exo-Binding of Na^+ between two fused calix[4]arenes and *endo* binding of Na^+ within the calix[4]arene cones in the disodium salt of 1,3-dimethyl ether *p-tert*-butylcalix[4]arene

Stuart R. Dubberley, Alexander J. Blake and Philip Mountford*

Department of Chemistry, University of Nottingham, Nottingham, UK NG7 2RD

Reaction of 1,3-dimethyl ether *p-tert*-butylcalix[4]arene (H_2L) with sodium hydride in tetrahydrofuran affords the dimeric metallocalixarene species $[Na_2L]_2$ which possesses a novel structure in which the Na^+ ions are coordinated in two very different environments.

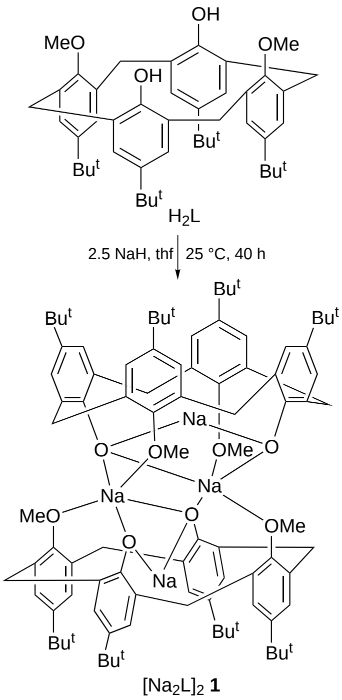
The study of calixarenes (and their derivatives) as receptor molecules *via endo*-binding of substrates within their cavities is a very active area of current research.[1] Furthermore, calixarenes can also act as polydentate O-donor ligands to main-group and transition-metal centres forming mononuclear[2] and fused binuclear[3] derivatives. O-Derivatised calixarenes with pendant arms containing Lewis-basic amide, ester, or polyether functionalities have also been widely studied for their ion-binding properties.[1*b,c*] In contrast, the simple O-alkylated calix[4]arenes have received very little attention and only a handful of metallo derivatives have been reported; these include mononuclear organometallic zirconium,[4] zinc,[3*a*] aluminium and gallium[5] derivatives of 1,3-dimethyl ether *p-tert*-butylcalix[4]arene (H_2L) and an Na^+ complex of tetramethyl ether *p-tert*-butylcalix[4]arene with the metal cation bonded in an *exo* fashion (with respect to the cavity of the cone) to the four ethereal oxygen atoms.[6]

Recent spectroscopic and structural studies have shown that complexation of alkali-metal cations within the calix[4]arene cavity involves cation–π interactions.[7] Furthermore, O-coordination of a transition metal at the lower rim of mononuclear *p-tert*-butylcalix[4]arenes can also allow for alkali-metal binding within the cavity.[2*f*] Binuclear derivatives wtih metals bridging the lower rims of two fused calixarene ligands may bind organic substrates within the divergent cavities.[3*b,c*] Here we show that simple metallation of 1,3-dimethyl ether *p-tert*-butylcalix[4]arene affords a lipophilic binuclear structure with both *exo* binding of Na^+ between the fused calixarene units and *endo* binding of Na^+ within the two calixarene cones.

A tetrahydrofuran (thf) solution of 1,3-dimethyl ether *p-tert*-butylcalix[4]arene (H_2L)[8] and sodium hydride (2.5 equiv.) was stirred at room temp. for 40 h (Scheme 1). Filtration and concentration afforded colourless crystals of the poly(thf) solvate of $[Na_2L]_2$ **1** suitable for X-ray diffraction analysis (*vide infra*). These crystals very readily lose thf; the total yield of pure base-free **1** on removal of all residual thf was 70%. The molecular structure of $[Na_2L]_2$ **1** is shown in Fig. 1.† Molecules of **1** lie on crystallographic twofold axes; the thf molecules of crystallisation (not shown) exhibit no unusual contacts to the Na^+ ions or calix[4]arene ligand and occupy lattice interstitial sites.

Molecules of $[Na_2L]_2$ **1** comprise two doubly deprotonated 1,3-dimethyl ether *p-tert*-butylcalix[4]arene dianions fused at the lower rim by two bridging sodium cations [Na(2) and Na(2A)], each of which possesses an approximately trigonal-bipyramidal coordination geometry. Each bridging sodium is coordinated to two ethereal O-donors and to three phenolate anionic O-donors, with three of the oxygen atoms belonging to one L^{2-} unit and the remainder to the other. The second pair of sodium cations [Na(1) and Na(1A)] are situated *endo* to the lower rim within the calixarene cone. Na(1) is tightly bonded to the two mutually opposite phenolate O-donors [namely O(2) and O(4)] and has bonding[9] contacts to all four phenol ring *ipso* (with respect to oxygen) carbons at $<$ *ca.* 2.9 Å [range 2.792(3)–2.900(5) Å]. There are further $Na\cdots C$(arene) π-contacts in the range 2.918(6)–3.056(6) Å to the two arene rings bearing O(1) and O(3) (Fig. 1). The former ring appears to be η^3-bonded (the *m* and *p*-carbons are not strongly bound) to Na(1) while the latter has effectively η^5-coordination (the *p*-carbon is significantly less closely bound). The Na(1)$\cdots$ring centroid distances for the two coordinated rings are 2.76 [for that supporting O(1)] and 2.65 Å. The normals to the least-squares planes of the two coordinated rings form an angle of 3.8°, whereas the non-coordinated rings are somewhat flattened with an angle of 75.1° between the normals to their planes. The four sodium ions and the oxygen donor atoms O(2), O(4), O(2A) and O(4A) in **1** comprise an unusual short, twisted ladder structure which may be viewed as an Na_4O_4 cubane that has been opened up along two of the $Na\cdots O$ vectors.[10*a*] Furthermore, **1** is a rare example of a structurally characterised, base-free sodium phenoxide.[10*b,c*] A search of the Cambridge Structural Database showed that the individual Na–O and $Na\cdots C$ distances in**1** lie within the ranges previously observed for non-calixarene systems.

The structure of $[Na_2L]_2$ is unusual in calixarene metal complex chemistry since it exhibits simultaneous bonding of



Scheme 1

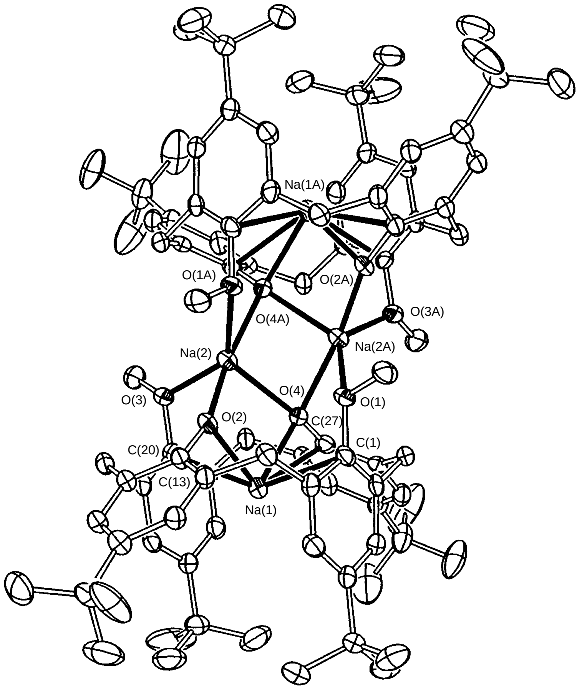


Fig. 1 Molecular structure of $[Na_2L]_2$ **1**. Hydrogen atoms and thf molecules of crystallisation omitted for clarity, principal bonds to the sodium ions are shown in black and thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Na(1)–C(1) 2.792(3), Na(1)–C(13) 2.800(6), Na(1)–C(20) 2.900(5), Na(1)–C(27) 2.797(5), Na(1)–O(2) 2.281(4), Na(1)–O(4) 2.283(4), Na(2)–O(1A) 2.538(4), Na(2)–O(2) 2.129(4), Na(2)–O(3) 2.343(4), Na(2)–O(4) 2.376(4), Na(2)–O(4A) 2.259(4); O(2)–N(2)–O(4A) 163.32(17), O(2)–Na(2)–O(1A) 90.84(15), O(2)–Na(2)–O(3) 89.86(15), O(2)–Na(2)–O(4) 88.55(15), O(1A)–Na(2)–O(3) 138.53(15), O(1A)–Na(2)–O(4) 127.84(14), O(3)–Na(2)–O(4) 93.63(15). Atoms denoted A are related to their counterparts by the symmetry operator: $1 - x, y, 3/2 - z$.

two pairs of otherwise Lewis-base free sodium ions in both possible coordination modes, namely between the fused calixarene units and also within the cones. It is also the first example of a fused dicalix[4]arene bridged by alkali (or alkaline earth) metals; only transition-metal- or post-transition-metal-fused dicalix[4]arenes have been reported previously.[2c–e] A fused derivative of the tetraanion of *p-tert*-butylcalix[4]arene featuring three bridging Zn or Zn(tmeda) units with *endo* ZnEt groups has very recently been described.[3a] Other examples of calix[4]arenes having an *endo* coordinated metal ion have also generally featured additional ligation by Lewis-base donors or other substituents.[2f,7b] In addition, Floriani has recently suggested that coordination of a transition metal to the lower rim O-donors can provide a general strategy for binding alkali-metal ions inside the calix[4]arene cavity.[2f] The homoleptic structure of **1** demonstrates that straightforward encapsulation of sodium ions within the cavity is achieved in a simple one-pot system without the need for transition-metal complexation or additional Lewis-base ligands. The structure of **1** also confirms that cation binding by deprotonated calix[4]arenes within the cone involves a substantial degree of metal–oxygen binding in addition to metal–π-ring interactions.

Preliminary experiments have indicated that $[Na_2L]_2$ is a precursor to new group 2 and early transition-metal complexes *via* sodium halide elimination reactions. We are currently studying the synthesis and structures of other base-free, group 1 and group 2 homoleptic derivatives of 1,3-dialkyl ether *p-tert*-butylcalix[4]arenes, and of *p-tert*-butylcalix[4]arene itself, to explore the relative importance of the metal–phenolate and metal–π-ring interactions.

This work was supported by grants from the EPSRC, Leverhulme Trust and Royal Society (to P. M.). We also thank the EPSRC for a studentship (to S. R. D.) and the provision of a diffractometer and Dr M. G. Davidson (University of Durham) and Professor V. C. Gibson (Imperial College, London) for sharing their results with us prior to publication (see pages 1605 and 1607 of this issue).

Footnotes and References

* E-mail: philip.mountford@nottingham.ac.uk

† *Crystal data* for $[Na_2L]_2\cdot 6thf$: $C_{84}H_{116}Na_4O_8\cdot 6C_4H_8O$, $M = 1778.43$, monoclinic, space group $C2/c$, $a = 18.606(5)$, $b = 30.461(10)$, $c = 20.228(5)$ Å, $\beta = 99.22(3)°$, $U = 11316(6)$ Å^3, $Z = 4$, $D_c = 1.044$ g cm^{-3}, $F(000) = 3872$, $T = 150$ K, Mo-Kα radiation, $5.7 \leqslant 2\theta \leqslant 47.1°$. The structure was solved by direct methods (SHELXS-96[11a]) and 591 parameters were refined (SHELXL-96[11b]) on F^2 for 8351 data to give final conventional $R_1 = 0.1097$ [for data with $F_o > 4\sigma(F_o)$] and $wR_2 = 0.3436$ (all data). Notes on the refinement: phenyl rings were restrained to have local C_{2v} symmetry and to be coplanar with their 1- and 4-substituent atoms. The fully occupied thf solvate molecues were refined with local C_2 symmetry. H atoms were included in geometrically calculated positions or located from Fourier difference syntheses; H atoms for partially occupied thf solvates were not included. All full-site occupancy, non-H atoms were refined anisotropically with extensive rigid bond restraints applied to the U^{ij} components. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/469.

1 (*a*) C. D. Gutsche, *Calixarenes*, Royal Society of Chemistry, Cambridge, 1989; (*b*) V. Böhmer, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 713; (*c*) *Calixarenes: A Versatile Class of Macrocyclic Compounds*, ed. J. Vicens and V. Böhmer, Kluwer Academic, Dordrecht, 1991.

2 (*a*) J. M. Harrowfield, M. I. Ogden, W. R. Richmond and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1991, 2153; (*b*) A. Zanotti-Gerosa, E. Solari, L. Giannini, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Chem. Commun.*, 1996, 119; (*c*) F. Corazza, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Inorg. Chem.*, 1991, **30**, 4465; (*d*) V. C. Gibson, C. Redshaw, W. Clegg and M. R. J. Elsegood, *J. Chem. Soc., Chem. Commun.*, 1995, 2371; (*e*) F. Corazza, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc., Chem. Commun.*, 1990, 640; (*f*) A. Zanotti-Gerosa, E. Solari, L. Giannini, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Chem. Commun.*, 1997, 183; (*g*) J. A. Acho, L. H. Doerrer and S. J. Lippard, *Inorg. Chem.*, 1995, **34**, 2542.

3 (*a*) M. G. Gardiner, S. M. Lawrence, C. L. Ratson, B. W. Skelton and A. H. White, *Chem. Commun.*, 1996, 2491; (*b*) J. L. Atwood, P. C. Junk, S. M. Lawrence and C. L. Raston, *Supramol. Chem.*, 1996, **7**, 15; (*c*) J. L. Atwood, S. G. Bott, C. Jones and C. L. Raston, *J. Chem. Soc., Chem. Commun.*, 1992, 1349; (*d*) F. Corazza, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc., Chem. Commun.*, 1990, 1083; (*e*) M. M. Olmstead, G. Sigel, H. Hope, X. Xu and P. P. Power, *J. Am. Chem. Soc.*, 1985, **107**, 8087.

4 L. Giannini, E. Solari, A. Zanotti-Gerosa, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 85.

5 J. L. Atwood, M. G. Gardiner, C. Jones, C. L. Raston, B. W. Skelton and A. W. White, *Chem. Commun.*, 1996, 2487.

6 S. G. Bott, A. W. Coleman and J. L. Atwood, *J. Am. Chem. Soc.*, 1986, **108**, 1709.

7 (*a*) F. Inokuchi, Y. Miyahara, T. Inazu and S. Shinkai, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1364; (*b*) J. M. Harrowfield, M. I. Ogden, W. R. Richmond and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1991, 1159.

8 A. Casnati, A. E. Arduini, A. Pochini and R. Ungaro, *Tetrahedron*, 1991, **47**, 2221.

9 E. Weiss, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1501.

10 (*a*) An example of a related Na_4O_4 ladder is found for the cyclohexano-15-crown-5 adduct of NaOPh: K. A. Watson, S. Forthier, M. P. Murchie and J. W. Bovenkamp, *Can. J. Chem.*, 1991, **69**, 687; (*b*) I. Cragg-Hine, M. G. Davidson, O. Kocian, T. Kottke, F. S. Mair, R. S. Snaith and J. F. Stoddart, *J. Chem. Soc., Chem. Commun.*, 1993, 1355; (*c*) M. P. Hogerheide, S. N. Ringelberg, M. D. Janssen, J. Boersma, A. L. Spek and G. van Koten, *Inorg. Chem.*, 1996, **35**, 1195.

11 (*a*) G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467; (*b*) SHELXL-96, Institut für Anorganische Chemie der Universität Göttingen, Germany, 1996.

Received in Basel, Switzerland, 7th March 1997; Com. 7/01639E