Shaping the cavity of calix[4]arene using transition metals and binding alkali-metal cations inside the cavity: the relevance of the alkali-metal cation–arene interaction

Antonio Zanotti-Gerosa,[a] Euro Solari,[a] Luca Giannini,[a] Carlo Floriani,*[a]† Angiola Chiesi-Villa[b] and Corrado Rizzoli[b]

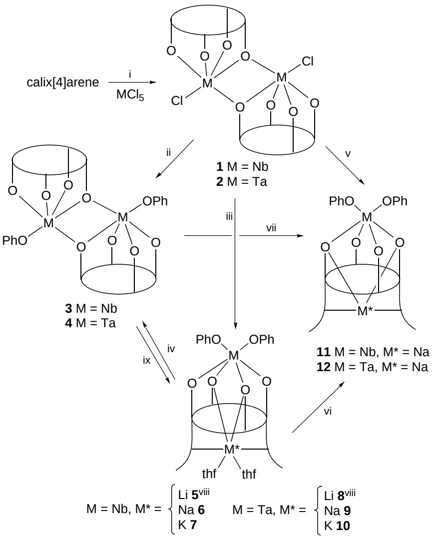
[a] *Institut de Chimie Minérale et Analytique, BCH, Université de Lausanne, CH-1015 Lausanne, Switzerland*
[b] *Dipartimento di Chimica, Università di Parma, I-43100 Parma, Italy*

Transition metals can be used for shaping and electronically enriching the calix[4]arene cavity; in this approach, the π-basic cavities can be adapted to alkali-metal cation complexation in a very hydrophobic environment and these cations can even be transferred into aliphatic hydrocarbons; the η^6-arene–alkali-metal cation interaction is structurally elucidated.

Complexation by transition metals[1,2] can be used as a methodology for shaping[2c] and tuning the binding properties of the calix[4]arene cavity.[3] The present report deals with a simple and general strategy for binding alkali-metal cations inside the calix[4]arene cavity. Solvation of the alkali-metal cations by a π-cavity is a quite remarkable phenomenon, in the context of the role played by the cation–π interactions in chemistry and biology.[4] Typically, complexation of alkali-metal cations is achieved using the chemically modified lower rim of calix[4]arenes, thus rendering complexation outside the cavity, using a set of conventional donor atoms.[3c,5–7]

The metallation of calix[4]arene has been achieved using $NbCl_5$ and $TaCl_5$ and the functionalizable dimers **1**‡ and **2** were obtained as analytically pure crystalline solids.

The reaction of **1** and **2** with alkali-metal phenoxides under the conditions briefly specified in Scheme 1 gave complexes **5–12**,‡ which can be considered as alkali-metal cation carriers in hydrophobic environments since they are very soluble in aliphatic hydrocarbons. The formation of **5–12** proceeds *via* the intermediacy of the monophenoxo derivatives **3** and **4**, as shown in Scheme 1. Attainment of the thf solvated (**5–10**) or unsolvated (**11**, **12**) forms of the alkali-metal cation depends on the reaction solvent. Unexpectedly, the desolvation of **6** and **9** to **11** and **12** was quite easy, thus confirming that the major binding effect of the alkali-metal cation is provided by the calix[4]arene oxygens and the arene rings. X-Ray structural information is available for **1**, **3**, **5**, **6**, **9**, **10** and **11**.§ In particular, we found that complexes **6**, **9** and **10** are isostructural. Structural details are reported only for **9** (see Fig. 1).



Scheme 1 *Reagents and conditions*: i, toluene, reflux; ii, 1 equiv. NaOPh, thf, room temp.; iii, excess of M*OPh, thf; iv, 1 equiv. of **1** in thf or 1 equiv. of **2** in C_6H_6; v, 2 equiv. NaOPh, C_6H_6, reflux; vi, azeotropic distillation, C_6H_{14}; vii, excess of NaOPh, C_6H_6; viii, a single thf is bonded to Li$^+$; ix, NaOPh, thf, room temp.

The two independent molecules A and B have an imposed crystallographic *m* symmetry so in the asymmetric unit of each complex there are two halves of crystallographically independent molecules. The mirror plane runs through the metal atoms and the oxygen atoms O(1) and O(3) bisecting the C(1)–C(4) and C(13)–C(16) rings. An alkali-metal cation is accommodated inside the cavity of the complex interacting with two oxygen atoms of the calixarene [O(2), O(2*)]. Two oxygen atoms from thf complete a planar (for symmetry requirements) coordination around the alkali metal.

As a consequence of the six-coordination of the metal, the calixarene ligand assumes a flattened cone conformation with the opposite C(5)···C(11) and C(5′)···C(11′) rings pushed outward and the opposite C(1)···C(4) and C(13)···C(16) rings inward relative to the cavity of the macrocycle. In both molecules A and B the sodium atom was found to be disordered over two positions (Na and Na′) which lie at a mean distance of 2.102(12) and 2.149(14) Å for molecules A and B respectively, from the reference plane. In both molecules, Na can be considered as η^6-bonded to the C(1)···C(4) ring [Na···C 3.005(17)–3.415(16) Å, Na$^+$··η^6-arene(centroid), 2.465(17) Å (molecule A) and 2.924(16)–3.231(16) Å (molecule B)]; Na$^+$ can be considered as η^3-bonded to atoms C(13), C(16) and C(13*) of the opposite ring [Na′···C 3.001(16)–3.125(14) Å (molecule A) and 3.168(16)–3.289(15) Å (molecule B)]. The

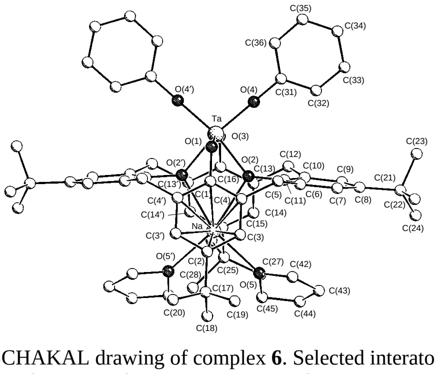


Fig. 1 A SCHAKAL drawing of complex **6**. Selected interatomic distances (Å) and angles (°): Nb–O(1) 2.015(2), Nb–O(2) 1.969(2), Nb–O(3) 2.016(2), Nb–O(4) 1.975(2), Nb–O(5) 1.901(2), Nb–O(6) 1.896(3), Na–O(1) 2.296(3), Na–O(3) 2.309(3), Na–C(22) 2.975(4), Na–C(23) 3.034(4), Na–C(24) 3.072(4), Na–C(25) 3.047(4), Na–C(26) 2.992(4), Na–C(27) 2.937(4), Na–arene(centroid) 2.666(4); O(5)–Nb–O(6) 98.8(1), O(4)–Nb–O(5) 97.8(1), O(3)–Nb–O(5) 168.2(1), O(3)–Nb–O(4) 83.4(1), O(2)–Nb–O(5) 93.6(1), O(2)–Nb–O(4) 162.7(1), O(2)–Nb–O(3) 82.8(1), O(1)–Nb–O(6) 168.6(1), O(1)–Na–O(3) 65.3(1).

directions of the η bonds are nearly perpendicular to the O(2)O(5)O(2*)O(5*) coordination plane, the dihedral angles between the Na–centroid directions and the normal to the plane are in the range 16.3(2)–17.0(3)°. The sodium atoms are displaced from the coordination plane by 0.440(12) and −0.360(12) Å for Na and Na′ respectively (molecule A) and 0.416(10) and 0.199(14) Å for Na and Na′, respectively (molecule B).

The complexation of alkali-metal cations was achieved by forcing open the calix[4]arene cavity using an appropriate coordination number of the metal.[2c] In the case of **5–11**, the negative charge is certainly a determining factor for the binding ability of the cavity. The complexation of the alkali metals by the cavity takes advantage of the cation–π interactions. This has been conveniently revealed by Shinkai *et al.* using mass spectrometry in the case of the alkali-metal cation–calixarene interactions.[8] The structural support for this kind of cation–π interaction comes from the X-ray analyses performed on **5**, **6**, **9**, **10** and **11**. The X-ray analysis revealed, at least in the solid state, how this kind of alkali-metal cation–arene interaction depends on the presence of thf and on the size of the alkali-metal cation. The interaction varies from bis-η^6-coordination for potassium [K^+–η^6-arene(centroid) 2.742(10), 2.819(10) Å in **10**] to a single η^6-coordination for sodium [Na^+–η^6-arene(centroid) 2.606(8) Å in **6** and 2.666(4) Å in **11**], to η^3-coordination for lithium [Li^+–η^3-arene(centroid) 1.98(4) Å in **5**], for the solvated forms of **5**, **6**, **9** and **10**. We should emphasize that, for **11** and **12**, the solvation of the alkali-metal cation is provided mainly by the arene rings. For a comparison of the structural parameters related to alkali-metal cations interacting with aromatic rings we refer to the excellent review by Weiss.[9]

Work is in progress (*i*) to elaborate the strategy for shaping the cavity of calix[4]arene in order to bind organic and inorganic cations inside; (*ii*) to study alkali-metal cation exchange processes; the reaction of **6** with LiCl in thf led, in fact, to the easy displacement of Na^+ by Li^+ in the cavity; (*iii*) to use these compounds as alkali-metal cation carriers in hydrocarbon media, the calix[4]arene cavity being a very hydrophobic environment.

We thank the Fonds National Suisse de la Recherche Scientifique (Grant No. 20-40268.94) and Ciba-Geigy SA (Basel, Switzerland) for financial support.

Footnotes

† E-mail: carlo.floriani@icma.unil.ch

‡ *Syntheses*: **1**: $NbCl_5$ (11.065 g, 41.0 mmol) was added to a suspension of calix[4]arene (H_4L) (26.58 g, 41.0 mmol) in toluene (200 cm^3) and the reaction mixture was refluxed for 14 h. The solvent was removed *in vacuo*, the red residue washed with toluene (150 cm^3), and collected (93%). Crystals suitable for X-ray analysis were grown from a saturated thf solution.

9: NaOPh (1.22 g, 10.5 mmol) was added to a suspension of $[TaL(Cl)]_2\cdot 2CH_2Cl_2$ (4.66 g, 2.4 mmol) in thf (100 cm^3). The reaction mixture was stirred at room temp. for 12 h, then refluxed for 6 h to give a white suspension. The solid was collected and extracted with the mother-liquors for 30 h. Volatiles were removed *in vacuo* and the solid residue was washed with *n*-hexane (100 cm^3), collected and dried *in vacuo* (88%).

11: NaOPh (0.91 g, 7.84 mmol) was added to a suspension of **1** (3.32 g, 3.81 mmol) in benzene (150 cm^3). The reaction mixture was refluxed for 12 h and the red suspension became a yellow solution. The solvent was removed *in vacuo* and fresh benzene (200 cm^3) was added. The mixture was filtered twice, the solvent was concentrated to 10 cm^3, and *n*-hexane (200 cm^3) was added. Upon concentration of this solution, a yellow solid precipitated and was collected and dried *in vacuo* (77%). Crystal suitable for X-ray analysis were grown by slowly cooling a saturated toluene–hexane solution to 9 °C.

§ *Crystal data*: **3**: $C_{108}H_{130}Nb_2O_{17}\cdot 5C_4H_8O$, M = 2166.6, monoclinic, space group $P2_1/n$, a = 19.617(3), b = 13.256(2), c = 22.489(5) Å, β = 100.52(2)°, U = 5749.8(18) Å^3, Z = 2, D_c = 1.251 g cm^{-3}, $F(000)$ = 2312, Cu-Kα radiation (λ = 1.541 78 Å), μ(Cu-Kα) = 21.49 cm^{-1}; crystal dimensions 0.18 × 0.32 × 0.62 mm.

5: $C_{62}H_{68}LiNbO_7\cdot C_{60}H_{70}LiNbO_7\cdot 0.5C_4H_8O\cdot 0.25C_6H_{14}$, M = 2085.7, triclinic, space group $P\bar{1}$, a = 12.467(6), b = 20.181(6), c = 24.954(2) Å, α = 93.69(4), β = 90.85(5), γ = 99.31(3)°, U = 6181(7) Å^3, Z = 2, D_c = 1.121 g cm^{-3}, $F(000)$ = 2205, Mo-Kα radiation (λ = 0.710 69 Å), μ(Mo-Kα) = 2.30 cm^{-1}; crystal dimensions 0.26 × 0.30 × 0.48 mm.

9: $C_{64}H_{76}NaO_8Ta\cdot 0.5C_6H_{14}$, M = 1220.3, monoclinic, space group $P2_1/m$, a = 12.545(2), b = 24.795(5), c = 20.031(3) Å, β = 99.38(1)°, U = 6147(2) Å^3, Z = 4, D_c = 1.319 g cm^{-3}, $F(000)$ = 2532, Mo-Kα radiation (λ = 0.710 69 Å), μ(Mo-Kα) = 4.02 cm^{-1}; crystal dimensions 0.10 × 0.32 × 0.68 mm. For 4538 unique observed reflections [$I > 2\sigma(I)$] collected at T = 295 K on a Enraf-Nonius CAD4 diffractometer ($6 < 2\theta < 50°$) and corrected for absorption the conventional R is 0.036 (wR_2 = 0.075).

11: $C_{56}H_{62}NaNbO_6\cdot 2C_7H_8\cdot 0.3C_6H_{14}$, M = 1157.1, monoclinic, space group $P2_1/n$, a = 12.090(2), b = 20.380(4), c = 25.079(5) Å, β = 91.36(2)°, U = 6178(2) Å^3, Z = 4, D_c = 1.244 g cm^{-3}, $F(000)$ = 2452, Mo-Kα radiation (λ = 0.710 69 Å, μ(Mo-Kα) = 4.02 cm^{-1}, crystal dimensions 0.13 × 0.16 × 0.32 mm.

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 182/316.

References

1 S. G. Bott, A. W. Coleman and J. L. Atwood, *J. Chem. Soc., Chem. Commun.*, 1986, 610; M. M. Olmstead, G. Sigel, H. Hope, X. Xu and P. P. Power, *J. Am. Chem. Soc.*, 1985, **107**, 8087; G. E. Hofmeister, F. E. Kahn and S. F. Pedersen, *J. Am. Chem. Soc.*, 1989, **111**, 2318; G. E. Hofmeister, E. Alvarado, J. A. Leary, D. I. Yoon and S. F. Pedersen, *J. Am. Chem. Soc.*, 1990, **112**, 8843; B. M. Furphy, J. M. Harrowfield, D. L. Kepert, B. W. Skelton, A. H. White and F. R. Wilner, *Inorg. Chem.*, 1987, **26**, 4231.

2 (*a*) F. Corazza, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc., Chem. Commun.*, 1990, 640; (*b*) 1083; (*c*) F. Corazza, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Inorg. Chem.*, 1991, **30**, 4465; (*d*) J. A. Acho, L. H. Doerrer and S. J. Lippard, *Inorg. Chem.*, 1995, **34**, 2542; (*e*) J. A. Acho, T. Ren, J. W. Yun and S. J. Lippard, *Inorg. Chem.*, 1995, **34**, 5226.

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

4 D. A. Dougherty, *Science*, 1996, **271**, 163.

5 F. Arnaud-Neu, G. Barrett, S. J. Harris, M. Owens, M. A. McKervey, M.-J. Schwing-Weill and P. Schwinté, *Inorg. Chem.*, 1995, **32**, 2644; 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**, 8681; 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; P. D. Beef, M. G. B. Drew, P. A. Gale, P. B. Leeson and M. I. Ogden, *J. Chem. Soc., Dalton Trans.*, 1994, 3479; F. Arnaud-Neu, S. Fanni, L. Guerra, W. McGregor, K. Ziat, M.-J. Schwing-Weill, G. Barrett, M. A. McKervey, D. Marrs and E. M. Seward, *J. Chem. Soc., Perkin Trans. 2*, 1995, 113; J. L. M. Gordon, V. Böhmer and W. Vogt, *Tetrahedron Lett.*, 1995, **36**, 2445.

6 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; F. Arnaud-Neu, M. J. Schwing, K. Ziat, S. Cremin, S. J. Harris and M. A. McKervey, *New J. Chem.*, 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; F. Arnaud-Neu, S. Cremin, D. Cunningham, S. J. Harris, P. McArdle, M. A. McKervey, M. A. McManus, M. J. Schwing and K. Ziat, *J. Inclusion Phenom.*, 1991, **10**, 329; M. J. Schwing-Weill, F. Arnaud-Neu and M. A. McKervey, *J. Phys. Chem.*, 1992, **5**, 496.

7 A very particular, non-extendible, single case of Cs^+ inclusion by an upper-rim bridged monoanionic calix[4]arene has been reported: R. Assmus, V. Böhmer, J. M. Harrowfield, M. I. Ogden, W. R. Richmond, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1993, 2427.

8 F. Inokuchi, Y. Miyahara, T. Inazu and S. Shinkai, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1364.

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

Received, 7th October 1996, Com. 6/06826J