1,3-Alternate and C-1,2-Alternate Tetrahomodioxacalix[4]crowns. Crystal Structures and Metal Ion Complexation

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Abstract

Two novel tetrahomodioxacalix[4]crowns with crown-5 and crown-6 rings were synthesized. From X-ray crystal structures, homooxacalix[4]crown-5 (**3**) and homooxacalix[4]crown-6 (**2**) were found to be in the 1,3-alternate and the C-1,2-alternate conformations, respectively. Homooxacalix[4]crown-5 (**1**) shows a marked selectivity for cesium ion over other metal ions tested.

Introduction

Calixarenes have drawn an intense interest as complexation hosts for both ions and neutral molecules [1–3]. Recently, the family of enlarged calixarenes termed homooxacalixarenes, and particularly tetrahomodioxacalix[4]arene, which contains two extra O–CH_2 groups in the macrocyclic ring, has also been studied [4–10]. No and Kim reported that there are five conformations in tetrahomodioxacalix[4]arene with appropriate nomenclature (cone, partial cone, C-1,2-alternate, COC-1,2 alternate, and 1,3-alternate) as indicated in Figure 1 [11]. Masci and coworkers [12] reported that the thermodynamically most stable conformation of tetrahomodioxa-*p-tert*-butylcalix[4]arene tetramethyl ether is C-1,2-alternate, as shown by temperature-dependent NMR spectral analysis.

Previously, we also reported that C-1,2-alternate *N,N*-diethyl tetrahomodioxacalix[4]arene tetraamide showed Pb^{2+} ion selectivity [13]. In the solid-state structure, the Pb^{2+} is bound to the carbonyl oxygen atoms of two adjacent amide substituents and an aryl-alkyl ether oxygen of one of them [13]. In the case of *mono*alkyl amide, however, its conformation changed to 1,3-alternate due to a strong hydrogen bonding, resulting in weak binding ability toward metal cations [11].

Calix[4]crown ethers in which the proper-sized crown rings are incorporated into the calix[4]arene framework have also been attractive as specific metal-selective extractants [14]. 1,3-Alternate calix-*bis*-crowns in their complexed form
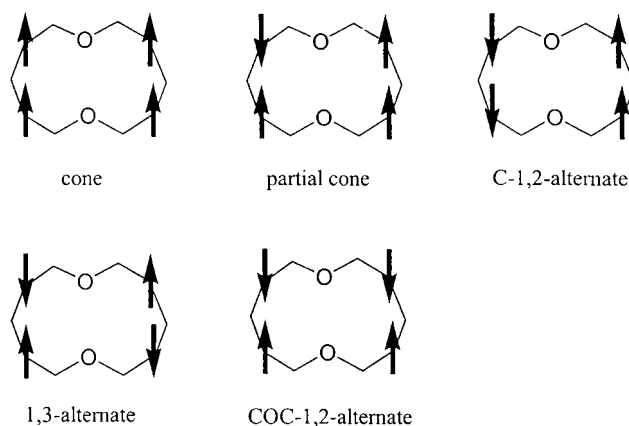

*Figure 1.* Schematic representation of the five conformations of homooxacalix[4]arenes.

display particularly interesting molecular features, including cation-π and electrostatic interactions [15].

With these previous studies in mind, we have investigated the synthesis, crystal structures and complexation behaviour toward alkali metal ions of tetrahomodioxa-*p*-phenylcalix[4]crown-5 and crown-6.

Results and discussion

The synthetic routes for homooxacalix[4]crown-5 (**1**) and -6 (**2**) are depicted in Scheme 1. Reaction of cone-**3** with tetraethylene glycol ditosylate and pentaethylene glycol ditosylate in the presence of K_2CO_3 gave 1,3-alternate **1** and C-1,2-alternate **2**, respectively. For **1**, cyclization using Cs_2CO_3 as a base took only 24 h with regard to TLC spot-
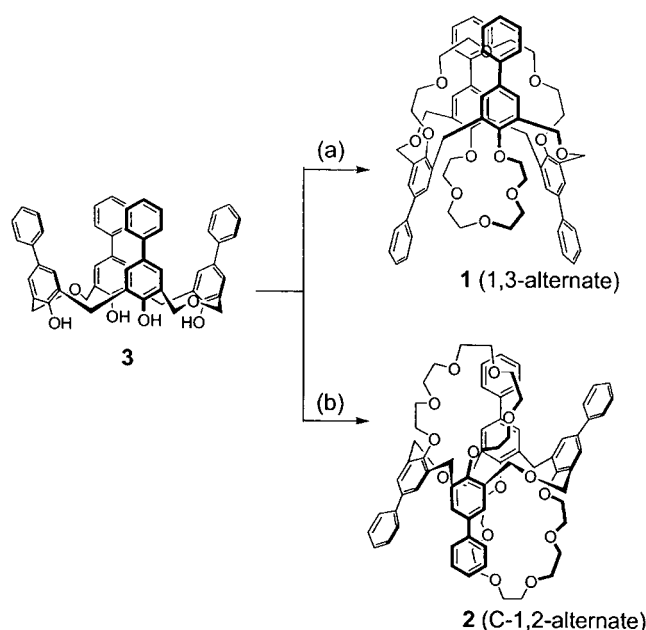
Scheme 1. Synthetic routes for homooxacalix-*bis*-crown ethers **1** and **2**. (a) K_2CO_3, tetraethylene glycol ditosylate, CH_3CN. (b) K_2CO_3, pentaethylene glycol ditosylate, CH_3CN.

Figure 2. Crystal structure of compound $\mathbf{1} \cdot 2.5py \cdot 0.5H_2O$. Hydrogen atoms and solvent molecules are omitted for clarity. Displacement ellipsoids are drawn at the 10% probability level.

ting, but in the case of K_2CO_3, the reaction took four days to complete. This indicates a template effect on the cyclization, which is in accordance with the binding ability for cesium ion (Table 2, see below). In contrast, we could not observe the template effect in the formation of compound **2**. The reaction took 4 days to complete regardless of the base species used (Na_2CO_3, K_2CO_3 or Cs_2CO_3).

Judging from ^{1}H and ^{13}C NMR spectroscopy, **1** and **2** were in the 1,3-alternate and C-1,2-alternate conformation, respectively. For **1**, in the ^{1}H NMR spectrum, the dimethylenoxy protons of the Ar*CH$_2$*O*CH$_2$*Ar bridge showed AB doublets at δ 4.75 and δ 4.27 (Δv = 192 Hz) with a geminal coupling constant of 12.4 Hz. In addition, a singlet peak for the methylene protons of Ar*CH$_2$*Ar appeared at δ 4.15. The ^{13}C NMR spectrum showed one peak at 65.80 ppm for the Ar*CH$_2$*O of bridge methyleneoxy carbons and one peak at 38.35 ppm for the Ar*CH$_2$*Ar bridge carbons implying that two adjacent benzene rings are in an *anti* orientation. So, it appears that **1** is in the stable 1,3-alternate conformation. In an earlier paper we gave a new nomenclature to differentiate between the two possible 1,2-alternate conformers in the following manner: The 1,2-alternate conformer in which the adjacent *syn* aryl moieties are joined by a CH_2 group is designated as the C-1,2-alternate, while the 1,2-alternate conformer in which the adjacent *syn* aryl moieties are joined by a CH_2OCH_2 moiety is designated as the COC-1,2-alternate [11]. For **2**, we observed AB doublets at δ 4.68 and δ 4.50 (Δv = 72 Hz) with a *geminal* coupling constant of 8.80 Hz corresponding to the dimethylenoxy protons of the Ar*CH$_2$*O*CH$_2$*Ar bridge as well as a doublet peaks at δ 4.70 and δ 3.47 (Δv = 492 Hz) with a *geminal* coupling constant of 11.20 Hz for the methylene protons of Ar*CH$_2$*Ar. In ^{13}C NMR spectrum we observed one peak at 66.75 ppm for the Ar*CH$_2$*O bridge methyleneoxy carbons and one peak
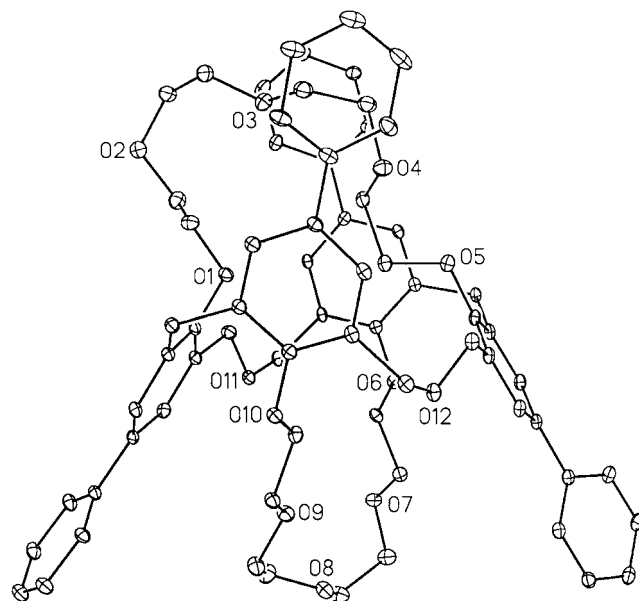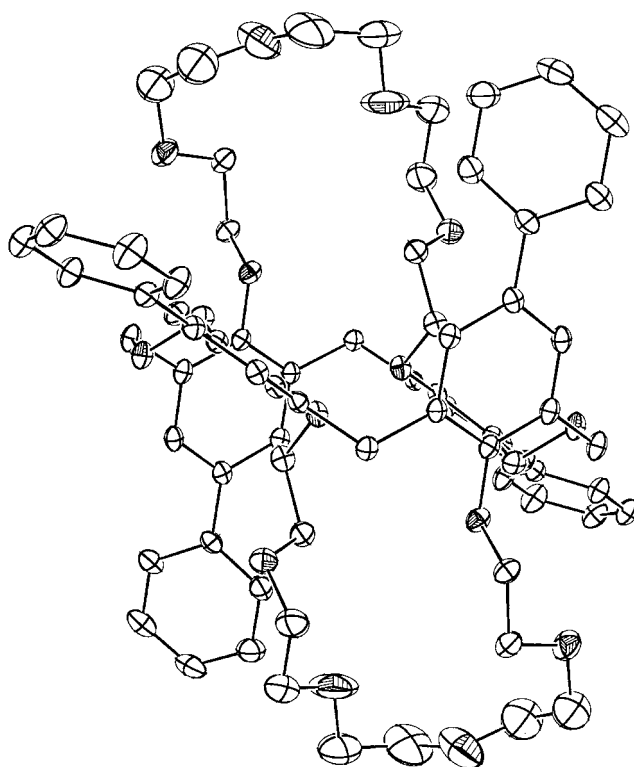
Figure 3. Crystal structure of compound **2**. Hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at the 10% probability level.

at 30.75 ppm for the Ar*CH$_2$*Ar bridge carbons. These NMR spectra for **2** indicate that two adjacent *syn* aryl moieties are joined by a CH_2 group in a *syn* orientation (C-1,2-alternate conformation).

X-ray crystal structures of $\mathbf{1} \cdot 2.5py \cdot 0.5H_2O$ and **2** are positive proofs for the 1,3-alternate and C-1,2-alternate conformation as shown in Figure 2 and 3, respectively. The corresponding crystal data are given in Table 1. The calix-

Table 1. Crystal data and refinement details for compounds **1** and **2**

Compound	**1** · 2.5py·0.5H$_2$O	**2**
Formula	C$_{82.5}$H$_{85.5}$N$_{2.5}$O$_{12.5}$	C$_{74}$H$_{80}$O$_{14}$
f.w.	1312.03	1193.38
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a (Å)	14.3680(19)	11.727(5)
b (Å)	15.7789(11)	13.260(5)
c (Å)	16.356(2)	11.226(5)
α (°)	87.615(7)	102.434(5)
β (°)	78.031(4)	109.638(5)
γ (°)	80.234(7)	92.964(5)
V (Å^3)	3574.9(7)	1590.9(11)
Z	2	1
$F(000)$	1396	636
Calculated density (g cm^{-3})	1.219	1.246
μ (mm^{-1})	0.082	0.09
Temperature (K)	110(2)	293(2)
Crystal size (mm)	0.30 × 0.25 × 0.25	0.35 × 0.30 × 0.30
Diffractometer	Nonius Kappa-CCD	Enraf-Nonius CAD-4
Data collection method	ϕ-scans	$\omega/2\theta$ scans
Absorption correction	None	None
No. of unique refl	12243	5589
No. of observed refl [$I_0 > 2\sigma(I_0)$]	5524	3522
θ_{max}	25.7	25.0
hkl range	0 17; −16 16; −19 19	−13 13; −15 15; 0 13
R_{int}	0.094	0.016
No. of parameters	922	428
R & R_w	0.091 & 0.204	0.064 & 0.201
GOF	1.005	1.045
$(\Delta/\sigma)_{max}$	<0.001	0.003
$(\Delta\rho)_{max}$ (e/Å^3)	0.71	0.77
$(\Delta\rho)_{min}$ (e/Å^3)	−0.48	−0.44
Extinction correction	None	0.005(2)

crown molecule in compound **1**·2.5py·0.5H$_2$O crystallizes with no crystallographic symmetry. The choice of a reference plane in such a molecule is not straight forward. In spite of a large maximum deviation of 0.741(4) Å, we have chosen to take the mean plane defined by all the six methylene bridges as a reference plane for the calixarene core. The dihedral angles between the four phenolic rings and this plane are 59.0(1), 81.6(1), 62.2(1) and 80.5(1)°, indicating that two opposite rings are closer to the mean plane than the two other ones, which in turn are more parallel to one another. Such a difference is likely related to the two crown ether chains displaying different conformations, which can be defined by the torsion angles. In the first one, containing oxygen atoms O1 to O5, the O–C–C–O torsion angles define an $ag^+g^-g^-$ sequence (where *a* and *g* represent *anti* and *gauche* torsion angles, respectively) and the C–O–C–C torsion angles are either *anti* or *gauche*. In the second crown ether chain, containing atoms O6 to O10, the O–C–C–O torsion angles sequence is similar but the C–O–C–C torsion angles are different, being either *anti* or intermediate between *anti* and *gauche*. Such flexibility of the crown ether chains in calixcrowns, in the absence of a co-

ordinated cation or of interactions with a solvent molecule, have previously been documented [15(a), 16]. The two 2-oxa-1,3-propylene bridges and the aromatic carbon atoms to which they are bound define both one *anti* and one *gauche* torsion angles and are not thus of the planar w shape sometimes encountered in tetrahomodioxacalix[4]arene [17]. In the present and other similar cases, four atoms only (including one aromatic carbon atom) are roughly planar. The dihedral angles between the phenolic rings and their phenyl *para* substituents are 29.2(2), 32.1(2), 36.5(2) and 36.7(2)°, the deviation from parallelism being rather low, probably in order to minimize the interactions between the substituents and the crown ether chains.

The calixcrown molecule in compound **2** crystallizes with half a calixcrown in the repeat unit, the other half being related to the first by a symmetry centre. The six methylene carbon atoms define a plane with a maximum deviation of 0.621 Å. The dihedral angles between the phenolic rings and this plane are 87.1 and 23.0°, indicating a conformation much different from that in **1**, with two opposite rings much closer to the mean plane. The conformation of the crown ether chains corresponds to a $g^+g^-g^+g^+g^+$ sequence for

the O–C–C–O torsion angles, with some C–O–C–C torsion angles being *gauche* instead of *anti*. This conformation, which does not direct all the oxygen lone pairs towards the crown centre, is not among those previously observed in calix[4]-bis-crowns in the 1,3-alternate conformation [16]. As in compound **1**, the two 2-oxa-1,3-propylene bridges and the aromatic carbon atoms to which they are bound define both one *anti* and one *gauche* torsion angles. The dihedral angles between the phenolic rings and their phenyl *para* substituents are 43.8 and 23.4°. In this case, and in contrast with calix[4]-bis-crowns, the crown-6 loop does not offer an appropriate cavity to encapsulate cesium ion probably due to the low size matching as well as the steric hindrance of methylene hydrogen atoms of the Ar*CH2*Ar, resulting in weak template effect on the cyclization and low extractability toward metal cations.

In order to get insight into the metal ion affinity of homooxacalixarene-based ligands, extractabilities toward metal ions by **1** and **2** were determined by the metal picrate extraction method. The results are listed in Table 2. Interestingly, the 1,3-alternate tetrahomodioxacalix[4]crown-5 (**1**) selectively binds Cs^+ ion over other cations while the C-1,2-alternate tetrahomodioxacalix[4]crown-6 (**2**) does not. For all cations tested, **2** gave a low extractability probably because of the steric hindrance by the methylene hydrogen atoms of the Ar*CH2*Ar for metal ion complexation as mentioned above. For **1**, we took a Job plotting experiment to obtain the complexation ratio between **1** and Cs^+pic^- under conditions of invariant total concentration as indicated in Figure 4. As a result, **1**-Cs^+ complex concentration approaches a maximum when the molar fraction of [**1**]/([**1**] + [Cs^+]) is about 0.4, meaning that it forms less than 1:2 complex (for instance 1:1.5). This can be ascribed to an electrostatic repulsion between the two metal ions [18]. Cesium ion selectivity of the 1,3-alternate **1** is probably due to the size agreement between the electron donors consisting of oxygen atoms in crown-5 ring as well as due to a π-metal complexation between inverted aromatic units and cesium ion. CPK molecular model also gave us a positive evidence for this concept. Thus, we took ^1H NMR spectra and observed the changes in the chemical shifts of the hydrogen atoms of **1** upon cesium ion complexation, which are shown in Figure 5. The chemical shift of H_d changed downfield by 0.07 ppm, implying that there is a π-metal complexation, but not as considerable as in the case of the calix[4]biscrown-5. H_c atoms do not seem to participate in the π-metal complexation presumably due to being far away from the crown unit. Distance between one pair of doublets corresponding to H_e became wider by 0.13 ppm, indicating that it is in more rigid conformation upon the cesium ion complexation.

In conclusion, two novel tetrahomodioxacalix[4]crowns having crown-5 and crown-6 rings were synthesized. From the ^1H, ^{13}C NMR and crystal structures, homooxacalix[4]crown-5 (**1**) and homooxacalix[4]crown-6 (**2**) were found to be in the 1,3-alternate and C-1,2-alternate conformations, respectively. The 1,3-alternate homooxacalix[4]crown-5 (**1**) showed cesium ion selectivity over other metal ions, the complexation probably involving
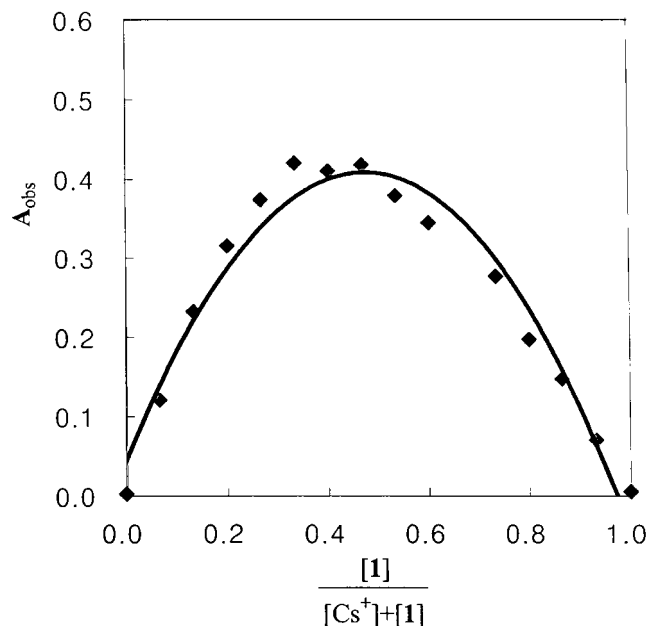

Figure 4. Job plot for Cs^+ ion complexation.

an electrostatic interaction between the Cs^+ ion and oxygen atoms of the crown-5 loop as well as a π-metal complexation between inverted phenoxy aromatic units and cesium ion, as usual. It may be noted that the crown ether complexation site in calix[4]-bis(crown-5) is too small for cesium, the enlargement of the calixarene platform resulting from the replacement of methylene by 2-oxa-1,3-propylene bridges in **1** being thus sufficient to provide the necessary crown size. The crystal structure of **1**·Cs^+ is presently under investigation and will be reported soon.

Experimental

Compound **3** was prepared from the adaptation of the reported procedures [11, 13, 19].

Synthesis

Tetrahomooxacalix[4]crown-5 (1)
Tetrahomodioxacalix[4]arene (1.18 g, 1.50 mmol), cesium carbonate (0.48 g, 1.50 mmol) and acetonitrile (120 mL) were stirred magnetically for 20 min in a 250mL round-bottomed reaction flask. Tetraethylene glycol ditosylate (0.78 g, 1.55 mmol) dissolved in acetonitrile (20 mL) was then added. After 4 days of refluxing, the same quantity of tetraethylene glycol ditosylate and potassium carbonate was added. The reflux was maintained for additional 3 days. After cooling to room temperature, the residue was acidified with dilute HCl and the mixture was extracted with CH_2Cl_2. The combined CH_2Cl_2 extracts were washed with water, dried over $MgSO_4$ and evaporated *in vacuo*. The residue was triturated with MeOH to give the product mixture which was separated with flash chromatography (eluent was 2:1 mixture of hexane and acetone) to afford 425 mg (25.7%) of **1** as a white solid with mp 220 °C. IR (KBr pellet, cm^{-1}):

Table 2. Extractabilities of **1** and **2** for alkali metal picrates[a]

Compd.	Extractability for metal cations (%)							
	Na^+	K^+	Rb^+	Cs^+	NH_4^+	Ag^+	Sr^{2+}	Ba^{2+}
1	1.19	7.44	22.82	72.96	0	16.96	1.64	0.84
2	1.19	1.40	1.68	3.04	0.42	10.97	0.18	0

[a]Conditions: ligand, 0.1 mM/ClCH$_2$CH$_2$Cl; metal picrate, 0.2 mM/water. The intensities of the extracted picrates (λ_{max} = 378 nm) from the water into the organic layer were measured.
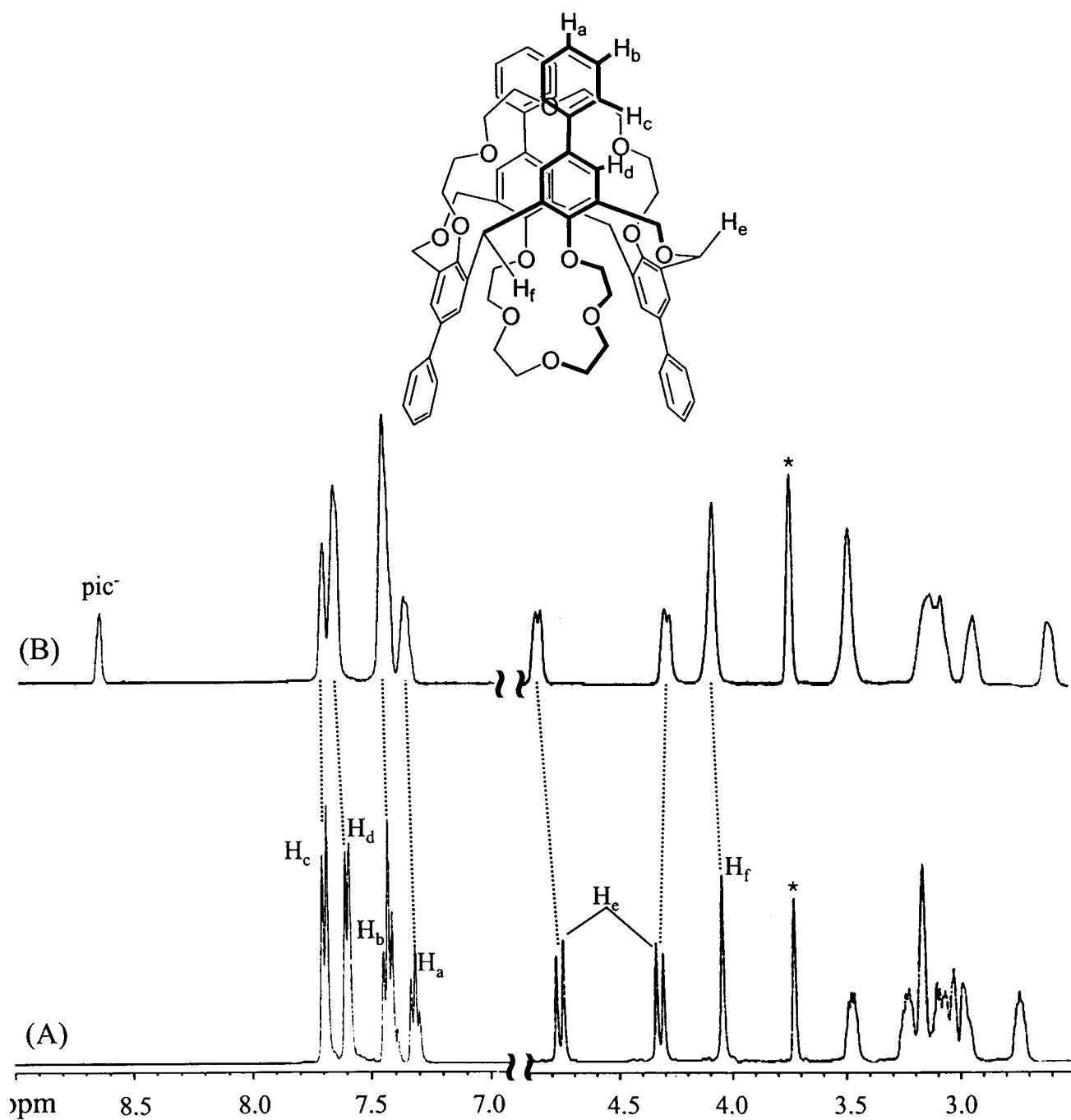

Figure 5. ^{1}H NMR spectra for ligand **1** (A) and the **1**·Cs$^+$pic- complex (B). *1,2-Dichloroethane-d$_4$.

1188.9, 1128.15, 1085.0. ^{1}H NMR (CDCl$_3$): 7.61 (d, 4, Ar*H*, *J* = 7.3 Hz), 7.52 (d, 4, Ar*H*, *J* = 2.6 Hz), 7.34 (t, 8, Ar*H*, *J* = 7.6 Hz), 7.23 (t, 8, Ar*H*, *J* = 7.3 Hz), 4.75 (d, 4, ArC*H$_2$*O, *J* = 12.3 Hz), 4.27 (d, 4, ArC*H$_2$*O, *J* = 12.3 Hz), 4.00 (s, 4, ArC*H$_2$*Ar), 3.38 (m, 4, OC*H$_2$*, *J* = 5.0 Hz), 3.24 (m, 4, OC*H$_2$*), 3.17 (b. t, 8, OC*H$_2$*, *J* = 3.6 Hz), 3.04 (m, 4, OC*H$_2$*), 3.00 (m, 4, OC*H$_2$*), 2.93 (m, 4, OC*H$_2$*), 2.68 (m, 4, OC*H$_2$*). ^{13}C NMR (CDCl$_3$): 156.39, 140.30, 136.41, 135.26, 131.73, 130.40, 128.80, 127.49, 127.19, 127.17 (Ar), 72.94, 71.17, 70.48, 70.32 (OC*H$_2$*), 65.72 (ArC*H$_2$*O), 38.37 (ArC*H$_2$*Ar) ppm. Anal. Calcd. for C$_{70}$H$_{72}$O$_{12}$; C: 76.06, H: 6.56, Found C: 76.12, H: 6.50.

Tetrahomooxacalix[4]crown-6 (2)

Method is same as for **1** except using K$_2$CO$_3$. 27.2% yield. A colorless crystal. Mp 256 °C. IR (KBr pellet, cm^{-1}): 1123.3, 1050.1. ^{1}H NMR (CDCl$_3$): 7.54 (d, 6, Ar*H*, *J* = 2.3 Hz), 7.53 (d, 6, Ar*H*, *J* = 2.3 Hz), 7.39 (t, 8, Ar*H*, *J* = 7.6 Hz), 7.37 (d, 4, Ar*HH*, *J* = 2.3 Hz), 7.29 (t, 4, Ar*H*, *J* = 7.2 Hz), 4.70 (d, 2, ArCH2Ar, J = 13.8 Hz), 4.68 (d, 4, ArCH$_2$O, J = 11.1 Hz), 4.51 (d, 4, ArC*H$_2$*O, *J* = 11.1 Hz), 3.87 (m, 4, OC*H$_2$*), 3.62 (m, 8, OC*H$_2$*), 3.48 (d, 2, ArC*H$_2$*Ar, *J* = 13.8 Hz), 3.45 (s. 8, OC*H$_2$*), 3.24 (m, 12, OC*H$_2$*), 3.20 (m, 4, OC*H$_2$*), 3.10 (m, 4, OC*H$_2$*). ^{13}C NMR (CDCl$_3$): 156.02, 140.56, 136.51, 135.37, 131.06, 128.94, 128.68, 128.64, 126.89 (Ar), 73.75, 70.56, 70.45, 70.25 69.75 (OC*H$_2$*), 66.75 (ArC*H$_2$$_2$*O), 30.75 (ArC*H$_2$*Ar) ppm. Anal. Calcd. for C$_{74}$H$_{80}$O$_{14}$; C: 74.48, H: 6.76, Found C: 74.42, H: 6.72.

Metal picrate extraction

Metal picrates were prepared by reaction of picric acid with the appropriate metal carbonate [20]. To determine the extractability of the ligand for a metal picrate, an aqueous solution (2.0 mL) containing 0.20 mM metal picrate and a 1,2-dichloroethane solution (2.0 mL) of the extractant (0.10 mM) were shaken for 30 min at 25 °C. The concentration of picrate anion extracted from the aqueous phase into the organic layer was determined by UV spectrophotometry (λ_{max} = 373 nm). Three independent experiments were carried out for each combination of ligand and metal picrate. The extractabilities listed in Table 2 are average values.

Crystal structures

The data for **1**·2.5py·0.5H$_2$O were collected on a Nonius Kappa-CCD area detector diffractometer [21] using graphite-monochromated Mo-Kα radiation (λ 0.71073 Å). The crystal was introduced in a glass capillary with a protecting "Paratone-N" oil (Hampton Research) coating. The unit cell parameters were determined from ten frames, then refined on all data. A 180° φ-range was scanned with 2° steps during data collection, with a crystal-to-detector distance fixed to 28 mm. The data were processed with DENZO-SMN [22]. The structure was solved by direct methods with SHELXS-97 [23] and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on F^2 with SHELXL-97 [23]. One pyridine molecule is disordered over two overlapping positions which have been

refined with occupancy factors of 0.25 each, so as to account for the impossibility of a simultaneous presence with the water molecule affected with a 0.5 occupancy factor. These two pyridine positions have been refined as idealized hexagons with some restraints on displacement parameters. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were introduced at calculated positions (except those of the disordered pyridine molecules, in which the nitrogen atoms have not been located, and those of the water molecule) and were treated as riding atoms with a displacement parameter equal to 1.2 times that of the parent atom. The molecular plots were drawn with SHELXTL [24]. All calculations were performed on a Silicon Graphics R5000 workstation.

Colorless crystals of **2** were obtained by slow evaporation of a solution of **2** in CH$_3$CN–CH$_2$Cl$_2$. Data were recorded on an Enraf-Nonius CAD-4 diffractometer [25]. Crystal data and refinement details for both compounds are given in Table 1. Crystal data were deposited with the Cambridge Crystallographic Data Centre, CCDC reference numbers 203560 (**1**) and 203561 (**2**).

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