Metal, Ammonium and Alkyl Ammonium Cation Recognition by a Novel Calix[4]arenediquinone Crown Ether

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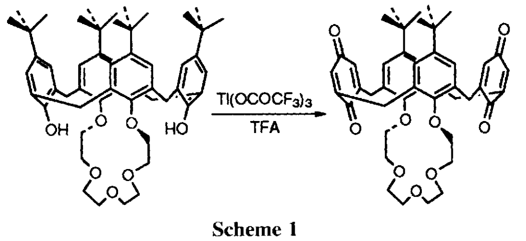
A novel calix[4]arenediquinone crown ether molecule **L** is prepared and shown to strongly complex and electrochemically recognise Na^+, K^+, Ba^{2+}, NH_4^+ and $BuNH_3^+$ guests; the X-ray crystal structure of the sodium complex of **L** is reported.

With the aim of advancing chemical sensor technology we[1] and others have incorporated transition metal[2] and organic[3] redox-active centres into a variety of crown ether, aza crown ether and cryptand macrocyclic structural frameworks and shown some of these host compounds to be selective and electrochemically responsive to the binding of cationic guest species. Although the synthesis[4,5] and electrochemical properties[6–8] of calix[4]arenequinones have been reported their potential use as prototype amperometric sensing molecules has not to our knowledge been utilised. We recently described the first example of such an application using simple diester- and diamide-functionalised calix[4]arenediquinones to complex and electrochemically recognise guest cations.[9] In an attempt to impart selectivity and greater thermodynamic cation stability into these types of systems we report here the synthesis, coordination chemistry and electrochemical properties of the first calix[4]arenediquinone crown ether molecule including a single crystal structure determination of a sodium cation complex.

Using the methodology of McKillop,[10] which was applied to calixarenes by Gutsche[5] and coworkers, the oxidation of *p-tert*-butylcalix[4]arene crown ether compound **1**[11] with thallium trifluoroacetate in trifluoroacetic acid for 2 h at room temp. in the dark produced the novel calix[4]arenediquinone crown ether **L** as a yellow powder in 35% yield (Scheme 1).

Proton NMR solution complexation investigations of Group 1 and 2 metal cations, and ammonium cations were carried out with **L** in deuteriated MeCN–$CHCl_3$ (4 : 1 v/v) solution. The evolution of a new set of resonances with Na^+, K^+, NH_4^+ and Ba^{2+}, corresponding to a respective solution complexed specie was observed. These new resonances evolved over the addition of 1 equiv. of cations suggesting 1 : 1 solution complex stoichiometries in which the cationic guests are bound *via* favourable electrostatic interactions with the crown polyether oxygen donor atoms and the quinone carbonyl moieties of **L**.

Crystals of the sodium cation complex of **L** suitable for X-ray crystallographic determination were grown from a CH_2Cl_2–ethyl acetate solvent mixture.† The structure is shown in Fig. 1. As found in previous structures of calix[4]arenediquinones, the disposition of the quinone and phenyl rings is significantly different.[9] The angle between the two quinone rings is 15.6° and between the two phenyl rings is 109.8°. The sodium is eight-coordinate being bonded to seven oxygen atoms at the bottom of the cone together with one oxygen atom from the $CF_3CO_2^-$ counterion. The shortest bonds are to the anion [Na–O(62) 2.243(9) Å] and to the quinone oxygen atoms at 2.523(6) and 2.301(6) Å, while the distance to the ethereal oxygens of the calix are Na–O(150) 2.707(6), Na–O(350) 2.917(8) Å and to the ethereal oxygens of the polyether linkage are Na–O(153) 2.993(8), Na–O(156) 2.640(7) and Na–O(159) 2.917(8) Å.



Scheme 1

UV–VIS spectroscopic titrations were used to determine association constant data for **L**[12] and for comparison purposes the calixarenediquinones **2** and **3**[9] with the metal and ammonium cations and the results are summarised in Table 1. It is noteworthy that with K^+, Ba^{2+} and NH_4^+ guests the cation association constant values with **L** are greater than the acyclic amide- and methoxy calix[4]arenediquinone analogues. The cation association constants are so large in these cases that UV–VIS titration can only accurately give a lower limit. A UV–VIS competition experiment revealed the order of the association constants to be $Ba^{2+} > K^+ > NH_4^+ > Na^+$

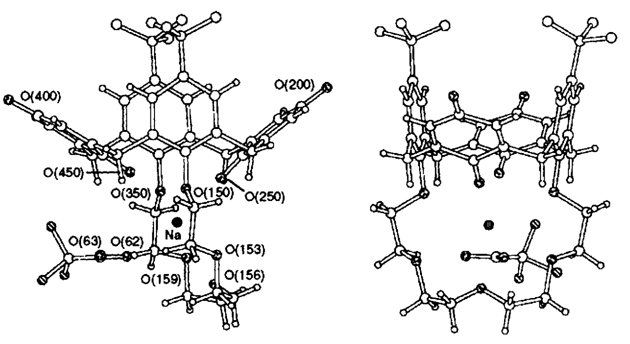
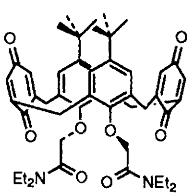


Fig. 1 Side view with oxygen numbering scheme and front view of the molecular structure of the sodium trifluoroacetate complex of **L**. The dichloromethane molecule is omitted for clarity.



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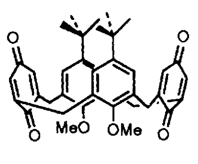

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Table 1 Association constants for the 1 : 1 complex of **L**, **2** and **3** with different cationic species determined by UV–VIS titration in acetonitrile at 296 K

Cations	log$K^{a,b}$ **L**	log$K^{b,c}$ **2**	log$K^{b,c}$ **3**
Na^+	>5.6	5.2	*d*
K^+	>6.0	4.7	4.3
Ba^{2+}	>6.0	5.3	3.7
NH_4^+	>6.0	3.1	*d*
$BuNH_3^+$	5.2	4.0	*d*

[a] Obtained by processing UV–VIS data using a SPECFIT. The results implied weak 1:2 complexation at high concentration of Na^+, K^+, Ba^{2+} and NH_4^+ cations. [b] K = [LC]/([L][C]). L, C and LC represent the ligand, the cationic specie and their 1 : 1 complex respectively. The maximum error for the reported values of log$K$ is less than 10%. [c] See ref. 9. [d] No evidence of complexation was observed.

> $BuNH_3^+$. Also of interest is the dramatic difference in selectivity of the amide derivative **2** for Na^+ over K^+ and the reverse selectivity trend observed for the calixarenediquinone crown ether. Unfavourable steric interactions between $BuNH_3^+$ and **L** may account for the reduced association constant value with this cationic guest.

The electrochemistry and electrochemical cationic recognition studies of **L** were investigated using cyclic and square wave (Osteryoung type) voltammetric techniques (Table 2). The receptor itself undergoes a reversible reduction at −1.15 V and an irreversible redox process at −1.93 V referenced to Ag/Ag^+ [Fig 2(*a*)]. Large anodic perturbations of the reduction waves were observed on addition of all the cationic guests with Ba^{2+}, which possesses the largest charge to radius ratio, producing the greatest effect (ΔE = 555 mV). On addition of substoichiometric equivalents of Na^+ cations [Fig. 2(*b*)] the evolution of a new redox couple, substantially anodically shifted (ΔE = 255 mV) results, until after 1 equiv. of Na^+ the uncomplexed original wave has disappeared [Fig. 2(*c*)]. Thus, this novel calix[4]arenediquinone crown ether receptor not only forms thermodynamically very stable complexes with Group 1, 2 and ammonium cations but can also electrochemically sense these cationic species *via* substantial anodic perturbation effects.

Table 2 Reduction potentials of **L** and the anodic shifts in the presence of 1.0–2.0 equiv. of different cationic species[a]

Compounds	Wave 1	Wave 2
$E_{1/2}$(free, V)	−1.155	−1.930
$\Delta E(K^+$, mV)[b]	210	250
$\Delta E(Na^+$, mV)[b]	255	290
$\Delta E(Ba^{2+}$, mV)[b]	555	*d*
$\Delta E(NH_4^+$, mV)[c]	405	*d*
$\Delta E(BuNH_3^+$, mV)[c]	355	*d*

[a] Obtained by both cyclic (100 mV s^{-1}) and square wave (10 Hz, Osteryoung-type) voltammetry in acetonitrile solution containing 0.1 mol dm^{-3} $[NBu_4]BF_4$ as supporting electrolyte. Solutions were *ca.* 1 × 10^{-3} mol dm^{-3} in compound with reference to a Ag/Ag^+ electrode (330 ± 5 mV *vs.* SCE) at 21 ± 1 °C. [b] Anodic shift of the reduction waves of **L** in the presence of 1.0 equiv. of the respective cationic species added as their perchlorate or hexafluorophosphate salts. [c] Anodic shift in the presence of 2.0 equiv. of the respective cations. [d] The second reduction wave of **L** became obscure or disappeared in the presence of more than 1 equiv. of the respective cations.

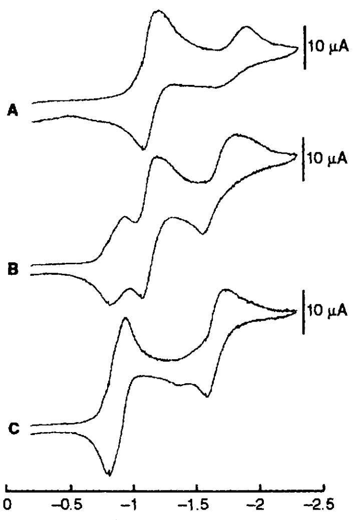

Fig. 2 Cyclic voltammograms of **L** (1.0 × 10^{-3} mol dm^{-3}) in acetonitrile in the absence (*a*) and presence of 0.3 equiv. (*b*) and 1.0 equiv. (*c*) of sodium cations added as its perchlorate salt. Supporting electrolyte: 0.1 mol dm^{-3} $[NBu_4]BF_4$. Scan rate: 100 mV s^{-1}. Working electrode: glassy carbon.

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Footnote

† *Crystal Data*, L, Na^+, $CF_3CO_2^-$, $0.5CH_2Cl_2$, $C_{46.5}H_{51}ClF_3NaO_{11}$: *M* = 901.35, Mo-Kα radiation, triclinic spacegroup $P\bar{1}$, *a* = 11.59(1), *b* = 14.29(1), *c* = 16.43 (1) Å, α = 78.7(1), β = 77.9(1) Å, γ = 72.6(1)°, *V* = 2513.8 $Å^3$, *z* = 2, D_c = 1.19 Mg m^{-3}. Data were collected with Mo-Kα radiation using the MARresearch Image Plate System. The crystal was positioned at 70 mm from the Image Plate. 90 frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program.[13] 7245 independent reflections were measured. The structure was solved using direct methods with the SHELX86 program.[14] There were several disordered features. The two *tert*-butyl groups were disordered and so was the CF_3 group. All three groups were described by two sets of atoms with a common thermal parameter and relative occupancy factors adding up to 1.0. A disordered dichloromethane molecule was also located containing a common carbon atom but two sites for each chlorine atom. The total occupancy was 0.50. All ordered non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions on ordered atoms but not on disordered atoms nor solvent. The structure was then refined on F^2 using SHELXL[15] to an *R* of 0.0896 for the 5342 data with $I > 3\sigma(I)$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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