ChemComm

An insight into ion-transport by calixarenes; the structure of the dipotassium complex of *p-tert*-butylcalix[8]arene crystallised from a protogenic, coordinating solvent [ethanol/diethylcarbonate (10 : 1)]

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Received (in Basel, Switzerland) 2nd December 1998, Accepted 20th January 1999

The structure of the dipotassium complex of the dianion of *p-tert*-butylcalix[8]arene crystallised from a protogenic, coordinating solvent (ethanol–diethylcarbonate, 10 : 1) shows that the metal ions are bound above and below the cavity of the calix[8]arene, which adopts a 'pinched' conformation.

The binding of metal ions to the calixarenes and their O-pendant derivatives is an area of intense research interest, in particular with regard to selective metal ion coordination and transport.[1] The discovery that the parent calixarenes effect the transport of Group 1 metal ions in [water | organic solvent | water] liquid membrane systems stimulated great interest in this family of compounds.[2] Recent research has concentrated on metal ion binding to O-pendant derivatives of the calixarenes (mostly calix[4]arenes in which the pendant groups are generally predominant in the metal ion binding and the calixarene is used in a preorganising role), and a great deal of X-ray crystallographic structural information has been accumulated for these systems.[1] In contrast, there is a paucity of structural data for Group 1 metal ion complexes of the parent calixarenes; the only reported structures are the Cs^+ complex of the mono-anion of *p-tert*-calix[4]arene (H_4L), $Cs(H_3L)(MeCN)$, which beautifully illustrates the importance of $\pi\cdots M^+$ interactions in these systems,[3] and two Li^+ complexes of fully deprotonated *p-tert*-butylcalix[4]arene: $Li_5L(OH)(hmpa)_4$ and $Li_8L_2(hmpa)_4$ (hmpa = hexamethylphosphoramide).[4] It has been proposed that the larger calix[*n*]arenes ($n \geqslant 6$) are able to bind and transport more than one metal ion at a time, and that this may be a result of their ability to adopt 'pinched' conformations.[5] However, as yet there are no crystal structures that detail the conformation of a larger calixarene upon binding to the Group 1 metal ions, the number of metal ions that may bind, the site(s) of metal ion binding, the effects of metal ion binding upon the pattern of hydrogen-bonding within the calixarene cavity or the number and disposition of other ligands bound to the metal ions (presumably water in the ion transport systems).

In this context, we herein report the preparation and crystal structure of the dipotassium complex of the dianion of *p-tert*-butylcalix[8]arene (H_8L'). The reaction of H_8L' (0.5 mmol) with 8 equiv. of KOH or $KOBu^t$ in ethanol–diethylcarbonate (10 : 1, 100 cm^3) under a dry atmosphere yielded colourless crystals of the dipotassium salt $K_2(H_6L')(EtOH)_{4.67}\{(EtO)_2CO\}_{1.33}$ **1** upon standing for 72 h. The same product was also isolated when ethanol–dimethylcarbonate (10 : 1) was used as solvent, indicating alcohol exchange of the dialkylcarbonate under these conditions.

The molecular structure of **1** is shown in Fig. 1. The molecule of **1** lies on a crystallographic inversion centre with the K^+ ions lying above and below the cavity of the calix[8]arene and a K(1)···K(1a) distance of 4.424(2) Å. The K^+ ion is six coordinate with a distorted octahedral geometry comprising three calix[8]arene ArOH ligands in a *fac* arrangement and two ethanol ligands, and is completed by a diethylcarbonate or ethanol ligand with occupancies of 0.66 and 0.34, respectively. The calix[8]arene is doubly deprotonated and adopts a 'pinched' conformation with two ArOH groups bridging the K^+ ions at the 'pinch' (Fig. 2). There are structurally characterised precedents for the doubly bridged $K_2(\mu\text{-OAr})_2$ moiety with the deprotonated acidic phenols 2,4,6-$(CF_3)_3C_6H_2OH$ and 2,4,6-$(NO_2)_3C_6H_2OH$.[6,7] However, in **1** the bridging phenol ligands remain protonated; the free refinement of the three unique calix[8]arene ArOH protons indicates that the formally deprotonated phenol, O(3), is furthest from the K^+ ions and all three calix[8]arene ArOH protons are involved in strong intra-calix[8]arene hydrogen-bonding. There is an additional hydrogen-bond between O(3) and one of the ethanol ligands (Fig. 2), and presumably the overall hydrogen-bonding arrangement favours the observed deprotonation of O(3). The presence of protons on the bridging phenol ligands is also consistent with their greater K–O bond distances (av. 2.92 Å) compared with the terminal ligands (av. 2.73 Å) and the reported examples of the $K_2(\mu\text{-OAr})_2$ moiety (av. 2.76 Å).

The isolation of a neutral, molecular, dipotassium complex from this protogenic, coordinating solvent medium is consistent with the ion transport properties of *p-tert*-butylcalix[8]arene. It is probable that the calix[8]arene complex responsible for K^+

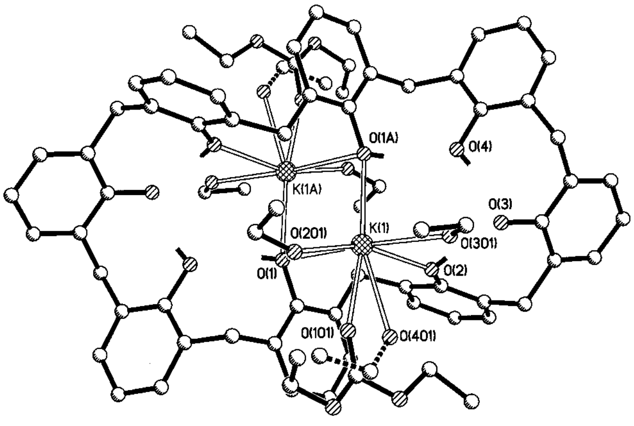

Fig. 1 Molecular structure of **1**. For clarity *tert*-butyl groups and C–H hydrogens have been omitted. Selected bond lengths (Å) and angles (°): K(1)–O(1) 2.949(2), K(1)–O(1a) 2.8963(19), K(1)–O(2) 2.7205(19), K(1)–O(101) 2.825(4), K(1)–O(201) 2.616(4), K(1)–O(301) 2.726(3); K(1)–O(401) 2.780(12); K(1)–O(1)–K(1a) 98.37(5), O(1)–K(1)–O(1a) 81.63(6), O(1)–K(1)–O(2) 97.28(6), O(1)–K(1)–O(301) 172.32(7), O(1a)–K(1)–O(101) 169.01(11), O(1a)–K(1)–O(401) 163.4(1), O(2)–K(1)–O(201) 160.68(11): symmetry operation; *a*, $-x$, $2-y$, $2-z$.

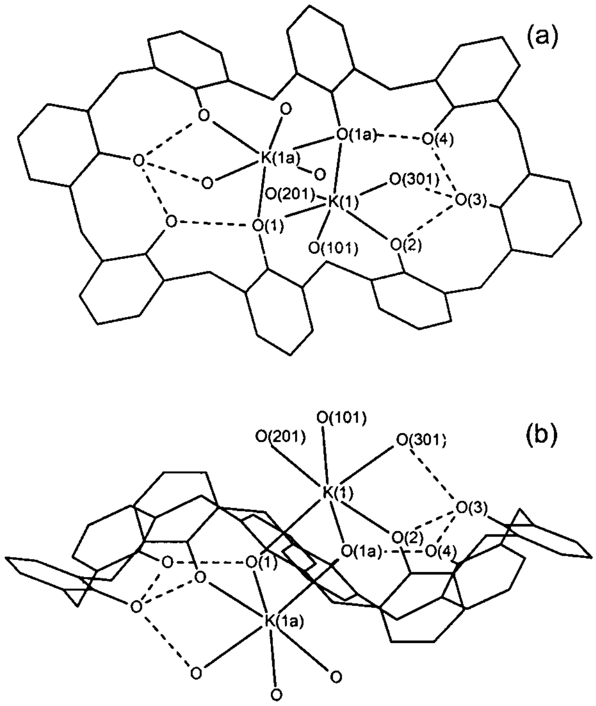

Fig. 2 Schematic representations of **1** showing the arrangement of hydrogen-bonds (O···O): (*a*) from above, (*b*) edge on. The *p-tert*-butyl groups are omitted for clarity and only the coordinated oxygen atom, O(101), of the partial occupancy diethylcarbonate ligand is shown. Hydrogen-bonds: O(1a)···O(4) 2.627(3), O(2)···O(3) 2.508(3), O(3)···O(4) 2.486(2), O(3)···O(301) 2.673(3), O(101)···O(201) 2.523(7) Å. (There are no other O···O interactions < 3.1 Å.)

ion transport in [water | organic solvent | water] liquid membrane systems is similar to **1** but with the ethanol and diethylcarbonate ligands replaced by water molecules. In this regard it is noteworthy that by comparison with the disposition of the ethanol molecules in **1**, these water molecules would be involved in intramolecular hydrogen-bonding to at least one of the ArOH groups of the calixarene cavity and probably also to each other, thus minimising unfavourable interactions with the organic solvent during ion transport.

This work was supported by the EPSRC, BP Chemicals (Additives) Ltd., (Industrial CASE studentship to NPC) and the University of Hull.

Notes and references

† *Crystal data*: $C_{104}H_{148.66}K_2O_{16.66}$, M_r = 1743.7, monoclinic, space group $P2_1/n$, a = 16.1867(3), b = 12.1515(2), c = 26.4092(4) Å, β = 105.827(2)°, U = 4997.57(15) Å^3, Z = 2, D_c = 1.159 g cm^{-3}, μ = 0.157 mm^{-1}, $F(000)$ = 1888. Crystal dimensions 0.10 × 0.05 × 0.03 mm. Data were collected at 160 K employing a wavelength of 0.6879 Å, on a Bruker AXS SMART CCD area detector diffractometer with a silicon (111) crystal monochromator and a palladium coated focusing mirror on the single crystal diffraction station (no. 9.8) at Daresbury Laboratory Synchrotron Radiation Source.[8] Coverage of a hemisphere of reciprocal space was achieved by 0.2° increments in ω, with $\theta_{\min}$ = 1.80° and $\theta_{\max}$ = 26.99° (index ranges $-20 \leqslant h \leqslant 17$, $-12 \leqslant k \leqslant 15$, $-34 \leqslant l \leqslant 34$). Corrections were applied to account for incident beam decay. A solution was provided *via* direct methods and refined by full-matrix least squares on F^2. 25725 reflections were measured, producing 10828 unique data with R_{int} = 0.0372. 649 parameters with 110 restraints refined to R_1 = 0.0802 and wR_2 = 0.2475 [$I > 2\sigma(I)$] with S = 1.060 and residual electron density extremes of 1.229 and −0.779 e Å^{-3}. Notes on the refinement: twofold orientational disorder was resolved for two independent *tert*-butyl groups and for one the minor components were refined isotropically with no hydrogen atoms; substitutional disorder of diethylcarbonate and ethanol was also modelled [refined occupancies 0.656:0.344(5)] as alternative ligands to K(1) with the aid of geometrical and displacement parameter constraints. CCDC 182/1151. See http://www.rsc.org/suppdata/cc/1999/379/ for crystallographic files in .cif format.

‡ A satisfactory elemental analysis for **1** could not be obtained due to the crystals rapidly desolvating upon removal from the solvent. The analysis of samples dried to constant weight in air over several days were consistent with decomposition to a formulation of $K_2(H_8L)(HCO_3)_2(H_2O)_5$. (Found C, 68.09; H, 7.67%. Calc. for $C_{90}H_{124}K_2O_{19}$: C, 68.07; H, 7.87%.)

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Communication 8/09401B