

New Lower Rim Calix(4)arene Derivatives with Mixed Pendent Arms and Their Complexation Properties for Alkali-Metal Cations. Structural, Electrochemical, and Thermodynamic Characterization

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The synthesis and characterization (¹H NMR) of two new lower rim calix(4)arene derivatives containing mixed pendent arms, namely, 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis[2-(methylthio)ethoxy]-26,28-bis[(pyrid-2-ylmethyl)oxy]calix(4)arene (**1**) and 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis[2-(methylthio)ethoxy]-26,28-bis[(pyrid-3-ylmethyl)oxy]calix(4)arene (**2**), are reported. Transfer thermodynamic parameters of these ligands to various solvents show that these macrocycles undergo selective solvation in nonaqueous media. As far as the alkali-metal cations are concerned, ¹H NMR measurements reflect that **1** in CD₃CN discriminates against the largest cations (K⁺, Rb⁺, and Cs⁺) but interacts with Li⁺ and Na⁺. These interactions appears to be more pronounced with the pendent arms containing the pyridyl ring (through the ethereal oxygens and nitrogen donor atoms) than with those containing the (methylthio)ethoxy arms (only ethereal oxygens are involved). No interaction takes place between its isomer **2** and alkali-metal cations in CD₃CN. The complexation of the lithium and the sodium complexes was established through conductometric titrations. In all cases investigated 1:1 (ligand: metal cation) complexes are formed in acetonitrile and in benzonitrile. On the basis of the semiquantitative information provided by conductance measurements regarding the strength of complexation of **1** and the sodium cation, the sodium monoacetonitrile complex of **1** was isolated and its structure determined by X-ray diffraction methods. Thus, the cation was found in the hydrophilic cavity while the hydrophobic cavity hosts a molecule of acetonitrile. The crystallographic results confirm the key role played in the chelating process by the ethereal oxygens and the pyridyl nitrogens at the 2-position in the terminal pyridyl groups, as found in solution. The thermodynamics of complexation of **1** and alkali-metal cations (Li⁺ and Na⁺) in two dipolar aprotic solvents is interpreted in terms of the solution thermodynamics of the reactants and the product. It is the availability of these data that allows interpreting the different enthalpic and entropic contributions resulting from cation, solvent, and ligand effects. Final conclusions are given.

Introduction

Calixarenes are cyclic oligomers of the base catalyzed condensation reaction between *p*-substituted phenols and formaldehyde.^{1–6}

The ability of calixarenes to interact with cations was established by Izatt and co workers⁷ in 1985 who showed that transport of alkali-metal cations from a basic aqueous source phase to an aqueous receiving phase could be accomplished through an organic chloroform membrane in which calixarenes were dissolved. Effort was subsequently devoted to the synthesis of new calixarene derivatives with improved solubility, capable of forming complexes with ionic species. An attractive building block upon which ligating arms containing donor atoms able to interact with cations is provided by the ease of alkylation of the phenolic hydrogens at the lower rim of the *p*-*tert*-butylcalix-(4)arene.^{1–6} A series of calixarene derivatives with arms

appended to the lower rim containing ester, amide, ketone, and amine functional groups among others have shown to bind metal cations.^{1–6}

The synthesis and study of calix(4)arenes with side chains appended to the lower rim containing soft donor atoms is also an area of current interest with the aim of producing selective receptors for soft metal cations. Representative examples are those reported by Ting et al.,⁸ Cobben et al.,⁹ Beer et al.,¹⁰ O'Conner et al.,¹¹ Gibbs and Gutsche,¹² Malinowska et al.,¹³ Koh et al.,¹⁴ Yordanov et al.,¹⁵ Delaigue et al.,¹⁶ Wróblewski et al.,¹⁷ Sone et al.,¹⁸ and Danil de Namor et al.¹⁹

We have recently reported the complexation of pyridinocalix-(4)arene derivatives with univalent cations and the X-ray structures of the sodium and the silver complexes of the 2-pyridinocalix(4)arene derivative (perchlorate as the counterion)^{20–22} Both structures have shown the presence of a molecule of acetonitrile in the hydrophobic cavity of the macrocycle.

We thought that the replacement of two pendent arms in the 2-pyridinocalix(4)arene by side chains containing (methylthio)-ethoxy groups may lead to macrocycles able to discriminate

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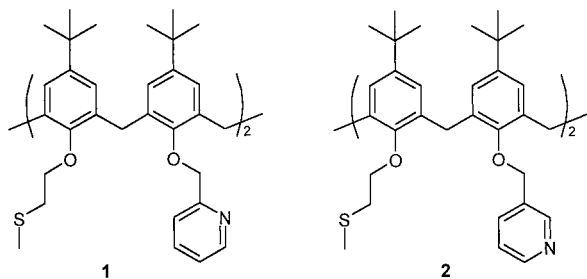
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between the small and large (lower charge density) alkali-metal cations, due to the reduction in the number of hard donor atoms, known to be suitable for interaction with these cations. In addition, the introduction of soft donor atoms in the pendent arms is likely to enhance the capability of these ligands for interaction with soft metal cations.

In this paper we report the following.

(i) The synthesis and the characterization (^1H NMR) of two isomers containing mixed pendent arms, namely 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis[2-(methylthio)ethoxy]-26,28-bis[(pyrid-2-ylmethyl)oxy]calix(4)arene (**1**) and 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis[2-(methylthio)ethoxy]-26,28-bis[(pyrid-3-ylmethyl)oxy]calix(4)arene (**2**).



(ii) The solubility of these ligands and derived standard Gibbs energies of solution ($\Delta_s G^\circ$) in a variety of solvents at 298.15 K and the standard transfer Gibbs energies ($\Delta_t G^\circ$) from acetonitrile. Whenever possible, the standard enthalpies of solution ($\Delta_s H^\circ$) were determined and the standard entropy of solution calculated.

(iii) The complexation properties of these ligands with alkali-metal cations as investigated from ^1H NMR (active sites of interaction of these ligands and metal cations) and conductance measurements.

(iv) The thermodynamics of complexation of **1** and alkali-metal cations in acetonitrile (MeCN) and benzonitrile (PhCN) at 298.15 K including the thermochemical characterization of the reactants and the product in these solvents.

Experimental Section

Chemicals. *p*-tert-Butylcalix(4)arene, sodium hydride 95%, 18-crown-6 (99%), 2-chloroethyl methyl sulfide (97%), 2- and 3-(chloromethyl)pyridine hydrochloride were purchased from Aldrich.

The tetra-*n*-butylammonium perchlorate from Fluka was used without further purification. Metal-ion perchlorate salts (Aldrich) were dried over P_4O_{10} under vacuum for 3 days before use.

Acetonitrile, benzonitrile, dichloromethane, hexane, methanol, *N,N*-dimethylformamide (HPLC grade) purchased from Fisher, ethanol (96%) from Hayman, and tetrahydrofuran from Aldrich were used.

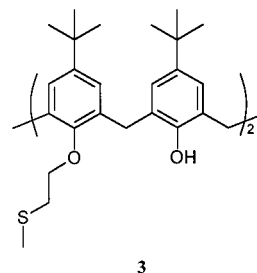
Purification of Solvents. Acetonitrile and benzonitrile used for electrochemical and thermodynamic measurements were purified as described elsewhere.^{20,21}

N,N-Dimethylformamide was further dried using A4 molecular sieves for a period of 24 h and then it was refluxed under reduced pressure. Only the middle fraction of the purified solvent was collected.²³

Tetrahydrofuran²³ was stored with a sodium metal wire for a period of 24 h. The solvent was then refluxed, whereupon benzophenone and metallic sodium in an atmosphere of nitrogen were added. A deep blue color resulting from the formation of the potassium/benzophenone ketal complex was developed. Then, the solvent was refluxed for several hours and the middle

fraction was collected. The water content verified by Karl Fisher titration was found to be lower than 0.02%.

Synthesis of 1 and 2. A two-step procedure was used to synthesize these ligands. The first step involved the preparation of 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-dihydroxy-26,28-bis[2-(methylthio)ethoxy]calix(4)arene (**3**), as described elsewhere.¹⁹



The second step is described as follows.

Synthesis of 1. A mixture of **3** (2.1 g, 0.03 mol) and dry sodium hydride (0.64 g, 0.03 mol), freshly distilled tetrahydrofuran (150 mL) and *N,N*-dimethylformamide (40 mL) was stirred for 15 min under a nitrogen atmosphere. Then, 2-(chloromethyl)pyridine hydrochloride (2.6 g, 0.017 mol) was added gradually, and refluxed at 90 °C for 24 h. The reaction was monitored by TLC using hexane:ethyl acetate (4:1) and dichloromethane:methanol (9:1) solvent mixtures as the developing solvents. The solvent was removed by rotary evaporation. The residue was then dissolved and extracted three times with dichloromethane and distilled water. The organic layer was dried using magnesium sulfate. After filtration the solvent was again removed. The viscous residue was then dissolved and treated with activated charcoal for further purification. After filtration and cooling, white crystals were obtained (90% yield). These were recrystallized from an ethanol:dichloromethane (4:1) mixture (mp: 256–258 °C). Anal. Calcd for $\text{C}_{62}\text{H}_{78}\text{O}_4\text{N}_2\text{S}_2$: C, 76.03; H, 8.03; N, 2.03. Found: C, 76.09; H, 8.18; N, 2.78.

^1H NMR (CDCl_3): δ (ppm) 8.66 (d, $J = 1.7$ Hz, 6-PyH, 2H), 7.67 (d, t , $J = 0.8$, 7.7 Hz, 4-PyH, 2H), 7.63 (d, $J = 7.7$ Hz, 3-PyH, 2H), 7.26 (d, t , $J = 0.8$, 1.7 Hz, 5-PyH, 2H), 7.12 (s, ArH, 4H), 6.48 (s, ArH, 4H), 4.82 (s, OCH_2Py , 4H), 4.02 (t, $J = 7.5$ Hz, SCH_2CH_2 , 4H), 3.19 and 4.4 (d, $J = 12.6$ Hz, ArCH_2Ar , 8H), 2.78 (t, $J = 7.5$ Hz, SCH_2CH_2 , 4H), 1.84 (s, SMe, 3H), 1.34 (s, C (Me)₃, 18H), 0.84 (s, C (Me)₃, 18H).

^{13}C NMR (CDCl_3): δ (ppm) 157.5 (C6–Py), 154.1 (C2–Py), 152.2 (C4–Py), 149.8 (C3–Py), 145.5 (C5–Py), 144.9, 136.9 (C_i), 135.7, 132.1 (C_p), 125.9, 124.9 (C_o), 123.6, 123.2 (C_m), 78.3, 76.8 (OCH_2), 34.3 (SCH_2), 33.9, 33.6 [$\text{C}(\text{CH}_3)_3$], 32.5, 31.4 [$\text{C}(\text{CH}_3)_3$], 31.9 (ArCH_2Ar), 15.5 (SCH_3).

Synthesis of 2. A similar procedure to that described for **1** was used, except that for the synthesis of **2**, 3-(chloromethyl)pyridine hydrochloride was used. White crystals were obtained (88.7%) (mp: 247–249 °C). Anal. Calcd for $\text{C}_{62}\text{H}_{78}\text{O}_4\text{N}_2\text{S}_2$: C, 76.03; H, 8.03; N, 2.03. Found: C, 76.03; H, 8.10; N, 2.84.

^1H NMR (300 MHz CDCl_3): δ (ppm) 8.65 (s, 2-PyH, 2H), 8.63 (d, $J = 4.8$ Hz, 6-PyH, 2H), 7.81 (d, $J = 7.6$ Hz, 4-PyH, 2H), 7.34 (dd, $J = 4.8$ and 7.6 Hz, 5-PyH, 2H), 7.04 (s, ArH, 4H), 6.5 (s, ArH, 4H), 4.77 (s, OCH_2Py , 4H), 4.02 (t, $J = 7.5$ Hz, SCH_2CH_2 , 4H), 4.24 and 3.1 (d, $J = 12.5$ Hz, ArCH_2Ar , 8H), 2.76 (t, $J = 4.2$ Hz, SCH_2CH_2 , 4H), 1.92 (s, SMe₃, 3H), 1.28 (s, C (Me)₃, 18H), 0.87 (s, C (Me)₃, 18H).

^{13}C NMR (CDCl_3): δ (ppm) 153.8 (C2–Py), 151.8 (C6–Py), 151.0 (C4–Py), 149.9 (C3–Py), 145.6 (C5–Py), 137.3, 135.1 (C_i), 133.1, 132.3 (C_p), 125.7, 125.0 (C_o), 123.7, (C_m),

75.4, 73.4 (OCH₂), 34.3 (SCH₂), 33.9, 32.8 [C(CH₃)₃], 31.6 (ArCH₂Ar), 31.4, 31.3 [C(CH₃)₃], 15.7 (SCH₃).

Solubility Measurements. Saturated solutions of **1** and **2** were prepared by adding an excess amount of the solid to the solvent. The mixtures were left in the thermostat bath at 298.15 K for several days until equilibrium was reached. Aliquots of the saturated solutions were taken and analyzed gravimetrically in triplicate. Blank experiments were carried out. Solvate formation was checked by exposing the solid to a saturated atmosphere of the solvent for several days, following the procedure described in the literature.²⁴ The samples were weighed from time to time to check for any uptake of solvent. Solvate formation was observed in CH₂Cl₂ and CHCl₃.

Determination of Standard Enthalpies of Solution. Enthalpies of solution were carried out with the Tronac 450 calorimeter. To check the reliability of the solution calorimeter, the standard enthalpy of solution of THAM in an aqueous solution of 0.1 mol dm⁻³ of HCl was determined. The value obtained ($\Delta_s H^\circ = -29.4 \pm 0.2$ kJ mol⁻¹) is in good agreement with that of -29.71 kJ mol⁻¹ given in the literature.²⁵

Standard solution enthalpies of the ligand or the metal-ion complex salt were determined as described elsewhere.²⁶

¹H NMR Measurements of **1 and **2** with Alkali-Metal Cations.** ¹H NMR measurements were recorded at 298 K using a Bruker AC-300 E pulsed Fourier transform NMR spectrometer. Typical operating conditions for routine proton measurements involved a "pulse" or flip angle of 30°, spectral frequency (SF) of 300.135 MHz, delay time of 1.60 s, acquisition time (AQ) of 1.819 s, and line broadening of 0.55 Hz. A solution of the samples was prepared in the appropriate deuterated solvent, and these were then placed in 5 mm NMR tubes using TMS as the internal reference. ¹H NMR titrations were performed under the same experimental conditions by adding small amounts of a metal cation salt solution (concentrations depending on the solubility of the salt in the solvent) to 500 μ L of a solution of **1** or **2** [$\sim(2-5) \times 10^{-4}$ mol dm⁻³]. Then, changes in the chemical shifts upon addition of the metal cation salt were recorded and compared with those for the free ligand.

Conductance Measurements. For these measurements, a Wayne-Kerr autobalance universal bridge was used. Measurements were carried out as described elsewhere.²⁷

Preparation and Isolation of the Lithium and Sodium Complex Salts Using Perchlorate as the Counterion. This was accomplished by mixing stoichiometric amounts of the ligand and the salt in acetonitrile. The mixture was stirred and heated at 50 °C for half an hour until a clear solution was obtained. The final product was recrystallized from an ethanol:acetone (4:1) mixture. Microanalysis was carried out at the University of Surrey. Anal. Calcd for the salt C₆₂H₇₈O₄N₂S₂·LiClO₄: C, 68.54; H, 7.24; N, 2.58. Found: C, 68.44; H, 7.36; N, 2.96.

Anal. Calcd for C₆₂H₇₈O₄N₂S₂NaClO₄: C, 67.58; H, 7.14; N, 2.54. Found: C, 67.67; H, 7.33; N, 3.53.

Determination of Stability Constants. (i) *Potentiometric Titrations.* Potentiometric titrations were carried out using the Metrohm, 716DMS Titrimatic automatic potentiometer, following the procedure previously described.²⁷⁻²⁹

(ii) *Titration Microcalorimetry.* The four channel heat conduction microcalorimeter (Thermometric 2277) designed by Suurkuusk and Wadsö³⁰ was used to determine the thermodynamic parameters of complexation of **1** and univalent cations in acetonitrile and benzonitrile at 298.15 K. In all cases, the calorimetric measurements were carried out by the slow titration procedure. The calorimetric vessel was filled with a solution

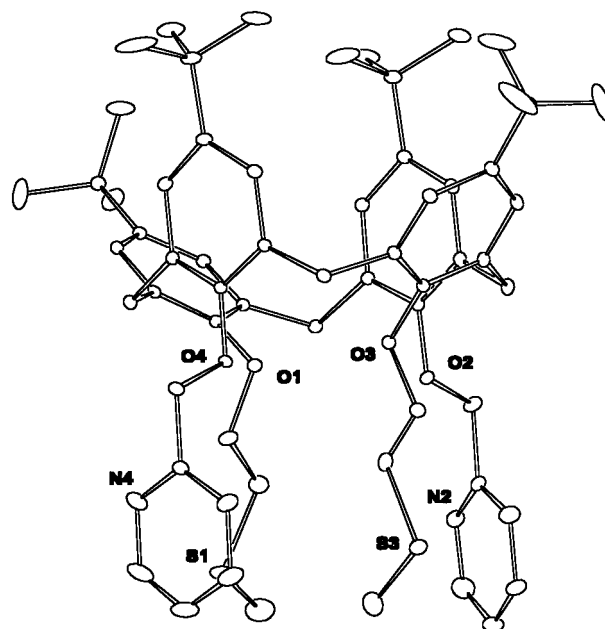


Figure 1. Side view of 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis[2-(methylthio)ethoxy]-26,28-bis[(pyrid-2-ylmethyl)oxy]calix(4)-arene (**1**). For clarity, only the labels of representative atoms are indicated in the plot.

of **1** ($\sim 2 \times 10^{-4}$ mol dm⁻³) in the appropriate solvent (2.5 cm³). Using a 500 μ L motor driven Hamilton syringe, fourteen additions (20 μ L each) of the metal-ion salt solution in the same solvent ($\sim 5 \times 10^{-3}$ mol dm⁻³) were made. Blank experiments were carried out in all cases to correct for the heat of dilution of the electrolyte in the given solvent.

A dynamic correction based on Tian's equation^{31,32} was used to calculate the integrals from the microcalorimetric curve. These experiments were carried out at different electrolyte concentrations (9×10^{-2} to 9×10^{-3} mol dm⁻³) to account for any additional heat effects due to ion-pair formation between the cation and its counterion.

Results and Discussion

Structural Conformations of **1 and **2** in Solution and in the Solid State.** The pair of doublets observed in the ¹H NMR data of these compounds which correspond to the equatorial (3.15 ppm for **1** and 3.12 ppm for **2**) and the axial (4.48 ppm for **1** and 4.26 ppm for **2**) protons of the methylene bridging groups provide evidence that these ligands adopt a "cone" conformation in solution.⁴ X-ray crystallographic studies of **1** and **2** show that this is also the case in the solid state. ORTEP³³ drawings of these molecules are shown in Figures 1 and 2. Atomic fractional coordinates and equivalent isotropic displacement parameters for **1** and **2** are reported elsewhere.³⁴ Essentially these structures show a hydrophobic cavity bounded by the phenyl rings and a hydrophilic pocket defined by OCH₂(2-Py) and O(CH₂)₂SCH₃ pendent groups. The chalices show a distorted "cone" conformation very similar to each other and to that found in other crystalline *p*-tert-butylcalix(4)arene derivatives.³⁵⁻³⁸ Following the structural characterization of **1** and **2**, we proceeded with the solution thermodynamics of these macrocycles in various solvents. Thus the following section discusses the standard solution Gibbs energies of **1**, **2**, and related ligands in different media derived from solubility data.

Solubility and Standard Gibbs Energies of Solution. *Transfer Functions.* Solubility data for **1** and **2** in various solvents at 298.15 K are listed in Table 1. These data are used

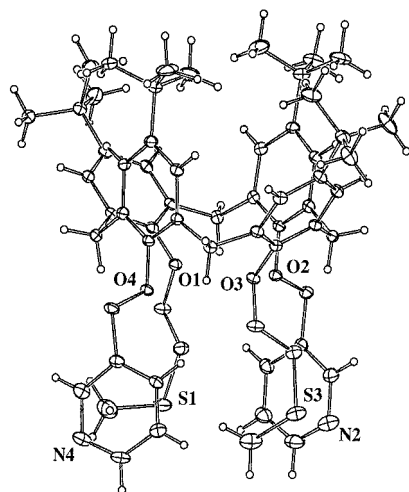


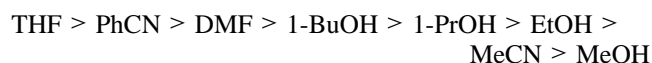
Figure 2. View of 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis[2-(methylthio)ethoxy]-26,28-bis[(pyrid-3-ylmethyl)oxy]calix(4)-arene (**2**) at 120 K with the atomic displacement ellipsoids at 30% probability level.

to calculate the standard Gibbs energies of solution $\Delta_s G^\circ$ of these ligands in the appropriate solvent using the relationship $\Delta_s G^\circ = -RT \ln S$, where S is the solubility on the molar scale referred to the standard state of 1 mol dm⁻³.

Taking acetonitrile as the reference solvent, standard Gibbs energies of transfer, $\Delta_t G^\circ$, of **1** and **2** from acetonitrile to other solvents are calculated.

These derivatives are very soluble in dichloromethane and in chloroform to the extent that solvate formation was observed when these were placed in a saturated atmosphere of these solvents. As a result, $\Delta_s G^\circ$ of these ligands in dichloromethane and in chloroform cannot be calculated since the derivation of $\Delta_s G^\circ$ requires the same composition for the solid in equilibrium with its saturated solution.

Data in Table 1 reflect that the equilibrium associated with the transfer process is shifted considerably by altering the nature of the solvent. Thus, the more negative the $\Delta_t G^\circ$ value is, the greater is the affinity of the receiving medium to solvate the ligand. The data show that these ligands undergo selective solvation in the various solvents. Thus, the following sequence is observed for **1**



A similar trend is observed for **2**, except that for this ligand, methanol is a better solvator than acetonitrile.

The ligand effect on the transfer process can be quantitatively assessed from the transfer constant ratio involving two ligands in a given solvent system. Since **1** and **2** are isomers, these data demonstrate that a change in the position of the nitrogen in the pyridyl ring relative to the ethereal oxygen leads to significant solvation changes. Thus **2** is better solvated by a factor of 2.1 in the MeCN–MeOH solvent system relative to **1** whereas the opposite is true in MeCN–EtOH (0.86) and MeCN–1-BuOH (0.56).

Since pyridinocalix(4)arenes (**3**–**5**) are related to these ligands (**1**, **2**), data available in the literature^{20–22} for these systems are also included in Table 1.

Thus, replacement of the pendant arms containing (methylthio)ethoxy substituents in **1** by pyridyl groups in **3** increases the solvation in the alcohols by factors of 4.40 (MeOH) to 8.3 (1-BuOH), whereas a decrease in solvation is observed in the

dipolar aprotic solvents (DMF, 0.21; PhCN, 0.29). When similar analysis was carried out with **4** relative to **2**, an increase in the solvation is found for the former with respect to the latter ligand in methanol (8.04) whereas in BuOH (0.11) the opposite trend is shown.

These changes in solvation upon transfer from one medium to another are likely to have implications on the stability of complex formation with metal cations in the various solvents.

Enthalpies of Solution and Derived Enthalpies of Transfer.

The problem encountered in the determination of the standard enthalpy of solution of calixarene derivatives by classical calorimetry is that these compounds are not soluble enough in the given solvent or their rate of dissolution is relatively slow. Therefore calorimetric measurements were carried out in two solvents, namely MeCN and PhCN.

No experimental difficulties were found with the latter solvent since at 298.15 K, **1** is soluble enough and the dissolution is fast. As far as MeCN is concerned, this compound is characterized by its low solubility in this solvent. Therefore for the calculation of the standard enthalpy of solution, $\Delta_s H^\circ$ of **1** in MeCN, the amount of compound dissolved was quantitatively measured (by using the gravimetric method) immediately after the calorimetric run was performed since total dissolution of the compound was not achieved. The standard enthalpy of solution ($\Delta_s H^\circ$) obtained calorimetrically is in excellent agreement with the $\Delta_s H^\circ$ obtained from the variation of the solubility with temperature. Details are given in Table 2. Combination of the $\Delta_s G^\circ$ values in Table 1 and $\Delta_s H^\circ$ values in Table 2 yield the standard entropy of solution $\Delta_s S^\circ$ of **1** in these solvents. Taking MeCN as the reference solvent, the standard transfer enthalpy $\Delta_t H^\circ$ and entropy $\Delta_t S^\circ$ to PhCN was calculated at 298.15 K, and these data are also reported in Table 2.

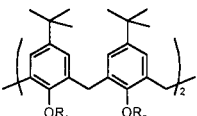
The higher solvation observed in PhCN relative to MeCN as reflected in the $\Delta_t G^\circ$ value for this ligand is enthalpy controlled since the process takes place with a loss of entropy. This is likely to have implications on the complexation ability of **1** for these metal cations in these media. In the following section, ¹H NMR measurements carried out with **1** and alkali-metal cations in CD₃CN at 298 K are discussed.

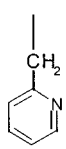
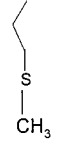
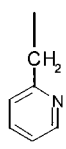
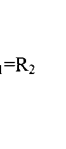
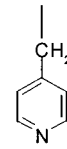
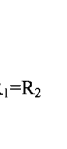
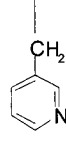
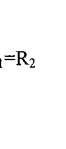
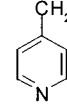
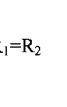
¹H NMR Measurements. ¹H NMR data for **1** and **2** and their interaction with alkali-metal cations in CD₃CN at 298 K are shown in Table 3.

Comparison of the ¹H NMR spectrum of the free calixarene in acetonitrile with that containing the lithium cation (1:1) in the same solvent shows a significant upfield shift of the 3-pyridyl proton signal ($\Delta\delta = 0.86$ ppm) and a downfield shift of the 6-pyridyl proton signal ($\Delta\delta = 0.64$ ppm), as well as for that corresponding to the methylene protons next to the pyridyl group ($\Delta\delta = 0.63$ ppm). This observation suggests an interaction of the cation with both, the oxygen and the nitrogen atoms of the pyridyl group, which results in a deshielding influence exerted on the protons adjacent to these donor atoms.

On the other hand, some weaker interaction seems to take place between lithium and the ethereal oxygen of the sulfur pendent arm, since a less pronounced downshift signal is observed for the resonance of the methylene proton close to the oxygen donor atom in this arm ($\Delta\delta = 0.23$ ppm). Parallel, though smaller, downfield shift changes appear to occur for the complexation of the ligand with sodium (Table 3), indicating a similar but weaker interaction of this cation with the macrocycle.

No chemical shift changes were observed by the addition of potassium, rubidium and cesium to **1** in CD₃CN. Again,

TABLE 1: Solubility and Derived Standard Gibbs Energies of Solution of 1 and 2 in Various Solvents at 298.15 K. Standard Transfer Gibbs Energies from Acetonitrile. Comparison with Data for Pyridinocalix(4)arenes^a


Ligand R ₁ — R ₂		Solvent (s)	Solubility mol dm ⁻³	Δ _s G° kJ mol ⁻¹	Δ _t G° kJ mol ⁻¹
 1	 2	MeCN	(2.90±0.30) × 10 ^{-4b}	20.20	0
		MeOH	(2.01±0.13) × 10 ^{-4b}	21.10	0.92
		EtOH	(1.13±0.10) × 10 ^{-3b}	16.82	-3.38
		1-PrOH	(2.56±0.07) × 10 ^{-3b}	14.80	-5.40
		1-BuOH	(3.18±0.01) × 10 ^{-3b}	14.26	-5.94
		DMF	(4.62±0.04) × 10 ^{-3b}	13.33	-6.87
		THF	(9.47±0.16) × 10 ^{-2b}	5.84	-14.36
		PhCN	(3.54±0.04) × 10 ^{-2b}	8.28	-11.92
 3	 4	MeCN	(5.32±0.11) × 10 ^{-4b}	18.69	0
		MeOH	(7.88±0.31) × 10 ^{-4b}	17.72	-0.97
		EtOH	(1.81±0.01) × 10 ^{-3b}	15.65	-3.03
		1-PrOH	(3.75±0.03) × 10 ^{-3b}	13.85	-4.84
		1-BuOH	(3.10±0.02) × 10 ^{-3b}	14.32	-4.37
		MeCN	4.08 × 10 ^{-3c}	19.35	0
		MeOH	1.24 × 10 ^{-3c}	16.59	-2.76
		EtOH	5.73 × 10 ^{-3c}	12.80	-6.55
 5	 6	1-PrOH	2.26 × 10 ^{-2c}	9.39	-9.96
		1-BuOH	3.74 × 10 ^{-2c}	8.15	-11.20
		DMF	1.88 × 10 ^{-3c}	15.56	-3.79
		PhCN	1.05 × 10 ^{-2c}	11.30	-8.05
		PC	3.44 × 10 ^{-4c}	19.77	0.42
		PhNO ₂	2.58 × 10 ^{-3c}	14.77	-4.58
		MeCN	3.53 × 10 ^{-3c}	14.00	0
		MeOH	4.19 × 10 ^{-2c}	7.86	-6.14
 7	 8	EtOH	2.80 × 10 ^{-2c}	8.86	-5.14
		1-BuOH	2.33 × 10 ^{-3c}	15.03	1.03
		DMF	8.18 × 10 ^{-3c}	11.91	-2.09
		PhCN	3.01 × 10 ^{-2c}	8.68	-5.32
		Me ₂ CO	6.25 × 10 ^{-3c}	12.58	-1.42
		MeCN	1.57 × 10 ^{-3c}	16.01	0
		MeOH	1.68 × 10 ^{-2c}	10.13	-5.88
		EtOH	8.60 × 10 ^{-3c}	11.79	-4.22
 9	 10	DMF	2.58 × 10 ^{-3c}	16.67	0.66
		PhCN	2.58 × 10 ^{-3c}	11.49	-4.52

^a Abbreviation; acetonitrile, MeCN; methanol, MeOH; ethanol, EtOH; 1-propanol, 1-PrOH; 1-butanol, 1-BuOH; *N,N*-dimethylformamide, DMF; tetrahydrofuran, THF; benzonitrile, PhCN. ^b This work. ^c References 20–22.

chemical shifts remain unaltered by the addition of any alkali-metal cation to **2** in this solvent.

Conductometric Measurements. Conductimetric titrations were carried out in order to establish the composition of the metal-ion complexes in MeCN and PhCN at 298.15 K.

Plots of molar conductances, Λ_m , against the ligand to metal ion mole ratio for **1** show well-defined changes in curvature at the reaction stoichiometry of 1:1 for Li⁺ and Na⁺ in acetonitrile at 298.15 K. These findings suggest the formation of reasonably strong complexes with these cations in this solvent. However slight (or zero) slopes and without any indication of a change in slope at any given molar ratio were found for K⁺, Rb⁺, and Cs⁺ in acetonitrile. Well-defined breaks in the titration curves were also found for Li⁺ and Na⁺ and **1** in benzonitrile. Again, no changes for K⁺, Rb⁺, and Cs⁺ were observed in this solvent.

Representative conductometric titration curves for Li⁺ and **1** in MeCN and PhCN at 298.15 K are shown in Figure 3.

In both cases, addition of the ligand to the metal-ion salt leads to a decrease in conductance suggesting that the mobility of the complex cation is lower than that for the free metal cation. This behavior can be justified given that the size of the former is greater than that of the uncomplexed cation. As far as **2** is concerned, the addition of this ligand to the metal-ion salt shows no indication of changes in the slopes for alkali-metal cations either in MeCN or in PhCN.

In summary, conductance measurements provide information regarding the following.

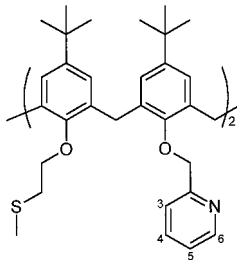
- The composition of the metal-ion complex in solution and
- The strength of complexation. The data also reflect that in moving from **1** to **2**, the distance between the donor atoms (O and N) of the pendent arms containing pyridine rings increases. Therefore, the cooperative effect of the ethereal oxygen and the pyridyl nitrogen atoms which appears to provide the sites of interaction for Li⁺ and Na⁺ does not operate in **2** as

TABLE 2: Enthalpies and Entropies of Solution of 1 in Acetonitrile and Benzonitrile. Derived Enthalpy and Entropy of Transfer of 1 from Acetonitrile at 298.15 K

MeCN				
T/K	solubility, mol dm^{-3}	$\Delta_{\text{s}}G^{\circ}$, kJ mol^{-1}	$\Delta_{\text{s}}H^{\circ}$, kJ mol^{-1}	$\Delta_{\text{s}}S^{\circ}$, $\text{J K}^{-1} \text{mol}^{-1}$
293.15	1.71×10^{-4}	21.50	51.23 ± 0.01^b (51.69) ^c	104.8 ^c
298.15	2.90×10^{-4} ^a	20.20 ^a		
303.15	4.42×10^{-4}	19.15		
322.15	1.26×10^{-3}	16.55		
PhCN				
T/K	solubility, mol dm^{-3}	$\Delta_{\text{s}}G^{\circ}$, kJ mol^{-1}	$\Delta_{\text{s}}H^{\circ}$, kJ mol^{-1}	$\Delta_{\text{s}}S^{\circ}$, $\text{J K}^{-1} \text{mol}^{-1}$
298.15	3.54×10^{-2}	8.28	12.92 ± 0.02	15.6 ^d
MeCN \rightarrow PhCN				
T/K	$\Delta_{\text{t}}G^{\circ}$, kJ mol^{-1}	$\Delta_{\text{t}}H^{\circ}$, kJ mol^{-1}	$\Delta_{\text{t}}S^{\circ}$, $\text{J K}^{-1} \text{mol}^{-1}$	
298.15	−11.92	−38.54	−89.20	

^a From Table 1. ^b Calorimetric value. ^c Derived from solubility data given in column 2 by the use of the van't Hoff equation. ^d Calculated from $\Delta_s G^\circ$ and $\Delta_s H^\circ$ values.

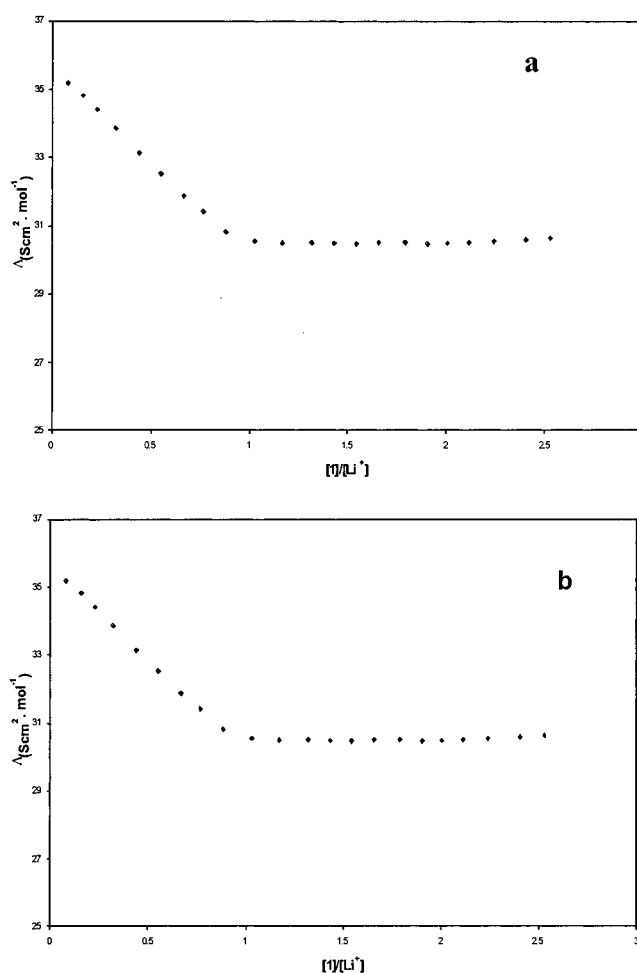
TABLE 3: Chemical Shift Changes of the Lithium and Sodium Complexes of 1 Relative to the Free Ligand in CD₃CN at 298 K

			
protons	ligand δ_{ppm}	Li ⁺ $\Delta\delta_{\text{ppm}}$	Na ⁺ $\Delta\delta_{\text{ppm}}$
<i>tert</i> -butyl(Py)	1.10	-0.07	-0.11
<i>tert</i> -butyl(S)	1.22	-0.01	-0.02
CH ₃ S	1.88	0.12	0.04
CH ₂ CH ₂ S	2.57	0.20	0.32
CH(Ax)	4.37	0.32	0.05
CH ₂ CH ₂ S	3.82	-0.23	-0.07
CH(Eq)	3.18	-0.18	-0.32
OCH ₂ Py	4.98	-0.63	-0.27
Ar(S)	7.03	-0.27	-0.33
Ar(Py)	7.20	-0.18	-0.13
Py(H3)	7.79	0.86	0.26
Py(H4)	7.34	-0.24	-0.13
Py(H5)	7.91	-0.05	-0.12
Py(H6)	8.63	-0.64	-0.18

also demonstrated by ¹H NMR (Table 3). As far as the interaction of **1** and alkali-metal cations in both solvents is concerned, the ligand discriminates against the larger metal cations.

As a result of the semiquantitative information from conductance measurements regarding the strength of complexation of **1** and these cations, we proceeded to investigate the thermodynamics of complexation of **1** with lithium and sodium in acetonitrile and benzonitrile at 298.15 K and this is now discussed.

Thermodynamic of Complexation of 1 with Lithium and with Sodium in Acetonitrile and Benzonitrile at 298.15 K. Stability constants (expressed as log *K*_s) and standard Gibbs energies of complexation, $\Delta_c G^\circ$, enthalpies, $\Delta_c H^\circ$, and entropies, $\Delta_c S^\circ$, of **1** and lithium and sodium in acetonitrile and benzonitrile at 298.15 K are listed in Table 4. These data were obtained from titration microcalorimetry, since the small heats and the slow kinetics of complexation of this ligand and these cations unable us to derive these from classical calorimetry.

**Figure 3.** Conductometric titration curves for lithium and **1** in acetonitrile (a) and in benzonitrile (b) at 298.15 K.

In addition, the stability constants of these cations and **1** in acetonitrile were also determined by competitive potentiometry using the silver electrodes. The stability constant for silver and **1** obtained by direct potentiometry is also included (see footnote of Table 4). A good agreement between the stability constants is found between the sets of data obtained by the two methods. An average value is used to calculate the standard Gibbs energy of complexation of **1** and Li⁺ and Na⁺ in acetonitrile. As shown by ¹H NMR, no complexation takes place between this ligand and the large alkali-metal cations (K⁺, Rb⁺, and Cs⁺) in

TABLE 4: Thermodynamics of Complexation of 1 and Metal Cations in Acetonitrile and Benzonitrile at 298.15 K

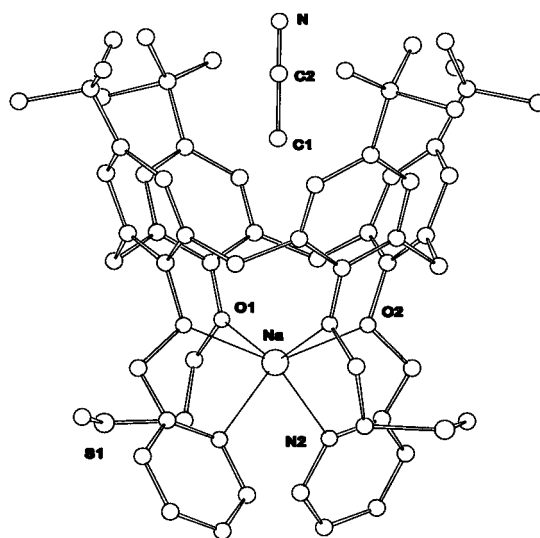
cation		$\log K_s$	$\Delta_c G^\circ$, kJ mol ⁻¹	$\Delta_c H^\circ$, kJ mol ⁻¹	$\Delta_c S^\circ$, J K ⁻¹ mol ⁻¹
Acetonitrile					
Li ⁺	5.43 ± 0.07 ^a	5.42 ± 0.01	-30.94 ± 0.41	-26.2 ± 0.6	16.0
	5.41 ± 0.18 ^b				
	5.95 ^c				
Na ⁺	5.20 ± 0.02 ^a	5.22 ± 0.02	-29.80 ± 0.10	-33.8	-13.4
	5.23 ± 0.02 ^b				
	5.48 ^c				
Benzonitrile					
Li ⁺	5.88 ± 0.01 ^a		-33.57 ± 0.06	-37.6 ± 0.1	-7.4
	5.10 ^c				
Na ⁺	5.11 ± 0.01 ^a		-29.17 ± 0.02	-17.5 ± 0.4	39.1
	4.74 ^c				

^a From titration microcalorimetry. ^b From competitive potentiometry using the silver electrode. log $K_s(1+Ag^+)$ in acetonitrile at 298.15 K, 4.4 ± 0.1. ^c Data for ligand 3.²⁰

acetonitrile. Conductance measurements suggest that this is also the case for these systems in benzonitrile. The results show that the ligand is slightly more selective for Li⁺ relative to Na⁺ in these solvents. While the $\Delta_c G^\circ$ values do not differ significantly between these two cations in a given solvent or indeed in these solvents, considerable differences are found in their enthalpic and entropic contributions. As far as the lithium cation is concerned, two patterns are observed. Thus in acetonitrile, lithium is enthalpically less stable than sodium, while the opposite is true in terms of entropy. This is the reverse trend to that observed in benzonitrile where the enthalpic stability of the process is greater for Li⁺ relative to Na⁺ and these are compensated by more favorable entropy for Na⁺ relative to Li⁺. For comparison purposes²¹ the values for the analogous derivative 3 and these cations in these solvents are also included in Table 4. Both ligands show a slightly higher affinity for lithium relative to sodium and the trend observed in terms of enthalpy and entropy in the two solvents is the same for 1 and 3. As far as the ligand effect is concerned, the most distinctive feature of the data is that while the stability of the complex is greater for 3 relative to 1 in acetonitrile, the opposite is true in benzonitrile. It is reasonable to expect that replacement of 2-pyridyl groups in 3 by two (methylthio)ethoxy groups in 1 will lead to a decrease in the complex stability of the latter with respect to the former. However, desolvation of ligand and metal cation as well as solvation of the metal-ion complex are likely to contribute significantly to the stability of complex formation and these are reflected in the changes observed in the $\Delta_c H^\circ$ and $\Delta_c S^\circ$ values in altering either the cation, the ligand and the solvent. A general feature is the considerable degree of enthalpy–entropy compensation effect, which are observed in the data reported in Table 4.

The availability of transfer thermodynamic data of the reactants and the product will help to gain understanding about the factors which contribute to the medium effect on the complexation process. Transfer thermodynamic data for the alkali-metal cations from MeCN and PhCN are available in the literature²⁶ while data for the ligand are those shown in Tables 2 and 3. Therefore, the following section discusses the solution thermodynamics of lithium and sodium 1 perchlorate salts in acetonitrile and benzonitrile at 298.15 K.

Solution Thermodynamics of Alkali-Metal 1 Complexes as Perchlorate Salts. The lithium and sodium 1 perchlorate salts were isolated as described in the Experimental Section. In addition, we obtained single crystals of the perchlorate salt of the Na1(MeCN) complex adequate for X-ray diffraction studies. An ORTEP molecular plot of the complex is shown in Figure

**Figure 4.** Molecular plot of the sodium and acetonitrile complex of 1, sited at a 2-fold crystallographic axis.**TABLE 5: Enthalpies of Solution of Lithium and Sodium Complexes as Perchlorates in Acetonitrile and Benzonitrile at 298.15 K**

[Li 1] ClO ₄			
MeCN		PhCN	
<i>c</i> , mol dm ⁻³	Δ _s <i>H</i> , kJ mol ⁻¹	<i>c</i> ,mol dm ⁻³	Δ _s <i>H</i> , kJ mol ⁻¹
1.49 × 10 ⁻⁴	14.1	4.74 × 10 ⁻⁴	-31.4
2.79 × 10 ⁻⁴	15.9	8.65 × 10 ⁻⁴	-33.8
4.84 × 10 ⁻⁴	13.1	1.20 × 10 ⁻³	-41.3
7.90 × 10 ⁻⁴	12.9	1.39 × 10 ⁻³	-50.9
9.25 × 10 ⁻⁴	14.6	1.62 × 10 ⁻³	-49.1
9.37 × 10 ⁻⁴	14.7	1.67 × 10 ⁻³	-52.4
Δ _s <i>H</i> ^o = 14.2 ± 1.1 kJ mol ⁻¹ <i>a</i>		Δ _s <i>H</i> ^o = -20.7 ± kJ mol ⁻¹ <i>b</i>	
[Na 1] ClO ₄			
<i>c</i> , mol dm ⁻³	Δ _s <i>H</i> , kJ mol ⁻¹		
MeCN			
4.94 × 10 ⁻⁴	3.1		
7.64 × 10 ⁻⁴	3.4		
1.03 × 10 ⁻³	3.1		
1.49 × 10 ⁻³	3.4		
1.76 × 10 ⁻³	3.8		
2.47 × 10 ⁻³	3.5		
Δ _s <i>H</i> ^o = 3.4 ± 0.2 kJ mol ⁻¹ <i>a</i>			

^a Average value. ^b Extrapolated value.

4. The corresponding structural details are reported elsewhere.³⁴ As can be seen from this figure, the cation is found in the hydrophilic cavity while the hydrophobic cavity hosts one molecule of acetonitrile. The crystallographic results confirm the key role played by the pyridyl nitrogens and the ethereal oxygens in the complexation process.

The lithium and sodium complex salts appear to undergo solvate formation when exposed to a saturated atmosphere of these solvents, particularly in benzonitrile. Hence we were unable to derive their solution Gibbs energies in these solvents from solubility measurements. As far as enthalpies are concerned, this is not a limitation. Therefore, calorimetric measurements were performed to determine the standard enthalpies of solution of these complex salts in acetonitrile and benzonitrile at 298.15 K. No reliable results were obtained for Na1ClO₄ in benzonitrile. Thus, Table 5 shows the $\Delta_s H$ values for Li1ClO₄ in MeCN and PhCN at different electrolyte concentrations. In cases where no systematic variation in the $\Delta_s H$ values were found by altering the concentration, the standard enthalpy of

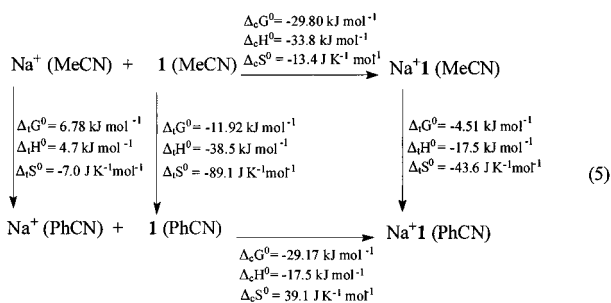
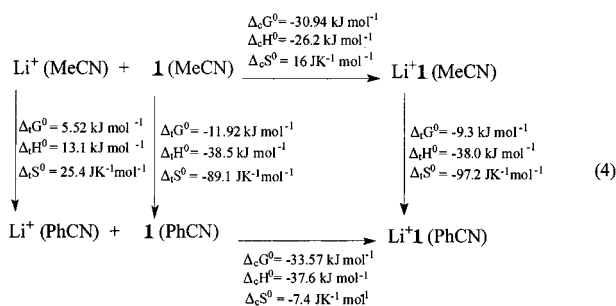
solution $\Delta_s H^\circ$ is taken as the average of the data. When $\Delta_s H^\circ$ values vary with changes in the electrolyte concentration, the $\Delta_s H^\circ$ value was calculated from the intercept at $c = 0$ of a plot of $\Delta_s H$ against the square root of the concentration $c^{1/2}$. Data for NaClO₄ in acetonitrile at 298.15 K are also shown in Table 5. As far as the lithium complex perchlorate salt is concerned, the results reflect that the complex salt interacts more strongly in benzonitrile than in acetonitrile. These data are now used to assess the medium effect on the complexation process and this is discussed in the following section.

Medium Effect on the Complexation of Lithium and Sodium with 1 in Dipolar Aprotic Media. The medium effect on the complexation process is controlled by the differences in the solvation of the reactants and the product³⁹ participating in the process between two solvents, as shown in eq 3

$$\Delta_c P^\circ(s_2) - \Delta_c P^\circ(s_1) = \Delta_t P^\circ(M^+1)(s_1 \rightarrow s_2) - \Delta_t P^\circ(M^+)(s_1 \rightarrow s_2) - \Delta_t P^\circ(1)(s_1 \rightarrow s_2) \quad (3)$$

These differences are reflected in the thermodynamic parameters of transfer, $\Delta_t P^\circ$ ($P = G, H, S$) of the ligand, the free (M^+) and the complexed metal-ion ($M1^+$) from a reference solvent (s_1) to another (s_2). As far as Gibbs energies are concerned, there is enough information as to assess the medium effect on complexation given that the single-ion values for these cations from acetonitrile to benzonitrile based on the Ph₄AsPh₄B convention⁴⁰ are well established.²⁶

Availability of the $\Delta_t G^\circ$ value for 1 from MeCN to PhCN (see Table 1) and the $\Delta_c G^\circ$ values for these cations and 1 in these solvents (Table 4) allows the calculation of the $\Delta_t G^\circ$ value for the metal-ion complex from MeCN to PhCN through eq 3. This is best illustrated via a thermodynamic cycle³⁹ in which the appropriate quantities for Li⁺ and Na⁺ are inserted.



As previously stated,³⁹ the complexation process will be favored in the solvent that offers the poorest solvating medium for the reactants and the better solvating medium for the product. On the basis of these concepts, the slightly higher stability (more favorable $\Delta_c G^\circ$) observed for Li⁺ and 1 in PhCN relative to MeCN is due to the favorable contribution of the free metal cation (better solvated in MeCN) and the complex cation (better

solvated in PhCN), which overcome the unfavorable contribution of the ligand for complexation in PhCN. Having stated this, it should be noted that the $\Delta_t G^\circ$ value for the ligand is quite close to that of the metal-ion complex. This finding may be taken as an indication that the cation may be well shielded in the hydrophilic cavity of the ligand and unable to enter direct interaction with the solvent.

For the complexation of Na⁺ and 1, again the free and complexed cations favor complexation in PhCN but their contributions are compensated by that of the ligand, which show the opposite trend. As a result, the stability of complex formation is about the same in both solvents.

To assess the medium effect in terms of enthalpy, we use the $\Delta_t H^\circ$ values for lithium and sodium from MeCN to PhCN based on the Ph₄AsPh₄B⁴⁰ given in the literature.²⁶ The $\Delta_t H^\circ$ value for the ligand, the lithium-ion complex salt and the $\Delta_c H^\circ$ values for these cations and 1 in these solvents are those given in Tables 2, 5, and 4, respectively.

Single-ion $\Delta_t H^\circ$ for the Li⁺ were calculated from data in Table 5 taking into account the transfer enthalpy single-ion value for the perchlorate ion from MeCN to PhCN based on the Ph₄AsPh₄B reported in the literature.²⁶ The $\Delta_t H^\circ$ value for Na⁺ from acetonitrile to benzonitrile was calculated via the cycle using the $\Delta_c H^\circ$ values for this cation and 1 in these solvents (Table 4) and the $\Delta_t H^\circ$ value for the sodium cation and the ligand (Table 2) from MeCN to PhCN (using the calculated $\Delta_t H^\circ$ value for NaClO₄ and the $\Delta_s H^\circ$ value for this salt in acetonitrile, an estimated value for the $\Delta_s H^\circ$ of this salt in benzonitrile can be calculated).

As far as Li⁺ is concerned, the data show that the higher enthalpic stability of complex formation in benzonitrile relative to acetonitrile is almost entirely due to the contribution of the free cation (enthalpically more stable in MeCN than in benzonitrile). The transfer enthalpy of the metal-ion complex is almost the same as that of the ligand and therefore the cation appears to be well shielded by the ligand. A similar pattern is also found in terms of entropy. This is not the case for sodium. For this cation, the joint contribution of both, the free and complex cations that favor complexation (in enthalpic terms) in benzonitrile, is not enough to overcome the higher enthalpic stability of the ligand in PhCN relative to MeCN. As a result, the complexation process is enthalpically more stable in the latter than in the former solvent. In terms of entropy, again the ligand plays a predominant role in the more favorable entropies of the complexation in PhCN relative to MeCN. It should be also noted that the differences in the entropic stability between these two solvents is reduced in the sodium metal-ion complex relative to the free ligand. It may well be that either the hydrophobic cavity is better pre-organized to interact with acetonitrile when the ligand is complexed with the sodium cation than on its free state or as shown in the transfer enthalpies, the ability of the ligand to interact with benzonitrile is greater for the free relative to the complex ligand.

Conclusions

From the above discussion, we reached the following conclusions.

(i) Two new lower rim calix(4)arene derivatives (isomers) containing mixed pendent arms have been successfully synthesized. These have been characterized by ¹H NMR and by X-ray diffraction studies.

(ii) Solution thermodynamic data for these ligands show that these macrocycles undergo selective solvation in nonaqueous media.

(iii) ^1H NMR measurements in CD_3CN at 298 K show that **1** interacts with the smaller alkali-metal cations (Li^+ and Na^+) but discriminates against the largest ones (K^+ , Rb^+ , and Cs^+). However, this interaction appears to be more pronounced when the pendent arms containing the pyridyl ring (through the ethereal oxygens and nitrogens) than with that containing the (methylthio)ethoxy arms (only ethereal oxygens are involved). This is not the case for **2**. For this ligand the distance between the ethereal oxygens and the pyridyl nitrogens increases and therefore **2** is unable to provide the sites of interaction required for complexation with alkali-metal cations

(iv) Conductance measurements demonstrated that 1:1 complexes are formed between **1** and lithium and sodium cations in acetonitrile and benzonitrile. Conductometric measurements corroborate the ^1H NMR results in that no interaction occurs between **1** and the large alkali-metal cations (K^+ , Rb^+ , and Cs^+)

(v) The complexation process involving **1** and lithium and sodium has been thermodynamically characterized in acetonitrile and in benzonitrile at 298.15 K. In acetonitrile, stability constants were derived from competitive potentiometry (using silver electrodes) and by titration calorimetry. The agreement found between the two sets of data encourages us to use the latter technique in benzonitrile since this allows the determination of not only the stability of complex formation but also the enthalpy and entropy.

(vi) The significance of transfer data of the reactants and the product in the interpretation of the medium effect on the thermodynamics of the complexation is demonstrated.

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