

Calix (aza-)crowns as potential ionophores for divalent and trivalent cations

Ryszard Ostaszewski^{a,*}, Tieme W. Stevens^b, Willem Verboom^a and David N. Reinhoudt^{a,*}

Laboratories of Organic Chemistry^a and Chemical Analysis^b, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

and

Frans M. Kaspersen

Organon International BV, Scientific Development Group, P.O. Box 20, 5340 BH Oss, The Netherlands

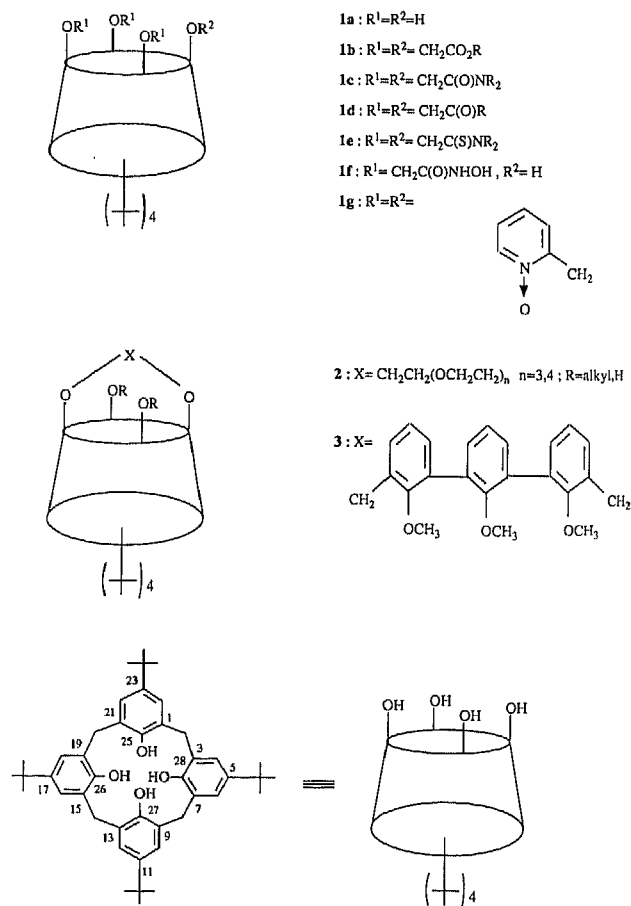
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Abstract. A series of calix (aza-)crowns **6a-f** and **11a,b** has been prepared by reaction of either calix dimethyl ester **4** or calix diacid dichloride **10** with an appropriate diamine. The complexation with both di- and trivalent cations has been qualitatively studied using fast-atom bombardment mass spectrometry.

Introduction

Calixarenes, which are phenol–formaldehyde cyclic oligomers, are becoming an important class of compounds in supramolecular chemistry^{1,2}. One property of this class of compounds is their ability to bind (selectively) cations upon appropriate functionalization of the phenolic OH groups (lower rim). Several calix[4]arenes tetraesters³, tetraamides⁴, and tetraketones⁵ (**1b**, **1c**, and **1d**, respectively) exhibit high affinity for alkali cations; in some cases, high selectivity for Na⁺ has been observed⁶. Only a limited number of lower-rim-functionalized calix[4]arenes are known to be capable of complexation of divalent and trivalent cations. Calix[4]arene tetrathioamides **1e** show strong complexation of heavy- and transition-metal cations, however, no selectivity has been observed⁷. Ungaro et al.⁸ prepared calix[4]arene trihydroxamate **1f**, which exhibits selectivity for Fe³⁺. It has been demonstrated that lanthanides can also be complexed by, for example, tetraamides **1c**⁹ and calix[4]arene derivative **1g** in which the phenolic OH groups are connected with methylpyridine *N*-oxide moieties¹⁰. Functionalization of the upper rim of calix[4]arene with 2-aminoethyl groups at the *para* positions resulted in compounds which showed interaction with several divalent metal ions, such as¹¹ Ni²⁺, Cu²⁺, Co²⁺, and Fe²⁺.

Very recently, we reported the selective 1,3-dialkylation^{12,13} of 4-*tert*-butylcalix[4]arene **1a**, followed by the introduction of a suitable poly(oxyethylene) bridge on the two remaining OH groups, to give the bridged¹⁴ calix[4]arenes **2**. These



* Present address: Institute of Organic Chemistry, Polish Academy of Sciences, 01-224 Warszawa, Kasprzaka 42, Poland.

compounds represent a new class of potassium-selective ionophores¹⁵ with K^+/Na^+ selectivities up to $1.18 \cdot 10^4$. The more rigidly bridged calix spherands **3** gave complexes that are kinetically stable, with Na^+ , K^+ , and Rb^+ . The excellent complexation properties of bridged calix[4]arenes **2**, **3** led us to investigate the poly-(azaethylene)-bridged calix[4]arenes **6** and **11** which, due to the presence of nitrogen atoms in the chain, may form complexes with softer cations. Furthermore, the two free OH groups may also act as a donor site and, in addition, force the calix[4]arenes into the cone conformation^{1,2}. We examine in this report a flexible synthetic method for calix (aza)-crowns **6a-f** and **11a,b** having a varying length of the bridge. We also report a qualitative study on the complexation behaviour of the compounds with a variety of cations, using fast-atom bombardment mass spectrometry (FAB-MS).

Results and discussion

Synthesis

Our strategy for the macrocyclization of the calix (aza)-crowns **6** is based on the reaction between a methyl ester and an amine¹⁶. Dimethyl ester **4**¹⁷ could easily be prepared in quantitative yield by transesterification of the corresponding diethyl ester **5**¹⁹ in methanol in the presence of 4-toluenesulphonic acid. Reaction of dimethyl ester **4** with an appropriate diamine in a 1:1 mixture of methanol and toluene gave the macrocyclic calix aza-crowns **6a-e** in yields varying from 17–90%. The reaction conditions (Table I) strongly depend on the diamine used. Apart from the absence of the original methoxy signals, the ¹H NMR spectra of **6a-e** clearly show a typical AB pattern for the methylene bridge protons (J 13.2–13.5 Hz), indicating the cone conformation. The mass spectra of **6a-e** (both electron impact and FAB) gave the correct molecular ion signals, proving that macrocyclization had taken place. Starting from diethyl ester **5**, bridging could only be achieved upon reaction with 1,2-ethanediamine; attempts with other diamines failed. In a similar way, the corresponding "oxa-bridged" calix[4]arene **6f** was synthesized in 22% yield by the reaction of dimethyl ester **4** with 3,6-dioxaoctane-1,8-diamine.

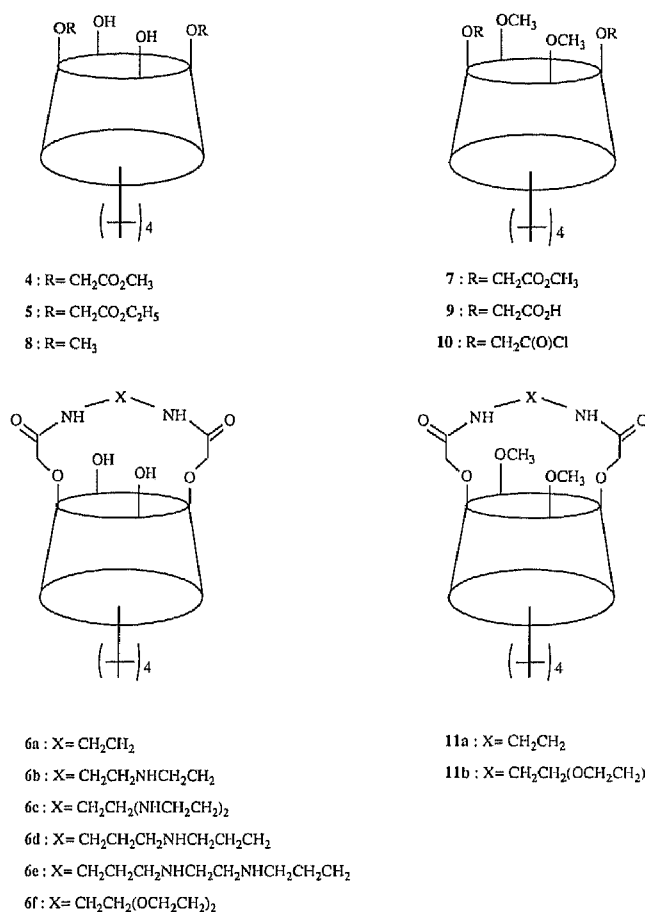


Chart 2

For comparison of complexing properties, the dimethoxy calix (aza)-crowns **11a** and **11b** were prepared²⁰. Reaction of dimethyl ester **4** with methyl iodide in the presence of K_2CO_3 in acetonitrile gave the 1,3-dimethoxy dimethyl ester **7**²¹ in 76% yield, as shown by the mass spectrum and a satisfactory elemental analysis. The ¹H NMR spectrum of **7** exhibits very broad signals, indicating coalescence between conformations. Lowering the temperature to $-30^\circ C$

Table I Reaction times, yields, melting points, and characteristic spectral data of compounds **6a-f**^{a,b}.

Compd.	Reaction time (d)	Yield (%)	M.p. (°C)	¹ H NMR (CDCl ₃), δ					¹³ C NMR (CDCl ₃), δ		FAB-MS ^g
				NH (s)	Ar H (s)	OCH ₂ (s)	ArCH ₂ Ar (ABq) ^c	<i>t</i> -Bu (s)	C=O (s)	OCH ₂ (t)	
6a	3 ^d	90	> 300	8.59	7.05	4.52	4.14 3.46	1.24 1.15	167.7	74.6	788.482 ^f (788.476)
6b	3 ^d	54	181–183	8.39	7.11 6.71	4.48	4.14 3.39	1.32 0.88	168.5	74.7	832.519 (832.526)
6c	3 ^e	55	152–154	8.64	7.11 6.99	4.52	4.21 3.37	1.32 0.88	169.3	75.1	875.565 (875.569)
6d	3 ^e	36	149–150	8.50	7.11 6.70	4.49	4.18 3.37	1.32 0.88	168.7	74.7	860.552 (860.558)
6e	7 ^e	17	155–157	8.40	7.10 6.75	4.53	4.20 3.37	1.31 0.91	168.8	74.8	903.591 (903.599)
6f	10 ^e	22	135–136	8.76	7.12 6.66	4.48	4.19 3.36	1.33 0.86	168.9	75.0	876.524 ^f (876.529)

^a All compounds gave satisfactory element analyses. ^b In IR spectra, C=O absorptions are located at 1665–1680 cm⁻¹. ^c J 13.2–13.5 Hz for ABq. ^d Room temperature. ^e Reflux temperature. ^f M⁺. ^g 3-Nitrobenzyl alcohol as matrix.

revealed the presence of the cone and partial cone conformations in a ratio of 1:2, as followed among others from the characteristic AB pattern for the methylene bridge protons at δ 4.64 and 3.11 (8H, J 15.1 Hz) for the cone and the two characteristic AB patterns¹ at δ 4.25 and 3.17 (4H, J 12.4 Hz) and 3.86 and 3.75 (4H, J 14 Hz) for the partial cone conformation. Saponification of **7**²² using NaOH in refluxing methanol/water gave diacid **9** in 99% yield; the ¹H NMR spectrum of **9** suggests a cone conformation. Subsequent reaction of diacid **9** with oxalyl chloride in CH₂Cl₂ gave the corresponding diacid dichloride **10** in 91% yield which, upon treatment with both 1,2-ethanediamine and 3,6-dioxaoctane-1,8-diamine in the presence of triethylamine under high dilution conditions in benzene, gave the bridged calix[4]arenes **11a,b** in 18% and 10% yield, respectively. The ¹H NMR spectrum of **11a** at room temperature indicates the presence of different conformers, viz. partial cone, cone, and 1,3-alternate in a ratio of 14:5:2, respectively. The cone conformation is concluded from the signals at δ 7.18 and 6.87 (s, Ar H) and the AB pattern at δ 4.26 and 3.28 (J 12.3 Hz) and the 1,3-alternate conformation from the absorptions at δ 7.08 and 7.00 (s, Ar H) and the characteristic singlet of the methoxy groups at δ 2.88 (compare Ref. 23). In the case of both **10** and **11b**, the ¹H NMR spectra show broad signals, again indicating coalescence of conformations. Spectroscopic evidence for the structures of **11a,b** was obtained, for example, from the shift in the carbonyl absorption in the infrared spectra, which moved from 1754 cm⁻¹ (**10**) to 1680 cm⁻¹ (**11a,b**), and a correct molecular ion signal in the mass spectra.

Complexation

The methods used for the investigation of complexation between macrocycles and various metal cations, such as calorimetry, potentiometry, NMR or absorption spectroscopy, are often not general and are rather cumbersome. For the compounds described in this paper, ¹H NMR spectroscopy showed changes in chemical shifts upon addition of a metal salt that were too small to draw definite conclusions about the complexation. Since we were interested in fast, qualitative screening of the complexation abilities of the calix (aza)-crowns **6a-f** and **11a,b**, fast-atom bombardment mass spectrometry (FAB-MS) appeared to be the method of choice. This soft-ionization method has been used for studying (semi-quantitatively) the complexation behaviour of, for example, crown ethers with different cations²⁴ and diazonium ions²⁵, and (bis-mono)aza-crown ethers with alkaline²⁶ and transition metal²⁷ cations. Poly(ethylene glycol) (PEG) 200 was found to be the best matrix for the experiments with the calix (aza)-crowns. A

control experiment showed that the intensity of the molecular ion peak was proportional to the concentration of the calix (aza)-crowns up to 10⁻¹ M and, therefore, the complexation study was performed at a concentration of about 10⁻² M in dioxane. Usually, this FAB technique is used as a competition method, in which one ligand is competing for several metal cations in one experiment, assuming that they form similar complexes. We have performed experiments in which, per experiment, the interaction with *only one cation* was studied. However, in the case of **6b**, a competition experiment was performed with Sc³⁺ and Y³⁺, giving rise to 1:1 formation (approximately) of the respective complexes (cf. Table II).

The results of the complexation of calix (aza)-crowns **6a-f** and **11a,b** with a series of both divalent and trivalent cations are summarized in Table II. The numbers indicate the ratio of the heights of the [L + M]⁺ (in some cases [L + M + H]⁺) and [L]⁺ peaks. For metals with different isotopes, only the most abundant isotope has been taken into account, for reasons of simplicity. Consequently, only the results of one cation can be compared with each other.

The relatively low numbers (cf., Ref. 24, for example) in Table II indicate that, in the different cases, only weak complexes are formed. Nevertheless, some general trends are observed. CPK-model examination reveals that compound **6a**, with the smallest cavity, should have an optimal fit for Be²⁺. However, in this case, no complex formation was observed. Complexation in the larger cavities (**6c** and **6e**), both having 4 nitrogen atoms, might be explained by assuming a zig-zag configuration of the bridge. For the other divalent cations²⁸, it can be concluded that the larger the radius of the ion, the larger the cavity must be in order to effect more efficient complexation. However, with the exception of Ba²⁺, the oxygen bridged ionophore **6f** gave the best results, indicating that for complexation the "harder" oxygen is preferred over the "softer" nitrogen for this type of divalent cation.

The effect of methylation of the free OH groups (**11a** and **11b**) is very striking, in all cases giving rise to much weaker complexation compared to the corresponding dihydroxy ionophores **6a** and **6f**. In the case of the trivalent cations, no relationship between the ion radius and the size of the cavity was observed. In³⁺ and Bi³⁺ show only very weak complexation with the compounds involved. Calix aza-crown **6a** appears to be by far the best ionophore for Sc³⁺, whereas the oxygen-bridged calix[4]arene **6f** is the best for Y³⁺ and Gd³⁺.

In general, we consider that the free OH groups are essential for stabilization of the complexes formed. However, it must be noted that, in the cases of ionophores with

Table II FAB-MS complexation studies of calix (aza)-crowns **6**, **11** with di- and trivalent cations^a.

Compd.	Cation									
	Be ²⁺	Mg ²⁺	Ca ²⁺	Sr ²⁺	Ba ²⁺	Sc ³⁺	Y ³⁺	In ³⁺	Gd ³⁺	Bi ³⁺
6a	^b	0.67	0.50	0.20	0.09	4.25	0.44	^b	0.41	^b
6b	^b	0.50	0.26	0.10	0.26	0.95	0.95	^b	0.20	0.03
6c	0.58	0.84	0.56	0.01	0.07	0.59	0.41	^b	0.13	^b
6d	^b	0.22	0.20	0.07	0.10	0.41	0.34	0.02	0.12	0.13
6e	1.25	0.46 ^c	0.67	0.42	0.89	0.33	0.86	^b	0.12	^b
6f	^b	1.22	0.67	0.45	0.50	0.51	0.96	^b	0.50	0.03
11a	^b	0.19	0.36	0.02	0.04	0.07	0.31	^b	0.03	0.01
11b	^b	0.10	0.05	^b	0.03	0.01	^b	^b	0.03	^b

^a Numbers indicate ratio of heights of [L + M]⁺ and [L]⁺ peaks. presence of Na⁺ complex.

^b Complex formation was not observed.

^c Complicated system by

methylated OH groups, the cavities are not completely comparable with those of **6a-f** because, in the former case, mixtures of conformers are present (*vide supra*). For the divalent cations, in addition to the hardness/softness (oxygen versus nitrogen) of the cavity, the concept of preorganization is important. In the case of Be^{2+} , the conformational flexibility of the bridge may also play a role. The behaviour of the trivalent cations is more complicated. Not only the ion radius and the size and type of heteroatoms in the bridge are important, but probably also the coordination number of the cation. Only a very limited number of macrocycles has been shown to be able to complex the trivalent cations studied^{29,30}.

Although the complexation of selected examples must be studied in more detail, the calix (aza)-crowns described in this paper represent an interesting class of compounds. Further work is in progress to develop other calix[4]arene-based ionophores for complexation of di- and trivalent cations.

Experimental

Melting points were determined with a Reichert melting point apparatus and are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded with a Nicolet NT-200 or a Bruker AC 250 spectrometer in CDCl_3 with Me_4Si as internal standard. Mass spectra were obtained using a Finnigan MAT 90 spectrometer and IR spectra using a Nicolet 55XC FT-IR spectrophotometer.

CH_2Cl_2 was distilled from CaH_2 and stored over molecular sieves. Silica gel (particle size 0.040–0.063 mm, 230–240 mesh) was obtained from Merck. All commercially available chemicals were obtained from Janssen except for ScCl_3 (Alfa) and BiCl_3 (Aldrich). All reactions were carried out under an argon atmosphere.

2,2'-[[5,11,17,23-Tetrakis(1,1-dimethylethyl)-26,28-dihydroxypentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacos-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-25,27-diyl]bis(oxy)]bis(acetic acid), dimethyl ester (4**)**

A suspension of diethyl ester **5**¹⁹ (1.91 g, 2.3 mmol) and 4-toluenesulphonic acid monohydrate (0.01 g, 0.05 mmol) in methanol (50 ml) was refluxed for 12 h. After removal of solvent, crystallization of the residue from ethanol gave pure **4** as a white powder; yield 99%; m.p. 195–197°C (heptane). Anal. $\text{C}_{50}\text{H}_{64}\text{O}_8$ calcd.: C 75.72, H 8.13; found: C 75.26, H 8.12%. ^1H NMR: δ 7.02 and 6.81 (s, 4H, Ar H), 7.01 (s, 2H, OH), 4.74 (s, 4H, OCH_2), 4.44 and 3.32 (ABq, 8H, J 13.1 Hz, ArCH_2Ar), 3.83 (s, 6H, OCH_3), 1.26 and 0.98 [s, 18H, $\text{C}(\text{CH}_3)_3$]. ^{13}C NMR: δ 169.7 (s, CO), 72.2 (t, OCH_2), 52.1 (q, OCH_3). IR (KBr): 1760 cm^{-1} (CO). MS (EI): accurate mass theor. 792.460; exp. 792.450.

General procedure for the preparation of the calix (aza)-crowns **6a-f**

A solution of dimethyl ester **4** (0.79 g, 1.0 mmol) and an appropriate diamine (1.0 mmol) in a mixture of methanol (50 ml) and toluene (50 ml) was stirred at room temperature (**a**, **b**), or at reflux temperature. After completion of the reaction, the solvents were evaporated and the resulting residue was purified by column chromatography (SiO_2 , CH_2Cl_2 /methanol 95/5) to give compounds **6a-f**, which were recrystallized from diethyl ether/methanol. The reaction conditions, yields, melting points and characteristic spectral data are summarized in Table I.

2,2'-[[5,11,17,23-Tetrakis(1,1-dimethylethyl)-26,28-dimethoxypentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacos-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-25,27-diyl]bis(oxy)]bis(acetic acid), dimethyl ester (7**)**

Starting from 4. A suspension of dimethyl ester **4** (0.73 g, 0.95 mmol), methyl iodide (1 ml, 16.1 mmol), and K_2CO_3 (1.68 g, 12.2 mmol) in acetonitrile (20 ml) was refluxed for 24 h. After removal of solvent, the residue was dissolved in EtOAc (75 ml) and washed with 1M HCl (30 ml) and water (20 ml). Crystallization of the crude mixture from ethanol gave pure **7** as white crystals in 76% yield.

Starting from 8. A suspension of 1,3-dimethoxycalix[4]arene **8**¹³ (7.70 g, 11.4 mmol), methyl bromoacetate (3.82 g, 25.0 mmol), and K_2CO_3 (3.45 g, 25.0 mmol) in acetone (150 ml) was stirred at room temperature for 2 days. Work-up as described above gave pure **7**; yield 60%; m.p. 144–147°C. Anal. $\text{C}_{52}\text{H}_{68}\text{O}_8$ calcd.: C 76.06, H 8.35; found: C 76.16, H 8.38%. ^1H NMR: δ 7.15–6.80 (br m, 4H, Ar H), 6.55–6.40 (br m, 4H, Ar H), 4.40–3.10 (br m, 24H, OCH_2 , OCH_3 and ArCH_2Ar). IR (KBr): 1761 cm^{-1} (CO). MS (EI): accurate mass 820.491; exp. 820.491.

2,2'-[[5,11,17,23-Tetrakis(1,1-dimethylethyl)-26,28-dimethoxypentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacos-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-25,27-diyl]bis(oxy)]bis(acetic acid) (9**)**

A suspension of **7** (3.10 g, 3.61 mmol) and NaOH (0.30 g, 17.5 mmol) in a mixture of ethanol (50 ml) and water (20 ml) was refluxed for 4 h. Upon cooling, the reaction mixture was acidified with 2N HCl to pH 2 and subsequently extracted with CH_2Cl_2 (2 \times 50 ml). After washing with water (2 \times 20 ml) and drying of the combined organic layers with MgSO_4 , evaporation of the solvent ultimately gave pure **9** as a white powder; yield 99%; m.p. 141–143°C. Anal. $\text{C}_{50}\text{H}_{64}\text{O}_8 \cdot 1\text{H}_2\text{O}$ calcd.: C 74.04, H 8.20; found: C 73.97, H 8.42%. ^1H NMR: δ 7.18 and 6.61 (s, 4H, Ar H), 4.67 (s, 4H, OCH_2), 4.21 and 3.32 (ABq, 8H, J 13.0 Hz, ArCH_2Ar), 3.82 (s, 6H, OCH_3), 1.34 and 0.84 [s, 18H, $\text{C}(\text{CH}_3)_3$]. ^{13}C NMR: δ 169.8 (s, CO), 72.0 (t, OCH_2), 63.8 (q, OCH_3). IR (KBr): 1759 cm^{-1} (CO). (FAB-MS): accurate mass theor. 793.5; exp. 793.5 (M + H)⁺.

2,2'-[[5,11,17,23-Tetrakis(1,1-dimethylethyl)-26,28-dimethoxypentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacos-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-25,27-diyl]bis(oxy)]bis(acetyl chloride) (10**)**

A solution of diacid **9** (1.81 g, 2.28 mmol) and oxalyl chloride (0.42 ml, 4.9 mmol) in CH_2Cl_2 (30 ml) was refluxed for 4 h. After evaporation of solvent and excess oxalyl chloride, the residue was dried under reduced pressure to give **10** as a yellowish foam, which could not be recrystallized due to decomposition; yield 91%; m.p. 107.5–109°C. Anal. $\text{C}_{50}\text{H}_{62}\text{Cl}_2\text{O}_6$ calcd.: C 72.36, H 7.53; found: C 72.11, H 7.78%. ^1H NMR: δ 7.25–6.50 (br m, 8H, Ar H), 5.0–3.0 (br m, 18H, OCH_2 , ArCH_2Ar and OCH_3), 1.30–0.85 [br m, 36H, $\text{C}(\text{CH}_3)_3$]. IR (KBr): 1755 cm^{-1} (CO). (FAB-MS): accurate mass theor. 792.42; exp. 792.47 (M – Cl)⁺.

2,17,22,32-Tetrakis(1,1-dimethylethyl)-8,9,10,11-tetrahydro-26,29-dimethoxy-25H-4,15-(methano[1,3]benzenomethano)-20,24-metheno-19H-dibenzo[k,t][1,10,4,7]dioxadiazacycloheptacosine-7,12(6H,13H)-dione (11a**)**

To a vigorously stirred solution of triethylamine (0.42 ml, 3 mmol) in benzene (100 ml), were added simultaneously solutions of diacid dichloride **10** (0.77 g, 0.93 mmol) in benzene (25 ml) and of 1,2-ethanediamine (0.057 g, 0.95 mmol) in benzene (25 ml), using a perfusor over a period of 5 h. After the mixture has been stirred overnight at room temperature, the solvent was evaporated off under reduced pressure. The resulting residue was purified by flash chromatography (SiO_2 , CH_2Cl_2 /methanol 95/5) to give pure **11a**, as a white powder, as a mixture of conformers (partial cone/cone/1,3-alternate 14/5/2); yield 18%; m.p. 155–158°C (CH_2Cl_2 /methanol). Anal. $\text{C}_{52}\text{H}_{68}\text{N}_2\text{O}_6 \cdot 0.5\text{CH}_2\text{Cl}_2$ calcd.: C 73.35, H 8.09, N 3.26; found: C 73.67, H 8.15, N 3.12%. ^1H NMR (partial cone): δ 8.6 (br s, 2H, NH), 7.29 and 7.03 (d, 2H, J 2.3 Hz, Ar H), 7.16 and 7.06 (s, 2H, Ar H), 4.41 and 4.04 (ABq, 4H, J 14.1 Hz, OCH_2), 4.22 and 3.38 (ABq, 4H, J 12.3 Hz, ArCH_2Ar), 3.93 and 3.83 (ABq, 4H, J 16.4 Hz, ArCH_2Ar), 3.63 (s, 3H, OCH_3), 3.6–3.4 (m, 4H, $\text{NCH}_2\text{CH}_2\text{N}$), 1.31 and 1.11 [s, 9H, $\text{C}(\text{CH}_3)_3$], 1.27 [s, 18H, $\text{C}(\text{CH}_3)_3$], 0.83 [s, 3H, OCH_3 (inside)]. ^{13}C NMR: δ 168.6 (s, CO), 71.8 (t, OCH_2), 64.1 and 59.8 (q, OCH_3). IR (KBr): 1679 cm^{-1} (CO). MS (EI): accurate mass theor. 816.508; exp. 816.504.

2,23,28,38-Tetrakis(1,1-dimethylethyl)-8,9,10,12,13,15,16,17-octahydro-32,35-dimethoxy-31H-4,21-(methano[1,3]benzenomethano)-26,30-metheno-25H-dibenzo[q,z][1,7,10,16,4,13]-tetraoxadiazacycloheptacosine-7,18(6H,19H)-dione (11b**)**

11b was prepared by a similar method to **11a** starting from diacid dichloride **10** (0.71 g, 0.86 mmol) and 3,6-dioxaoctane-1,8-diamine

(0.13 g, 0.86 mmol); yield 10%; m.p. 295–298°C (CH₂Cl₂/methanol). Anal. C₅₆H₇₆N₂O₈ · 0.5CH₂Cl₂ calcd.: C 71.61, H 8.19, N 2.95; found: C 72.01, H 8.09, N 3.01%. ¹H NMR: δ 7.2 and 6.4 (br s, 4H, Ar H), 4.2–3.15 (br m, 30H, OCH₂, OCH₃, NCH₂ and ArCH₂Ar), 1.4–0.8 [br m, 36H, C(CH₃)₃]. IR (KBr): 1671 cm⁻¹ (CO). MS (EI): accurate mass theor. 904.560; exp. 904.558.

Complexation studies using FAB-MS

The mass spectrometer was equipped with a standard Finnigan FAB source and an ion tech gun. Xenon was employed as the primary atom beam, accelerated to 8 KeV with an ion current of 1 μA. The spectra were obtained in the positive ion mode. PEG 200 appeared to be the best matrix.

For the measurements 1 μl of a 0.01M solution of calix (aza-)crown **6**, **11** in dioxane and 0.5 μl of a 0.2M (or 1 μl of 0.1M) solution of inorganic salt in water [CHCl₃ in the case of Be(OAc)₂ and ethanol in the case of BiCl₃] were mixed with 2 μl of PEG 200 as the matrix and stirred for 1 min before use.

Be(OAc)₂, BaBr₂, SrCl₂, CaBr₂, Mg(NO₃)₂, InBr₃, GdCl₃, YCl₃, ScCl₃ and BiCl₃ were used as inorganic salts.

Complex formation³¹, indicated by the ratio of the heights of the [L + M]⁺ (in some cases [L + M + H]⁺) and [L]⁺ peaks, is summarized in Table II.

Acknowledgements

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