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Synthesis, Crystal Structures, Cation-Binding Properties and the Influence of Intramolecular C–H···O Interactions on the Complexation Behaviour of a Family of Cone *p-tert*-Butylcalix[4]arene-crown-5 Compounds

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A family of cone *p-tert*-butylcalix[4]arene-crown-5 compounds with various substituents (H, $COCH_3$, $CH_2CO_2C_2H_5$ and CH_2CO_2H) appended at the opposite phenolic oxygen atoms have been synthesised to evaluate their efficiency and selectivity towards different alkali and alkaline-earth metal ions, and also to ascertain the role of the appended side-arms in the complexation process. The selectivity of these ionophores towards Na^+, K^+, Mg^{2+}, and Ca^{2+} has been evaluated with an aqueous solution containing an equimolar mixture of these ions. The concentration of metal ion in the extract (organic phase) has been estimated by ion chromatographic assay. Among these ions, K^+ shows the highest selectivity in all cases except one, where the two phenolic oxygen atoms contain $COCH_3$ substituents. All the ionophores show poor selectivity towards Mg^{2+} and Ca^{2+}. Association constants (K_a) for the binding of Na^+ and K^+ to these ionophores have been determined spectrophotometrically. K_a (7.2×10^7) is highest for the binding of K^+ to the ionophore with $CH_2CO_2C_2H_5$ substituents. The molecular structures of four of the ionophores and four of the metal complexes have been established by single-crystal X-ray crystallography. Analysis of the structures revealed that in case of the ionophore with two $COCH_3$ substituents, the C–H···O interactions form an eight-membered zigzag ring almost perpendicular to the crown ring, which prevents entry of the metal ions into the calix-crown cavity. The ionophore with $CH_2CO_2C_2H_5$ substituents, where no such interaction is observed, forms metal complexes easily and exhibits the highest association constant. ^1H and ^{13}C NMR studies have also been carried out to investigate the conformational behaviour of these ionophores and their metal complexes in solution.

Introduction

Calixarenes, which are macrocyclic oligomers made up of phenol units linked by a methylene bridge, are receiving increasing attention because of their ability to bind guest molecules or ions.[1] In the calixarene family, calix[4]arenes are most popular because of their rigid structures, which make them ideal candidates for the complexation of neutral molecules or ions.[1,2] This chemistry has become even more versatile because of the ease with which calix[4]arenes can be modified with functional groups at either the lower or upper rims, or both, depending on the requirements. These modified calixarenes provide a highly pre-organized architecture for the assembly of converging binding sites.[3] Among these calixarene derivatives, calix[4]arene-crown ethers have attracted intense interest as selective alkali metal extractants.[4] The ion selectivity of this class of compounds is controlled mainly by the conformation of the calixarene platform, the size of the crown ether ring, the substituents at the upper rim of the calixarene and the appended functional groups at the two sides of the crown ring. Among various conformations of the calixarene, 1,3-alternate conformers have been studied more extensively as complexing agent for alkali metal ions.[4b,4c,4f,5] Other conformers have also been prepared but metal ion complexation studies are rare.[4a,4d] Among various crown ether rings, crown-5- and crown-6-containing calixarene derivatives have been found to be more suitable for complexation with alkali metal ions.[4] A number of calix[4]-bis(crown ethers) and their complexation behaviour, mainly with cations of large size, have also been reported.[6]

It has been observed that the substituents at the lower rim determine the conformations of the calixarenes. Calix[4]arene-crown ether derivatives in 1,3-alternate conformation have been studied most since they are more efficient and selective in the complexation of potassium ions.[5] The ionophores *p-tert*-butylcalix[4]arene-crown derivatives, which have not been studied extensively, exist in cone, partial cone and 1,3-alternate conformations.[4a,4g,7] In the latter case, the desired conformation can be obtained by manipulating the experimental conditions and reagents.[4g,8] It should be noted that the selectivity and efficiency of extraction of alkali and alkaline-earth metal ions is maximal with

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the cone conformation of *p-tert*-butylcalix[4]arene-crown derivatives, except for one report in which a partial cone conformation was reported to exhibit high K^+/Na^+ selectivity.[4a]

As part of our effort to identify suitable options for selective extraction of K^+ from natural sources such as brine and bittern, which mainly contain Na^+, K^+, Ca^{2+} and Mg^{2+},[9] we here report our studies on competitive binding of these ions with *p-tert*-butylcalix[4]arene-crown-5 derivatives in the cone conformation (Figure 1). The effect of appended substituents on complexation and the structural features of the ionophores before and after complexation in solution and the solid state, as probed by NMR spectroscopic and single-crystal X-ray studies, are reported. These studies have enabled us to unravel structural features of the ionophores and their complexes; in particular, the influence of intramolecular hydrogen bonding on complexation.

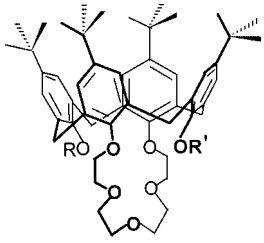
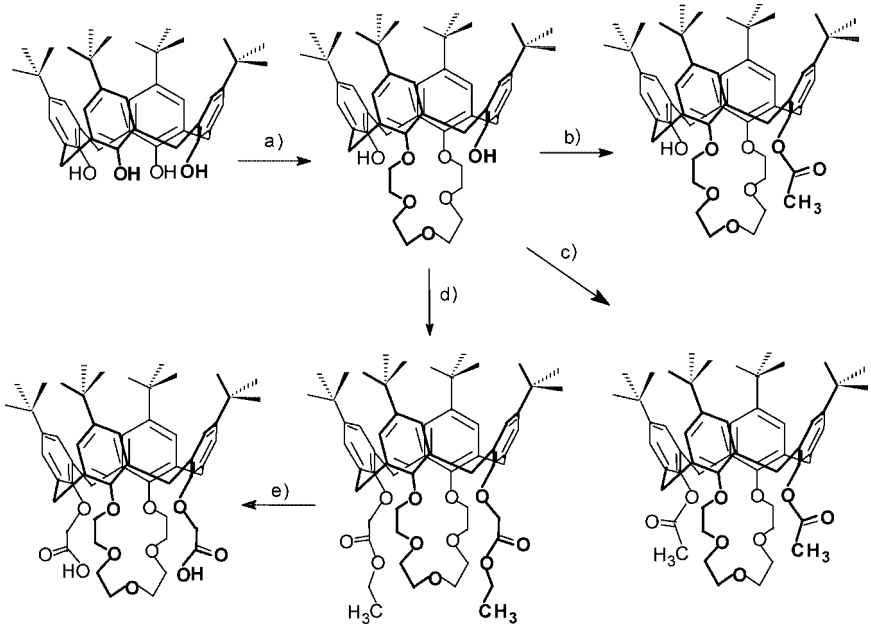


Figure 1. Structures of the ionophores (**1**–**5**) used in this study.

Results and Discussion

Synthesis of Ligands 1–5

The compound *p-tert*-butylcalix[4]arene-crown-5 (**1**) was synthesised by the reaction of *p-tert*-butylcalix[4]arene, tetraethylene glycol ditosylate and *t*BuOK (Scheme 1) according to a modified literature procedure.[4a] The conformation of the calix-crown products depends on the reaction conditions and reagents used; the cone conformation needed for the complexation study could be obtained in good yield. For the synthesis of acetyl derivatives of **1**, we attempted the reaction at room temperature with acetyl chloride and acetyl bromide, using NaH as base and diethyl ether as solvent. However, a mixture of mono- and diacetyl derivatives was obtained, with the former as the major product even after extended (3 d) stirring. We optimised the reaction conditions in diethyl ether to maximize the yield of the monoacetyl derivative, and compound **2** was obtained in cone conformation after purification by column chromatography. By switching the solvent from diethyl ether to THF and conducting the synthesis under reflux conditions, we were successful in obtaining the diacetyl derivative **3** in good yield. Compound **4** was obtained in cone conformation by the reaction of **1** with ethyl bromoacetate in the presence of K_2CO_3 under reflux in acetonitrile. Hydrolysis of **4** yielded the corresponding acid **5** in good yield. During preparation of this manuscript, a paper has appeared on the synthesis of **4** and **5** and use of the latter as a proton di-ionisable extractant for Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}; however, this study is quite different from that reported here.[10]



Scheme 1. Synthesis of *p-tert*-butylcalix[4]arene-crown-5 compounds; a) $OTsCH_2(CH_2OCH_2)_2CH_2OTs$, *t*BuOK, benzene; b) CH_3COBr, NaH, diethyl ether; c) CH_3COBr, NaH, THF; d) $BrCH_2CO_2C_2H_5$, K_2CO_3, CH_3CN; e) NaOH, ethanol.

Synthesis of Na^+ and K^+ Complexes of 1–5

Reaction of the ligands with a ten-fold excess of metal picrate in chloroform resulted in the formation of 1:1 metal complexes. In the case of **3**, however, the Na^+ complex (**3**·Na^+Pic^-, Pic = picrate) was only obtained in poor yield, and virtually no complex formation took place with K^+, as evident from the ^1H NMR spectrum. Hence, the K^+ complex of **3** is not discussed further.

All of these ligands and metal complexes gave satisfactory C, H, and N analyses. The mass spectra of all these ligands and metal complexes were recorded and the observed *m*/*z* values show excellent agreement with the calculated values. It may be noted that the *m*/*z* values (100%) of all ligands correspond to the Na^+ adduct [ligand + Na]$^+$, which is a well-known phenomenon in LC mass spectrometry. The potassium and sodium complexes of the ligands (complex formation was confirmed by NMR studies and X-ray structure determination; vide infra) exhibit molecular ion peaks corresponding to [ligand + K]$^+$ and [ligand + Na]$^+$, respectively.

NMR Study

The ^1H and ^{13}C NMR spectra of all compounds were recorded in $CDCl_3$ and the data are presented in the Experimental Section. The NMR spectroscopic data established the conformation of the ligands and complexes in solution. The ^1H NMR spectra of these compounds exhibit two signals for the aromatic protons, two doublets for the bridging methylene groups of the calixarene unit and two singlets for the *tert*-butyl groups. In the case of **2** and its complexes, however, the spectra are more complex because of asymmetric substituents at the *p*-hydroxy positions of the opposite benzene rings (OH and $COCH_3$). In all of these ionophores and complexes, a typical AB pattern was observed for the methylene bridge (ArCH_2Ar) protons, that is, two widely separated doublets at δ = 3.90–4.65 and 3.12–3.36 ppm (J = 12–13.8 Hz), which suggests that these ionophores exist in a cone conformation in solution.[4a,11] The low-field doublet is due to the axial H atom and the high-field doublet is due to the equatorial H atom of the methylene bridge. The chemical shift difference ($\Delta\delta$) between H_{axial} and $H_{equatorial}$ serves as a measure of the "flattening" of each phenyl unit.[1a,12] In general, $\Delta\delta$ = 0.9 ppm for a system in the regular cone conformation, and for a more "flattened" conformation the value of $\Delta\delta$ decreases. For compounds **1**–**5**, the $\Delta\delta$ values are 0.78, 0.89 (1.31 for another ring), 0.78, 1.48 and 1.10 ppm, respectively. These data indicate that the "flattening" of the phenyl rings is greater in **1** and **3** and lesser in **4** and **5** than that of the regular cone conformation.[4a] The reduced "flattening" in **4** and **5** is because of steric crowding caused by bulky substituents at the narrow lower rim of the calix[4]arene-crown moiety. The $\Delta\delta$ values for the metal complexes of **1**–**3** could not be calculated because of the overlapping of signals from the high-field doublet and crown moiety. However, for the complexes of **4** and **5** these values are in the range 1.07–1.12 ppm, thus indicating that the structures of the metal complexes in solution are close to a regular cone conformation. The difference between the two signals due to phenyl groups and also due to *tert*-butyl groups observed for the free ligand are significantly reduced ($\leq$0.1) in the complexed state. This is presumably because insertion of a metal ion into the crown cavity provides a similar geometrical shape of the complexed molecule. It should be noted that the two appended $CH_2CO_2C_2H_5$ groups of **4**·Na^+Pic^- and **4**·K^+Pic^- exhibit one set of signals [δ = 4.77 (s), 4.32 (q) and 1.33 (t) ppm for **4**·Na^+Pic^- and δ = 4.57 (s), 4.32 (q) and 1.33 (t) ppm for 4·K^+Pic^- (Figure 2)] thus indicating that both groups in each compound are chemically equivalent in solution. A similar observation was also noted for the complexes of **3** and **5**, in which two appended $COCH_3$ and CH_2CO_2H groups are present, respectively. Interestingly, the crystal structures of **4**·Na^+Pic^-, **4**·K^+Pic^- and **5**·K^+Pic^- (see below) show that only one of the two appended groups in each complex is connected to a metal ion through its oxygen atom. Therefore, two sets of signals for two non-equivalent appended groups in each complex are expected. The appearance of only one set of signals suggests exchange of coordination between the appended groups and the metal ion in solution. This exchange process is fast enough on the NMR timescale to make them indistinguishable. Another unprecedented observation is noted for the signals for the phenyl and *tert*-butyl protons of the complexes of **1**. Ligand **1** shows two signals for the phenyl protons and two signals for the *tert*-butyl protons. However, in the complexes one of the signals (high-field) of the phenyl protons is found to split to produce two signals at δ = 6.73 (1 H) and 6.63 (3 H) ppm for **1**·Na^+Pic^- and δ = 6.74 (1 H) and 6.61 (3 H) ppm for **1**·K^+Pic^-. The high-field signal for *tert*-butyl is also seen to split to produce signals at δ = 1.20 (3 H), 0.92 (3 H) and 0.83 (12 H) ppm for **1**·Na^+Pic^- and δ = 1.20 (3 H), 0.93 (3 H) and 0.81 (12 H) ppm for **1**·K^+Pic^-. The possibility of the formation of other conformations can be ruled out on the basis of full NMR spectroscopic data. The crystal structure of **1**·K^+Pic^- shows that the picrate anion is coordinated to the metal ion in a bidentate fashion through the oxygen atoms of the deprotonated phenolic group and one of the nitro groups. Beer et al. have noted similar observations in the lanthanide picrate complexes of their *tert*-butylcalix[4]arene diamide ligand.[13]

Analysis of the crystal structure of **1**·K^+Pic^- shows that the benzene ring of the picrate anion is in proximity, and almost parallel to, one of the benzene rings of the calixarene (C_g–C_g distance is 3.76 Å and the dihedral angle between the planes of the rings is 13.72°). The structural analysis shows that one of the phenyl protons and a few of the *tert*-butyl protons of one of the benzene rings of the calixarene are pointed towards the deshielding zone of the benzene ring of the picrate anion, which results in a splitting of the signals for the phenyl and *tert*-butyl protons.[14] Because of this deshielding effect, the signals of one of the phenyl protons and two methyl groups of the *tert*-butyl moiety are shifted downfield; the shift of one of the methyl groups is quite pronounced.

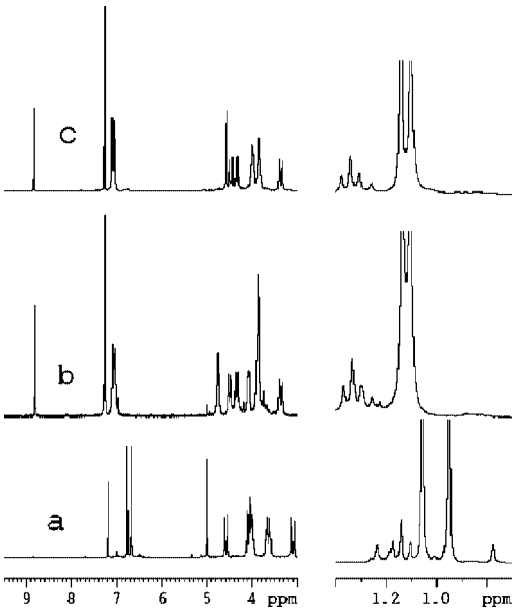


Figure 2. ^{1}H NMR spectra of ionophore **4** (a), its Na^+ (**4**·Na^+Pic^-) (b) and K^+ complexes (**4**·K^+Pic^-) (c), recorded in $CDCl_3$ at room temperature.

In the ^{13}C NMR spectra, the signals of the carbon atoms of the four methylene bridges (ArCH_2Ar) appear at the same position (one peak), with a chemical shift of $\delta \approx$ 31 ppm, which is typical for the cone conformation of *tert*-butylcalix[4]arene derivatives.[4g,15] The other observation is that the C-1 and C-4 carbon atoms (see Figure 3 for the numbering scheme) show two signals each, which could be due to different substituents attached to the carbon atoms at the lower rim of the calixarene. In the metal complexes, the ^{13}C NMR signals are consistent with the cone conformation of the calixarene moiety albeit with some changes in chemical shift for the carbon atoms of the crown moiety, due to complex formation, compared to the free ligand.

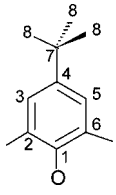


Figure 3. Numbering scheme for carbon atoms of the *p-tert*-butylcalix[4]arene used in the NMR discussion.

Crystal Structures

X-ray crystal structures of four ionophores and four complexes have been determined; ORTEP views of the ionophores are displayed in Figure 4. The structures of the ionophores clearly show the flattened cone conformation, as suggested by the NMR spectroscopic data. However, the extent of flattening differs from ligand to ligand. The interplanar angles between the two opposite rings are 71.89° and 41.10° (82.67° and 35.60° for the other molecule in the unit cell) for **1**, 87.00° and 7.40° for **2**, 60.66° and 39.82° for **3** and 78.10° and 29.18° for **4**. The opposite benzene rings, which are connected to the crown moiety, are less flattened, as evident from their low inter-planar angles. The wide variations in flattening of the rings are due to steric overcrowding of the bulky substituents at the lower rim of the rings and also due to intramolecular C–H···O interactions. It should be noted that the oxygen atoms of the CO groups of the $COCH_3$ substituent in **2** and **3** and the $CH_2COOC_2H_5$ substituent of **4** are directed away from the polyether rings, which could be due to minimisation of the electrostatic repulsion between the lone pairs of the oxygen atoms of the CO and polyether rings. Most of the appended groups show hydrogen-bonding interactions with the oxygen atoms of the polyether rings. There are many examples of hydrogen-bonding interactions involving OH groups at the lower rim of the calixarene,[16] although hydrogen-bonding interactions involving other groups are not common. In case of **1**, the hydrogen atoms of the OH groups (O6–H6 and O7–H7) make strong O–H···O interactions with O5 and O1, which act as donors; O7, on the other hand, acts as an acceptor, making C–H···O interactions with H48A and H50B of the methylene groups of the polyether ring. The interesting feature of the packing is the dimeric association of the two ligands A and B present in the asymmetric unit. This occurs by an intermolecular C–H···O interaction involving H10K attached to C101 and the phenolic oxygen atom O6. Two such hydrogen-bonded dimers are further associated by a C–H···π interaction to form a tetrameric unit (Figure 5). Details of C–H···O, C–H···N, and C–H···π interactions of **1**–**3** and **4** are given in Table S1 in the Supporting Information. In the case of **2**, the hydrogen atom (H1) of the phenolic oxygen atom O1 is involved in a strong intramolecular O–H···O interaction with O4. Two of the methyl hydrogen atoms of the acetyl moiety (H46B and H46C) make intramolecular C–H···O interactions with O4 and O8 of the crown moiety. A packing diagram of **2** showing the one-dimensional array formed by intermolecular hydrogen-bonding interactions between adjacent molecules is depicted in Figure S1 (Supporting Information).

The intramolecular hydrogen-bonding pattern of **3** is interesting and provides important information regarding its robustness towards complexation with K^+. In this compound, it has been observed that the two H atoms of each methyl group of the two appended $COCH_3$ groups (H46B, H48C and H46C, H48B) are close to the oxygen atoms of the polyether ring and are held strongly by C–H···O interactions with O6 and O8 of the crown moiety (Table 1) In fact, this hydrogen bonding forms an eight-membered puckered ring, which is nearly perpendicular to the crown ring (79.33°) and crosses it through the middle (Figure 6). We believe this interaction also exists in solution and, therefore, metal ions such as K^+ cannot enter into the cavity to form metal complexes. The packing diagram of **3**, which shows a dimeric association of the molecule through intermolecular interactions involving surrounding lattice solvent molecules, is shown in Figure S2 (Supporting Information).

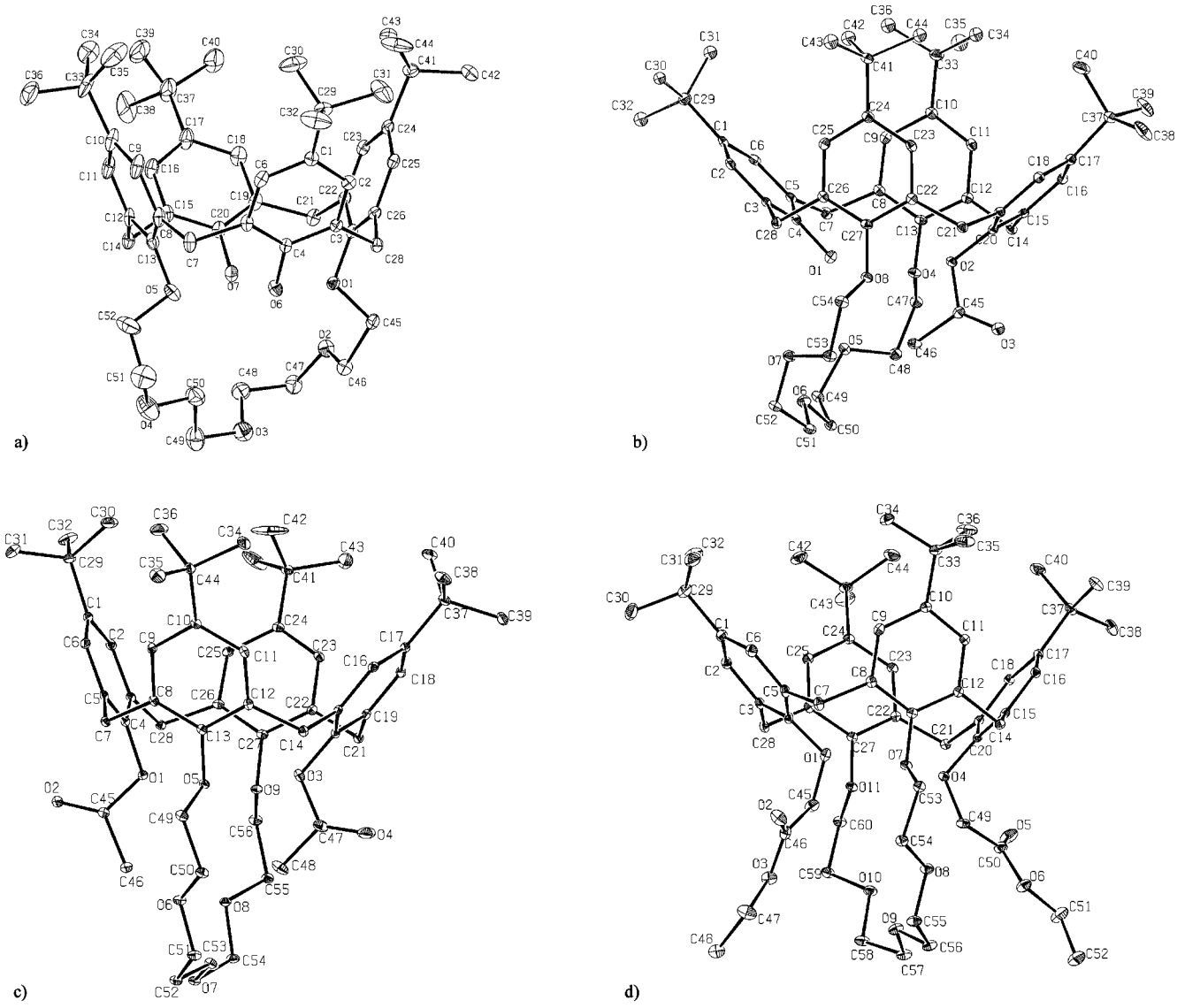


Figure 4. ORTEP views of compounds **1** (a), **2** (b), **3** (c) and **4** (d).

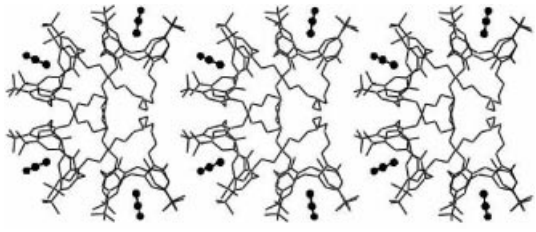


Figure 5. Packing diagram of **1** viewed along the *a*-axis showing the tetrameric association of the compound with acetonitrile (ball-and-stick model) in the cavity of the calix cone.

Table 1. Intramolecular C–H···O interactions involving methyl hydrogen atoms of $COCH_3$ and oxygen atoms of the crown ring for **3**.

D–H···A	H···A [Å]	D···A [Å]	<(D–H···A) [°]
C46–H46B···O6	2.30	3.240(3)	167
C46–H46C···O8	2.32	3.269(3)	168
C48–H48B···O8	2.44	3.315(4)	151
C48–H48C···O6	2.40	3.255(4)	149

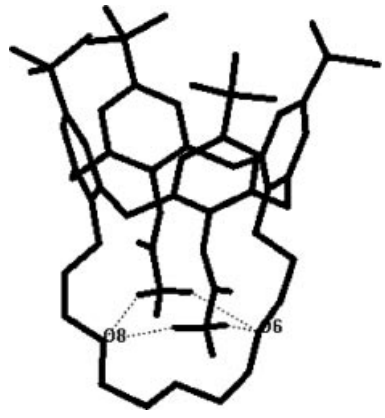


Figure 6. Capped stick model of compound **3**, showing C–H···O interactions (dotted line) involving methyl hydrogen atoms of $COCH_3$ groups and oxygen atoms (O6 and O8) of the crown moiety.

In the case of **4** the C–H···O interactions involving the crown ring are not significant. The only interaction observed is that between the hydrogen atoms (H49A) of the $CH_2COOC_2H_5$ moiety and O9 of the crown ring. However, the oxygen atoms of the CO groups of both $CH_2COOC_2H_5$ moieties form C–H···O interactions with the hydrogen atoms of the bridging methylene group. The packing diagram of **4** is also available as Supporting Information (Figure S3).

All of the above ligands contain lattice solvent molecule(s) and these appear to play a role in crystal formation. One of the acetonitrile molecules present in the crystal occupies the cone cavity of the calixarene unit in all cases. This acetonitrile molecule is held in the cavity and forms C–H···N interactions with the hydrogen atom of one of the bridging ethylene groups and C–H···π interactions with the benzene rings of the calixarene moiety.

The crystal structures of the metal complexes reveal that the K^+ ion is coordinated to eight oxygen atoms in all complexes whereas the Na^+ ion in **4**·Na^+Pic^- is coordinated to six oxygen atoms (Figure 7). In **1**·K^+Pic^-, where eight coordination sites with oxygen atoms as donor are not available,

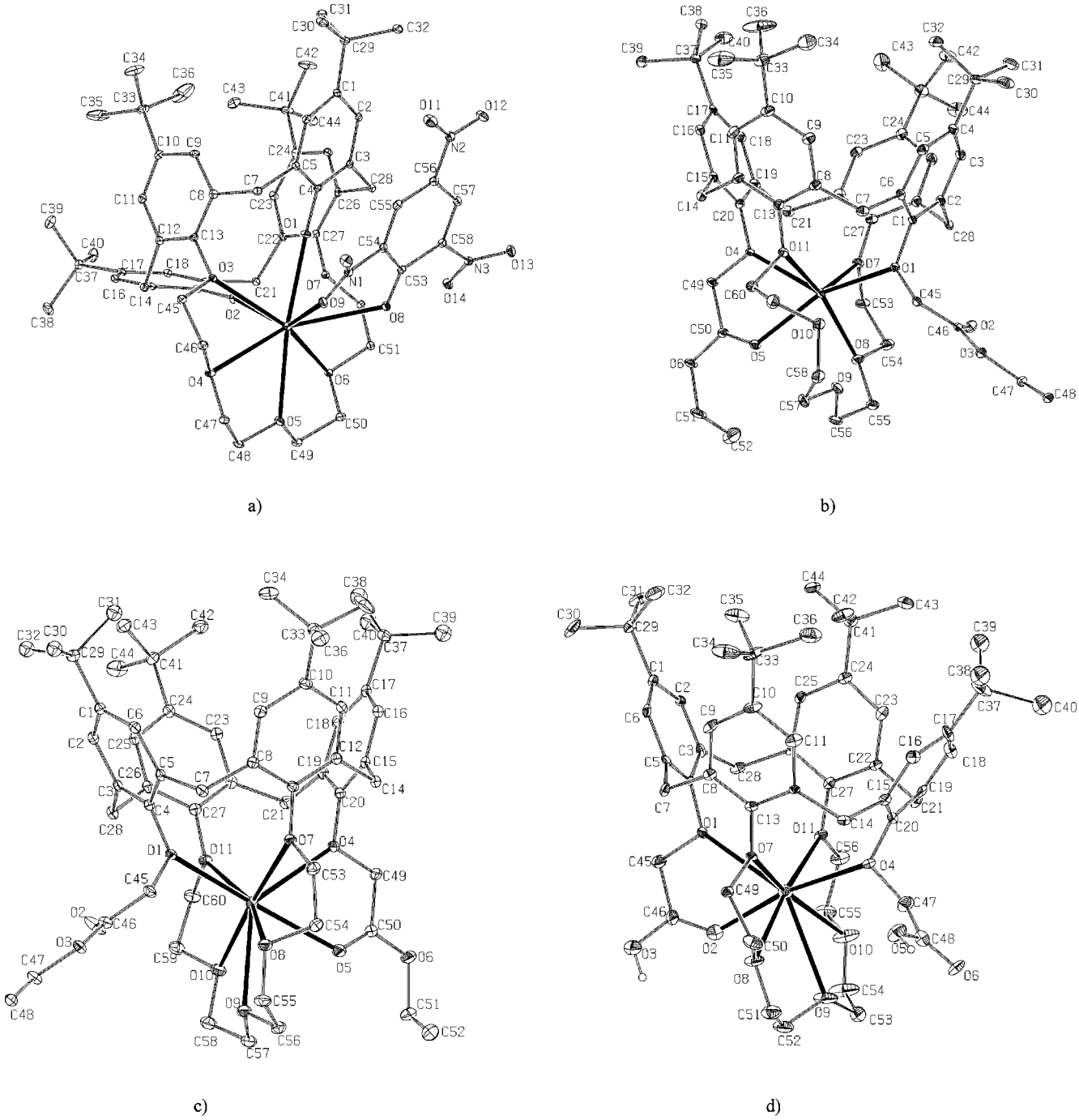


Figure 7. ORTEP views of complexes **1**·K^+Pic^- (a), **4**·Na^+Pic^- (b), **4**·K^+Pic^- (c), and **5**·K^+Pic^- (d).

the picrate anion acts as a bidentate ligand to make K^+ octacoordinate. For complexes **4**·Na^+Pic^-, **4**·K^+Pic^- and **5**·K^+Pic^-, out of two $CH_2CO_2C_2H_5$ and CH_2CO_2H appended arms, the oxygen atom of the CO group of one arm is coordinated to K^+. In the case of **4**·Na^+Pic^-, however, two oxygen atoms (O9 and O10) of the crown moiety are not coordinated to Na^+. The M–O distances of all complexes are given in Table 2. In the metal complexes, the cone conformations of the calixarene moieties are more symmetric than those of the corresponding free ligands. For example, all the four phenyl rings of **4**·K^+Pic^- make similar angles of intersection with the plane of the four rim methylene groups (64.50–69.92°) and the inter-planar angles between the two opposite rings are 45.63° and 54.25°, which suggests an almost symmetric cone conformation of the calixarene unit.

Table 2. Metal–oxygen bond lengths [Å] for complexes **1**·K^+Pic^-, **4**·Na^+Pic^-, **4**·K^+Pic^-, and **5**·K^+Pic^-.

1·K^+Pic^-			
K1–O9	2.700(2)	K1–O2	2.824(2)
K1–O5	2.703(2)	K1–O4	2.845(2)
K1–O1	2.711(2)	K1–O8	2.890(2)
K1–O3	2.726(2)	K1–O6	3.013(2)
4·Na^+Pic^-			
Na1–O5	2.367(3)	Na1–O7	2.405(3)
Na1–O11	2.375(3)	Na1–O8	2.420(3)
Na1–O1	2.394(3)	Na1–O4	2.543(3)
4·K^+Pic^-			
K1–O1	2.657(2)	K1–O7	2.801(2)
K1–O5	2.659(3)	K1–O4	2.803(2)
K1–O11	2.712(2)	K1–O9	2.836(3)
K1–O10	2.758(3)	K1–O8	2.931(3)
5·K^+Pic^-			
K1–O1	2.742(6)	K1–O8	2.760(6)
K1–O2	2.561(8)	K1–O9	2.971(8)
K1–O4	2.566(5)	K1–O10	2.926(6)
K1–O7	2.703(4)	K1–O11	2.704(4)

Analysis of the crystal structures revealed that each of these structures make a number of intra- and intermolecular C–H···O interactions, leading to layered or zigzag chain network of packing. Packing diagrams (Figures S4–S7) and a table of hydrogen-bonding interactions (Table S2) for all these complexes are available as Supporting Information. Some of the solvent molecules and picrate anions are highly disordered, as discussed in the Experimental Section.

Selectivity

The selectivities of these ionophores toward metal ions such as Na^+, K^+, Mg^{2+} and Ca^{2+} were determined by a two-phase extraction method followed by ion chromatographic assay of the metal ions in the extract.[9] The experiments were carried out with an aqueous solution containing equimolar amounts of Na^+, K^+, Mg^{2+} and Ca^{2+} as their picrate salts, as described in the Experimental Section. Chromatograms of the original solution and that of the extract obtained using **4** are given in Figure 8. The distributions of metal ions in the organic extracts, together with values of the observed selectivity ratios, are given in Table 3. As can be seen from the data, all ionophores except **3** show high selectivity towards K^+, this selectivity being highest for **4** (82.1%). From the crystal structures it appears that the calix-crown cavity fits well with K^+, allowing it to coordinate to all the oxygen donors of the cavity. Na^+ also coordinates, but it does not fit well in the cavity and leaves two oxygen atoms of the crown ring uncoordinated. Mg^{2+} and Ca^{2+} show poor selectivity.

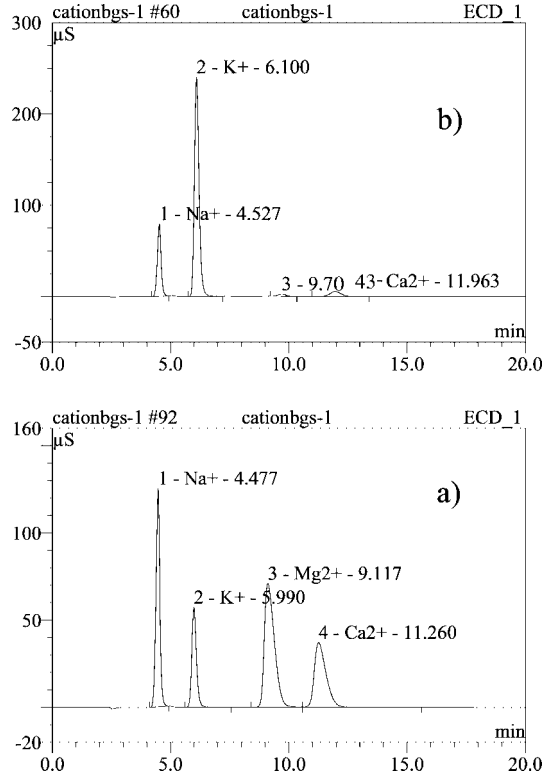


Figure 8. Ion chromatograms of a) a solution containing an equimolar mixture of Na^+, K^+, Mg^{2+}, and Ca^{2+} and b) the extract obtained from the equimolar mixture by two-phase extraction using ionophore **4**.

Apart from cavity size, the C–H···O interactions involving oxygen atoms of the crown ring observed in some of these compounds play an important role in complex formation. In the ionophores **2**–**5**, the main coordination core (calix-crown moiety) for all of them is the same, with one of the appended arms taking part in coordination. However, the selectivity for a particular metal ion (e.g. K^+) differs significantly. The crystal structures show that in the case of **2**, one side of the crown ring is blocked by strong C–H···O interactions between two of the methyl protons of $COCH_3$ and the oxygen atoms of the crown rings. For **3**, both the sides are blocked (Figure 6), and in this case the effect is so severe that K^+ cannot enter into the cavity for complex formation. For **4**, however, the C–H···O interaction involving oxygen atoms of the crown ring is not significant and the metal ion can interact easily with the calix-

Table 3. Concentration of metal ions in the extract and selectivity ratio with respect to potassium ion.

Compound	Concentration [%] of metal ion in extract[a]				Selectivity ratio[b]		
	Na^+	K^+	Mg^{2+}	Ca^{2+}	K^+/Na^+	K^+/Mg^{2+}	K^+/Ca^{2+}
1	22.0	63.8	3.2	10.9	1.7	12.2	6.0
2	28.3	57.5	2.15	12.0	1.2	16.5	4.9
3	56.5	25.3	–[c]	18.1	0.3	–	1.4
4	17.9	82.1	–[c]	–[c]	2.7	–	–
5	26.6	69.4	0.7	4.2	1.5	60.9	16.9

[a] Concentration [%] of metal ion in the original solution (before extract): Na^+ = 18.2, K^+ = 30.9, Mg^{2+} = 19.9, Ca^{2+} = 31.7. [b] Ratio calculated by [% of K^+ in the extract][% of M^{n+} in the original solution]/[% of M^{n+} in the extract][% of K^+ in the original solution]. [c] Trace amount.

crown moiety. This is consistent with the selectivity data and the association constants determined. It should be noted that apart from the appended arms, the remainder of all five ionophores is identical, therefore the observed variation in complex formation/selectivity is obviously due to the effect of the appended arms. Steric crowding is not a significant factor in this case as the ionophore with the most bulky appended arms (**4**) shows the highest selectivity. This suggests that the intramolecular hydrogen-bonding interactions involving the lower rim of the ionophore play an important role in complex formation with metal ions. The appended functional groups, which are expected to act cooperatively as an axial ligand to stabilise the complex, may not always work in this manner and could even inhibit complex formation.

Association Constants

The association constants (K_a) of the ionophores **1**–**5** with Na^+ and K^+ picrates were determined spectrophotometrically, as described in the Experimental Section. Metal picrates in aqueous solution were extracted with chloroform both in the presence and absence of host. The amount of picrate ion in the chloroform layer was determined from its extinction coefficient at 380 nm after appropriate dilution in CH_3CN. The association constants were determined using Equation (1), where K_a is the association constant, K_d the distribution constant, R the molar ratio of picrate to host in the organic layer, $[G_i]_{H_2O}$ the initial concentration of the guest (metal ion/picrate), $[H_i]_{CHCl_3}$ the initial concentration of the host (ionophore) in chloroform, V_{CHCl_3} the volume of the organic layer (chloroform) and V_{H_2O} the volume of the aqueous layer.[17]

$$K_a = \frac{R}{(1-R)K_d\{[G_i]_{H_2O} - [H_i]_{CHCl_3}(V_{CHCl_3}/V_{H_2O})\}^2} \quad (1)$$

The molar ratios of picrate to host (R) were determined from Equation (2), where A is the observed absorbance in the aqueous phase, D the dilution factor, ε the extinction coefficient of the picrate salt at 380 nm in CH_3CN (ε = 16900), $[G_i^+]$ the initial concentration of guest in the aqueous phase, V_{aq} the volume of the aqueous phase, V_{org} the volume of the organic phase, and $[H_i^*]$ the initial concentration of the host in the $CHCl_3$ phase.[18]

$$R_{CHCl_3} = \frac{\{[G_i^+] - A(D/\varepsilon)\}(V_{aq}/V_{org})}{[H_i^*]} \quad (2)$$

The distribution constants were determined using Equation (3).[17]

$$K_d = \frac{[G^+X^-]_{CHCl_3}}{[G^+]_{H_2O}[X^-]_{H_2O}} \quad (3)$$

The values of association constants (K_a) and R for all ionophores are given in Table 4. The data show that the values of K_a for K^+ with various ionophores decrease in the order **4** > **5** > **1** > **2** >> **3**, which is consistent with the selectivity data and the C–H···O interactions observed in the crystal structures. For Na^+, the values of K_a are approximately 10–100 times lower than those for K^+, in line with the selectivity data.

Table 4. Molar ratio of picrate/host in the organic layer (R) and association constants (K_a) with Na^+ and K^+.

Ionophore	R		K_a	
	Na^+	K^+	Na^+	K^+
1	0.02	0.24	1.06×10^4	1.82×10^6
2	0.02	0.08	8.70×10^4	3.25×10^5
3	0.01	–	5.17×10^4	–
4	0.26	0.68	3.12×10^6	7.20×10^7
5	0.34	0.66	5.96×10^6	5.80×10^7

Conclusions

A series of *p*-*tert*-butylcalix[4]arene-crown ethers with various substituents attached to the opposite phenolic oxygen atoms have been synthesised in the cone conformation to evaluate their performance as ionophores towards Na^+, K^+, Mg^{2+} and Ca^{2+}. NMR and crystal structure studies suggest that these ionophores exist in a "flattened" cone conformation both in solution and the solid state. Na^+ and K^+ complexes of these ionophores have been synthesised and the crystal structures show that, in all cases, one of the two appended substituents coordinates to the metal ion and the size of the calix-crown cavity is most suited to K^+ among the ions studied. The ^1H NMR study also revealed that there is fast exchange of coordination between the two appended groups and the metal ion in solution. The selectivity study with a mixture of cations showed the highest

selectivity towards K^+; the association constants also follow the same order. The one exception is compound **3**, where access to the metal ion is blocked as a result of strong C–H···O interactions between the pendant $COCH_3$ substituents and the crown moiety. Such deleterious interactions are apparently nonexistent in the case of the $CH_2CO_2C_2H_5$ substituents as the ligand interacts strongly with the metal ions. Evidently, although appended functional groups (like "lariat" crown ethers) are known to act as a stabilizing axial ligand, these may, in fact, act in the opposite way if strong intramolecular hydrogen bond involving the crown ring is operational. The X-ray structure determination of the ionophores therefore provides an insight into the effect of intramolecular interactions on the structure–selectivity correlation.

Experimental Section

Reagents and Methods: The ligand *p-tert*-butylcalix[4]arene was synthesised according to a literature procedure.[19] Metal picrate salts were prepared by the reaction of picric acid and the metal hydroxide in aqueous media. All the reagents used in this study were purchased from Aldrich and S. D. Fine Chemicals. All solvents were of analytical grade and purified by standard procedures before use.[20] Milli-Q (Millipore Corporation) water was used for extraction and ion chromatographic study. Elemental analyses (C and H) were performed with a model 2400 Perkin–Elmer elemental analyzer. NMR spectra were recorded with a model DPX 200 Bruker FT-NMR instrument. Infrared spectra were recorded with a Perkin–Elmer Spectrum GX FT-IR system. Mass spectra were recorded with a Q-TOF Micro™ LC-MS instrument. The UV/Vis spectra were recorded with a model 8452A Hewlett–Packard diode array spectrophotometer. Cation concentration was measured with a Dionex 500 ion chromatograph. Single crystal structures were determined using a Bruker SMART 1000 (CCD) diffractometer.

Synthesis of 1: A mixture of *p-tert*-butylcalix[4]arene (1.46 g, 2.25 mmol) and *t*BuOK (0.23 g, 2 mmol) in 150 mL of dry benzene was refluxed under an inert gas with stirring for 1.5 h, then tetraethylene glycol ditosylate (1.06 g, 2 mmol) was added. After refluxing for 24 h, a second portion of *t*BuOK (0.23 g, 2 mmol) was added, and the reaction mixture was refluxed for an additional 24 h. It was then cooled to room temperature, treated with 1 N HCl (125 mL), and extracted five or six times with 30 mL of diethyl ether each time. The combined organic layers were finally washed three times with water (100 mL each time) and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography using silica gel as packing material and dichloromethane/ethyl acetate (4:1) as eluent. Yield: 0.75 g (43%). ^{1}H and ^{13}C NMR spectroscopic data are similar to those reported earlier.[4a,10] LC-MS: *m*/*z* = 829.51 (calcd. for [**1** + Na^+] 829.50). $C_{52}H_{71}O_{7.5}$ (**1**·0.5H_2O, 815.50): calcd. C 76.59, H 8.78; found C 76.48, H, 8.69.

Synthesis of 2: Compound **1** (0.27 g, 0.3 mmol), NaH (0.04 g, 1.75 mmol), and acetyl bromide (0.4 mL, 5.4 mmol) were dissolved in 70 mL of diethyl ether and the mixture was stirred at room temperature under an inert gas for 3 d. After removing the solvent with a rotary evaporator, the solid mass was treated with 10% HCl (50 mL) and extracted with dichloromethane (50 mL). The organic layer was washed twice with water (50 mL each time) and the solvent was removed by rotary evaporation. The product was purified by column chromatography using silica gel as packing material and ethyl acetate/hexane (1:5) as eluent. Initially, some starting materials were separated and then the desired product was eluted. The solvent was removed from the desired fraction and the solid compound was dried in vacuo. Yield: 0.11 g (39%). ^{1}H NMR (200 MHz, [D_3]chloroform): δ = 7.20 (s, 2 H, ArH), 7.08 (s, 2 H, ArH), 6.79 (s, 1 H, OH), 6.64 (d, *J* = 2.4 Hz, 2 H, ArH), 6.59 (d, *J* = 2.4 Hz, 2 H, ArH), 4.55 (d, *J* = 13.0 Hz, 2 H, Ar*CH*$_2$Ar), 4.13 (d, *J* = 12.8 Hz, 2 H, Ar*CH*$_2$Ar), 4.07–3.46 (m, 16 H, crown-*CH*$_2$), 3.24 (dd, J_1 = 13.1, J_2 = 3.6 Hz, 4 H, Ar*CH*$_2$Ar), 2.90 (s, 3 H, O*CH*$_3$), 1.35 (s, 9 H, *t*Bu), 1.34 (s, 9 H, *t*Bu), 0.83 (s, 18 H, *t*Bu) ppm. ^{13}C NMR: δ = 171.18 (*CO*CH_3), 151.45, 151.25, 150.44 (C-1), 147.43, 146.24 (C-4), 135.71, 135.44, 133.11, 132.01, 131.96 (C-2, C-6), 128.47, 126.05, 125.58, 125.36, 125.33, (C-3, C-5), 74.98, 72.39, 71.69, 71.52, 70.99, 70.38, (O*CH*$_2$*CH*$_2$O*CH*$_2$*CH*$_2$O), 32.49, 32.29, (C-7), 32.40, 31.62 (C-8), 31.97 (Ar*CH*$_2$Ar), 22.10 (CO*CH*$_3$) ppm. LC-MS: *m*/*z* = 871.7 (calcd. for [**2** + Na^+]: 871.53). $C_{54}H_{73}O_{8.5}$ (**2**·0.5H_2O, 857.53): calcd. C 75.63, H 8.58; found C 75.64, H 8.55.

Synthesis of 3: NaH (0.02 g, 0.8 mmol) was added to a solution of **1** (0.20 g, 0.25 mmol) in THF (70 mL) and the reaction mixture was refluxed. After 30 min of reflux, a solution (10 mL) of acetyl bromide (0.5 mL, 7.0 mmol) in THF was added dropwise to the reaction mixture and refluxing was continued. After 6 h, the solution was cooled to room temperature, filtered and the solvent of the filtrate was removed by rotary evaporation. The residue was treated with 2 N HCl (50 mL), the mixture filtered and the solid mass washed twice with water (25 mL each time). The product thus obtained was recrystallised from dichloromethane/acetonitrile. Yield: 0.16 g (81%). ^{1}H NMR (200 MHz, [D_3]chloroform): δ = 7.06 (s, 4 H, ArH), 6.48 (s, 4 H, ArH), 4.28–4.06 (m, 8 H, crown-*CH*$_2$), 3.90 (d, *J* = 12.8 Hz, 4 H, Ar*CH*$_2$Ar), 3.77–3.61 (m, 8 H, crown-*CH*$_2$), 3.12 (d, *J* = 12.8 Hz, 4 H, Ar*CH*$_2$Ar), 2.56 (s, 6 H, O*CH*$_3$), 1.25 (s, 18 H, *t*Bu), 0.78 (s, 18 H, *t*Bu) ppm. ^{13}C NMR: δ = 171.39 (*CO*CH_3), 154.95, 152.44 (C-1), 146.66, 145.43 (C-4), 135.53 (C-2), 132.16 (C-6), 126.68, 125.51 (C-3, C-5), 74.02, 73.62, 71.89, 71.57 (O*CH*$_2$*CH*$_2$O*CH*$_2$*CH*$_2$O), 32.42, 31.82, 31.74 (C-7, C-8), 32.04 (Ar*CH*$_2$Ar), 22.25 (CO*CH*$_3$) ppm. LC-MS: *m*/*z* = 913.53 (calcd. for [**3** + Na^+]: 913.52). $C_{56}H_{76}O_{10}$ (**3**·H_2O, 908.52): calcd. C 74.03, H 8.43; found C 74.12, H, 8.07.

Synthesis of 4: A mixture of **1** (0.20 g, 0.25 mmol) and K_2CO_3 (0.08 g, 0.53 mmol) in 70 mL of acetonitrile was refluxed with stirring for 3 h, then ethyl bromoacetate (0.09 g, 0.53 mmol) was added dropwise and refluxing was continued for 24 h. The reaction mixture was then cooled to room temperature, treated with 5% HCl (50 mL) and extracted with 50 mL of dichloromethane. The organic layer thus obtained was washed twice with water (50 mL in each time) and the solvent was removed by rotary evaporation. The crude product was recrystallised from dichloromethane/acetonitrile. Yield: 0.18 g (71%). ^{1}H NMR (200 MHz, [D_3]chloroform): δ = 6.84 (s, 4 H, ArH), 6.74 (s, 4 H, ArH), 5.07 (s, 4 H, O*CH*$_2$CO), 4.65 (d, *J* = 12.6 Hz; 4 H, Ar*CH*$_2$Ar), 4.20–4.05 (m, 8 H, crown-*CH*$_2$), 3.76–3.66 (m, 8 H, crown-*CH*$_2$), 3.17 (d, *J* = 12.6 Hz, 4 H, Ar*CH*$_2$Ar), 1.21 (t, *J* = 6.8 Hz, 6 H, CH_3), 1.13 (s, 18 H, *t*Bu), 1.01 (s, 18 H, *t*Bu) ppm. ^{13}C NMR: δ = 171.53 (OCH$_2$*CO*OCH$_2$CH$_3$) 153.98, 152.79 (C-1), 145.28, 145.13 (C-4), 134.67 (C-2), 134.09 (C-6), 125.46 (C-3, C-5), 73.40, 71.81, 71.49, 71.18, (O*CH*$_2$*CH*$_2$O*CH*$_2$-*CH*$_2$O), 70.98 (O*CH*$_2$COOCH$_2$CH$_3$), 60.69 (OCH$_2$COO*CH*$_2$CH$_3$), 34.37, 34.25 (C-7), 32.68 (Ar*CH*$_2$Ar), 32.18, 31.83 (C-8), 14.82 (OCH$_2$COOCH$_2$*CH*$_3$) ppm. LC-MS: *m*/*z* = 1001.58 (calcd. for [**4** + Na^+]: 1001.57). $C_{60}H_{86}O_{13}$ (**4**·2H_2O, 1014.6): calcd. C 71.03, H 8.54; found C 71.01, H, 8.46.

Synthesis of 5: An aqueous solution (0.25 mL) of NaOH (15%) was added to an ethanolic solution (70 mL) of **4** (0.10 g, 0.1 mmol) and the reaction mixture was heated under reflux. After 24 h, it was cooled to room temperature and the solvent was removed by rotary evaporation. Then, 50 mL of cold water was added to the solid mass and 30% HCl was added dropwise with vigorous stirring until the pH of the solution reached 1. The solid product thus produced was isolated by filtration. The crude product was then dissolved in chloroform (50 mL) and washed with HCl (30%) followed by concentrated brine. The organic layer was separated, the solvent removed, and the product dried in vacuo. Yield: 0.065 g (70%). ^{1}H NMR (200 MHz, [D$_3$]chloroform): δ = 7.12 (s, 4 H, ArH), 6.60 (s, 4 H, ArH), 5.29 (s, 4 H, O*CH$_2$*CO), 4.37 (d, *J* = 12.0 Hz, 4 H, Ar*CH$_2$*Ar), 4.08–3.85 (m, 16 H, crown-CH$_2$), 3.27 (d, *J* = 12.0 Hz, 4 H, Ar*CH$_2$*Ar), 1.33 (s, 18 H, *t*Bu), 0.83 (s, 18 H, *t*Bu) ppm. ^{13}C NMR: δ = 172.99 (OCH$_2$*CO*OH), 153.69, 152.18 (C-1), 146.69, 146.19 (C-4), 135.49 (C-2), 132.89 (C-6), 126.39, 126.19 (C-3, C-5), 74.09, 71.13, 71.07, 70.99 (O*CH$_2$CH$_2$*O*CH$_2$CH$_2$*O), 70.44 (O*CH$_2$*-COOH), 34.89, 34.39 (C-7), 32.89 (Ar*CH$_2$*Ar), 32.39, 31.99 (C-8) ppm. LC-MS: *m*/*z* = 945.52 (calcd. for [**5** + Na$^+$]: 945.51). $C_{56}H_{80}O_{14}$ (**5**·3H$_2$O, 976.51): calcd. C 68.87, H 8.26; found C 69.14, H, 8.32.

General Procedure for the Synthesis of Na$^+$ and K$^+$ Complexes of 1–5: A mixture of 0.05 mmol of the required ionophore (**1**–**5**) and Na$^+$/K$^+$ picrate (0.5 mmol, ten-fold excess) was stirred in chloroform at room temperature for 24 h. The reaction mixture was then filtered to remove unreacted picrate salt and the complex was obtained by removing the solvent from the filtrate by rotary evaporation. The yellow complex thus obtained was dissolved in a minimum amount (ca. 3 mL) of dichloromethane (in which Na$^+$/K$^+$ picrate is almost insoluble) and filtered to remove trace quantities of unreacted Na$^+$/K$^+$ picrate. The solvent was then removed from the filtrate and the yellow product was dried in vacuo. The ^{1}H NMR spectra of the product did not show any signal corresponding to free ligand or excess picrate anion. Yield: 90–95%.

Sodium Complex of 1 (1·Na$^+$Pic$^-$): ^{1}H NMR (200 MHz, [D$_3$]chloroform): δ = 8.69 (s, 2 H, picrate), 7.03 (s, 2 H, OH), 7.03 (s, 4 H, ArH), 6.73 (s, 1 H, ArH), 6.63 (s, 3 H, ArH), 4.22–4.16 (m, 12 H, Ar*CH$_2$*Ar and crown-*CH$_2$* overlapped), 3.98–3.80 (m, 8 H, crown-*CH$_2$*), 3.30 (d, *J* = 13.6 Hz, 4 H, Ar*CH$_2$*Ar), 1.29 (s, 18 H, *t*Bu), 1.20 (s, 3 H, *t*Bu), 0.92, 0.83 (s, 15 H, *t*Bu) ppm. ^{13}C NMR: δ = 150.15, 148.15 (C-1), 143.27, 142.18 (C-4), 132.61 (C-2), 128.62 (C-6), 127.50 (C-3), 126.35 (C-5), 125.99 (picrate), 75.84, 71.27, 70.24 (O*CH$_2$CH$_2$*O*CH$_2$CH$_2$*O), 34.59 (C-7), 32.40, 32.24, 31.60 (C-8), 31.93 (Ar*CH$_2$*Ar) ppm. LC-MS: *m*/*z* = 829.10 (calcd. for [**1** + Na$^+$]: 829.50). $C_{58}H_{72}N_3NaO_{14}$ (1057.51): calcd. C 65.84, H 6.85, N 3.96; found C 65.46, H, 6.49, N 3.68.

Potassium Complex of 1 (1·K$^+$Pic$^-$): ^{1}H NMR (200 MHz, [D$_3$]chloroform): δ = 8.70 (s, 2 H, picrate), 7.05 (s, 2 H, OH), 7.05 (s, 4 H, ArH), 6.74, (s, 1 H, ArH), 6.61 (s, 3 H, ArH), 4.37–4.18 (m, 12 H, Ar*CH$_2$*Ar and crown-*CH$_2$*), 3.90–3.73 (m, 8 H, crown-*CH$_2$*), 3.30 (d, *J* = 13.8 Hz, 4 H, Ar*CH$_2$*Ar), 1.30 (s, 18 H, *t*Bu), 1.20 (s, 3 H, *t*Bu), 0.93 (s, 3 H, *t*Bu), 0.81 (s, 12 H, *t*Bu) ppm. ^{13}C NMR: δ = 50.35, 148.17 (C-1), 143.74, 142.15 (C-4), 132.65 (C-2), 129.03 (C-6), 127.74 (C-3), 126.55 (C-5), 125.89 (picrate), 75.75, 71.56, 71.35, 70.14 (O*CH$_2$CH$_2$*O*CH$_2$CH$_2$*O), 34.69, 34.59 (C-7), 32.43, 32.26, 31.62 (C-8), 31.85 (Ar*CH$_2$*Ar) ppm. LC-MS: *m*/*z* = 845.41 (calcd. for [**1** + K$^+$]: 845.50). $C_{58}H_{72}KN_3O_{14}$ (1073.5): calcd. C 64.89, H 6.76, N 3.91; found C 65.15, H 6.54, N 3.67.

Sodium Complex of 2 (2·Na$^+$Pic$^-$): ^{1}H NMR (200 MHz, [D$_3$]chloroform): δ = 8.78 (s, 2 H, picrate), 7.05 (s, 2 H, ArH), 6.98 (s, 2 H, ArH), 6.66 (br., 2 H, ArH), 6.63 (br., 2 H, ArH), 4.30–3.62 (m, 20 H, ArCH$_2$, crown-CH$_2$), 3.30 (d, *J* = 12.8 Hz, 4 H, ArCH$_2$), 2.27 (s, 3 H, OCH$_3$), 1.35 (s, 9 H, *t*Bu), 1.30 (s, 9 H, *t*Bu), 0.82 (s, 18 H, *t*Bu) ppm. ^{13}C NMR: δ = 171.36 (*CO*CH$_3$), 150.34, 150.06, (C-1), 148.59, 148.00 (C-4), 132.55 (C-2), 128.51 (C-6), 127.22, 126.44 (C-3, C-5), 125.85 (picrate), 75.88, 71.93, 71.21, 70.22 (O*CH$_2$CH$_2$*-O*CH$_2$CH$_2$*O), 34.57, 32.20 (C-7), 32.30, 31.51 (C-8), 31.83 (Ar-*CH$_2$*Ar), 21.74 (CO*CH$_3$*) ppm. LC-MS: *m*/*z* = 871.9 (calcd. for [**2** + Na$^+$]: 871.53). $C_{60}H_{76}N_3NaO_{16}$ (with H$_2$O, 1117.5): calcd. C 64.49, H 6.86, N 3.76; found C 64.23, H 6.88, N 3.57.

Potassium Complex of 2 (2·K$^+$Pic$^-$): ^{1}H NMR (200 MHz, [D$_3$]chloroform): δ = 8.72 (s, 2 H, picrate), 7.20 (s, 1 H, ArH), 7.08 (s, 1 H, ArH), 7.06 (s, 2 H, ArH), 6.79 (s, 1 H, OH), 6.64–6.56 (m, 4 H, ArH), 4.16–3.46 (m, 20 H, ArCH$_2$, crown-CH$_2$), 3.33–3.19 (m, 4 H, ArCH$_2$), 2.90 (s, 3 H, OCH$_3$), 1.34 (s, 9 H, *t*Bu), 1.30 (s, 9 H, *t*Bu), 0.83 (s, 18 H, *t*Bu) ppm. ^{13}C NMR: δ = 174.56 (*CO*CH$_3$),150.56, 150.33 (C-1), 147.88, 146.28 (C-4), 132.80 (C-2), 128.75 (C-6), 127.49, 126.31 (C-3, C-5), 125.73 (picrate), 75.01, 72.39, 71.44, 70.43 (O*CH$_2$CH$_2$*O*CH$_2$CH$_2$*O), 34.46, 32.48 (C-7), 32.28, 31.56 (C-8), 31.85 (Ar*CH$_2$*Ar), 21.82 (CO*CH$_3$*) ppm. LC-MS: *m*/*z* = 887.57 (calcd. for [**2** + K$^+$]: 887.53). $C_{60}H_{74}KN_3O_{15}$ (1115.5): calcd. C 64.60, H 6.69, N 3.76; found C 65.13, H 6.37, N 3.85.

Sodium Complex of 3 (3·Na$^+$Pic$^-$): ^{1}H NMR (200 MHz, [D$_3$]chloroform): δ = 8.82 (s, 2 H, picrate), 7.16 (s, 4 H, ArH), 6.53 (s, 4 H, ArH), 4.28–3.72 (m, 20 H, ArCH$_2$, crown-CH$_2$), 3.35 (d, *J* = 13.0 Hz, 4 H, ArCH$_2$), 2.61 (s, 6 H, OCH$_3$), 1.26 (s, 18 H, *t*Bu), 0.75 (s, 18 H, *t*Bu) ppm. ^{13}C NMR: δ = 171.58 (*CO*CH$_3$), 151.77, 151.51 (C-1), 146.64, 144.50 (C-4), 135.67 (C-2), 132.38 (C-6), 127.20 (picrate), 126.71, 125.88 (C-3, C-5), 75.23, 71.98, 71.17, 70.53 (O*CH$_2$CH$_2$*O*CH$_2$CH$_2$*O), 34.70, 32.32, 32.20, 31.93 (C-7, C-8), 31.49 (Ar*CH$_2$*Ar), 21.34 (CO*CH$_3$*) ppm. LC-MS: *m*/*z* = 914.0 (calcd. for [**3** + Na$^+$]: 913.52). $C_{62}H_{77}N_3NaO_{16.5}$ (with 0.5H$_2$O, 1150.5): calcd. C 64.73, H 6.75, N 3.65; found C 64.75, H, 6.92, N 3.32.

Sodium Complex of 4 (4·Na$^+$Pic$^-$): ^{1}H NMR (200 MHz, [D$_3$]chloroform): δ = 8.80 (s, 2 H, picrate), 7.10 (s, 4 H, ArH), 7.04 (s, 4 H, ArH), 4.77 (s, 4 H, O*CH$_2$*CO), 4.48 (d, *J* = 12.4 Hz, 4 H, Ar-*CH$_2$*Ar), 4.32 (q, *J* = 7.4 Hz, 4 H, O*CH$_2$*CH$_3$), 4.09 (m, 4 H, crown-*CH$_2$*), 3.86 (br., 12 H, crown-*CH$_2$*), 3.36 (d, *J* = 12.2 Hz, 4 H,Ar), 1.33 (t, *J* = 7.0 Hz, 6 H, OCH$_2$*CH$_3$*), 1.13 (s, 18 H, *t*Bu), 1.10 (s, 18 H, *t*Bu) ppm. ^{13}C NMR: δ = 171.44 (OCH$_2$*CO*OCH$_2$CH$_3$) 151.85, 150.53 (C-1), 148.78, 148.23 (C-4), 134.73 (C-2, C-6), 127.16 (picrate), 126.60 (C-3, C-5), 77.04, 73.93, 71.27, 70.33, (O*CH$_2$CH$_2$*-O*CH$_2$CH$_2$*O), 70.57 (O*CH$_2$*COOCH$_2$CH$_3$), 62.60 (OCH$_2$-COO*CH$_2$*CH$_3$), 34.83, 34.80 (C-7), 31.95 (C-8), 31.10 (Ar*CH$_2$*Ar), 14.84 (OCH$_2$COOCH$_2$*CH$_3$*) ppm. LC-MS: *m*/*z* = 1001.57 (calcd. for [**4** + Na$^+$]: 1001.57). $C_{66}H_{84}N_3NaO_{18}$ (1229.6): calcd. C 64.47, H 6.89, N 3.42; found C 64.77, H 6.88, N 3.66.

Potassium Complex of 4 (4·K$^+$Pic$^-$): ^{1}H NMR (200 MHz, [D$_3$]chloroform): δ = 8.82 (s, 2 H, picrate), 7.10 (s, 4 H, ArH), 7.06 (s, 4 H, ArH), 4.57 (s, 4 H, O*CH$_2$*CO), 4.46 (d, *J* = 12.2 Hz, 4 H, Ar-*CH$_2$*Ar), 4.32 (q, *J* = 7.4 Hz, 4 H, O*CH$_2$*CH$_3$), 4.40–3.84 (m, 16 H, crown-*CH$_2$*), 3.36 (d, *J* = 12.6 Hz, 4 H, Ar*CH$_2$*Ar), 1.33 (t, *J* = 6.8 Hz, 6 H, CH$_3$), 1.13 (s, 18 H, *t*Bu), 1.10 (s, 18 H, *t*Bu) ppm. ^{13}C NMR: δ = 170.76 (OCH$_2$*CO*OCH$_2$CH$_3$) 151.76, 151.12 (C-1), 148.31, 147.74 (C-4), 134.47, 134.37 (C-2, C-6), 127.17 (picrate), 126.68 (C-3, C-5), 77.13, 73.87, 71.50, 70.64, (O*CH$_2$CH$_2$*O*CH$_2$-*CH$_2$*O), 70.57 (O*CH$_2$*COOCH$_2$CH$_3$), 62.63 (OCH$_2$COO*CH$_2$*CH$_3$), 34.79 (C-7), 31.97 (C-8), 30.16 (Ar*CH$_2$*Ar), 14.86 (OCH$_2$-COOCH$_2$*CH$_3$*) ppm. LC-MS: *m*/*z* = 1017.1 (calcd. for [**4** + K$^+$]: 1017.6). $C_{66}H_{84}KN_3O_{18}$ (1245.6): calcd. C 63.66, H 6.79, N 3.37; found C 64.15, H, 6.94, N 3.40.

Sodium Complex of 5 (5·Na^+Pic^-): ^{1}H NMR (200 MHz, [D_3]chloroform): δ = 8.85 (s, 2 H, picrate) 7.06 (s, 4 H, ArH), 7.10 (s, 4 H, ArH), 4.65 (s, 4 H, OCH_2CO), 4.43 (d, J = 12.0 Hz, 4 H, $ArCH_2$), 4.08–3.86 (m, 16 H, crown-CH_2), 3.36 (d, J = 12.0 Hz, 4 H, $ArCH_2$), 1.14 (s, 18 H, *t*Bu), 1.11 (s, 18 H, *t*Bu) ppm. ^{13}C NMR: δ = 172.23 (OCH_2*CO*OH), 151.61, 150.18 (C-1), 148.77, 148.24 (C-4), 134.75 (C-2, C-6), 126.69 (picrate), 126.60, 126.49 (C-3, C-5), 74.03, 71.45, 70.68, 69.96 (O*CH*$_2$*CH*$_2$O*CH*$_2$*CH*$_2$O), 68.25 (O*CH*$_2$-COOH), 34.81, 34.74 (C-7), 31.93, 31.89 (C-8) 30.37 (Ar*CH*$_2$Ar) ppm. LC-MS: m/z = 945.0 (calcd. for [**5** + Na^+]: 945.51). $C_{62}H_{78}N_3NaO_{19}$ (with H_2O, 1191.5): calcd. C 62.50, H 6.60, N 3.52; found C 62.67, H, 6.75, N 3.64.

Potassium Complex of 5 (5·K^+Pic^-): ^{1}H NMR (200 MHz, [D_3]chloroform): δ = 8.87 (s, 2 H, picrate), 7.12 (s, 4 H, ArH), 7.04 (s, 4 H, ArH), 4.65 (s, 4 H, OCH_2CO), 4.47 (d, J = 12.0 Hz, 4 H, $ArCH_2$), 4.07–3.82 (m, 16 H, crown-CH_2), 3.36 (d, J = 12.2 Hz, 4 H, $ArCH_2$), 1.17 (s, 18 H, *t*Bu), 1.07 (s, 18 H, *t*Bu) ppm. ^{13}C NMR: δ = 171.50 (OCH_2*CO*OH), 153.81, 152.13 (C-1), 148.43 (C-4), 134.56, 134.38 (C-2, C-6), 126.83, 126.63 (picrate, C-3, C-5), 74.05, 71.62, 70.69, 70.32 (O*CH*$_2$*CH*$_2$O*CH*$_2$*CH*$_2$O), 68.72, (O*CH*$_2$-COOH), 34.77 (C-7), 32.01, 31.90 (C-8) 30.37 (Ar*CH*$_2$Ar) ppm. LC-MS: m/z = 961.57 (calcd. for [**5** + K^+]: 961.51). $C_{62}H_{78}KN_3O_{19}$ (with H_2O, 1207.5): calcd. C 61.67, H 6.51, N 3.48; found C 61.16, H, 6.80, N 3.24.

Determination of Selectivity of the Ionophores: The selectivity of the ionophores towards Na^+, K^+, Mg^{2+}, and Ca^{2+} was determined using an equimolar mixture of the picrate salts of these ions according to a procedure described in the literature.[9] In a typical procedure, equal volumes (15 mL) of an aqueous solution of an equimolar mixture of picrate salts (Na^+, K^+, Mg^{2+}, Ca^{2+}; 0.005 M each) and a CH_2Cl_2 solution (15 mL) of the required ionophore (0.005 M) were mixed and vigorously shaken in a vortex mixer for 15 min. The solution was then transferred to a separating funnel and allowed to stand for 4–5 h. The dichloromethane layer was then separated and transferred to a crucible, stripped of solvent by gentle heating in a water bath, and then heated in a furnace at 550 °C for 4–5 h. The residue was dissolved in deionized water (ca. 5 mL) and filtered through 0.2-μm filter paper. The relative concentrations of the cations in the filtrate were determined by ion chromatography on an Ion Pac CS12 (2 mm) analytical column and 20 mM methylsulfonic acid as eluent with a flow rate of 0.25 mL min^{-1}. Quantification was made using a standard solution containing a mixture of NaCl, KCl, $MgCl_2$, and $CaCl_2$ (15 ppm each). A blank experiment, without added ionophore, was carried out under similar experimental conditions; no detectable amount of picrate was observed in the dichloromethane layer.

Determination of Association Constants (K_a) with Na^+ and K^+ Picrate: Association constants of the ionophores **1**–**5** with Na^+ and K^+ were determined according to a published procedure using picrate as anion.[17,18] This involves two-phase (water/chloroform) extraction of the metal complex followed by determination of the ratios of picrate to host (R) in the organic phase and determination of the distribution constants (K_d) of the picrate salts between water and chloroform [Equations (1)–(3)].

Determination of Molar Ratio of Picrate/Host in the Organic Layer (R): Aqueous solutions were prepared that were 0.01 M in the picrate of Na^+ and K^+. Into each of two 10-mL centrifuge tubes was transferred 1 mL of the appropriate picrate solution with a syringe; 1-mL aliquots of a previously prepared chloroform solution that was 0.01 M in host were then added with a syringe to each tube. The tube was covered immediately with a rubber septum to prevent evaporation and the two layers in each tube were mixed thoroughly with a Vortex Genie mixer for 5 min. The tubes were then placed in a centrifuge for 15 min. Aliquots of 0.5 mL of the organic phase were carefully removed from each phase with a syringe and transferred to a 10-mL volumetric flask, which was brought to the mark with acetonitrile. The absorbance of each sample was then determined (λ = 380 nm) after appropriate dilution (to make absorbance within measuring limit). The molar ratio of picrate/host (R) was then calculated from Equation (2).

Determination of Distribution Constants (K_d) of Picrate Anion: A 0.02 M metal picrate solution in 100 mL of water was added to 100 mL of chloroform and the mixture was shaken in a separating funnel for 5–6 h. The layers of the mixture were then allowed to separate overnight (ca. 12 h). The lower layer (chloroform) was then carefully transferred into a round-bottomed flask and the solvent evaporated with a rotary evaporator. The residue was quantitatively transferred with acetonitrile to a 10-mL volumetric flask and diluted with acetonitrile up to the mark. The absorbance of the organic layer was measured spectrophotometrically and the value of K_d was determined from Equation (3).

X-ray Crystallography for 1–4, 1·K^+Pic^-, 4·Na^+Pic^-, 4·K^+Pic^- and 5·K^+Pic^-: Crystal data collection and refinement parameters for all eight compounds are given in Table 5. A suitable crystal of each compound was selected, coated with Paratone oil and mounted with epoxy cement on the tip of a fine glass fibre. Data sets were obtained with a Bruker Smart APEX diffractometer with a CCD area detector using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at liquid nitrogen temperature (100 K). Data frames were processed using the Bruker SAINT program.[21] Intensities were corrected for Lorentz, polarisation, decay effects and an absorption correction was applied using SADABS.[22] The structure was solved by direct methods using SHELXS-97[23] and refined on F^2 using SHELXL-97.[24] The non-hydrogen atoms were located directly by successive Fourier calculations and were refined anisotropically in all the solvated ligand structures except for **2**. In **2**, three of the *tert*-butyl groups attached to the phenyl rings were found to be disordered over two positions (with occupancy factor 0.50) and these disordered *tert*-butyl groups were refined only isotropically. In the case of **1**·K^+Pic^-, the lattice THF molecule is disordered extensively, and in the case of **4**·K^+Pic^- two of the *tert*-butyl groups, the lattice solvent molecules (benzene and THF) and the nitrate groups of the picrate anions showed dynamic disorder; all these disordered atoms were refined isotropically. Since it was very difficult to determine the dynamic disorder present in both the *tert*-butyl groups and lattice solvent molecules, these disorders were taken care of by assigning a tentative occupancy factor for the reasonably good peaks appearing in the difference Fourier map depending upon their peak heights. Anisotropic full-matrix refinement of all atoms, except the disordered atoms, was carried out using SHELXL-97 until convergence was reached (no significant peaks in the difference Fourier map). The inclusion of all the disordered atoms with the occupancy factor tentatively assigned, depending upon the peak height, significantly reduced the refinement parameters, thus implying the correct treatment of the disorder; a constrained or rigid model refinement was not possible in this case. In the case of **4**·Na^+Pic^-, it was not possible to locate the picrate anions and severely disordered solvents (THF and toluene from which crystals for X-ray study were grown) present in the lattice from the difference Fourier map. A suitable disorder model was not obtained and the picrate anion and solvent contribution was subtracted from the reflection data using the program SQUEEZE.[25] A combination of SQUEEZE and PLATON was applied to resolve severely disordered molecules of solvents (THF and toluene) within the asymmetric unit, which also contains one

Table 5. Experimental data for the X-ray diffraction studies on single crystals of **1**–**4**, **1**·K^+Pic^-, **4**·Na^+Pic^-, **4**·K^+Pic^-, and **5**·K^+Pic^-.

Compound	**1**	**2**	**3**	**4**	**1**·K^+Pic^-	**4**·Na^+Pic^-	**4**·K^+Pic^-	**5**·K^+Pic^-
Empirical formula	$C_{108}H_{142}N_2O_{14}$	$C_{58}H_{51}N_2O_8$	$C_{76}H_{84}N_3O_9$	$C_{64}H_{88}N_2O_{11}$	$C_{62}H_{72}KN_3O_{15}$	$C_{60}H_{82}NaNO_{12}$	$C_{82}H_{70}KN_3O_{19}$	$C_{62}H_{58}N_3KO_{19}$
Formula mass	1692.24	904.01	1133.68	1061.36	1138.33	1002.25	1440.51	1188.21
a [Å]	12.2085(12)	20.9878(13)	14.3741(9)	12.9539(9)	12.4879(11)	13.570(3)	15.4140(12)	19.1372(13)
b [Å]	35.618(4)	12.7867(8)	14.7658(9)	13.7659(9)	15.1378(13)	32.711(8)	20.1863(16)	16.0996(12)
c [Å]	46.261(5)	21.2898(13)	17.2358(11)	16.9973(11)	16.1659(14)	19.403(5)	24.673(2)	20.0525(14)
α [°]	90	90	66.2500(10)	82.6790(10)	92.793(2)	90	90	90
β [°]	90	111.2090(10)	78.6250(10)	88.1120(10)	94.146(2)	105.859(5)	97.7120(10)	97.772(2)
γ [°]	90	90	67.2500(10)	80.4720(10)	100.515(2)	90	90	90
Z	8	4	2	2	2	4	4	4
V [Å^3]	20116(4)	5326.4(6)	3084.2(3)	2964.6(3)	2990.8(4)	8285(3)	7607.6(10)	6121.5(8)
Crystal system	orthorhombic	monoclinic	triclinic	triclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	*Pbca*	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	*P*21/*n*	*P*21/*n*	*P*21/*c*
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
$\rho_{calcd.}$ [g cm^{-3}]	1.118	1.127	1.221	1.189	1.264	0.804	1.258	1.289
μ [mm^{-1}]	0.073	0.075	0.205	0.080	0.157	0.059	0.143	0.162
F(000)	7328	1908	1212	1148	1208	2164	3032	2488
Temp. [K]	100	100	100	100	100	100	100	100
Rflns collected/unique	60303/13142	20483/6939	18195/13407	25645/13342	18244/13194	39935/14475	44443/17616	24283/7976
R(int)	0.1332	0.0247	0.0172	0.0160	0.0247	0.0981	0.0367	0.084
GOF on F^2	1.065	1.195	1.013	1.038	1.009	0.856	1.044	1.073
R_1/wR_2 ($[I>2\sigma(I)]$	0.1203/ 0.2972	0.0764/ 0.2149	0.0651/ 0.1669	0.0518/ 0.1427	0.0665/ 0.1633	0.0910/ 0.2134	0.0945/ 0.2720	0.1180/ 0.3039
R_1/wR_2 (all data)	0.1867/ 0.3498	0.0816/ 0.2184	0.0809/ 0.1801	0.0592/ 0.1492	0.0908/ 0.1778	0.1527/ 0.2404	0.1360/ 0.3056	0.1631/ 0.3356

crystallographically independent picrate anion. Within the 3460 Å^3 void space occupied by solvent molecules and the unresolved anion, a total of 810 electrons were calculated per unit cell. After correction for the one unresolved counteranion per asymmetric unit, corresponding to 115 electrons, the rest of the electron density per asymmetric unit (87.6) can be equated for by the presence of approximately one molecule of THF and one molecule of toluene in the asymmetric unit. A refinement using reflections modified by the SQUEEZE procedure behaved well, and the geometry of **4**·Na^+Pic^- and, of course, the *R* factors and GOF values were significantly improved. H atoms (except for the H atoms attached to the disordered non-hydrogen atoms and some of the lattice solvent hydrogen atoms) were calculated on the basis of geometric criteria and were treated with a riding model in subsequent refinements using the SHELXL default parameters. The molecular graphics of the crystal structures were generated using ORTEP, PLATON and Mercury.[26–28] CCDC-297554 to -297561 (for complexes **1**–**4**, **1**·K^+Pic^-, **4**·Na^+Pic^-, **4**·K^+Pic^-, and **5**·K^+Pic^-, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information Available (see footnote on the first page of this article): Tables S1 and S2 contain hydrogen-bonding parameters of the ionophores and metal complexes, respectively. Figures S1–S7 show packing diagrams of **2**–**4**, **1**·K^+Pic^-, **4**·Na^+Pic^-, **4**·K^+Pic^-, and **5**·K^+Pic^-, respectively.

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