

Encapsulated Potassium Cation in a New Calix[4]arene Neutral Ligand: Synthesis and X-Ray Crystal Structure¹

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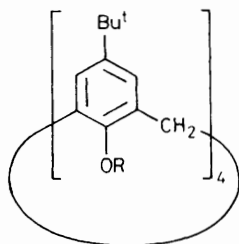
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The X-ray crystal structure of a *p*-*t*-butylcalix[4]arene tetra-amide and its 1 : 1 KSCN complex shows the ligand in a fixed cone conformation and the cation completely encapsulated in an eight-oxygen antiprism; the hydrophobic cavity contains a methanol molecule.

We have recently reported¹ the synthesis, X-ray structure, and ion binding properties in solution of the *p*-*t*-butylcalix[4]arene tetraester (2), and other authors² have reported extraction data on a similar compound (3). All data available, and in particular the ¹H n.m.r. and u.v.-visible complexation studies,¹ show these calix[4]arene derivatives³ to be a new class of efficient cation receptors, whose binding properties are closer to cryptands⁴ and spherands⁵ than to classical crown ethers.⁶ Ligands (2) and (3) have ester groups located on a

lipophilic framework which becomes rigid after functionalization. The preorganization of the binding sites prior to



- (1) R = H
- (2) R = CH₂CO₂Bu^t
- (3) R = CH₂CO₂Et
- (4) R = CH₂CONEt₂

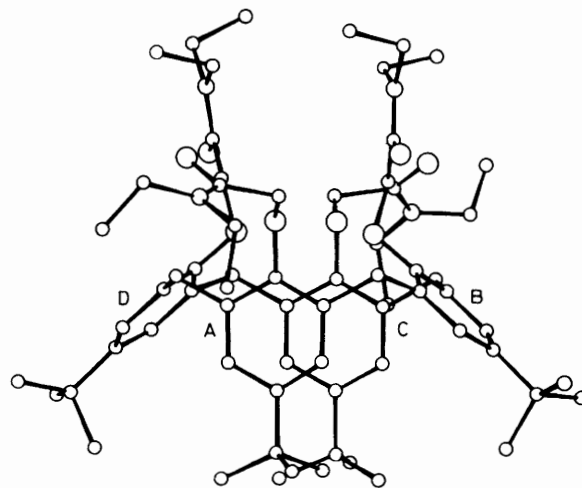


Figure 1. A view of the free ligand (4) along the mean molecular plane.

complexation,⁵ although less pronounced than with Cram's spherands, is the most relevant factor which determines the complexing ability of these new cation ligands.¹

So far, there is evidence for the complexation of alkali cations by ligands (2) and (3) in solution,^{1,2} but there is no report on the solid state structures of these complexes, which would show the groups involved in complexation and their spatial arrangement.

With the aim of further improving the binding abilities of these calix[4]arene ligands and isolating crystalline complexes with alkali cations suitable for X-ray analysis, we have introduced amide groups on the phenolic oxygen atoms of calixarenes.

The reaction of *p*-*t*-butylcalix[4]arene (1) with α -chloro-*N,N*-diethylacetamide (NaH, tetrahydrofuran–dimethylformamide, 1:1 v/v) gave the ligand (4), m.p. 228–229 °C (from MeOH), in 95% yield.† Figure 1 shows the X-ray crystal structure of the free ligand (4)‡ which shows a slightly distorted cone conformation with the four amide groups on one side and the Bu^t groups on the other side of the plane containing the bridging methylene groups of the macrocycle.

The molecular conformation is similar to that reported¹ for the tetraester (2) and may be defined by the angles which the four aromatic rings (A–D) make with the plane containing the four CH₂ groups: A (87.4°), B (43.5°), C (89.5°), and D (135.1°). Two opposite aromatic rings (A,C) are almost parallel to each other, and the other two (B,D) are almost perpendicular (\angle A–C, 2.2; B–D 92.4°).

The equilibrium constants K_e for the extraction of alkali metal picrates from water to chloroform at 20 °C by the ligand (4), $K_e = 1.9 \times 10^9$ (for Na⁺), 2.8×10^7 (K⁺), and 1.3×10^7 dm⁶ mol⁻² (Li⁺), are among the highest reported to date for neutral ligands under the same conditions.⁷ The selectivity order Na⁺ > K⁺ > Li⁺ is the same as that observed previously

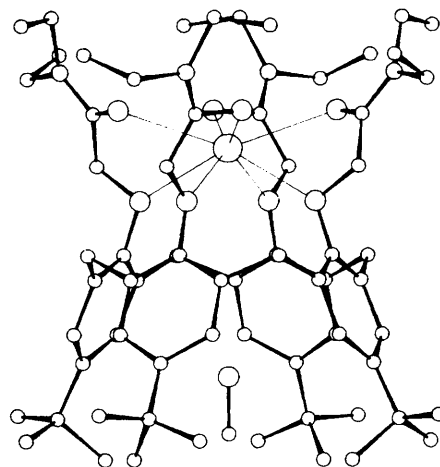


Figure 2. X-Ray crystal structure of the (4)·KSCN·MeOH complex showing the 'encapsulation' of K⁺ in the ether–amide oxygen cavity. One methanol molecule occupies the intramolecular apolar cavity.

for the tetraester (2), but the tetra-amide (4) appears to be more efficient and slightly less selective. Crystalline 1:1 adducts of ligand (4) with sodium and potassium salts have been isolated, but only the structure of the KSCN complex has been solved.

The molecular and crystal structures of the potassium complex, Figure 2, shows that the molecule possesses four-fold symmetry, with the cation completely encapsulated in a polar environment of eight oxygen atoms, which form an antiprism. The hydrophobic pocket of the macrocycle contains a methanol molecule for which there is no evidence of a short contact with the host molecule.

The ether and amide oxygen atoms lie on two distinct parallel planes. The projection of the K···O bonds on the *xy* plane appears tilted by almost 32°. The K···O bond distances are 2.708(7) and 2.74(1) Å for the ether and amide atoms respectively. The distance between two opposite ether oxygen atoms is 4.7 Å, while that between two opposite amide oxygens is close to 5.2 Å.

The conformation of the four amide chains in the complex is more symmetrical than that of the free ligand. This change to higher symmetry around the bound cation than in the free ligand results from rotation of the amide groups around the ArO–CH₂ bonds, which brings the carbonyl groups into the interior and the CH₂ towards the exterior of the hydrophilic cavity. The torsion angles involved increase from a mean value of 94(1)° in the free ligand to a value of 149(1)° within the complex. In contrast to the free ligand, the dihedral angles between the aromatic rings and the plane of the methylene groups are all equal, 113.1(3)°, in the complex.

Since ¹H n.m.r. experiments show that the complexed potassium cation exchanges slowly in solution with the free ligand at room temperature, it is reasonable for us to assume that the structure of the complex in solution is the same as that in the solid state (Figure 2).§

The complex described represents the first example of an encapsulated alkali cation in this new class of strong ion

† Satisfactory elemental analysis was obtained for compound (4): ¹H n.m.r. (200 MHz, CDCl₃, Me₄Si): δ 1.08 (s, 36H), 1.05–1.24 (m, 24H), 3.19 (d, 4H, *J*_{AB} 12.8 Hz), 3.33 (m, 16H), 5.02 (s, 8H), 5.30 (d, 4H), and 6.77 (s, 8H).

‡ Crystal data: (4), (C₁₇H₂₅O₂N)₄·CH₃OH, *M*_r = 1133.61, orthorhombic, space group *Pbca*, *a* = 28.828(3), *b* = 19.120(2), *c* = 26.236(3) Å, *U* = 14461 Å³, *Z* = 8, *D*_c = 1.04 g cm⁻³, 3171 observed unique reflections, *R* = 0.101. (4)·KSCN (C₁₇H₂₅O₂N)₄·KSCN·CH₃OH, *M*_r = 1230.79, tetragonal, space group *I4/mmm*, *a* = 15.192(4), *c* = 37.040(6) Å, *U* = 8549 Å³, *Z* = 4, *D*_c = 0.956 g cm⁻³ (does not take into account the presence within the crystal of unresolved solvent molecules), 1121 observed unique reflections, *R* = 0.113. Intensity data were collected at room temperature to $\theta \leq 60^\circ$ and 65° respectively in the θ – 2θ step-scanning mode using Ni-filtered Cu-*K*_α radiation (λ = 1.54178 Å). The reflection profiles were analysed with the Lehmann–Larsen algorithm (M. S. Lehmann and F. K. Larsen, *Acta Crystallogr., Sect. A*, 1974, **30**, 580). In both cases the reflections with $I > 3\sigma(I)$ [$\sigma(I)$ based on counting statistics] were retained as observed and used in the refinement. The structures were solved by direct methods and refined by full matrix anisotropic least squares calculations using SHELX.⁹ The structure of the complex is disordered, showing two different (but energetically equivalent) types of chain folding with 50% statistical distribution in the crystal. The description of the structure in the space group *I4/mmm* represents the 'average' structure. The SCN⁻ anion is disordered around the centre of an intermolecular cavity surrounded by several electron density peaks (probably attributable to disordered methanol molecules) which could not be refined because of too strong correlation between partial occupancies and high thermal motion. One methanol molecule was located in the hydrophobic cavity of the calixarene. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ The ¹H n.m.r. spectrum of the KSCN complex of ligand (4) shows chemical shifts in accord with the proposed structure (200 MHz, CDCl₃, Me₄Si), δ 1.19 (s, 36H), 1.07–1.23 (m, 24H), 3.35 (d, 4H), 3.36–3.50 (m, 16H), 4.61 (d, 4H), 4.65 (s, 8H), and 7.16 (s, 8H).

receptors and, together with a recently reported sodium complex of *p*-t-butylmethoxycalix[4]arene,⁸ solid-state evidence for the co-ordination of an alkali metal by a calixarene.

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