A supramolecular assembly of a multifunctional calix[4]arene with alkali and alkaline earth cations in solution and in the solid state

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A supramolecular assembly of a multifunctional calix[4]arene with alkali and alkaline earth cations in solution and in the solid state

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p-tert-Butylcalix[4]arene derivatives 2 and 4 bearing one carboxylic acid, one ester and two phenolic groups on the lower rim form pH-dependent mononuclear or binuclear assemblies with alkali (excluding lithium) and alkaline earth cations. The structures of binuclear K$^+$ complexes 5 and 6 of 2 and 4, respectively, have been determined by X-ray diffraction.

Calixarenes chemically modified with ligating groups on either the upper or lower rim show great versatility in their ability to form mononuclear complexes with metal cations, notably alkali and alkaline earths and heavy metals such as silver and lead.[1] The most effective ligating groups on the lower rim are those containing polyether[2] or teranisyl[2] bridges or carbonyl moieties in the form of esters[3], ketones[3], amides[4], thioamides[5], and carboxylic acids.[6] Substituent effects within the ligating groups can be used to "fine-tune" complexation selectivity.[7] More extensive calixarene assemblies are also known. For example, several crystalline metallocalixarenes containing Ti(IV), Fe(III), Co(II) and Eu(III) exist as binuclear dimers. Atwood et al[9] have found recently that water-soluble upper rim sulfonates form Na$^+$ (pyridinium) inclusion complexes which adopt dimer supramolecular assemblies in the solid state through a combination of hydrophobic effects and either hydrogen bonding or secondary bonding. It is also possible to construct supramolecular assemblies on the lower rim of calix[4]arenes through the use of combinations of ligating groups and we now present evidence for the exist-

ence of binuclear complexes, in solution and in the solid state, between metal cations and p-tert-butylcalixarenes containing a carboxylic acid, an ester and two phenolic functions. Partial hydrolysis of the known diethyl ester 1[10] employing potassium hydroxide in ethanol furnished monoacid 2, m.p. 119–121°C, in excellent yield. Similarly, partial hydrolysis of the corresponding di-tert-butyl ester 3 furnished monoacid 4, m.p. 130–133°C.

Compounds 2 and 4, defined here as the ligand LH$_3$, contain three ionisable groups. The following protonation constants for 2, measured potentiometrically in methanol at 25°C with constant ionic strength (0.01 M in Et$_4$N$^+$ClO$_4^-$) and expressed as acidity pK$_a$'s, were obtained: 8.2 ± 0.1 for the carboxylic acid and > 13.0 for the two phenolic functions. For the alkali cations, pH-dependent complexation was observed with the exception of Li$^+$ which was not complexed to any detectable extent. A small pH lowering, with respect to the titration of the ligand without the cation, was observed on the titration curves (represented in Figure 1a for three cations) from 5.0 < pH < 8.0, i.e. before the first inflection point, corresponding to one equivalent of ligand. For a ligand concentration of 10^{-3} M and different concentrations of cations, the best fit was obtained by assuming the formation of a binuclear neutral species M$_2$L$_2$H$_4$, LH$_2^-$ being the ligand in carboxylate monoanionic form. Table 1a contains the logarithms of the stepwise stability constants K$_{224}$ as defined by the equilibrium in equation 1:

$$2M^{n+} + 2LH_2^- \rightleftharpoons M_2L_2H_4^{2(n-1)+} \qquad (1)$$

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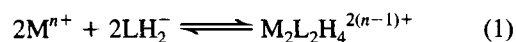
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Table 1a   Complexation in Methanol (log K_{224})[a]

Species	Li^+	Na^+	K^+	Rb^+	Cs^+
$M_2L_2H_4$		9.4 ± 0.3	10.4 ± 0.2	10.2 ± 0.1	9.8 ± 0.1
	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	
$M_2L_2H_4^{2+}$	11.1 ± 0.1	11.4 ± 0.1	11.4 ± 0.3	11.5 ± 0.2	

After the first inflection, the extent of complexation is small, as the measured pH's are high and comparable to those of the free ligand. Accordingly, interpretation of this zone of the titration curve was not attempted.

Alkaline earth cations also displayed a pH-dependent complexation profile. The logarithms of the stability constant K_{224}, relating to equation 1, are given in Table 1a. In contrast to the alkali cations, a pronounced pH lowering was observed in the more alkaline region, i.e. after the first inflection. In this region, between pH ~ 8 and 11, $M_2L_2H_4^{2+}$ undergoes further deprotonation to give new species which are cation dependent. With all cations, the new species are a binuclear complex $M_2L_2H_3^+$ and a mononuclear fully deprotonated complex ML^-, the latter resulting from deaggragation and deprotonation of the binuclear complex. For Ca^{2+} and Ba^{2+}, in addition to $M_2L_2H_3^+$ and ML^- species, we cannot discount the formation of a third species, MLH and $M_2L_2H_2$, respectively. Little discrimination by the

ligand within the alkali and alkaline earth series was observed.

In ethanol, the acidity pK_a's for all three ionisable groups of 2 were slightly higher than in methanol: 8.6 ± 0.3 for the carboxylic acid and >14.5 for both phenols. Na^+ and Ca^{2+} were the only cations measured in this medium as K^+ led to precipitation in the presence of the ligand. Complexation was found to be stronger than in methanol as shown by the titration curves (Figure 1b). Surprisingly, no binuclear species were detected between pH ~ 5.5 and 11.0; only the three mononuclear species $ML^{(n-3)+}$, $MLH^{(n-2)+}$ and $MLH_2^{(n-1)+}$ were observed. The third combination was the only complex present before the first inflection for both Na^+ and Ca^{2+}. The logarithms of the overall stability constants, β_{11m}, relating to the equilibrium (2)

$$M^{n+} + L^3 + mH^+ \rightleftharpoons MLH_m^{(n-3+m)+} \qquad (2)$$

are given in Table 1b.

Crystalline Na^+ and K^+ complexes of 2 could be isolated. Although we did not conduct a detailed examination of the pH-dependent behaviour of the *tert*-butyl ester 4 on complexation, we did, for comparative purposes, isolate its crystalline K^+ complex. The K^+ complexes 5 and 6 (of 2 and 4 respectively) when recrystallised from ethanol, yielded crystals suitable for X-ray analysis which establish that both complexes are binuclear centrosymmetric dimers (Fig. 2 to 5) with the calixarene moieties adopting distorted cone conformations in the solid state.

The binuclear K^+ centrosymmetric calixarene complex 5 of 2 has two ethanol molecules associated with it. The major feature in this centrosymmetric dimer is the presence of two K^+ cations encapsulated between the carboxylate and ester moieties of two calixarene molecules. Each K^+ cation is bonded to (i) two phenolic and one ethereal oxygen atoms, {O(1B), O(1D), O(1C)} of the calixarene core {K-O(1B) 3.13(1), K-O(1D) 2.81(1), K-O(1C) 2.74(1) Å} and (ii) the two oxygen atoms of the
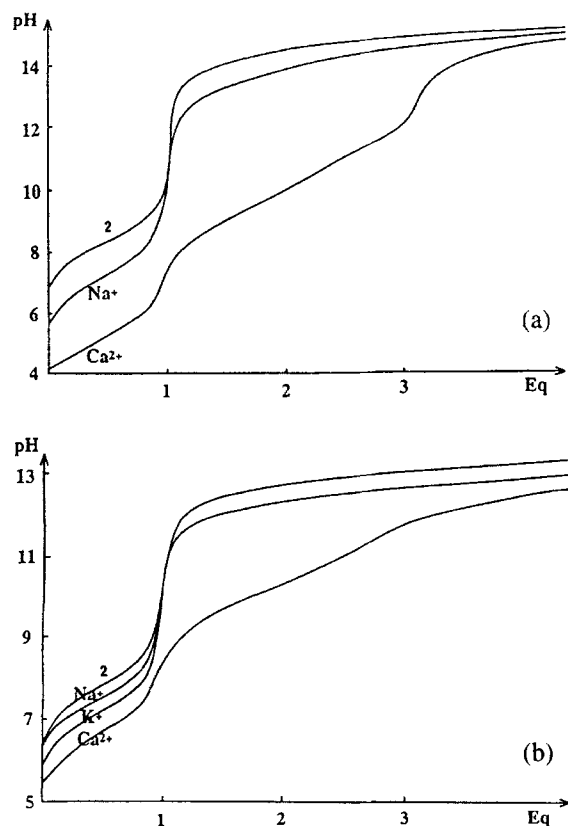
Figure 1   Titration curves for compound 2.

Table 1b   Complexation in Ethanol (log β_{11m})[a]

Species[b]	Na^+	Ca^{2+}
ML	5.5 ± 0.3	15.3 ± 0.1
MLH	20.0 ± 0.2	26.5 ± 0.1
MLH_2	33.76 ± 0.05	35.7 ± 0.1

[a]The precision given is the σ_{n-1} on the average of several measurements   [b]Charges omitted for clarity
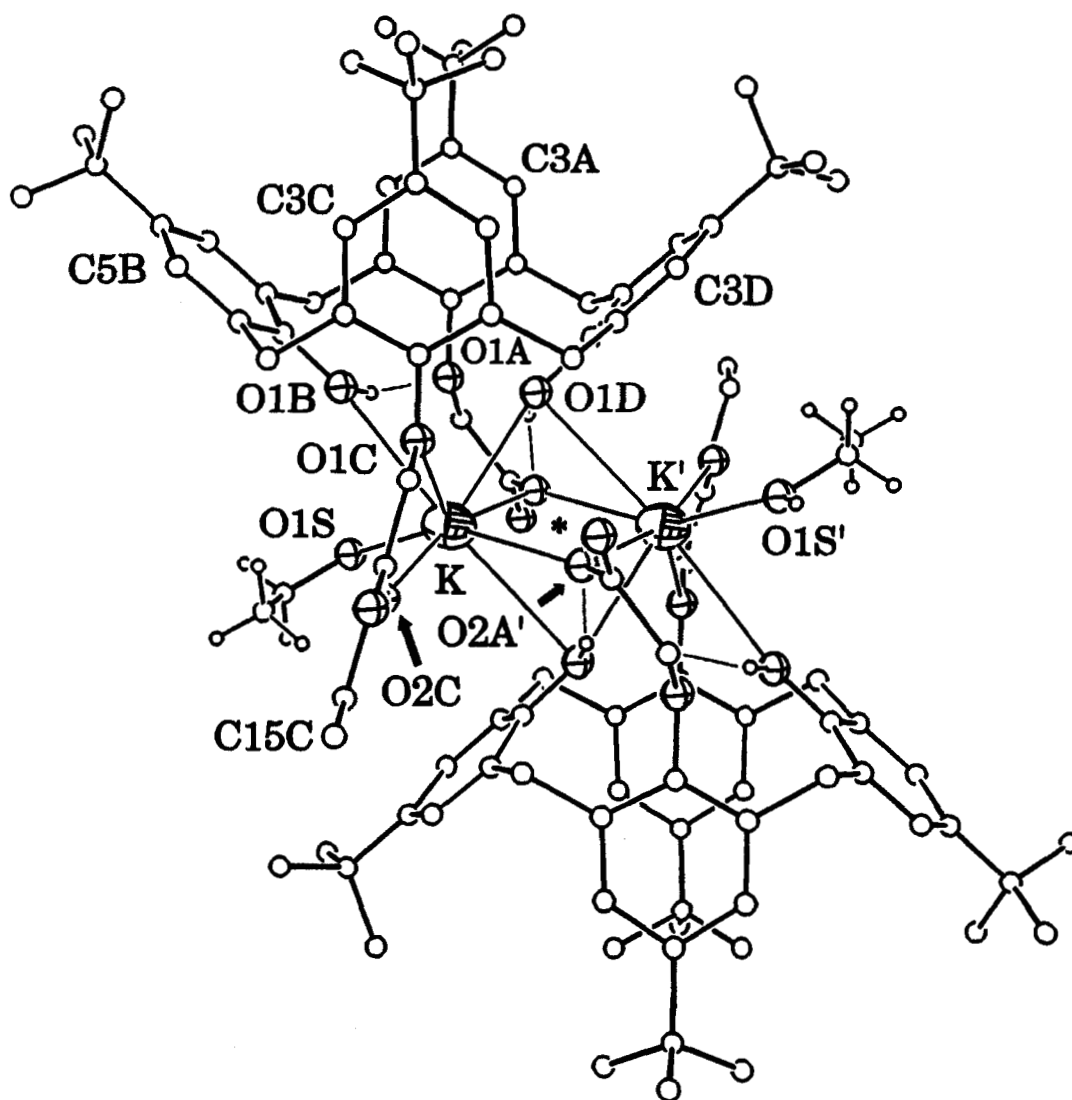
Figure 2 A view of (5) with our labelling scheme. The K^+ ions are depicted with their thermal ellipsoids at the 50% probability level. The oxygen, carbon and hydrogen atoms, (of the ethanol molecule), are drawn as small spheres of an arbitrary size.

carboxylate and ester moieties, {O(2A), O(2C)}, that are attached to this calixarene core, {K-O(2A) 2.88(1), K-O(2C) 2.78(1) Å}. The K^+ cations are separated by 3.800(5) Å and are bridged by the phenolic oxygens O(1D) and O(1D)*, {K-O(1D)* 3.27(1) Å} and carboxylate oxygens O(2A) and O(2A)*, {K-O(2A)* 2.96(1) Å, * is the symmetry equivalent: -x, 1-y, 2-z}. The carboxylate group bonds to the K^+ cations only in a monodentate fashion through O(2A). An ethanol molecule per calixarene is bonded to the K^+ cation {K-O(1S) 2.75(1) Å} and fills the remaining coordination site making each of the K^+ ions eight coordinate; the arrangement of oxygen atoms around each K^+ ion corresponds to a distorted square anti-prism. The eight K-O distances are in the range 2.74(1) to 3.27(1) Å, with the nearest other K...O contact involving the ethereal oxygen of the carboxylate

moiety, (K...O(1A), 3.74(1) Å). The ethanol molecule which is bonded to the K^+ through its oxygen atom O(1S) is also involved in O-H...O hydrogen-bonding with the carboxylate oxygen atom of a neighbouring calixarene dimer that is not engaged in bonding to a K^+ cation, O(1S)...O(3A)** 2.73(1) Å, (** is the symmetry equivalent: 1-x, 1-y, 2-z). This linkage gives rise to a one dimensional hydrogen-bonded polymer with the K^+ calixarene dimers linked by ethanol molecules about inversion centres, Figure 3.

Other important conformation determining features in this dimer are the presence of (a) an intramolecular O-H...O hydrogen bond between a phenolic oxygen and an adjacent ethereal oxygen atom, {O(1B)...O(1A) 2.83(1) Å, HOB...O(1A) 1.94 Å, O(1B)-HOB...O(1A) 160.5°} and (b) an intramolecular bifurcated O-H...O
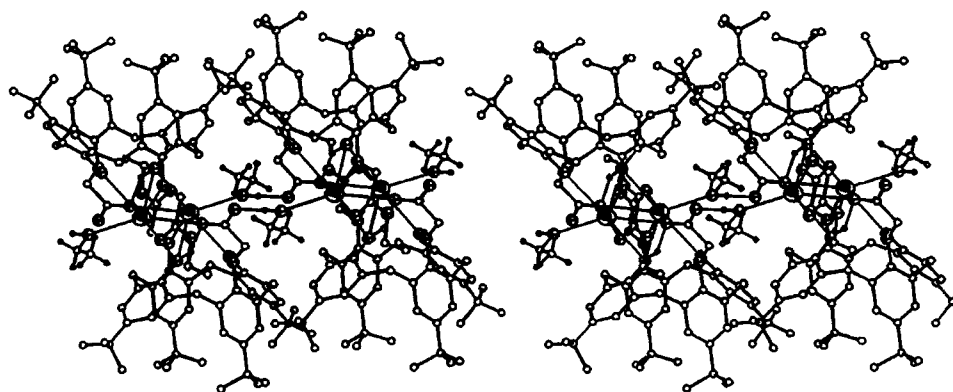
Figure 3   A stereoview of the hydrogen bonded polymeric chain in (5).

hydrogen bond involving the phenolic hydroxyl group O(1D)-H with the adjacent oxygen atom O(2A) (of the carboxylate group) and the ethereal oxygen O(1A), with dimensions {O(1D)...O(2A) 2.71(1) Å, HOD...O(2A) 1.80 Å, O(1D)-HOD...O(2A) 150.1°, O(1D)...O(1A) 2.81(1) Å, HOD...O(1A) 2.13 Å and O(1D)-HOD...O (1A) 123.4°}. The hydroxyl hydrogen coordinates were obtained from difference Fourier maps in the final stages of refinement.

The conformation of the calixarene core in (5) is defined by the angles which the aromatic rings make with the plane of the four methylene carbon atoms which link them, *viz.*, 104.7(3)° (A), 138.1(3)° (B), 81.0(3)° (C) and 137.6(3)° (D), [interplanar angles >90° indicate that the aromatic ring system is tilted so that its *t*-butyl group is directed *away from* the ring cavity; angles <90° indicate that these groups are directed *in towards* the cavity]. Two opposite rings (A) and (C) are almost parallel to one another (interplanar angle 6.0(4)°), carboxylate substituted ring (A) tilted so that its *t*-butyl group is pitched away from the calix cavity, ester substituted ring (C) tilted so that its *t*-butyl group is pitched slightly towards the cavity. The phenolic rings (B) and (D) are almost normal to one another, (interplanar angle 95.8(3)°), both rings (B) and (D) being tilted so that their *t*-butyl groups are pitched well away from the calix cavity. This conformation leads to O...O separations between O(1A) and O(1C) across the calixarene cavity of 5.03(1) and 3.43(1) Å between O(1B) and O(1D).

The binuclear K$^+$ centrosymmetric calixarene complex 6 of 4 has two partial occupancy ethanol and two partial occupancy water molecules associated with it in the crystal lattice. As in 5, complex 6 also has the calixarene moiety with a distorted cone conformation in the solid state (Figure 4). The major conformation determining feature in this dimer is the presence of two K$^+$ cations encapsulated between the carboxylate and ester moieties of two calixarene molecules. The K$^+$

coordination is quite different in 5 and in 6 although the calixarene conformation and internal hydrogen-bonding are very similar. The major differences in the K$^+$ coordination between (5) and (6) are (*a*) the ethereal oxygen O(1D) bridges both K$^+$ ions in (5), whereas in (6) it is bonded to one K$^+$ ion and (*b*) only one of the carboxylate oxygen atoms on each calixarene is involved in K$^+$ binding in (5), (bridging both K$^+$ ions), whereas in (6) both carboxylate oxygens of each calixarene are involved in K$^+$ bonding (one as a unidentate and one as a bridging atom). Each K$^+$ cation in (6) is bonded to (*i*) two phenolic and one ethereal oxygen atoms, {O(1B), O(1D), O(1C)} of a calixarene core {K-O(1B) 2.92(1), K-O(1D) 2.81(1), K-O(1C) 2.69(1) Å} and (*ii*) the two oxygen atoms of the carboxylate and ester moieties, {O(2A), O(2C)}, that are attached to this calixarene core {K-O(2A) 2.79(1), K-O(2C)} 2.69(1) Å}. The two K$^+$ cations (K and K*) are separated by 4.181(3) Å and are bridged by the carboxylate oxygens O(2A) and O(2A)*, {K-O(2A)* 2.68(1) Å, * is the symmetry equivalent: -x, 1-y, -z}. The other carboxylate oxygen O(3A) is *only* involved in bonding to one K$^+$ cation, {K-O(3A)* 3.34(1) A}, (unlike in (5) where it is not in contact with a K$^+$ cation). Thus the carboxylate group behaves as both a monodentate bridging and a bidentate chelating ligand, Figure 4. An ethanol molecule is bonded to the K$^+$, {K-O(1E) 2.80(1) Å}, in the remaining coordination site and makes each K$^+$ eight coordinate. All eight K-O distances are in the range 2.68(1) to 3.34(1) Å with the nearest other K...O contact involving the ethereal oxygen of the carboxylate moiety, {K...O(1A), 3.61(1) Å}. The ethanol molecule which is bonded to the K$^+$ through its oxygen atom O(1E) is also involved in O-H...O hydrogen-bonding with a water molecule; the hydroxyl H-atom could not be located but the O(1E)...O(1W) distance (2.61(1) Å) is clearly consistent with an O-H...O hydrogen bond. This water molecule is presumably involved in hydrogen bonding with its symmetry related
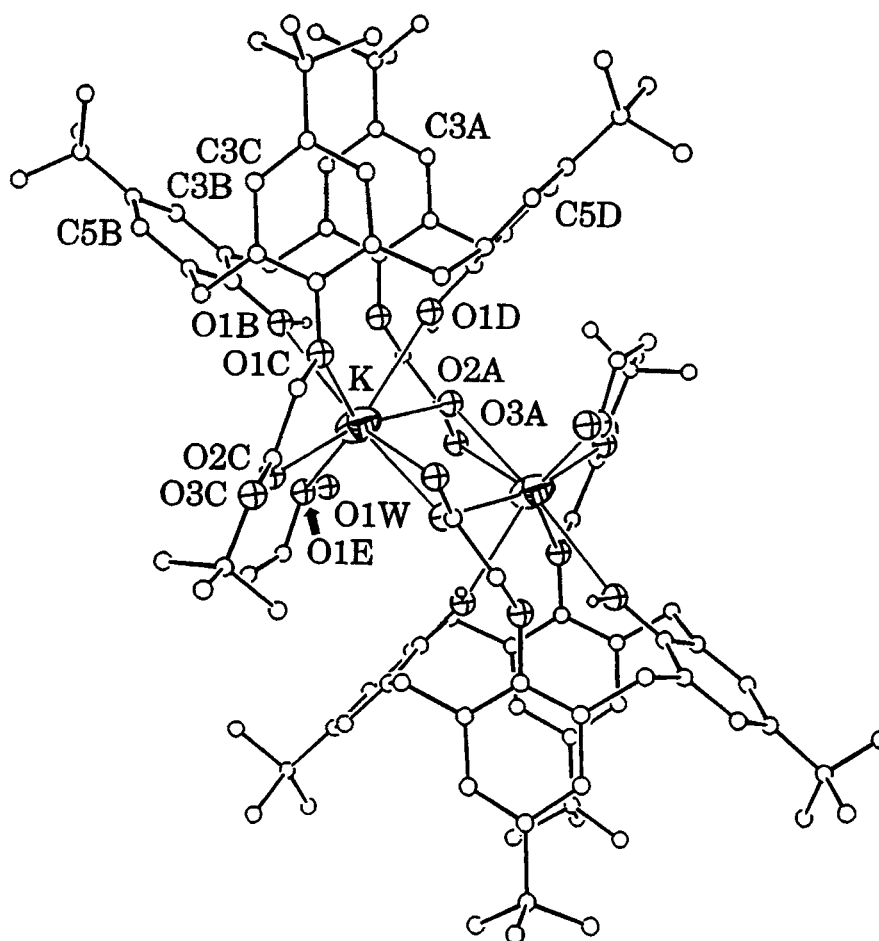
Figure 4 A view of (6) with our labelling scheme and ellipsoids and atom size as in Figure 1.

equivalent across an inversion centre, {O(1W)...O (1W)** 2.72(3). ** is the symmetry equivalent: -1-x, 1-y, -z}, and also involved in hydrogen-bonding with carboxylate oxygen O(3A)**, 2.58(1) Å. As in molecule (5), this gives rise to a one-dimensional hydrogen-bonded polymer with the K$^+$ calixarene dimers linked by the partial occupancy water and disordered partial occupancy ethanol molecules, Figure 5.

Other important conformation determining features in molecule (6) are the presence of (a) an intramolecular O-H...O hydrogen bond between the phenolic hydroxyl group O(1B)-H and the adjacent ethereal oxygen atom O(1A), {(O(1B)...O(1A) 2.78(1) Å, HOB1...O(1A) 1.91 Å, O(1B)-HOB1...O(1A) 159.4°} and (b) an intramolecular bifurcated O-H...O hydrogen bond between the phenolic hydroxyl group O(1D)-H and adjacent oxygen
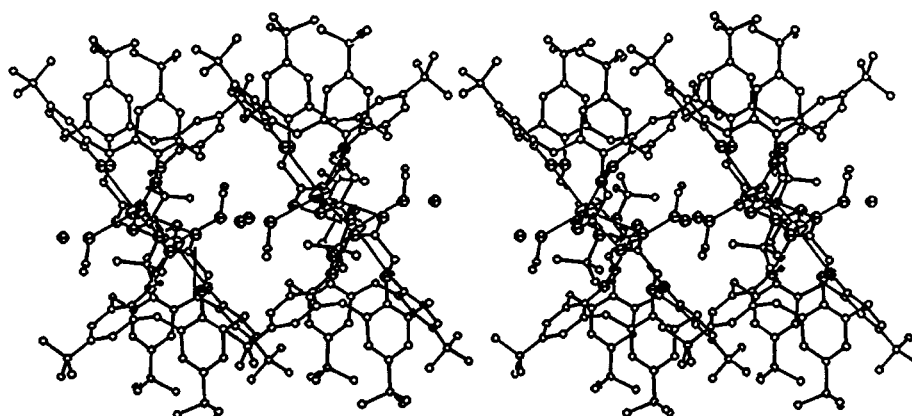

Figure 5 A stereoview of the hydrogen bonded polymeric chain in (6).

atom O(2A) (of a carboxylate group) and ethereal oxygen atom O(1A), {O(1D)...O(2A) 2.71(1) Å, HOD...O(2A) 1.99 Å, O(1D)-HOD...O(2A) 141.3°, O(1D)...O(1A) 2.87(1) Å, HOD...O(1A) 2.20 Å and O(1D)-HOD...O(1A) 135.1°}. The hydroxyl hydrogen coordinates were obtained from difference Fourier maps in the final stages of refinement.

The conformation of the calixarene core in (6) is similar to that described in (5) above and is defined by the angles which the aromatic rings make with the plane of the four methylene carbon atoms which link them, *viz.*, 105.0(2)° (A), 137.2(2)° (B), 83.4(2)° (C) and 139.6(2)° (D). Two opposite rings (A) and (C) are almost parallel to one another (interplanar angle 8.5(2)°), the carboxylate substituted ring (A) tilted so that its *t*-butyl group is pitched away from the calix cavity and the ester substituted ring (C) tilted so that its *t*-butyl group is pitched slightly towards the cavity. The phenolic rings (B) and (D) are almost normal to one another, (interplanar angle 96.8(2)°), both rings (B) and (D) being tilted so

that their *t*-butyl groups are pitched well away from the calix cavity. This conformation leads to O...O separations between O(1A) and O(1C) across the calixarene cavity of 5.06(1) and 3.34(1) Å between O(1B) and O(1D).

EXPERIMENTAL SECTION

Structural Analysis for the binuclear K^+ calix[4]arenes 5 and 6

Details of the X-ray experimental conditions, cell data, data collection and refinement for molecules 5 and 6 are summarised in Table 2.

In (5), an ethanol molecule of solvation was located in the early stages of refinement. The hydroxyl hydrogen of the ethanol molecule was clearly visible in difference maps at an intermediate stage of the refinement and included in the structure factor calculations at 0.95 A from the ethanol oxygen along the O1S...O3A' vector. The *t*-butyl methyl carbon atoms of ring C were disordered

Table 2 Summary of Data Collection, Structure Solution and Refinement Details

	5	6
(a) Crystal Data		
empirical formula	$C_{100}H_{126}O_{16}K_2 \cdot 2C_2H_5OH$	$C_{104}H_{134}O_{16}K_2 \cdot 1.5C_2H_5OH \cdot 1.5H_2O$
fw	1754.4	1814.5
color, habit	colorless, plate	colorless, block
crystal size, mm	0.10 × 0.25 × 0.30	0.35 × 0.40 × 0.50
cryst syst	Triclinic	Triclinic
a, A	9.8650(6)	10.2885(9)
b, A	12.9711(8)	12.8369(14)
c, A	20.6463(11)	21.6006(24)
α, °	105.445(5)	76.184(9)
β, °	90.564(5)	86.041(8)
γ, °	95.712(5)	86.870(8)
V, A^3	2532.0(3)	2761.6(5)
space group	$P\bar{1}$	$P\bar{1}$
Z	1	1
molecular symmetry	$\bar{1}$	$\bar{1}$
$F(000)$	944	978
d_{calc}, g cm^{-3}	1.15	1.08
μ, cm^{-1}	1.5	1.4
(b) Data acquisition[a]		
temp, °C	21	21
unit-cell reflcns (2θ-range°)	25 (18–32)	25 (18–36)
max. 2θ (°) for reflcns	44	48
hkl range of reflcns	−10 10, 0 13, −21 20	−11 11, 0 14, −23 24
variation in 3 standard reflcns	<1%	<1%
reflcns measured	6235	8646
unique reflcns	6235	8646
reflcns with $I > 2\sigma(I)$,	2324	3442
(c) Structure Solution and Refinement[b]		
solution method	SHELXS86[c]	SHELX86
H-atom treatment	C-H riding; O-H from Δ-map	C-H riding; O-H from Δ-map
no. of variables in LS	587	636
k in $w = 1/(\sigma^2 Fo + kFo^2)$	0.0015	0.0015
R, R_w, gof	0.062, 0.072, 1.32	0.062, 0.081, 1.67
density range in final Δ-map, e A^{-3}	−0.22, 0.31	−0.28, 0.32
final shift/error ratio	0.06	0.06

[a]Data collection on an Enraf Nonius CAD4 diffractometer with graphite monochromatised Mo-Kα radiation (λ 0.7093 A). [b]All calculations were done on a Silicon Graphics 4D-35TG computer system with the NRCVAX system of programs (E.J. Gabe, Y. Le Page, J-P. Charland, F.L. Lee and P.S. White, *J. Appl. Cryst.* (1989), **22**, 384–389). [c]G.M. Sheldrick, *SHELX86*. Crystallographic computing 3; G.M. Sheldrick, C. Kruger, R. Goddard, Oxford University Press: London, 1986; pp. 175–189.

over two orientations with equal occupancy. The hydrogens attached to these half occupancy carbons were allowed for by positioning at geometrically idealised positions, C-H 0.95 Å, with appropriate occupancies. The two phenolic hydrogens HOB and HOD were located from a difference map; the hydrogens attached to the other carbon atoms were positioned on geometric grounds but were restrained to ride on the carbon atom to which they were bonded (C-H 0.95 Å) and were included as such in the structure factor calculations. All non-hydrogen atoms were subsequently refined with anisotropic thermal parameters.

In (6), it was clear in early stages of refinement that there was considerable disorder in the structure. From analysis of difference maps and peak heights, it became apparent that there was a partial occupancy water (0.75) and a partial occupancy ethanol molecule (0.75) (with its terminal methyl group disordered), located in the lattice in a volume element similar to that occupied by the ethanol molecule in calixarene (5). The ethanol oxygen in (6) is bonded to the K^+ cation and engaged in hydrogen bonding with the water molecule which is located near an inversion centre. The minor carbon atom sites of the ethanol were located from difference maps and only their thermal parameters were refined isotropically. Hydrogens were not included on either the water or ethanol molecules as they had high thermal parameters associated with them and could not be clearly resolved. The two phenolic hydrogens HOB and HOD were located from a difference map at an intermediate stage of the refinement and included as such in the structure factor calculations and both directed towards proximal ethereal oxygen atoms O(1A) and O(1C). The t-butyl methyl carbon atoms of rings A, B and C were disordered over two orientations with occupancies of (0.85, 0.15), (0.5, 0.5) and (0.67, 0.33) for each of the three disordered t-butyl groups. The hydrogens associated with these partial occupancy carbon atoms and all other hydrogens of the calixarene carbon atoms (visible in difference maps) were positioned on geometric grounds with appropriate occupancies and included as riding atoms, (C-H 0.95 Å), in the structure factor calculations. All non-hydrogen atoms were subsequently refined with anisotropic thermal parameters except for the carbon atoms of the minor orientation of the t-butyl group attached to ring A and the partial occupancy carbon atom sites associated with the ethanol molecule. All the figures were prepared with the aid of $ORTEPII$.[11]

Partial hydrolysis of diethyl ester 1

Diethyl ester 1 (5.0g, 6.1 mmol) was stirred in dry ethanol (100mL) containing potassium hydroxide (0.4g, 7.3mmol) for 30 hours. The reaction mixture was concentrated to dryness and the solid residue was taken up in dichloromethane and washed with hydrochloric acid (3 × 20mL). The organic layer was separated, dried

over magnesium sulfate and concentrated to afford the crude monoacid 2 (4.8g). The product was purified by dissolving it in dichloromethane containing potassium carbonate. The mixture was stirred for 1 hour and then filtered, the filtrate was evaporated to dryness and the residue was recrystallised from ethanol to afford the K^+ salt 5 (4.0g, 79%). Quantitative conversion of 5 to the free acid 2 was achieved by treatment with 1N HCl. Recrystallisation of 2 from ethanol afforded an analytically pure sample, m.p. 119–121°C; ^{1}HNMR (300MHz, CDCl$_3$) δ_H 1.06 (9H, s, Bu^t), 1.07 (9H, s, Bu^t), 1.26 (18H, s, Bu^t), 1.37 (3H, t, OCH$_2$CH$_3$), 3.43 (4H, d, J = 13.4Hz, (9H, s, Bu^t), 1.26 (18H, s, Bu^t), 1.37 (3H, t, OCH$_2$CH$_3$), 3.43 (4H, d, J = 13.4Hz, ArCH$_2$Ar), 4.09 (2H, d, J = 13.4Hz, ArCH$_2$Ar), 4.27 (2H, d, J = 13.4Hz, ArCH$_2$Ar), 4.41 (2H, q, OCH$_2$CH$_3$), 4.69 (2H, s, OCH$_2$CO), 6.95 (4H, s, ArH), 7.06 (4H, s, ArH), 4.78 (2H, s, OH) [Found: C, 74.9; H, 8.3. C$_{50}$H$_{64}$O$_8$.CH$_2$CH$_2$OH requires C, 74.4; H, 8.4%].

Partial hydrolysis of di tert-butyl ester 3

Di tert-butyl ester 3 was hydrolysed with potassium hydroxide exactly as described above for the diethyl ester to afford monoacid 4, m.p. 130–133°C (from ethanol); ^{1}HNMR (300MHz, CDCl$_3$) δ_H 0.98 (9H, s, Bu^t), 0.99 (9H, s, Bu^t), 1.19 (18H, s, Bu^t), 1.50 (9H, s, OBu^t), 3.34 (4H, d, J = 13.3Hz, ArCH$_2$Ar), 4.05 (2H, d, J = 13.3Hz, ArCH$_2$Ar), 4.24 (2H, d, J = 13.3Hz, ArCH$_2$Ar), 4.53 (2H, s, OCH$_2$CO), 4.56 (2H, s, OCH$_2$CO), 6.92, 6.94 (2H, ArH), 6.98 (4H, s, ArH) 7.41 (2H, s, OH) [Found: C, 74.5; H, 8.5. C$_{52}$H$_{68}$O$_8$. CH$_3$CH$_2$OH requires C, 74.6; H, 8.8%].

K^+ complex 5

^{1}HNMR (300MHz, CDCl$_3$)δ_H 0.57 (9H, s, Bu^t), 0.99 (9H, s, Bu^t), 1.26 (3H, t, HOCH$_2$CH$_3$), 1.28 (3H, t, OCH$_2$CH$_3$), 1.34 (18H, s, Bu^t), 3.05 (2H, d, J = 14.1Hz, ArCH$_2$Ar), 3.17 (2H, d, J = 14.1Hz, ArCH$_2$Ar), 3.72 (2H, q, HOCH$_2$CH$_3$), 3.76 (2H, d, J = 14.1Hz, ArCH$_2$Ar), 4.30 q, OCH$_2$CH$_3$), 4.40 (2H, s, OCH$_2$CO), 4.45 (2H, s, OCH$_2$CO), 4.45 (2H, d, ArCH$_2$Ar), 6.30 (2H, s, ArH), 6.75 (2H, s, ArH), 6.97 (2H, d, ArH), 7.07 (2H, d, ArH), 7.75 (2H, bs, OH) [Found: C, 71.1; H, 7.8. C$_{100}$H$_{126}$O$_{16}$K$_2$.2CH$_3$CH$_2$OH requires C, 71.2; H, 8.0%].

K^+ complex 6

^{1}HNMR (300MHz, CDCl$_3$)δ_H 0.60 (9H, s, Bu^t), 1.00 (9H, s, Bu^t), 1.34 (18H, s, Bu^t), 1.51 (9H, s, Bu^t), 3.15 (2H, d, J = 14.1Hz, ArCH$_2$Ar), 3.21 (2H, d, J = 14.1Hz, ArCH$_2$Ar), 3.83 (2H, d, J = 14.1Hz, ArCH$_2$Ar), 4.37 (2H, s, OCH$_2$CO), 4.41 (2H, s, OCH$_2$CO), 4.41 (2H, d, ArCH$_2$Ar), 6.30 (2H, s, ArH), 6.78 (2H, s, ArH), 7.00 (2H, d, ArH), 7.08 (2H, d, ArH), 7.70 (2H, bs, OH) [Found: C, 69.2; H, 7.5. C$_{104}$H$_{134}$O$_{16}$K$_2$. 1.5 CH$_3$CH$_2$OH.1.5 H$_2$O requires C, 70.3; H, 8.1%].

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REFERENCES

1 For a recent survey see *Calixarenes: A Versatile Class of Macrocyclic Compounds*, eds. J. Vicens and V. Böhmer, Kluwer Academic Publishers, Dordrecht, 1991.

2 D.N. Reinhoudt, P.J. Dijkstra, P.J.A. in't Veld, K.E. Bugge, S. Harkema, R. Ungaro and E. Ghidini, *J. Am. Chem. Soc.*, 1987, **109**, 4761; P.J. Dijkstra, J.A.J. Brunink, K.E. Bugge, D.N. Reinhoudt, S. Harkema, R. Ungaro, F. Ugozzoli and E. Ghidini, *J. Am. Chem. Soc.*, 1989, **111**, 7567.

3 F. Arnaud-Neu, E.M. Collins, M. Deasy, G. Ferguson, S.J. Harris, B. Kaitner, A.J. Lough, M.A. McKervey, E. Marques, B.L. Ruhl, M.J. Schwing-Weill and E.M. Seward, *J. Am. Chem. Soc.*, 1989, **111**, 6881; S.K. Chang and I. Cho, *J. Chem. Soc., Perkin Trans 2*, 1986, 211; A. Arduini, A. Pochini, S. Reverberi, R. Ungaro, G.D. Andreetti and F. Ugozzoli, *Tetrahedron*, 1986, **42**, 2089.

4 F. Arnaud-Neu, M.J. Schwing, K. Ziat, S. Cremin, S.J. Harris and M.A. McKervey, *New J. Chemistry*, 1991, **15**, 33; A. Arduini, E. Ghidini, A. Pochini, R. Ungaro, G.D. Andreetti, G. Calestani and F. Ugozzoli, *J. Inclusion Phenom.*, 1988, **6**, 119; S.K. Chang, S.K. Kwon and I. Cho, *Chem. Lett.*, 1987, 947.

5 M.J. Schwing-Weill, F. Arnaud-Neu and M.A. McKervey, *J. Phys. Org. Chem.*, 1992, **5**, 496.

6 F. Arnaud-Neu, G. Barrett, S.J. Harris, M. Owens, M.A. McKervey, M.J. Schwing-Weill and P. Schwinte, *Inorg. Chem.*, **32**, 2644.

7 F. Arnaud-Neu, G. Barrett, S. Cremin, M. Deasy, G. Ferguson, S.J. Harris, A.J. Lough, L. Guerra, M.A. McKervey, M.J. Schwing-Weill and P. Schwinte, *J. Chem. Soc., Perkin Trans 2*, 1992, 1119.

8 For a survey of metallocalixarenes see the chapters by R. Ungaro and A. Pochini and J.-C. G. Bunzli and J. MacB. Harrowfield in reference 1.

9 J.L. Atwood, G. William Orr, F. Hamada, S.G. Bott and K.D. Robinson, *Supramol. Chem.*, 1992, **1**, 15.

10 E.M. Collins, M.A. McKervey, E. Madigan, M.B. Moran, M. Owens, G. Ferguson and S.J. Harris, *J. Chem. Soc., Perkin Trans 1*, 1991, 3137.

11 C.K. Johnson, *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA, 1976.