COMMUNICATION

OBC
www.rsc.org/obc

Alkali metal ion complexes of functionalised calixarenes – competition between pendent arm and anion bonding to sodium

Rym Abidi,[a] Lassaad Baklouti,[a] Jack M. Harrowfield,[b] Alexandre N. Sobolev,[b] Jacques Vicens[c] and Allan H. White *[b]

[a] *Faculté des Sciences, Université de Bizerte, 7021 Zarzouna-Bizerte, Tunisia*
[b] *Chemistry, School of Biomedical and Chemical Sciences, University of Western Australia, Crawley, WA 6009, Australia. E-mail: ahw@chem.uwa.edu.au*
[c] *Ecole Européene de Chimie, Polymères, Matériaux, Université Louis Pasteur de Strasbourg, 25 rue Becquerel, Cronenbourg 67087, France*

Received 26th June 2003, Accepted 11th August 2003
First published as an Advance Article on the web 20th August 2003

Determination of the crystal structure of the acetonitrile inclusate of the complex formed between sodium trifluoromethanesulfonate (triflate, $CF_3SO_3^-$) and the narrow-rim functionalised calix[4]arene, 5,11,17,23-tetra-*tert*-butyl-25,27-di(phenylmethoxy)-26,28-di(2′-methoxyethoxy)calix-[4]arene, has shown, somewhat unexpectedly, that the diether pendent arms do not chelate the sodium cation, although coordination of all four phenolic oxygen atoms does draw the calixarene into a nearly symmetrical cone form, consistent with conclusions drawn earlier from solution ^1H NMR data. Crystals of $C_{64}H_{80}O_6{\cdot}NaO_3S.CF_3{\cdot}CH_3CN$ obtained from acetonitrile solvent are monoclinic, *C*2/*c*, a structure determination at 'low' temperature (153 K) resolving several difficulties encountered in earlier attempts to analyse data acquired at ~295 K, and indicative of an interesting temperature dependence of substituent and anion orientations.

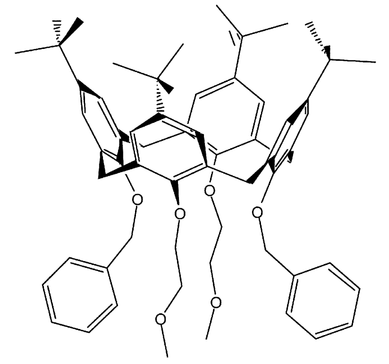
Introduction

Alkali metal ion binding to calixarenes[1] has been of interest for reasons ranging from the possible usage of calixarenes in ion-selective electrodes[2] to the treatment of nuclear waste.[3] A remarkable variety of functional groups has thus been grafted to the calixarene framework, though polyether entities have been particularly prominent.[4,5] One of the useful features of the calix[4]arene scaffold in particular is that it can be sequentially and selectively modified,[6] providing, at least in principle, a subtle way of controlling the strength and selectivity of metal ion binding. As part of an investigation of such chemistry, we synthesised the 1,3-dibenzyl-2,4-(2-methoxyethyl)tetraether of *p*-*tert*-butylcalix[4]arene, **1**.[7] In solution, this molecule does indeed act as an alkali metal ion complexant, with some degree of selectivity for sodium ions and it was assumed that this was a consequence, at least in part, of the ability of the methoxyethyloxo pendent arms to act as chelating units.[7] To confirm this assumption, the crystal structure of the complex of **1** with sodium triflate (trifluoromethanesulfonate) was, with some difficulty, determined and found to be of the somewhat unexpected form described herein.

Experimental

Crystallisation of $1{\cdot}NaO_3SCF_3{\cdot}CH_3CN$

Equimolar amounts of **1** and sodium triflate were dissolved in acetonitrile and the solution allowed to evaporate slowly at room temperature to give a mass of colourless crystals. The composition given above is that deduced from the structure solution for the one selected crystal.



1

Structure determinations †

An initial attempt at determining the structure was undertaken some years ago, a capillary mounted single crystal being chosen from a rather inauspicious bulk sample, a hemisphere of room-temperature data being measured with a 'four-circle'/single counter instrument ($2\theta/\theta$ scan mode; monochromatic MoKα radiation, $\lambda = 0.7107_3$ Å; *T ca.* 295 K) yielding $N_{t(otal)}$ reflections, these merging to N unique (R_{int} quoted) without absorption correction, N_o with $I > 2\sigma(I)$ being considered 'observed'. The structure was solved but considered 'unsatisfactory' with high displacement parameters and disorder and was not carried through to completion. More recently, with the availability of a 'low'-temperature CCD area detector facility, the specimen having been preserved in the interim, a revisitation was undertaken. A full sphere of data was measured (Bruker AXS instrument, *T ca.* 153 K), data being processed prior to merging with the inclusion of 'empirical'/multiscan 'absorption' correction (proprietary software). In the full-matrix least squares refinement, anisotropic thermal parameter forms were refined for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being included constrained at estimated values. The structure refined unproblematically and without disorder, giving a definitive result, albeit, with rather weak data, of limited precision. Conventional residuals R, R_w (statistical weights) on F^2 are quoted at convergence, neutral atom complex scattering factors being employed within the context of SHELXL[8] and XTAL 3.7[9] program systems; pertinent results are given below and in Fig. 1. After consideration of these results, their implications for the nature of the room-temperature attempt were considered in the light of a recent diffraction study[10] of a compound (3,5-di-*tert*-butylpyrazole) wherein *tert*-butyl disorder (rotation about the pendent bond between potential minima?), was found to be temperature dependent – was it likely that a similar phenomenon existed here, accounting, at least in part, for the initial difficulties? This was plausibly found to be the case, disorder clearly distinguish-

DOI: 10.1039/b307193f

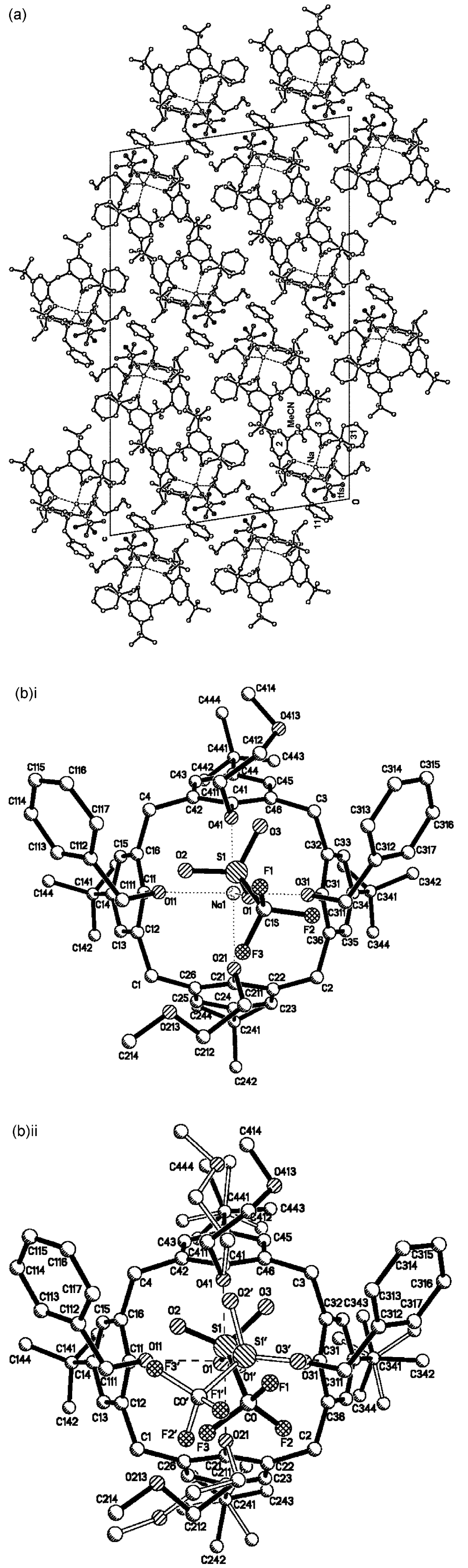


Fig. 1 (a) Unit cell contents projected down *b*, (b) A single aggregate of the complex as modelled at (i) 153 K, (ii) 295 K.

able in the room-temperature study but absent in the low-temperature study, the result described below. [Obviously, the possibility of dependence in the *time* dimension cannot be fully ruled out; at the time of measurement of the low temperature data, the consequences for the room-temperature study had not yet been realized and the specimen was not preserved, regrettably, nor was any bulk sample currently available, so that immediate remeasurement of data at room-temperature was not feasible].

Crystal/refinement data

$C_{64}H_{80}O_6{\cdot}NaO_3S.CF_3{\cdot}CH_3CN$, $M = 1158.4$. Monoclinic, space group *C*2/*c* (C_6^{2h}, No. 15), $Z = 8$, specimen: 0.18 × 0.16 × 0.08 mm (colourless).

(a) *T ca.* 153 K, CCD diffractometer data. $a = 39.501(9)$, $b = 13.177(3)$, $c = 24.959(6)$ Å, $\beta = 98.709(5)°$, $V = 12841(5)$ Å, $D_c = 1.19_8$ Mg m^{-3}, $\mu_{Mo} = 0.12$ mm^{-1}; $T_{min/max} = 0.99$, $2\theta_{max} = 50°$, $N_t = 45658$, $N = 11500$ ($R_{int} = 0.11$), $N_o = 5550$; $R = 0.097$, $R_w = 0.24$. $|\Delta\rho_{max}| = 0.89(8)$ e Å^{-3}. *Variata.* Refinement, difference map and geometrical considerations, indicated modelling of the acetonitrile with the methyl group included in the cavity to be appropriate.

(b) *T ca.* 295 K, single-counter instrument data. $a = 40.086(8)$, $b = 13.339(3)$, $c = 25.135(5)$ Å, $\beta = 98.58(3)°$, $V = 13289(5)$ Å^3. $D_c = 1.15_8$ Mg m^{-3}, $\mu_{Mo} = 0.12$ cm^{-1}, $2\theta_{max} = 45°$; $N_t = 17087$, $N = 8674$ ($R_{int} = 0.15$), $N_o = 2723$; $R = 0.14$, $R_w = 0.36$. $|\Delta\rho_{max}| = 0.65(8)$ e Å^{-3}. *Variata.* With the result of the 3,5-di-*tert*-butyl-pyrazole study in mind, *tert*-butyl groups *n*4, *n* = 2–4, were modelled as rotationally disordered over two sets of sites, occupancies set at 0.5 after trial refinement; data being weak and limited, rigid body constraints were applied in the refinement. Beyond this, the anionic moiety was now also much less clearly defined, and consideration of the nature of the residues in its vicinity prompted its modelling as also disordered over two sets of sites pivoting about the Na–O interaction, while similar considerations modelled the pendants at O(21,41) similarly, all being modelled with geometrical constraints applied in the refinement and site occupancies set at 0.5. It is not evident from the experiment whether the disorder is concerted *in toto* or made up of independent components.

Results and discussion

Our previous observation[7] that the structure of the unbound ligand seemed not to be "preorganised" for complexation may be seen as a considerable understatement given the structure now found for the sodium triflate complex. The results of the present 'low'-temperature study define the complex unambiguously as $[Na(\{CH_3CN\}\mathbf{1})(O_3SCF_3)]$, one formula unit, devoid of crystallographic symmetry, comprising the asymmetric unit of the structure, the packing of these entities being shown in Fig. 1(a) and the individual aggregate in Fig. 1(b). A striking difference from the free ligand structure is the splaying of the four pendent ether arms away from the axis of the calixarene cup, the two methoxyl-*O* donor atoms thus becoming much too remote from the sodium to be considered coordinated to it. The four originally phenolic oxygen atoms of the calixarene are bound equivalently to the metal, forming themselves a good plane (χ^2 5.3) from which the sodium atom is deviant by 0.589(2) Å. The aromatic C_6 planes make dihedral angles to the O_4 plane of 64.5(1), 68.9(1), 65.2(1) and 66.1(1)°, *i.e.* the calixarene cone is essentially fourfold symmetric, consistent with the form of the complex in solution as deduced by ^{1}H NMR spectroscopy.[7] Square-pyramidal five-coordination about Na is completed by O(1) of the anion (Table 1). Despite the difficulties of the room-temperature determination, the calyx remains well-defined, the geometry of the base of the pyramid about Na being closely similar to that of the low-temperature study. The anionic oxygen at the apex, however, is disordered over a pair of sites 0.49(3) Å apart, with the sulfur atom also separated into a pair of components 0.55(2) Å apart.

The structure is remarkably similar to that of the complex of the tetramethylether of *p*-*tert*-butylcalix4arene with the sodium salt of a methylaluminoxobenzoate.[11] There, included toluene

Table 1 The sodium environment. *r* Å is the sodium oxygen distance; other entries in the matrix are the angles (degrees) subtended at the sodium by the relevant atoms at the head of the row and column. θ is the associated Na–O(*n*1)–C(*n*1),S angle and ϕ,χ are Na–O(*n*1)–C(*n*11), C(*n*1)–O(*n*1)–C(*n*11). Values for the room-temperature study are given (italicised) below those for the low-temperature study

Atom	*r*	O(11)	O(21)	O(31)	O(41)	θ	ϕ	χ
O(1)	2.219(6) *2.08(2)* *2.17(2)*	116.1(2) *102.4(7)* *115.2(6)*	101.6(2) *104.3(6)* *102.3(6)*	93.3(2) *107.5(7)* *94.6(6)*	107.5(2) *106.3(6)* *107.8(6)*	138.5(3) *160(2)* *166(1)*		
O(11)	2.303(4) *2.285(9)*		87.5(1) *87.0(3)*	150.6(1) *150.1(3)*	84.3(1) *84.9(3)*	126.4(3) *127.4(7)*	119.3(3) *119.4(7)*	113.3(4) *112.2(9)*
O(21)	2.341(4) *2.320(8)*			84.4(1) *84.6(3)*	150.5(1) *149.4(3)*	125.9(3) *126.4(6)*	119.3(3) *118.5(6)*	113.7(3) *118.5(6)*
O(31)	2.304(4) *2.299(9)*				89.1(1) *88.0(3)*	125.6(3) *125.8(6)*	121.0(3) *120.8(7)*	113.1(4) *113.0(9)*
O(41)	2.332(4) *2.347(9)*					125.5(3) *127.4(7)*	118.7(3) *119.4(7)*	114.8(4) *112.2(9)*

O(1) ··· O(1′) in the 295 K study is 0.49(3) Å.

replaces included acetonitrile, and the very weakly bound aluminate anion replaces triflate but the sodium atom is again essentially square-pyramidal in its coordination geometry, with <Na–O(ether)> 2.30 Å, and a displacement from the O_4 plane of 0.44 Å (at room temperature), slightly less than in the present complex, perhaps in consequence of the weaker interaction with the axially coordinating anion. Clearly, the methoxyethyl arms of **1** have no significant influence upon the binding of the sodium ion, at least in the solid state and it is intriguing to consider why this might be so. The free ligand structure certainly indicates that coordination of all six ether oxygen atoms should be possible and even that cation-π interactions[12] involving the benzyl ether arms could assist in sodium binding. In solution, it may be that the anion dissociates to become solvated and the two ether arms do then chelate and, if so, it could be argued that in the highly concentrated medium which is a crystal lattice, insufficient solvent would be present to prevent direct interaction between cation and anion. Nonetheless, since the triflate, which is expected to be a rather weak ligand,[13] binds only as a unidentate species and sodium ion is commonly found with coordination numbers greater than 5 (though there are certainly precedents for five-coordination by functionalised calixarenes and related aryloxides[14,15]), it seems surprising that at least one arm does not bind in conjunction with triflate. Careful inspection of the lattice array has not allowed us to identify any obviously unusual intermolecular attractions of the diether arms which might explain why they do not chelate, though there is a rather tenuous approach (to *ca* 3.8 Å) of methoxyl carbon to triflate fluorine which may indicate preferential "solvation" of the anion over the cation.

References

† CCDC reference numbers 205946 and 207213. See http://www.rsc.org/suppdata/ob/b3/b307193f/ for crystallographic data in .cif or other electronic format.

1 F. Arnaud-Neu, M. A. McKervey and M-J. Schwing-Weill in *Calixarenes 2001*, eds. Z. Asfari, V. Böhmer, J. M. Harrowfield and J. Vicens, Kluwer Academic Publishers, Dordrecht, 2001, ch. 21, p. 385.

2 F. Cadogan, K. Nolan and D. Diamond, in *Calixarenes 2001*, eds. Z. Asfari, V. Böhmer, J. M. Harrowfield and J. Vicens, Kluwer Academic Publishers, Dordrecht, 2001, ch. 34, p. 627.

3 F. Arnaud-Neu, M.-J. Schwing-Weill, J.-F. Dozol, in *Calixarenes 2001*, eds. Z. Asfari, V. Böhmer, J. M. Harrowfield and J. Vicens, Kluwer Academic Publishers, Dordrecht, 2001, ch. 35, p. 642.

4 I. Thondorf, A. Shivanyuk, V. Böhmer, in *Calixarenes 2001*, eds. Z. Asfari, V. Böhmer, J. M. Harrowfield and J. Vicens, Kluwer Academic Publishers, Dordrecht, 2001, ch. 2, p. 26.

5 A. Casnati, R. Ungaro, Z. Asfari, J. Vicens, in *Calixarenes 2001*, eds. Z. Asfari, V. Böhmer, J. M. Harrowfield and J. Vicens, Kluwer Academic Publishers, Dordrecht, 2001, ch. 20, p. 365.

6 P. Thuéry, M. Nierlich, V. Lamare, J-F. Dozol, Z. Asfari and J. Vicens, *J. Inclusion Phenom. Macrocycl. Chem.*, 2000, **36**, 275.

7 R. Abidi, J. M. Harrowfield, B. W. Skelton, A. H. White, Z. Asfari and J. Vicens, *J. Inclusion Phenom. Mol. Recognit. Chem.*, 1997, **27**, 291.

8 G. M. Sheldrick, SHELXL-97, Program for refinement of crystal structures, University of Göttingen, Germany, 1997 .

9 Xtal 3.7 System, eds. S. R. Hall, D. J. du Boulay and R. Olthof-Hazekamp, University of Western Australia, 2000 .

10 G. B. Deacon, A. Gitlits, P. W. Roesky, M. R. Bürgstein, B. W. Skelton and A. H. White, *Chem. Eur. J.*, 2001, 127.

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

12 R. Ferdani, J. Hu, W. M. Leevy, J. Pajlewska, R. Pajlewski, V. Villalobos, L. J. Barbour and G. W. Gokel, *J. Inclusion Phenom. Macrocycl. Chem.*, 2001, **41**, 7.

13 G. A. Lawrance, *Adv. Inorg. Chem.*, 1989, **34**, 145.

14 (*a*) A. Bilyk, A. K. Hall, J. M. Harrowfield, M. W. Hosseini, B. W. Skelton and A. H. White, *Inorg. Chem.*, 2001, **40**, 672; (*b*) Z. Asfari, J. M. Harrowfield, P. Thuéry, M. Nierlich and J. Vicens, *Aust. J. Chem.*, 1999, **52**, 403; (*c*) P. Thuéry, Z. Asfari, J. Vicens, V. Lamare and J.-F. Dozol, *Polyhedron*, 2002, **21**, 2497.

15 B. W. F. Gordon and M. J. Scott, *Inorg. Chim. Acta*, 2000, **297**, 206.