

New Metal Cation-Selective Ionophores Derived from Calixarenes: Their Syntheses and Ion-Binding Properties

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Various derivatives (ethoxycarbonylmethyl, carboxymethyl, and ethoxyethyl, *etc.*) of calix[4]arene, calix[6]arene, and calix[8]arene have been synthesized and their ion-binding properties investigated by solvent extraction, ion-transport through liquid membranes, and u.v. spectroscopy. The extraction of various metal ions (as picrate salts) from the aqueous phase into dichloromethane by the calixarene derivatives showed that the ethoxycarbonylmethyl derivatives exhibited markedly increased extraction efficiency compared with their unsubstituted phenol analogues, and the efficiency was in general comparable to those of crown ethers. The most notable feature was the selectivities exhibited by their ethoxycarbonylmethyl derivatives; calix[4]arene for Na^+ , calix[6]arene for Cs^+ , and calix[8]arene for K^+ . A liquid membrane study with a water-chloroform-water system also indicated that the ion-transport efficiencies exhibited by calixarenes were found to be in accordance with their extraction abilities, confirming the strong participation of the ester carbonyl oxygen in this function. However, the ester derivative of calix[4]arene was an exception in that inefficient carrier activity was observed in spite of high extraction efficiency. The pronounced Cs^+ selectivity exhibited by the calix[6]arene ester was further confirmed by the changes in the u.v. spectrum of the ester from 277 and 270 nm to 275 and 267 nm upon interaction with Cs^+ ion in methanol.

There has been much work on the synthesis and ion-binding properties of macrocyclic multidentate ligands.¹ Further, many attempts have been made to create pseudocavities by introducing specifically interacting functional groups onto podand and polypodand structures.²

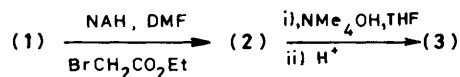
The calixarenes prepared by base-catalyzed condensation of *p*-substituted phenols with formaldehyde are attractive matrices, their phenolic hydroxy groups being ordered in well shaped cyclic arrays^{3,4} which may be functionalized^{5,6} into novel metal ion-complexing blocks.

Although many publications⁷ have dealt with the synthesis and crystal structures of calixarene complexes with molecules such as toluene and acetone, there have been few reports on the complexation properties of these potential ionophores with metal ions.⁸⁻¹⁰ The preliminary results of our study on the podands (**2b**) and (**2c**) as complexing ligands have been already reported.¹¹ These compounds showed higher affinity toward

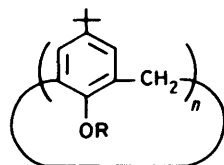
conversion of the phenolic moieties of calixarenes into the corresponding carboxylic acid and carboxylic ester functions, provided further binding sites so situated⁹ as to exhibit interesting complexation characteristics.

Results and Discussion

The syntheses of (**2a-c**) and (**3a-c**) are shown in the Scheme. That alkylation of the phenolic group was complete was shown by the disappearance of the phenoxide absorption band in the



Scheme.



(a) $n = 4$

(b) $n = 6$

(c) $n = 8$

- (1) $R = \text{H}$
 (2) $R = \text{CH}_2\text{CO}_2\text{Et}$
 (3) $R = \text{CH}_2\text{CO}_2\text{H}$
 (4) $R = \text{Me}$
 (5) $R = \text{CH}_2\text{CH}_2\text{OEt}$

alkali metals, with unique selectivities, as compared with the parent calixarenes. Here we report the syntheses and ion-binding properties of new podands containing additional carboxylic acid and carboxylic ester functions which have often been claimed to act as binding sites in the complexation of certain enzymes and antibiotics.¹² In the present work

u.v. spectrum,¹³ although the crude products were found to contain trace impurities on t.l.c.

Unusually, the tetraester (**2a**) was obtained as a sodium bromide complex,¹⁴ as shown by elemental analysis as well as by t.l.c., and was difficult to obtain in salt-free form. Upon treatment with silver nitrate the tetraester solution in methanol turned turbid, indicating the presence of bromide ion. Attempts to prepare the ester (**2a**) by employing other bases, such as potassium *t*-butoxide,¹³ instead of NaH resulted in the formation of an unworkable mixture of products as indicated by t.l.c. The incorporation of sodium bromide as a tight complex was also indicated by i.r. spectroscopy. The i.r. spectrum of the sodium bromide complex of (**2a**) exhibited the carbonyl stretching band at 1750 cm^{-1} , which can be compared with those of the free ligands (**2b**) and (**2c**) at 1765 and 1770 cm^{-1} , respectively.

Hydrolysis of the esters to the acids (**3a-c**) was achieved by the use of tetramethylammonium hydroxide which prevents possible contamination of the resulting carboxylic acids by metallic impurities. Unfortunately, the carboxylic acids thus

Table 1. Extraction of picrate salts with derivatives of calixarenes

Ligand	Fraction of cation extracted (%)						
	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	Ca ²⁺	Ba ²⁺
(1a), (1b), (1c) and (4b)	<1	<1	<1	<1	<1	<1	<1
(2a)-NaBr	48.9	87.7	51.2	41.0	52.8	45.7	47.3
(2b)	6.7	15.6	66.2	60.5	88.9	5.3	8.2
(2c)	<1	4.5	21.5	16.4	17.0	6.4	17.9
(4a)	<1	6.2	3.8	<1	<1	<1	<1
(4c)	<1	<1	<1	<1	2.9	<1	1.7
(5a)	<1	3.8	<1	<1	<1	3.2	2.3
(5b)	<1	2.9	<1	<1	2.6	2.0	2.4
(5c)	2.3	1.3	1.7	1.8	2.7	2.0	3.0
18-crown-6 ^a	<1	4.2	55.5	30.7	20.0		2.1

^a Taken from ref. 25.

obtained have limited solubility in most common organic solvents¹⁵ except alcoholic tetra-alkylammonium hydroxide, and a study of complexation behaviour under the relevant experimental conditions was unsuccessful.

In order to compare the complexation characteristics of the podands (2a–c), the liquid–liquid extraction of alkali metal cations with the picrate ion into dichloromethane by these compounds was performed at 25 °C.¹⁶ The results obtained are summarized together with the values of 18-crown-6 in Table 1. As can be seen from the Table, the extraction efficiencies of ester derivatives of calixarenes (2a–c) vary considerably; the remarkable selectivities are notable. Under the same experimental conditions, the parent calixarenes (1a–c) which have only a phenolic hydroxy group as a complexing site failed to show any significant extraction ability. This suggests the strong participation of the carbonyl oxygen of the side-arm ester functions. An illustrative example of such participation is shown by naturally occurring valinomycin, the particular complexation properties of which arise from its ability to fold its backbone into a precise conformation where its six ester carbonyl groups form a sphere.¹²

The strong participation of the ester carbonyl group in the complexation with metal ions in the present case was further confirmed by the results of extraction experiments with methyl ether derivatives (4a–c). In some cases phenolic ether groups are known to act as good ligands and are an important part of crown ethers;¹⁷ interesting examples have been reported by Cram.¹⁸ Cram's spherands exhibit remarkable selectivities in their complexation with metal ions. Contrary to expectation, however, the ether derivatives (4b) and (4c) exhibited virtually no extraction of metal ions. This result seems to indicate that in the complexation of metal ions by various podands the rigidity of the complexing site and positioning of functional groups are probably more important than the type of ligand involved.

The importance of the ester carbonyl function in complex formation was underlined by the results obtained with (5a–c), which although similar to the preceding compounds contains ether rather than ester groups, and show poor ability in the extraction of metal ions.

As with other ion-selective podands, the selectivities exhibited by the present calixarene esters were strongly dependent on ionic size as indicated by the data in Table 1. This trend is similar to the size selectivity exhibited by typical crown ether type ionophores in that they are generally more selective toward alkali metal ions than alkaline earth metal ions. However, the extraction behaviour of (2a) is rather nonselective, all the cations being extracted to a similar extent except sodium ion. This is because (2a) was already complexed by sodium ion during the preparation of this compound and other cations

Table 2. Transport rates of alkali metal cations by derivatives of calixarenes^a

Ligand	Transport rate (mole × 10 ⁻⁷ h ⁻¹)		
	Na ⁺	K ⁺	Cs ⁺
(1a)	2.0	2.3	1.2
(1b)	1.0	2.5	1.4
(1c)	8.6	3.6	4.0
(2a)-NaBr	140	71	21.9
(2b)	106	473	556
(2c)	25.8	100	75.2
(4a)	4.1	10.9	3.2
(4b)	11.1	10.6	21.2
(4c)	22.5	24.2	20.8

^a The experimental values deviate from the reported values by no more than 10%.

cannot compete with sodium ion in binding with the tetraester. Simple exchange of bromide and picrate ions between the aqueous and organic phase results in all the original sodium remaining in the organic phase, no selectivity being observed.

The extractability of alkali metal picrate ions by various calixarene derivatives decreases in the sequence; Na⁺ > Cs⁺ > K⁺ > Li⁺ > Rb⁺ for (2a); Cs⁺ > K⁺ > Rb⁺ > Na⁺ > Li⁺ for (2b); K⁺ > Rb⁺ > Cs⁺ > Na⁺ > Li⁺ for (2c). It is interesting to note that the order of selectivity exhibited by (2b) follows the unusual sequence found for the acyclic ionophoric antibiotics X-537A.¹²

A further interesting observation was that (2c), which was derived from the largest compound in the calixarene family, showed a puzzling extraction ability toward potassium ion. Gutsche *et al.*³ noted that the cyclic octamer calix[8]arene behaves as though it were a cyclic tetramer or exists in a transannularly pinched conformation which has the superficial aspect of a pair of cyclic tetramers 'stuck' together. With this conformation, the octaester obtained from the octamer occurs similarly in a loosely pinched state and potassium ion can fit snugly into the pseudocavities of this podand. A further plausible explanation could be that above a certain value for ratio of crown ether cavity size to cation size, a conformation with a twisted polyether ring could be formed as was observed in complex formation of monobenzo-26-crown-8 and alkali metal trichloro(ethylene) platinum(II) salts.¹⁹

In order to understand more clearly the ion-binding properties of these new podands we carried out transport experiments with them and found that the transport rate was effectively governed by the metal ion size; this is consistent with the results of extraction experiments. A plot of moles of cation transported *vs.* time was obtained for each system studied and the rates of transport were estimated. Such plots were invariably linear as in other experiments.²⁰ For each cation–ligand pair triplicate determinations were carried out and in no case was transport of the cation across the chloroform membrane detected in the blank runs. This type of transport experiment could not be carried out for carboxylic acid derivatives because precipitates formed. Transport rates are collected in Table 2.

The results of the transport experiments showed a similar trend to that obtained in the extraction experiments, again confirming the unique participation of the ester function in the formation of complexes. However, an unexpected observation was that (2a) did not exhibit efficient transport behaviour, probably because it forms a tight complex with Na⁺, thus becoming resistant to releasing the complexed cation into the outer phase. The podand simply retains the cation in the chloroform layer.²¹

The changes in the u.v. spectrum of the aromatic crown com-

pounds containing the phenolic ether moiety upon the addition of metal salts were used by Pedersen for the qualitative detection of complexation.²² We estimated a qualitative extent of complexation by calixarenes (**2a–c**) with various metal ions by obtaining a u.v. spectrum of this ligand in methanol with a 50-fold excess of salt so as to maximize the possible complexation.

With a caesium ion, the absorption bands of (**2b**) at 277 and 270 nm shifted to 275 and 267 nm, respectively upon complexation, and the degree of shift was parallel with those of dibenzo-18-crown-6-ether.²³ However, with other ions such as barium, potassium, and rubidium which were extracted to a moderate degree, small shifts of <1 nm in the absorption peaks occurred upon complexation, the intensity of the bands being affected somewhat randomly. Also, the u.v. spectra of (**2a**) and (**2c**) were not affected notably upon interaction with various metal ions, indicating that complex formation is not significant enough to change the absorption spectra of the ligands in methanol.

Experimental

M.p.s were taken on a Thomas-Hoover apparatus and were uncorrected. Most of the solvents used were dried by distillation over barium oxide, lithium aluminium hydride, or by storage with a molecular sieve. ¹H N.m.r. spectra were obtained on a Hitachi R-600 spectrometer at 60 MHz using SiMe₄ as an internal standard. I.r. spectra were recorded on a Perkin-Elmer Model 283B spectrophotometer and u.v. spectra were recorded on a Shimadzu UV-240 spectrophotometer. T.l.c. was done on silica gel precoated plates (Merck Silica gel 60 F254). The solvent was dichloromethane–hexane–isopropyl alcohol (16:3:1, by volume). The high temperature melting behaviour of some compounds was examined by Du Pont 990 thermal analyzer.

The calixarenes (**1a–c**) were prepared from the base-catalyzed condensation of *p*-*t*-butylphenol with formaldehyde by the published method.³

The esters (**2a–c**) were prepared generally as follows. A calixarene (1 mmol) was suspended in dry DMF (20 ml) in a flask equipped with a CaCl₂ drying tube and was then treated with NaH (4 mmol). Ethyl bromoacetate (5 mmol) was added and the mixture was stirred at 80 °C. After *ca.* 2 h the reaction mixture was cooled and treated with a second portion of NaH (2 mmol). Ethyl bromoacetate (2.4 mmol) was then added. The mixture was stirred again at 80 °C for a further 2 h. This operation was repeated until no phenolic OH was detectable by the u.v. spectroscopy.¹³ The reaction was also followed by t.l.c. The solvent was evaporated under reduced pressure, and the residue was washed with water and the product extracted with chloroform. The chloroform solution was then dried over 3A molecular sieves, and evaporated to give the solid crude product. Column chromatography on silica gel eluting with dichloromethane–isopropyl alcohol gave the following esters:

(**2a**) (72%), m.p. 208–210 °C, ν_{\max} (KBr) 1750 cm⁻¹; δ (CDCl₃) 7.4–7.0 (8 H, two s at δ 7.15 and 7.3, ArH), 4.8–3.2 (24 H, m, ArCH₂Ar, CH₂CO₂, and CH₂Me), and 1.7–0.8 (48 H, m, CH₂Me and CMe₃ with s at δ 1.2 and t centred at δ 1.4) (Found: C, 65.5; H, 7.6. C₆₀H₈₀O₁₂·NaBr requires C, 65.7; H, 7.4%). (**2b**) (65%), m.p. 252–255 °C, ν_{\max} (KBr) 1765 cm⁻¹; δ (CDCl₃) 7.7–6.4 (12 H, m, ArH), 5.0–3.3 (36 H, m, ArCH₂Ar, CH₂CO₂, and CH₂Me), and 1.7–0.7 (72 H, m, CH₂Me and CMe₃ with s at δ 0.97 and t centred at δ 1.3) (Found: C, 71.3; H, 8.4. C₉₀H₁₂₀O₁₈·H₂O requires C, 71.7; H, 8.2%). (**2c**) (75%), m.p. 200–205 °C, ν_{\max} (KBr) 1770 cm⁻¹; δ (CDCl₃) 6.9 (16 H, s, ArH), 4.4–3.6 (48 H, m, ArCH₂Ar, CH₂CO₂, and CH₂Me), and 1.4–0.8 (96 H, m, CMe₃ and CH₂Me with s at δ 1.1) (Found: C, 71.0; H, 8.2. C₁₂₀H₁₆₀O₂₄·2H₂O requires C, 71.25; H, 8.2%).

Hydrolysis of the Esters.—The ester (1 mmol) in THF (50 ml) was added to 10% aqueous tetramethylammonium hydroxide (50 ml) and heated under reflux for 24 h. After cooling, the reaction mixture was acidified with concentrated HCl and stirred overnight. The resulting precipitate was filtered off, washed thoroughly with water, and dried in an air oven. Yields were quantitative: (**3a**), m.p. >267 °C (decomp.) (lit.,¹⁵ m.p. 264–267 °C); ν_{\max} 1740 (CO) and 3600–2700br cm⁻¹ (OH); δ [(CD₃)₂SO–CDCl₃] 7.0 (8 H, br s, ArH), 4.6–3.8 (16 H, br, ArCH₂Ar and CH₂CO₂H), and 1.2 (36 H, br s, CMe₃). (**3b**), m.p. >250 °C (decomp.); ν_{\max} (KBr) 1735 (CO) and 3600–2700br cm⁻¹ (OH); δ [(CD₃)₂SO–CDCl₃] 6.8–7.4 (12 H, br s, ArH), 4.8–3.6 (24 H, br, ArCH₂Ar and CH₂CO₂H), and 1.2 (54 H, br s, CMe₃). (**3c**), m.p. >255 °C (decomp.); ν_{\max} (KBr) 1735 (CO) and 3600–2700br cm⁻¹ (OH); δ [(CD₃)₂SO–CDCl₃] 6.9 (16 H, s, ArH), 4.3–3.0 (32 H, br, ArCH₂Ar and CH₂CO₂H), and 1.1 (72 H, s, CMe₃).

Methyl ethers (**4a–c**) and ethoxyethyl ethers (**5a–c**) were obtained by the alkylation of calixarenes with dimethyl sulphate and with 2-bromoethyl ether, respectively, in the presence of NaH in DMF, and the crude products were purified by recrystallization from acetonitrile and chloroform–methanol, (**4a**)⁵ (87%), m.p. 238–240 °C; ν_{\max} (KBr) 1210 cm⁻¹; δ (CDCl₃) 6.95 (8 H, s with small sharp shoulder at δ 7.25, ArH), 4.4–2.7 (20 H, br m, CH₂ and OMe), 1.2 (36 H, s, CMe₃) (Found: C, 82.1; H, 8.9. Calc. for C₄₈H₆₄O₄: C, 81.8; H, 9.1%). (**4b**) (82%), m.p. 210–213 °C; ν_{\max} (KBr) 1210 cm⁻¹; δ (CDCl₃) 7.05 (12 H, s, ArH), 4.0 (12 H, s, ArCH₂Ar), 3.0 (18 H, s, OMe), and 1.15 (54 H, s, CMe₃) (Found: C, 80.25; H, 8.7. C₇₂H₉₆O₆·MeOH requires C, 80.5; H, 9.25%). (**4c**)⁹ (90%), m.p. 274–277 °C; ν_{\max} (KBr) 1210 cm⁻¹; δ (CDCl₃) 6.9 (16 H, s, ArH), 4.05 (16 H, s, ArCH₂Ar), 3.4 (24 H, s, OMe), and 1.1 (72 H, s, CMe₃) (Found: C, 79.3; H, 9.6. Calc. for C₉₆H₁₂₈O₈·2MeOH: C, 79.8; H, 9.3%). (**5a**) (85%), m.p. 175–176 °C; ν_{\max} (KBr) 1200 and 1120 cm⁻¹; δ (CDCl₃) 6.8 (8 H, s, ArH), 4.5 (4 H, d, *J* 12 Hz, ArCH₂Ar), 4.2–3.9 (16 H, m, CH₂CH₂), 3.6 (8 H, q, *J* 7 Hz, CH₂Me), 3.2 (4 H, d, *J* 12 Hz, ArCH₂Ar), 1.25 (12 H, t, *J* 7 Hz, CH₂Me), and 1.1 (36 H, s, CMe₃) (Found: C, 76.2; H, 9.9. C₆₀H₈₈O₈ requires C, 76.9; H, 9.5%). (**5b**) (80%), m.p. 242–245 °C ν_{\max} (KBr) 1210, 1200, and 1120 cm⁻¹; δ (CDCl₃) 7.5–6.8 (12 H, br m, ArH), 4.1–3.1 (48 H, br m, ArCH₂Ar, OCH₂CH₂OCH₂), 1.25 (18 H, br, CH₂Me), 1.05 (54 H, s, CMe₃) (Found: C, 74.9; H, 9.4. C₉₀H₁₃₂O₁₂· $\frac{1}{3}$ CHCl₃ requires C, 75.0; H, 9.2%). (**5c**) (85%), m.p. 189–193 °C; ν_{\max} (KBr) 1210 and 1120 cm⁻¹; δ (CDCl₃) 7.0 (16 H, s, ArH), 4.1 (16 H, s, ArCH₂Ar), 3.9–3.1 (48 H, m, CH₂CH₂OCH₂), and 1.4–0.8 (96 H, m, CH₂Me and CMe₃ with s at δ 1.1) (Found: C, 77.5; H, 9.6. C₁₂₀H₁₇₆O₁₆ requires C, 76.9; H, 9.5%).

Extraction Experiment.—A dichloromethane solution of a calixarene (35 × 10⁻⁵M) and an aqueous solution of metal picrate were placed in a centrifuge tube stoppered with a Teflon-lined screw cap and the mixture was shaken for 5 min in a temperature-regulated water bath (25 ± 0.1 °C).¹¹ The mixture was then centrifuged to complete the phase separation before measurements. The metal picrate solution was prepared by mixing metal hydroxides or metal chloride (in case of calcium ion) and picric acid (7 × 10⁻⁵M) in deionized water. The initial volume of each phase was 5 ml in all cases. Concentration of the picrates in the organic and aqueous phases were determined spectrophotometrically and the molar absorptivities reported by Pedersen (λ_{\max} 354 nm; ϵ , 1.5 × 10⁴ in water; and λ_{\max} 378

* Full characterization of this acid was difficult because of its lack of volatility and its poor solubility in solvents. The only way was its conversion to other characterizable derivatives, such as amides and amines, which will be reported in a subsequent publication.

nm; ϵ , 1.8×10^4 in dichloromethane) were used.¹⁶ For each cation-calixarene system three separate measurements were taken to ensure the values.

Transport Experiments.—Transport across the liquid membrane was conducted using apparatus similar to that employed by Lamb *et al.*²⁴ A chloroform solution (80 ml) containing carrier (7×10^{-5} M) was placed at the bottom of the apparatus. On the outer phase was placed deionized water (40 ml) and at the top of the inside of the cylinder was carefully added 0.01M picrate salt solution (10 ml). The chloroform layer was agitated by a stirring bar at the bottom of the cell. Thermolyne synchronous motors provided constant reproducible stirring at 100 r.p.m. The entire apparatus was maintained at $25 \pm 0.5^\circ\text{C}$ using a thermostatted circulator. The appearance of the picrate anion in the outer phase was followed by u.v. spectrometry (λ_{max} , 354 nm; ϵ , 1.5×10^4).

Acknowledgements

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