, 6.89. Found: C, 70.13; H, 6.86.

Crystals suitable for X-ray diffraction measurements were obtained by dissolving (**4**) in chloroform, adding an equal volume of acetonitrile and allowing the solution to stand at room temperature for several hours.

2.3. STRUCTURE DETERMINATION

A unique room-temperature diffractometer data set ($T \sim 295$ K; monochromatic Mo K_α radiation, λ 0.71073 Å; $2\theta/\theta$ scan mode; $2\theta_{\max}$ 45°) was measured, yielding 6675 independent reflections, 2231 with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least squares refinement after gaussian absorption correction. Despite weak and limited data, anisotropic thermal parameter refinement was stable for all non-hydrogen atoms (excepting C of the solvent) and was retained; $(x, y, z, U_{\text{iso}})_{\text{H}}$ were included constrained at estimated values. Conventional R, R_w on $|F|$ at convergence were 0.088, 0.088, statistical weights being the derivative of $\sigma^2(I) = \sigma^2(I_{\text{diff}}) + 0.0004\sigma^4(I_{\text{diff}})$. Neutral atom complex scattering factors were employed, computation using the XTAL 3.2 program system [24] implemented by S.R. Hall. Pertinent results are given in the figures and tables; material deposited comprises thermal and hydrogen parameters, full non-hydrogen molecular geometries and structure factor amplitudes.*

Crystal data. C₅₃H₆₂O₁₃ · ~0.57CHCl₃, $M \sim 978.7$. Triclinic, space group $P\bar{1}$ (C_i^1 , No. 2), a 18.95(3), b 12.394(9), c 11.756(7) Å, α 106.93(5), β 101.77(8), γ 94.63(8)°, V 2557 Å³. D_c ($Z=2$) ~ 1.27 g cm⁻³; $F(000) \sim 1037.6$. μ_{Mo} 1.8 cm⁻¹; specimen: 0.55 × 0.4 × 0.40 mm; $A_{\text{min,max}}^*$ 1.06, 1.08.

Abnormal features/variations in procedure. Difference map residues were modelled in terms of CHCl₃ solvent, site occupancy from refinement being set at

0.570(5). O(24) was disordered over a pair of sites, occupancy set at 0.5 from the refinement.

3. Results and Discussion

3.1. SYNTHESIS

As with many related compounds [1–3], the syntheses, outlined in Figure 2, of the calixcrowns (**1**), (**3**) and (**4**), proceed in excellent yields for such macrocycle formation processes [25], so justifying optimism with regard to practical applications of such materials [2–7]. The introduction of crown ether “straps” within the calixarene structure formally removes some symmetry elements and so complicates relationships between ^1H NMR spectra and the molecular conformations. However, it is worthy of note that the 1,3-alternate conformations which must be taken for both (**3**) and (**4**) on the basis of the present structure determination are reflected in singlet resonances for the calixarene methylene protons (as expected for a simple 1,3-alternate calix[4]arene [26]) despite the fact that the dissimilar crown chains render these protons diastereotopic. Given this apparently undetectable influence of the crown chains, we assume that the observation of an AX doublet pair for the calixarene methylene resonances in (**1**) indicates that it adopts the cone and not the 1,3-alternate conformation.

3.2. CRYSTALLOGRAPHY

The results of the room-temperature, single crystal X-ray study of (**4**) are consistent in terms of stoichiometry and connectivity with the above formulation, accompanied by solvent modelled as $\sim 0.57 \text{ CHCl}_3$. The chemical identity of this adduct species is simply assumed on the basis of the solvent used for crystallisation being retained in the larger, undried crystals used for the structure determination, as analysis of the bulk, air-dried material indicated it to be unsolvated. In any event, this solvent has no association with either cavity of the calixcrown, simply occupying lattice sites. Despite the “unsymmetrical” nature of (**4**) in respect of the crown loops, the molecular symmetry is close to twofold about an axis perpendicular to the calixarene mean plane (Figure 3(a)) and is certainly higher than that of the “symmetrical” analogue in which both loops contain a 1,3-phenylene spacer [15]. It remains true, nonetheless, that neither loop of (**4**) can be regarded as “preorganised” for metal ion binding in that the oxygen atom lone pairs cannot all be considered oriented towards a central point of a cavity. Within the calix[4]arene moiety, the four bridging methylene carbon (C(n)) atoms define a good plane (χ^2 6.5), with the C_6 phenyl planes 1 - 4 making dihedral angles of 83.6(7), 84.3(3), 82.7(4) and 81.9(3) $^\circ$ with it. These dihedrals are, however, of opposite sense to those commonly observed in calix[4]arenes [8, 17] and define ring tilts which place the C4 carbons of 1,3; 2,4 ring pairs into closer proximity than the C1 (*O*-substituted) carbons, as previously observed in the symmetrically bridged

Table I. Non-hydrogen positional and isotropic displacement parameters

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) Å ²
O(1)	0.1987(4)	1.1903(6)	0.3089(6)	0.055(4)
C(11)	0.1445(6)	1.114(1)	0.314(1)	0.058(6)
C(12)	0.1419(6)	1.097(1)	0.428(1)	0.053(6)
C(13)	0.0854(7)	1.026(1)	0.433(1)	0.072(7)
C(14)	0.0332(7)	0.958(1)	0.329(1)	0.077(8)
C(15)	0.0399(6)	0.968(1)	0.214(1)	0.061(6)
C(16)	0.0953(6)	1.0420(9)	0.207(1)	0.050(6)
C(1)	0.1071(6)	1.045(1)	0.0837(9)	0.051(6)
O(2)	0.1128(4)	0.8051(6)	0.0244(6)	0.060(4)
C(21)	0.1762(6)	0.879(1)	0.0362(9)	0.048(6)
C(22)	0.1744(6)	0.9964(9)	0.568(9)	0.051(6)
C(23)	0.2363(6)	1.060(1)	0.059(1)	0.060(6)
C(24)	0.2993(6)	1.016(1)	0.047(1)	0.068(7)
C(25)	0.3009(6)	0.902(1)	0.033(1)	0.066(7)
C(26)	0.2389(6)	0.8336(9)	0.0283(9)	0.047(6)
C(2)	0.2427(6)	0.709(1)	0.026(1)	0.064(7)
O(3)	0.3568(4)	0.7954(6)	0.2447(6)	0.058(4)
C(31)	0.2917(6)	0.742(1)	0.255(1)	0.066(7)
C(32)	0.2363(6)	0.693(1)	0.148(1)	0.065(7)
C(33)	0.1705(7)	0.637(1)	0.156(1)	0.069(7)
C(34)	0.1641(7)	0.637(1)	0.275(1)	0.086(8)
C(35)	0.2189(7)	0.691(1)	0.378(1)	0.078(8)
C(36)	0.2801(6)	0.744(1)	0.369(1)	0.058(6)
C(3)	0.3362(7)	0.818(1)	0.481(1)	0.072(7)
O(4)	0.2216(4)	0.9381(7)	0.5569(6)	0.069(4)
C(41)	0.2787(6)	0.996(1)	0.5301(9)	0.055(6)
C(42)	0.3364(6)	0.943(1)	0.5012(9)	0.057(6)
C(43)	0.3928(6)	1.008(1)	0.476(1)	0.068(7)
C(44)	0.3898(7)	1.118(1)	0.480(1)	0.083(8)
C(45)	0.3292(7)	1.116(1)	0.502(1)	0.073(7)
C(46)	0.2724(6)	1.107(1)	0.5274(9)	0.052(6)
C(4)	0.2045(7)	1.158(1)	0.540(1)	0.065(7)
C(51)	0.5101(7)	1.261(1)	0.252(1)	0.081(8)
C(52)	0.5174(8)	1.380(1)	0.291(1)	0.097(9)
C(53)	0.5844(8)	1.446(1)	0.301(1)	0.092(8)
C(54)	0.6418(7)	1.394(1)	0.272(1)	0.089(8)
C(541)	0.714(1)	1.461(2)	0.284(1)	0.17(1)
O(541)	0.7361(8)	1.536(1)	0.371(1)	0.29(1)

Table I. (Continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) Å ²
C(55)	0.6335(7)	1.275(1)	0.226(1)	0.088(8)
C(56)	0.5698(6)	1.216(1)	0.222(1)	0.069(7)
C(11')	0.1744(7)	1.296(1)	0.313(1)	0.072(7)
C(12')	0.2316(8)	1.372(1)	0.293(1)	0.095(8)
O(12')	0.2897(4)	1.4143(7)	0.3955(7)	0.081(5)
C(13')	0.3522(8)	1.470(1)	0.375(1)	0.091(8)
C(14')	0.4004(8)	1.384(1)	0.339(1)	0.100(9)
O(14')	0.4631(5)	1.4389(8)	0.3222(9)	0.108(6)
C(21')	0.0698(7)	0.761(1)	-0.101(1)	0.087(8)
C(22')	0.0128(7)	0.668(1)	-0.113(1)	0.093(8)
O(22')	-0.0419(5)	0.7019(8)	-0.0498(8)	0.094(5)
C(23')	-0.037(1)	0.668(1)	0.053(2)	0.15(1)
C(24')	-0.1011(9)	0.691(2)	0.099(2)	0.18(1)
O(24A')#	-0.078(1)	0.604(2)	0.168(2)	0.19(2)
O(24B')#	-0.0923(9)	0.716(1)	0.234(1)	0.068(9)
C(25')	-0.1113(8)	0.613(1)	0.259(2)	0.13(1)
C(31')	0.4085(7)	0.721(1)	0.230(1)	0.078(8)
C(32')	0.4795(7)	0.786(1)	0.234(1)	0.099(9)
O(32')	0.4740(4)	0.8177(7)	0.1290(8)	0.089(5)
C(33')	0.5303(7)	0.907(1)	0.137(1)	0.100(9)
C(34')	0.5109(6)	1.024(1)	0.182(1)	0.086(8)
O(34')	0.5700(5)	1.0977(8)	0.1799(8)	0.099(6)
C(41')	0.2350(8)	0.944(1)	0.684(1)	0.092(8)
C(42')	0.1679(8)	0.904(1)	0.711(1)	0.100(9)
O(42')	0.1396(6)	0.7907(8)	0.6529(8)	0.123(6)
C(43')	0.082(1)	0.773(1)	0.548(1)	0.13(1)
O(44')	0.0005(6)	0.613(1)	0.3892(9)	0.148(7)
C(44')	0.046(1)	0.652(2)	0.509(2)	0.18(1)
C(45')	-0.0693(9)	0.630(2)	0.392(2)	0.17(1)
Cl(1)#	0.308(1)	1.278(1)	-0.128(2)	0.42(2)
Cl(2)#	0.415(1)	1.417(1)	-0.017(1)	0.35(1)
Cl(3)#	0.3090(9)	1.404(2)	0.025(2)	0.47(2)
C(0)*#	0.346(1)	1.347(2)	-0.018(2)	0.15(1)

Site occupancy factors: O(24A'), O(24B') 0.5; Cl(1) to C(0) 0.570(5).

* Isotropic thermal parameter.

Table II. Torsion angles in the polyether strings (atoms are denoted by number only, *O* italicised)

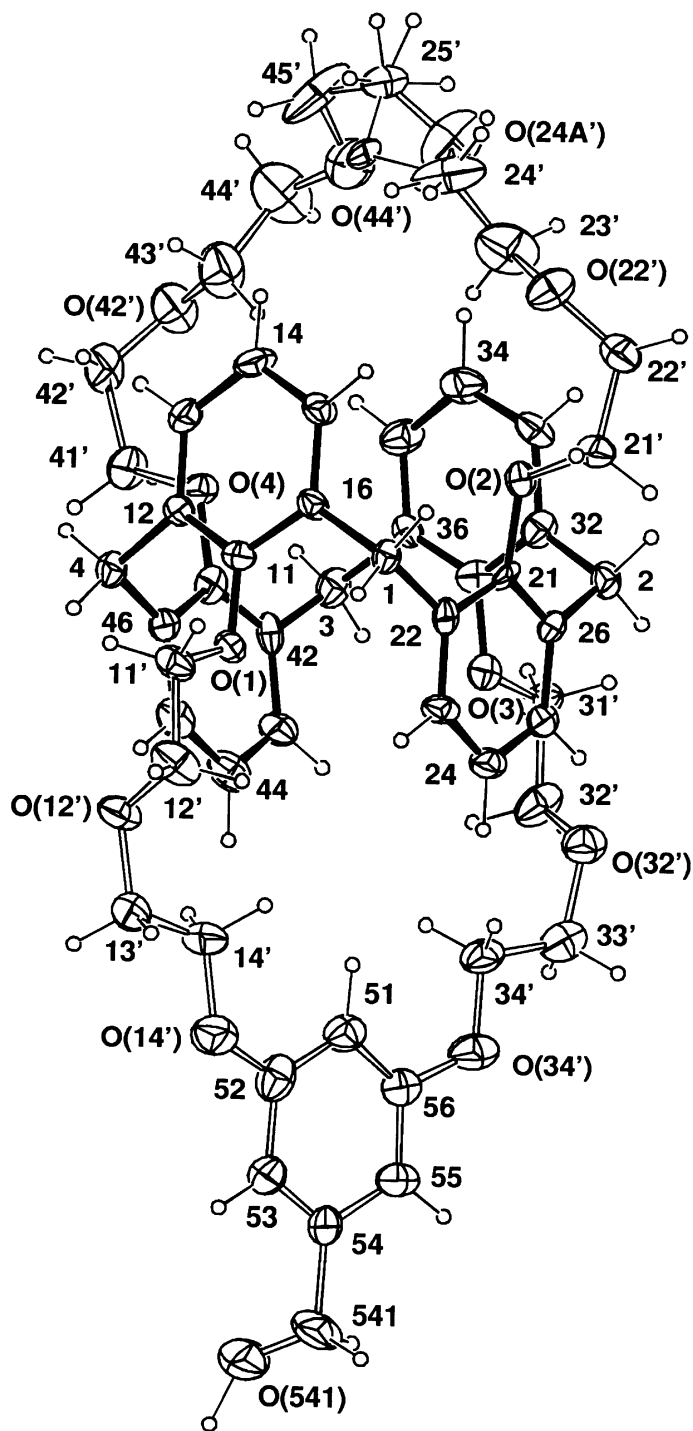
n	1	2	3	4
n1-n-n1'-n2'	-173.6(9)	168(1)	-174(1)	168(1)
n-n1'-n2-n2'	-74(1)	67(1)	-70(1)	65(2)
n1'-n2'-n2'-n3'	169(1)	-108(1)	163(1)	-99(2)
n2'-n2'-n3'-n4'	-91(1)	-169(1)	-91(1)	-169(1)
n2'-n3'-n4'-n4'	178(1)	162(1); -151(1)	-178(1)	-164(1)
n3-n4'-n4'-n5 [*]	179(1)	163(2); -93(2)	177(1)	-91(2)

* n5' being C(45) or C(52, 56) as appropriate.

calixbis(1,3-phenylene-crown-6).[15] Some strain is evident at the bridging C(n) atoms; angles subtended at them are 112(1), 111.3(9), 113(1) and 110.6(9)°, not greatly deviant from the tetrahedral norm, but the atoms are nevertheless displaced inwards from the corners of the “square” obtained by taking its edges as the lines joining the aromatic carbon atoms to which the methylene groups are bound (Figure 3(b)) by, for rings 1–4, respectively, 0.24(2), 0.19(2); 0.19(2), 0.18(2); 0.21(2), 0.24(2); and 0.24(2), 0.18(2) Å, with C(n1') out of plane (outwards) by 1.40(2), 1.47(2), 1.35(2) and 1.36(2) Å. With the exception of the substituent on ring 5 and the disorder at O(24), the overall symmetry of the molecule is, as noted above, a good approximation to 2; torsions in the polyether strings differ between the two ends of the molecule, presumably as a consequence of the different chemical structures.

3.3. COORDINATION CHEMISTRY

Extended reaction of a chloroform solution of (4) with excess solid caesium picrate results in the formation of a solution of a complex of 1 : 1 stoichiometry (as judged by integration of the ¹H NMR spectrum). Changes in the ligand spectrum resulting from complexation are most readily discerned in the well-resolved resonances attributable to the aromatic hydrogen atoms *para* to the calixarene phenolic oxygen atoms and to the ethoxycarbonyl group of the bridging phenyl group. All these signals, however, are significantly shifted, so that although it is clear that only a single product complex results, it is not obvious on this basis where the caesium is actually bound. Unfortunately, we have not yet been able to obtain the solid complex in a form suitable for determination of its structure by X-ray crystallography. In the light of the behaviour of the symmetrical analogues of (4), [12, 15] we interpret the formation of a 1 : 1 complex as indicative of an ability to bind Cs⁺ within the oxoethylene-crown-6 cavity only, with weak binding to the 1,3-phenylene-linked polyether arm possibly retarded by the binding at the other site. Thus, with respect to the caesium ion, (4) may be considered a monotopic ligand



(a)

Figure 3.

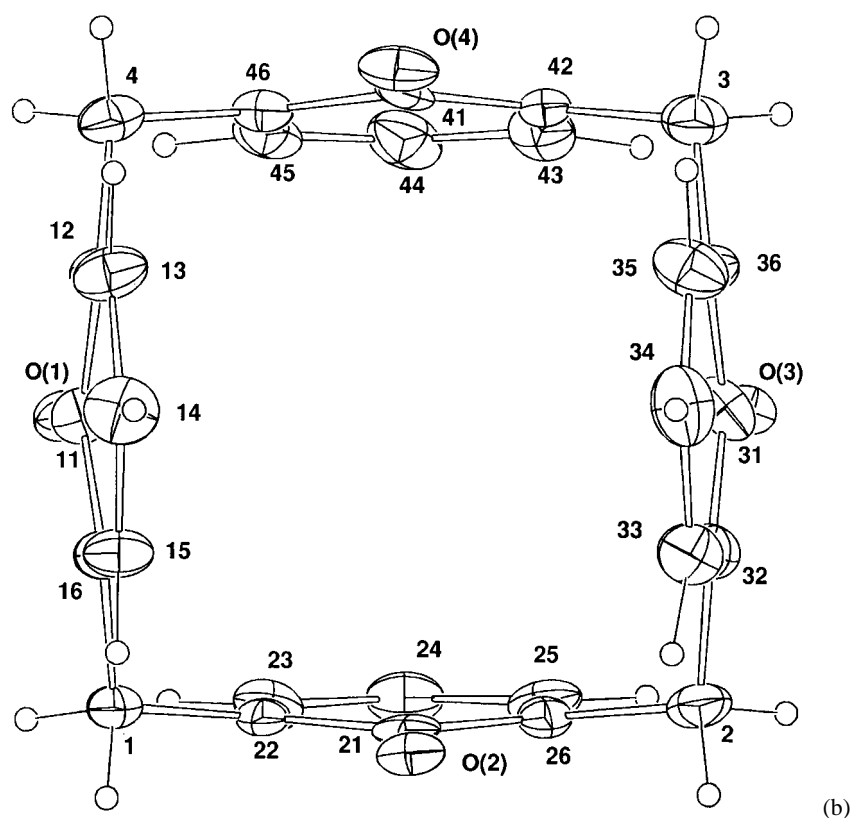


Figure 3. (a) Projection of a single molecule of (4) normal to the molecular "axis". 20% thermal ellipsoids are shown for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. (b) Projection of the calix[4]arene component of (4) down the molecular axis, showing the difference in inclination of opposed pairs of phenoxy groups and their "square" disposition; the slight "inward" deviation of the bridging ("corner") atoms from their associated phenyl rings is also apparent.

with its coordination site remote from the hydroxymethyl group which might be used as a means of immobilising the ligand, so that it might be anticipated that immobilisation should not lead to significant modification of the caesium-binding ability of the ligand. Investigations of these prospects are in progress.

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References

1. Z. Asfari, S. Wenger, and J. Vicens: in J. Vicens, Z. Asfari, and J.M. Harrowfield (eds.), *Calixarenes' 50th Anniversary*, Kluwer Academic Publishers, Dordrecht (1995), p. 137. (Also

- published as *J. Incl. Phenom. Mol. Recogn. Chem.* **19**, 137 (1994).) See also Z. Asfari, J.-P. Astier, C. Bressot, J. Estienne, G. Pèpe, and J. Vicens: p. 291.
2. C. Hill, J.-F. Dozol, V. Lamare, H. Rouquette, S. Eymard, B. Tournois, J. Vicens, Z. Asfari, C. Bressot, R. Ungaro, and A. Casnati: in J. Vicens, Z. Asfari, and J.M. Harrowfield (eds.), *Calixarenes' 50th Anniversary*, Kluwer Academic Publishers, Dordrecht, 1995, p. 399. (Also published as *J. Incl. Phenom. Mol. Recogn. Chem.* **19**, 399 (1994).)
 3. S. Wenger, Z. Asfari, and J. Vicens: *Pure J. Chem.* **67**, 1037 (1995).
 4. Z. Asfari, C. Bressot, J. Vicens, C. Hill, J.-F. Dozol, H. Rouquette, S. Eymard, V. Lamare, and B. Tournois, *Anal. Chem.* **67**, 3133 (1995).
 5. A. Casnati, A. Pochini, R. Ungaro, F. Ugozzoli, F. Arnaud, S. Fanni, M.-J. Schwing, R.J.M. Egberink, F. De Jong, and D.N. Reinhoudt: *J. Am. Chem. Soc.* **117**, 2767 (1995) and references therein.
 6. L. Cecille, M. Casarici, and L. Pietrelli (eds.): in *New Separation Chemistry Techniques for Radioactive Waste and Other Specific Applications*, Elsevier Applied Science, London (1991).
 7. R. Ungaro, A. Casnati, F. Ugozzoli, A. Pochini, J.-F. Dozol, C. Hill, and H. Rouquette: *Angew. Chem., Int. Ed. Engl.* **33**, 1506 (1994).
 8. F. Arnaud-Neu, Z. Asfari, B. Souley, and J. Vicens: *New J. Chem.* **20**, 453 (1996).
 9. Z. Asfari, C. Bressot, J.-F. Dozol, V. Lamare, C. Naumann, M. Nierlich, P. Thuéry, and J. Vicens: *New J. Chem.* **20**, 1183 (1996).
 10. K.N. Koh, K. Araki, S. Shinkai, Z. Asfari, and J. Vicens: *Tetrahedron Lett.* **36**, 6095 (1995).
 11. R. Abidi, Z. Asfari, J.M. Harrowfield, A.N. Sobolev, and J. Vicens: *Aust. J. Chem.* **49**, 183 (1996).
 12. P. Thuéry, M. Nierlich, C. Bressot, V. Lamare, J.-F. Dozol, Z. Asfari, and J. Vicens, *J. Incl. Phenom., Mol. Recogn. Chem.* **23**, 305 (1995). Structures of the 'free' ligands are given by P. Thuéry, M. Nierlich, Z. Asfari, and J. Vicens, *J. Incl. Phenom., Mol. Recogn. Chem.* **27**, 127 (1997).
 13. R. Ungaro, A. Arduini, A. Casnati, O. Ori, A. Pochini, and F. Ugozzoli: in G. Wipff (ed.), *Computational Approaches in Supramolecular Chemistry*, NATO ASI Series, Mathematical and Physical Sciences, No. 426, Kluwer Academic Publishers, Dordrecht (1994), p. 277.
 14. D.A. Dougherty, P.C. Kearney, L.S. Mizoue, R.A. Kumpf, J.E. Forman, and A. McCurdy: in G. Wipff (ed.), *Computational Approaches in Supramolecular Chemistry*, NATO ASI Series, Mathematical and Physical Sciences, No. 426, Kluwer Academic Publishers, Dordrecht (1994), p. 301.
 15. R. Abidi, Z. Asfari, J.M. Harrowfield, C. Naumann, A.N. Sobolev, and J. Vicens: *Annales de Chimie* **92**, 51 (1996).
 16. Z. Asfari, J.M. Harrowfield, A.N. Sobolev, and J. Vicens, *Aust. J. Chem.* **47**, 757 (1994).
 17. R. Abidi, Z. Asfari, J.M. Harrowfield, A.N. Sobolev, and J. Vicens: *Aust. J. Chem.* **49**, 183 (1996).
 18. Z. Asfari, J. Vicens and S. Wenger, *Tetrahedron Lett.* **35**, 8369 (1994).
 19. Z. Asfari, J. Vicens, and S. Wenger: *J. Incl. Phenom. Mol. Recognit. Chem.* **20**, 293 (1995).
 20. B. Pulpoka: Doctoral Thesis, Université Louis Pasteur de Strasbourg (1997).
 21. A. Ikeda, T. Tsudera, and S. Shinkai: *J. Org. Chem.* **62**, 3568 (1997).
 22. C.D. Gutsche and M. Iqbal: *Org. Synth.* **68**, 234 (1990).
 23. C.D. Gutsche and L.-G. Lin: *Tetrahedron* **42**, 1633 (1986).
 24. S.R. Hall, H.D. Flack, and J.M. Stewart (Eds): *The XTAL 3.2 Reference Manual*, Universities of Western Australia, Geneva and Maryland (1992).
 25. G. Gokel: in J.F. Stoddart (ed.), *Crown Ethers and Cryptands, Monographs in Supramolecular Chemistry*, No. 3, Royal Society of Chemistry, Cambridge (1991).
 26. C.D. Gutsche: in J.F. Stoddart (ed.), *Calixarenes, Monographs in Supramolecular Chemistry*, No. 1 Royal Society of Chemistry, Cambridge (1989), p. 108.