Solvation Effect of Guest, Supramolecular Host, and Host−Guest Compounds on the Thermodynamic Selectivity of Calix(4)arene Derivatives and Soft Metal Cations

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This paper reports thermodynamic data for the transfer of calixarene derivatives and their metal−ion complexes in dipolar aprotic solvents. These data are used to assess the effect of solvation of these compounds on the selective complexation shown by these macrocycles for soft metal cations in different media. Thus, solubilities and derived Gibbs energies of solution of 5,11,17,23-tetra-*tert*-butyl[25,27-bis(hydroxyl)-26,28-bis-(ethylthioethoxy)]calix(4)arene, **1**, and 5,11,17,23-tetra-*tert*-butyl-[25,27-bis(ethylenethanoate)-26,28-bis-(ethylthioethoxy)]-calix(4)arene, **2**, in various solvents at 298.15 K are reported. Solvation of these ligands in one medium relative to another is analyzed from their standard transfer Gibbs energies using acetonitrile as the reference solvent. These data are combined with transfer enthalpies (derived from standard solution enthalpies obtained calorimetrically) to calculate the corresponding entropies of transfer of these calix(4)-arene derivatives from acetonitrile to methanol and *N,N*-dimethylformamide. As far as the metal−ion salts (silver and mercury) in their free and complex forms are concerned, standard solution enthalpies were determined in acetonitrile, methanol, and *N,N*-dimethylformamide. These data are used to derive their transfer enthalpies from one medium to another. It is concluded that the extent of complexation of these macrocycles with soft metal cations is controlled by not only the solvation changes that the free cation undergoes in moving from one medium to another but also those for the ligand and its complex cation in these solvents.

Introduction

Transfer thermodynamic parameters of a compound from a reference solvent to another provide information related to the extent of its solvation in one medium relative to another.[1−3] Although these data are available for a wide range of neutral and ionic species[4] not much use of this information is made. Supramolecular chemistry defined by Lehn[5] as "the chemistry of molecular assemblies and of intermolecular bonds" is one of the most active areas of chemical research as demonstrated by the huge amount of literature in this field.[6] As far as supramolecular hosts and host−guest compounds are concerned, the availability of transfer thermodynamic data on these systems is indeed very limited.[3] However, the extent of solvation of reactants and products in a given medium plays a key role in the selective, nonselective, or absent interaction between supramolecular hosts and guest species. This statement is evident from the relationship (eq 1) between the thermodynamic parameters of complexation ($\Delta_c P^\circ$, $P = G^\circ$, H°, S°) and those for the transfer ($\Delta_t P^\circ$) of the host, H, the guest, G, and the host−guest, H−G, from one solvent s_1 to another s_2.[9,10] The medium

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

effect on cation complexation processes involving cryptands[7−9] and crown ethers,[10,11] although significant, does not generally alter the selectivity pattern of these ligands for metal cations. This is not the situation for processes involving calixarene

derivatives[12] and metal cations where remarkable solvent effects are observed to an extent that changes from one solvent to another may result in reverse or loss of selectivity or lack of complexation. Changes in the complex composition with the medium have also been observed.[13] An illustrative example is that involving two lower rim calix(4)arene derivatives, namely, 5,11,17,23-tetra-*tert*-butyl[25,27-bis(hydroxy)-26,28-bis(eth-ylthioethoxy)]calix(4)arene, **1**,[14] and 5,11,17,23-tetra-*tert*-butyl-[25,27-bis(ethylethanoate)oxy-26,28-bis(ethylthioethoxy)]calix-(4)arene, **2**,[15]

1   **2**
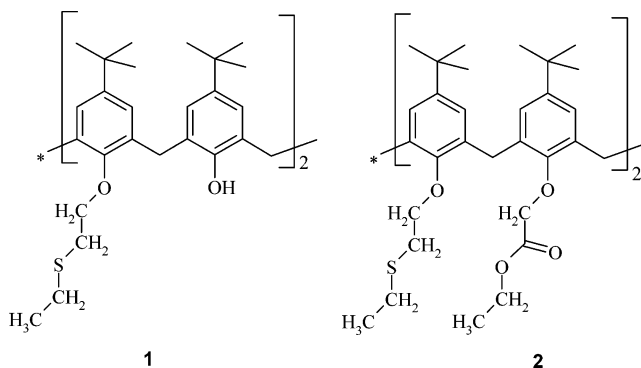
with soft metal cations (Hg^{2+} and Ag^+) in different solvents. As far as **1** is concerned, the selectivity of this ligand for Hg^{2+} relative to Ag^+ in acetonitrile is reversed in methanol and lost in *N,N*-dimethylformamide, while no complexation was found in propylene carbonate. Therefore, this paper aims to establish the solvation changes that these cations, the supramolecular hosts, and their host−guest complexes undergo in these solvents. To fulfill this aim, we proceeded with the calculation of the

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transfer parameters ($\Delta_t G°$, $\Delta_t H°$, $\Delta_t S°$) of **1** and **2** and their metal−ion complex salts from solution thermodynamic data of these compounds in these solvents. The implications of transfer data on the complexation thermodynamics of these ligands (**1** and **2**) and the cations in different medium are discussed.

Experimental Section

Synthesis and Characterization of Ligands 1 and 2. Ligands **1** and **2** were synthesized and characterized as reported elsewhere.[14,15]

Chemicals. Mercury(II) perchlorate 98%, silver perchlorate 99%, and tris(hydroxymethyl)aminomethane ultrapure grade 99.9% were all purchased from Aldrich Chemical Co. These were dried over P_4O_{10} under vacuum for several days before use.

Acetonitrile, MeCN (Aldrich, HPLC grade), was purified by refluxing the solvent in a nitrogen atmosphere and distilled over calcium hydride. The middle fraction of the distilled solvent was used.[16]

N,*N*-Dimethylformamide, DMF (Fisher, HPLC grade), was dried over 3 Å molecular sieves (which have been dried in an oven at 300 °C overnight) for 72 h followed by distillation under reduced pressure.[16] The water contents of these solvents as determined by Karl Fisher titration were not greater than 0.01%.

Methanol, MeOH (Fission, HPLC grade), was used without further purification.

Solubility Measurements. The solubility of **1** and **2** was determined in several nonaqueous solvents at 298.15 K. Saturated solutions of these ligands were prepared and kept in a thermostated bath at 298.15 ± 0.05 K for several days, to reach equilibrium between the solid (sol) and its saturated solution (s) (eq 2). In eq 2, *K* is the thermodynamic equilibrium

$$\textbf{1 or 2 (sol)} \xrightarrow{K} \textbf{1 or 2 (s)} \qquad (2)$$
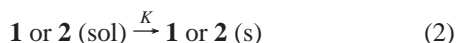
constant.

Aliquots of the saturated solution were placed into preweighed porcelain crucibles. The solvent was evaporated, and the solid left inside the crucibles was kept in a desiccator under calcium chloride to reach room temperature. The crucibles were weighed over several days until constant weight was recorded. Separate blank experiments were carried out to ensure the absence of any involatile material in the pure solvent. All analyses were carried out in triplicate.

Solvate formation was checked by placing a known amount of the ligand on a watch glass for several days over the appropriate solvent located at the bottom of a closed desiccator, to ensure a saturated atmosphere of the solvent.[17]

Isolation of the Mercury(II) and Silver(I) Complexes of 1 and 2 from MeCN and/or MeOH. Stoichiometric quantities of the mercury(II) and silver(I) perchlorate salts and **1** and **2** were dissolved in acetonitrile or methanol accordingly, mixed, and refluxed, then the solutions were left at room temperature until crystals were formed. Elemental analyses performed at the University of Surrey are as follows: (i) Ag**1**ClO₄ recrystallized from MeOH, calcd C, 60.49; H, 7.03; found C, 60.33; H, 7.18; (ii) Hg**1**(ClO₄)₂ recrystallized from MeOH, calcd C, 50.98; H, 5.93; found C, 50.79; H, 6.07; (iii) Hg**1**(ClO₄)₂ recrystallized from MeCN, found C, 50.65; H, 6.07.

Determination of Standard Enthalpy of Solution. The enthalpies of solution, $\Delta_s H$ (kJ mol⁻¹), of the ligand **2**, metal−ion salt [Hg(ClO₄)₂], and the metal−ion complexes [Hg**1**(ClO₄)₂, Ag**1**ClO₄, Hg**2**(ClO₄)₂, and Ag**2**ClO₄] at different concentrations (1×10^{-4} to 1×10^{-3} mol dm⁻³) were determined calori-

metrically using the Tronac 450 macrocalorimeter in the corresponding solvent at 298.15 K. Glass ampules (at least five) were filled with different amounts of the corresponding compound and sealed. These were then placed into a stainless steel basket and mounted on a plunger in the reaction vessel. The solvent (50 cm³) of interest was loaded in the vessel, and the system was placed in a water bath until thermal equilibrium was attained. The ampule was broken by means of the plunger, and the resulting temperature changes were recorded. After each experiment, electrical calibration was performed. The heat of solution was calculated by subtracting the heat of breaking of the empty ampule from the total recorded heat. When **1** and **2** metal−ion complexes were investigated, these experiments were performed in the presence of an excess of the ligand dissolved in the solvent placed in the reaction vessel to ensure that no dissociation of the complex would occur during these measurements.

As far as the standard enthalpy of solution of **1** in MeCN and MeOH is concerned, the van't Hoff equation (eq 3) was used to evaluate $\Delta_s H°$ (kJ mol⁻¹). Therefore, solubility measurements at three different temperatures (278.15, 285.15, and 308.15 K) were carried out. In eq 3, $K = s$ is the equilibrium

$$\log K = \frac{-\Delta_s H°}{2.303R} \times \frac{1}{T} + C \qquad (3)$$

constant, *T* is the temperature in K, *R* is the gas constant, 8.314 J K⁻¹ mol⁻¹, *C* is a constant, and $\Delta_s H°$ is the enthalpy of solution in kJ mol⁻¹.

Taking eq 3 into account, it follows that a plot of $-\log K$ vs $1/T$ will give a slope of $\Delta_s H°/2.303R$ from which $\Delta_s H°$ can be calculated.

Results and Discussion

Solubility of 1 and 2 and Derived Standard Gibbs Energies of Solution. Table 1 reports the solubility on the molar scale of **1** and **2** in different solvents at 298.15 K for the process described in eq 4. The standard deviation of the data is also included in this table.

$$\textbf{1}(sol) \rightarrow \textbf{1}(s)$$

$$\textbf{2}(sol) \rightarrow \textbf{2}(s) \qquad (4)$$

When equilibrium between the solid (sol) and the solution (s) was reached and the solid phase was not altered by solvation, solubility data were used to calculate the standard Gibbs energy of solution, $\Delta_s G°$, referred to the standard state of 1 mol dm⁻³. Given that $\Delta_s G°$ involves the contribution of the crystal lattice and the solvation Gibbs energy, the former is removed by calculating the standard Gibbs energies of transfer, $\Delta_t G°$, of these ligands using acetonitrile as the reference solvent. As far as **1** is concerned, the strength of solvation follows the sequence

$$n\text{-BuOH} > \text{DMF} > \text{MeCN} > \text{EtOH} > \text{PC} > \text{MeOH}$$

However, this sequence was slightly altered when the hydroxyl groups of **1** were functionalized by aliphatic pendant arms containing ester ($-CH_2COOC_2H_5$) groups to yield **2**. Thus, for the latter the following trend of solvation is observed

$$n\text{-BuOH} > \text{DMF} > \text{EtOH} > \text{MeCN} > \text{PC} > \text{MeOH}$$
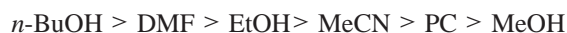
Furthermore, in moving from **1** to **2** an increase in solvation is observed ($\Delta_t G°$ values are slightly more negative for **2** relative to **1**). These data reflect quantitatively the ligand effect on the

TABLE 1: Solubilities (molar scale) and Derived Standard Gibbs Energies of Solution of 1 and 2 in Various Solvents at 298.15 K

	1			**2**		
solvent[a]	solubility/mol dm^{-3}	$\Delta_s G°$/kJ mol^{-1}	$\Delta_t G°$/ kJ mol^{-1}(MeCN−s)[b]	solubility/mol dm^{-3}	$\Delta_s G°$/kJ mol^{-1}	$\Delta_t G°$/ kJ mol^{-1}(MeCN−s)
MeCN	$(8.01 \pm 0.02) \times 10^{-3}$	11.97 ± 0.02	0.00	$(3.91 \pm 0.02) \times 10^{-3}$	13.78 ± 0.01	0.00
MeOH	$(1.48 \pm 0.02) \times 10^{-3}$	16.13 ± 0.01	4.16	$(2.31 \pm 0.04) \times 10^{-3}$	15.04 ± 0.02	1.26
EtOH	$(4.52 \pm 0.03) \times 10^{-3}$	13.38 ± 0.01	1.41	$(6.01 \pm 0.03) \times 10^{-3}$	12.68 ± 0.02	−1.10
n-BuOH	$(1.05 \pm 0.04) \times 10^{-2}$	11.30 ± 0.03	−0.67	$(1.28 \pm 0.02) \times 10^{-2}$	10.80 ± 0.03	−2.98
PC	$(2.20 \pm 0.02) \times 10^{-3}$	15.17 ± 0.03	3.20	$(3.23 \pm 0.04) \times 10^{-3}$	14.24 ± 0.02	0.46
DMF	$(9.71 \pm 0.03) \times 10^{-3}$	11.48 ± 0.02	−0.49	$(8.46 \pm 0.01) \times 10^{-3}$	11.82 ± 0.03	−1.96
PhCN	very soluble	solvate formation		very soluble	solvate formation	
Hex	very soluble	solvate formation		very soluble	solvate formation	
PhNO$_2$	very soluble	solvate formation		very soluble	solvate formation	
DCM	very soluble	solvate formation		very soluble	solvate formation	
THF	very soluble	solvate formation		very soluble	solvate formation	

[a] Abbreviations for solvents: acetonitrile; MeCN, methanol, MeOH; ethanol, EtOH; n-butanol, n-BuOH; propylene carbonate, PC; N,N-dimethylformamide, DMF; benzonitrile, PhCN; hexane, Hex; nitrobenzene, PhNO$_2$; dichloromethane, DCM; tetrahydrofuran, THF. [b] Transfer Gibbs energies from acetonitrile.

TABLE 2: Enthalpies of Solution of 1 and 2 at Different Concentrations in Various Solvents at 298.15 K Determined by Calorimetry

1		**2**					
DMF		MeCN		MeOH		DMF	
c/mol dm^{-3}	$\Delta_s H$/kJ mol^{-1}	c/mol dm^{-3}	$\Delta_s H$/kJ mol^{-1}	c/mol dm^{-3}	$\Delta_s H$/kJ mol^{-1}	c/mol dm^{-3}	$\Delta_s H$/kJ mol^{-1}
2.51×10^{-4}	−11.20	1.11×10^{-4}	16.80	1.02×10^{-4}	26.80	1.58×10^{-4}	22.70
5.15×10^{-4}	−11.35	1.15×10^{-4}	16.94	1.43×10^{-4}	26.60	2.30×10^{-4}	22.91
8.30×10^{-4}	−11.05	1.40×10^{-4}	17.50	1.85×10^{-4}	27.13	2.50×10^{-4}	21.54
9.55×10^{-4}	−10.92	2.55×10^{-4}	17.48	2.70×10^{-4}	27.02	2.72×10^{-4}	22.25
4.84×10^{-3}	−10.94	2.85×10^{-4}	17.63	3.55×10^{-4}	26.61	3.60×10^{-4}	22.89
6.91×10^{-3}	−11.10	3.91×10^{-4}	16.92	5.35×10^{-4}	27.40	4.13×10^{-4}	21.81
8.00×10^{-3}	−11.14	8.41×10^{-4}	16.70			4.36×10^{-4}	21.97
		1.03×10^{-3}	17.10			6.00×10^{-4}	22.20
						8.80×10^{-4}	22.32
$\Delta_s H = -11.1 \pm 0.6$ kJ mol^{-1}		$\Delta_s H = -17.1 \pm 0.4$ kJ mol^{-1}		$\Delta_s H = -26.9 \pm 0.3$ kJ mol^{-1}		$\Delta_s H = -22.3 \pm 0.5$ kJ mol^{-1}	

TABLE 3: Solubility of 1 in Acetonitrile and Methanol at Different Temperatures and Derivation of Solution Enthalpy

T/K	solubility/mol dm^{-3}	$\Delta_s H$/kJ mol^{-1} [a]
	MeCN	
278.15	$(4.15 \pm 0.01) \times 10^{-3}$	24 ± 1
285.15	$(6.02 \pm 0.02) \times 10^{-3}$	
298.15	$(8.01 \pm 0.02) \times 10^{-3}$	
308.15	$(1.21 \pm 0.02) \times 10^{-2}$	
	MeOH	
278.15	$(9.12 \pm 0.01) \times 10^{-4}$	19 ± 1
285.15	$(9.82 \pm 0.02) \times 10^{-4}$	
298.15	$(1.48 \pm 0.02) \times 10^{-3}$	
308.15	$(1.96 \pm 0.01) \times 10^{-3}$	

[a] Used the van't Hoff equation to derive enthalpy data.

TABLE 4: Thermodynamic Parameters of Transfer of 1 and 2 from MeCN to MeOH and DMF at 298.15 K

solvent system	$\Delta_t G°$/ kJ mol^{-1} [a]	$\Delta_t H°$/ kJ mol^{-1} [b]	$\Delta_t S°$/ J K^{-1} mol^{-1} [c]
	1		
MeCN → MeCN	0	0	0
MeCN → MeOH	4.2	−5.0	−31
MeCN → DMF	−0.5	−35.1	−116
	2		
MeCN → MeCN	0	0	0
MeCN → MeOH	1.3	9.8	29
MeCN → DMF	−2.0	5.2	24

[a] From data in Table 1. [b] From data in Table 2. [c] Calculated from $\Delta_t G°$ and $\Delta_t H°$ values.

transfer process, which may not be necessarily attributed to the contribution of the ethyl ethanoate group in **2** given that the $\Delta_t G°$ value for the tetraester derivative from acetonitrile to methanol is about 2.79 kJ mol^{-1}. As far as the alcohols (protic solvents) are concerned, both ligands show a parallel behavior. However, by increasing the hydrophobic character of the aliphatic chain in moving from MeOH to n-BuOH, stronger interactions between these ligands and these solvents are observed. In dipolar aprotic solvents (DMF, MeCN, and PC) a similar solvation pattern is observed for these ligands. The changes of solvation observed upon transfer from one solvent to another, although not very significant, are likely to affect the stability of complex formation with metal cations. To gain further insight into the ligand−solvent (solute−solvent) interactions, the enthalpy and entropy of transfer of these ligands are

required. Enthalpy data were determined in selected solvents (solvents used as complexation media).[14,15] These are now discussed.

Standard Enthalpies of Solution of 1 and 2 and Derived Enthalpies of Transfer from Acetonitrile. For the determination of the standard enthalpies of solution, $\Delta_s H°$, of **1** and **2** in various solvents (MeCN, MeOH, and DMF) by calorimetry, measurements were carried out at different concentrations of these ligands in the appropriate solvent. Details are given in Table 2. Since hardly any variations are observed in the $\Delta_s H$ values by altering the ligand's concentration, the standard enthalpy of solution, $\Delta_s H°$, is taken as the average value of these measurements. The standard deviations of the data are also included. The dissolution of **1** in MeOH and MeCN was found to be relatively slow as to derive enthalpy data from calorimetry. Therefore, solubility measurements at four different

TABLE 5: Enthalpies of Solution of the Free and the Complex Metal−Ion Salts at Various Electrolyte Concentration in Acetonitrile, Methanol, and *N,N*-Dimethylformamide at 98.15 K

MeCN		MeOH		DMF	
c/mol dm^{-3}	$\Delta_s H$/kJ mol^{-1}	c/mol dm^{-3}	$\Delta_s H$/kJ mol^{-1}	c/mol dm^{-3}	$\Delta_s H$/kJ mol^{-1}
Hg(ClO$_4$)$_2$					
4.04×10^{-4}	-52.01	1.97×10^{-4}	-70.80	1.63×10^{-4}	-138.52
6.70×10^{-4}	-51.43	4.22×10^{-4}	-71.50	1.86×10^{-4}	-137.54
6.92×10^{-4}	-52.10	5.31×10^{-4}	-70.91	5.51×10^{-4}	-140.03
1.21×10^{-3}	-51.92	5.80×10^{-4}	-72.10	9.46×10^{-4}	-139.51
1.83×10^{-3}	-51.30	5.94×10^{-4}	-71.40	1.36×10^{-3}	-139.60
2.84×10^{-3}	-52.70	1.27×10^{-3}	-71.63		
3.24×10^{-3}	-51.90	1.93×10^{-3}	-71.42		
4.30×10^{-3}	-52.30	3.24×10^{-3}	-72.10		
$\Delta_s H°$ $^a = -52.0 \pm 0.5$ kJ mol^{-1}		$\Delta_s H°$ $^a = -71.5 \pm 0.5$ kJ mol^{-1}		$\Delta_s H°$ $^a = -139 \pm 1$ kJ mol^{-1}	
Hg1(ClO$_4$)$_2$					
8.21×10^{-5}	-53.56	1.44×10^{-4}	-10.0	7×10^{-5}	-104.8
5.45×10^{-5}	-52.35	2.38×10^{-4}	-8.3	1.07×10^{-4}	-103.0
1.55×10^{-4}	-56.15	2.63×10^{-4}	-6.3	2.28×10^{-4}	-94.5
2.95×10^{-4}	-58.57	2.64×10^{-4}	-7.7	2.65×10^{-4}	-93.3
3.29×10^{-4}	-58.92	4.43×10^{-4}	-4.8	7.40×10^{-4}	-45
4.05×10^{-4}	-59.87	8.57×10^{-4}	-0.3		
$\Delta_s H°$ $^b = -48.3 \pm 0.4$ kJ mol^{-1}		$\Delta_s H°$ $^b = -17.6 \pm 0.2$ kJ mol^{-1}		$\Delta_s H°$ $^b = -119 \pm 0.5$ kJ mol^{-1}	
Hg2(ClO$_4$)$_2$					
1.14×10^{-4}	1.86	9.58×10^{-5}	15.40	5.40×10^{-5}	-46.77
1.23×10^{-4}	1.30	8.60×10^{-5}	15.45	8.45×10^{-4}	-55.65
2.13×10^{-4}	-4.73	2.33×10^{-4}	15.04	1.26×10^{-4}	-59.74
3.13×10^{-4}	-9.53	2.55×10^{-4}	14.90	2.40×10^{-4}	-77.00
4.54×10^{-4}	-11.18	3.13×10^{-4}	14.72	4.56×10^{-4}	-90.24
4.84×10^{-4}	-11.85	4.48×10^{-4}	14.40	7.08×10^{-4}	-114.50
$\Delta_s H°$ $^b = 14.29 \pm 1.3$ kJ mol^{-1}		$\Delta_s H°$ $^b = 16.27 \pm 0.8$ kJ mol^{-1}		$\Delta_s H°$ $^b = -23.05 \pm 0.8$ kJ mol^{-1}	
Ag1ClO$_4$					
6.97×10^{-5}	8.94	7.02×10^{-6}	9.46	7.65×10^{-5}	-50.20
7.26×10^{-5}	9.38	6.49×10^{-5}	9.35	5.52×10^{-5}	-50.22
1.30×10^{-4}	10.50	1.98×10^{-4}	9.47	1.45×10^{-5}	-50.17
2.37×10^{-4}	12.46	2.17×10^{-4}	9.19	4.47×10^{-4}	-50.24
2.63×10^{-4}	12.65	2.42×10^{-4}	9.29	6.41×10^{-4}	-50.21
3.61×10^{-4}	13.70	$3.0 \times 10^{-4}4$	9.50	6.47×10^{-4}	-50.20
3.70×10^{-4}	14.20	3.17×10^{-4}	9.36		
		5.15×10^{-4}	9.22		
$\Delta_s H°$ $^b = 5.4 \pm 0.22$ kJ mol^{-1}		$\Delta_s H°$ $^b = 9.4 \pm 0.1$ kJ mol^{-1}		$\Delta_s H°$ $^b = -50.20 \pm 0.03$ kJ mol^{-1}	
Ag2ClO$_4$					
8.3×10^{-5}	-2.02	1.42×10^{-4}	8.24	9.20×10^{-5}	-14.20
1.12×10^{-4}	-2.26	1.54×10^{-4}	8.44	3.68×10^{-4}	-9.92
2.47×10^{-4}	-3.10	2.10×10^{-4}	10.34	4.42×10^{-4}	-9.77
3.24×10^{-4}	-3.47	3.97×10^{-4}	13.90	5.54×10^{-4}	-8.56
4.20×10^{-4}	-3.81	5.30×10^{-4}	15.72	6.96×10^{-4}	-7.10
8.70×10^{-4}	-5.90			8.70×10^{-4}	-5.90
$\Delta_s H°$ $^b = -0.21 \pm 0.12$ kJ mol^{-1}		$\Delta_s H°$ $^b = 0.18 \pm 0.1$ kJ mol^{-1}		$\Delta_s H°$ $^b = -18.2 \pm 0.3$ kJ mol^{-1}	

^{a} Average value. ^{b} Extrapolated value.

temperatures were carried out. The van't Hoff equation was used to derive the solution enthalpies of this ligand in these two solvents. Details are given in Table 3. Since solution enthalpies are made from the contribution of the standard enthalpy of solvation, $\Delta_{solv} H°$ (exothermic process), and the standard crystal lattice enthalpy, $\Delta_{cl} H°$ (endothermic process), it is quite clear from the $\Delta_s H°$ values reported in Tables 2 and 3 that in most cases (except in DMF) the crystal lattice process predominates over the solvation process. To remove the contribution of the crystal lattice to the solution enthalpy, transfer data from acetonitrile to various solvents were calculated. Thus, Table 4 lists the thermodynamics of transfer of **1** and **2** from acetonitrile to various solvents. Transfer entropies were calculated by the combination of $\Delta_t G°$ and $\Delta_t H°$ values.[6] As far as $\Delta_t H°$ values are concerned, the results show that **1** is enthalpically more stable in the following sequence

$$DMF > MeOH > MeCN$$

For **2**, the trend is altered

$$MeCN > DMF > MeOH$$

For **1**, the results shown in Table 4 indicate that the solvation patterns observed in terms of Gibbs energies are enthalpically controlled with the higher $\Delta_t H°$ values for the transfer of **1** to DMF. For transfers from MeCN to MeOH, the loss of entropy observed (negative $\Delta_t S°$ value) may be attributed to hydrogen bond interactions between the hydroxyl group of **1** and MeOH.

In the case of DMF, a protophilic aprotic solvent,[8] the interaction may occur between the phenolic hydrogens and the carboxyl oxygen atoms of the solvent. This is reflected in the high loss of entropy observed in the transfer of **1** from MeCN to DMF. On the other hand, the transfer of **2** to these solvents is accompanied by a gain in entropy (favorable) while the process is destabilized in terms of enthalpy. The X-ray structure of **2** referred to the solid state shows that a molecule of MeCN

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TABLE 6: Enthalpies of Solution of Hg1(ClO$_4$)$_2$, Hg2(ClO$_4$)$_2$, Ag1ClO$_4$, and Ag2ClO$_4$ in Various Solvents at 298.15 K

| solvent	$\Delta_s H°$/kJ mol^{-1}	$\Delta_t H°$/kJ mol^{-1} (MeCN → s)[a]
	Hg1(ClO$_4$)$_2$	
MeCN	−48.3 ± 0.4	0
MeOH	−17.6 ± 0.2	30.7
DMF	−119.0 ± 0.5	−70.7
	Hg2(ClO$_4$)$_2$	
MeCN	14.30 ± 1.3	0
MeOH	16.3 ± 0.8	2
DMF	−23.1 ± 0.8	−39.4
	Ag1ClO$_4$	
MeCN	5.4 ± 0.22	0
MeOH	9.4 ± 0.1	4
DMF	−50.2 ± 0.03	−55.6
	Ag2ClO$_4$	
MeCN	−0.2 ± 0.12	0
MeOH	0.2 ± 0.1	0.4
DMF	−18.2 ± 0.3	−18.0

[a] Derived enthalpies of transfer from MeCN at 298.15 K.

sits in the hydrophobic cavity of **2** while recrystallization of this ligand from DMF shows the absence of this solvent from the cavity of the ligand.[14,15] Having established the thermodynamic parameters of the transfer of **1** and **2** from MeCN to DMF and MeOH, the following section discusses the solution enthalpies of the free and the complex metal−ion salts in these solvents.

Thermodynamics of Solution of the Free and Complex Metal−Ion Salts. Most metal−ion calix(4)arene complex salts are solvated in MeCN, MeOH, and DMF. Therefore, we report here the enthalpies of solution of Hg(ClO$_4$)$_2$, Hg1(ClO$_4$)$_2$, Hg2(ClO$_4$)$_2$, Ag1ClO$_4$, and Ag2ClO$_4$ in MeCN, MeOH, and DMF. Details are given in Table 5. In cases where the $\Delta_s H$ values do not change with the electrolyte concentration, the standard enthalpy of solution, $\Delta_s H°$, is the average value of enthalpy data carried out at various concentrations. When variations in the $\Delta_s H$ values were found by altering the electrolyte concentration, the standard enthalpy of solution was calculated from the intercept at $I = 0$ of a plot of $\Delta_s H$ against the square root of the ionic strength of the solution, $I^{1/2}$.

Negative values of $\Delta_s H°$ (exothermic process) indicate that the solvation process predominates in solution. For most of the compounds listed in Table 5, this is indeed the case. Endothermic processes are indicative that the crystal lattice process is predominant in solution.

Before proceeding with the derivation of the transfer enthalpies, it is important to check the accuracy of the enthalpy data through the calculation of the standard enthalpy of coordination, $\Delta_{coord} H°$, from solution data referred to the process where the reactants (MX and L) and the product (MLX) are in their pure physical state as shown by eq 5
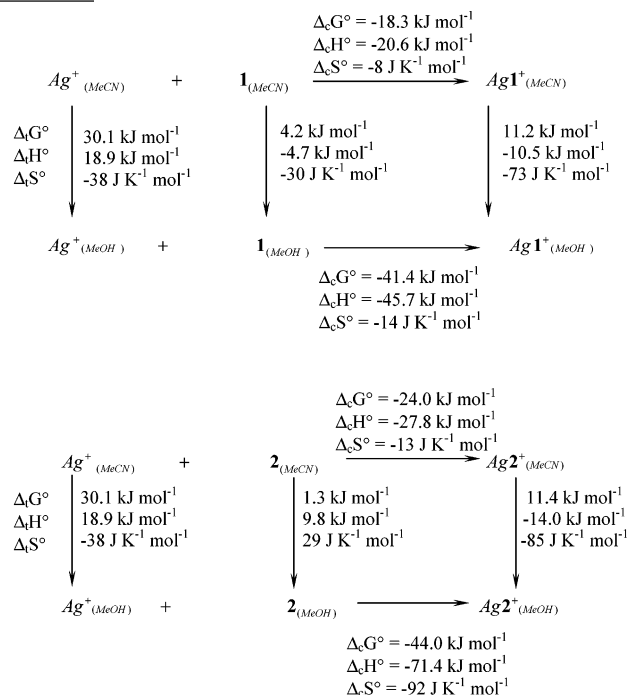
$$MX(sol) + L(sol) \xrightarrow{\Delta_{coord}H°} MLX(sol) \quad (5)$$
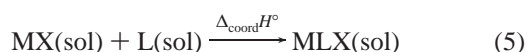
For this purpose, the following relationship is used

$$\Delta_{coord}H° = \Delta_s H°(L)_{(s)} + \Delta_s H°(M^{n+}X^-)_{(s)} + \Delta_s H° - \\ \Delta_s H°(ML^{n+}X^-)_{(s)} \quad (6)$$

By inserting the appropriate quantities in eq 6, the $\Delta_{coord} H°$ value is calculated for the various systems. Details are given in Table 6. The good agreement found between the $\Delta_{coord} H°$ values

SCHEME 1

MeCN-MeOH

derived from different solvents for a given system confirm the accuracy of the enthalpy data reported in this paper. Thus, average values for the enthalpies of coordination (kJ mol^{-1}) are as follows: −50.2 ± 0.5, −132.4 ± 0.65, −53.9 ± 0.5, and −58.51 ± 0.41 for Ag1ClO$_4$, Ag2ClO$_4$, Hg1(ClO$_4$)$_2$, and Hg2(ClO$_4$)$_2$, respectively.

Having confirmed the accuracy of the data we proceeded to calculate the transfer enthalpies of the complex salts from MeCN to MeOH and to DMF. These data are listed in Table 6.
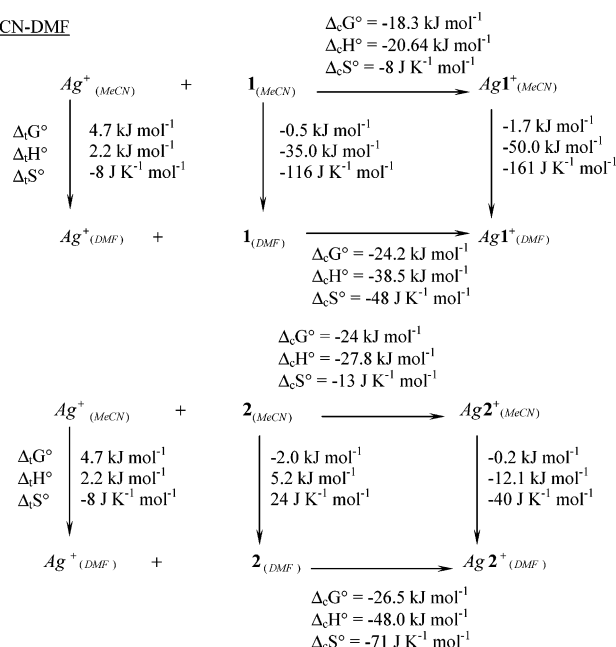
The results are striking in that for all complexes, the enthalpic stability in DMF is much greater than that in MeCN and in MeOH. For the last two solvents the medium effect is almost negligible except for Hg1(ClO$_4$)$_2$ which is enthalpically more stable by about 30 kJ mol^{-1} in MeCN relative to MeOH. Quite clearly, the metal−ion complex (see eq 1) will contribute favorably to the enthalpy of complexation of these metal cations and these ligands in DMF relative to MeCN and MeOH. However in assessing the medium effect on the complexation process, metal cation−solvent and the ligand−solvent interactions must be considered and this is now discussed.

Medium Effect on the Complexation Process. It is important to emphasize that thermodynamic data for the transfer process involving reactants and product allow the calculation of $\Delta(\Delta_c P°)$ (eq 1), and therefore, this information can be used to establish the most favorable complexation medium for a given metal cation−ligand system. It should be noted that in eq 1, the contribution of the counterion is canceled if this is a common component of the free and the complex salt. However, to assess the medium effect on the selective behavior of a ligand for a metal cation in a given medium, the thermodynamic parameters for the complexation process previously reported by us are used.[14,15] Thus, eq 1 is best illustrated by the following thermodynamic cycle in which the appropriate quantities for Ag$^+$, **1**, and **2** in the MeCN−MeOH (Scheme 1) and MeCN−DMF (Scheme 2) solvent systems are inserted.

Single-ion transfer parameters for Ag$^+$ from acetonitrile to methanol and to *N,N*-dimethylformamide at 298.15 K based on the Ph$_4$AsPh$_4$B convention are those from the literature.[18] The

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SCHEME 2

MeCN-DMF

$\Delta_cG° = -18.3$ kJ mol^{-1}
$\Delta_cH° = -20.64$ kJ mol^{-1}
$\Delta_cS° = -8$ J K^{-1} mol^{-1}

$Ag^+{}_{(MeCN)}$ + $\mathbf{1}_{(MeCN)}$ $\longrightarrow$ $Ag\mathbf{1}^+{}_{(MeCN)}$

$\Delta_tG°$	4.7 kJ mol^{-1}	-0.5 kJ mol^{-1}	-1.7 kJ mol^{-1}
$\Delta_tH°$	2.2 kJ mol^{-1}	-35.0 kJ mol^{-1}	-50.0 kJ mol^{-1}
$\Delta_tS°$	-8 J K^{-1} mol^{-1}	-116 J K^{-1} mol^{-1}	-161 J K^{-1} mol^{-1}

$Ag^+{}_{(DMF)}$ + $\mathbf{1}_{(DMF)}$ $\longrightarrow$ $Ag\mathbf{1}^+{}_{(DMF)}$

$\Delta_cG° = -24.2$ kJ mol^{-1}
$\Delta_cH° = -38.5$ kJ mol^{-1}
$\Delta_cS° = -48$ J K^{-1} mol^{-1}

$\Delta_cG° = -24$ kJ mol^{-1}
$\Delta_cH° = -27.8$ kJ mol^{-1}
$\Delta_cS° = -13$ J K^{-1} mol^{-1}

$Ag^+{}_{(MeCN)}$ + $\mathbf{2}_{(MeCN)}$ $\longrightarrow$ $Ag\mathbf{2}^+{}_{(MeCN)}$

$\Delta_tG°$	4.7 kJ mol^{-1}	-2.0 kJ mol^{-1}	-0.2 kJ mol^{-1}
$\Delta_tH°$	2.2 kJ mol^{-1}	5.2 kJ mol^{-1}	-12.1 kJ mol^{-1}
$\Delta_tS°$	-8 J K^{-1} mol^{-1}	24 J K^{-1} mol^{-1}	-40 J K^{-1} mol^{-1}

$Ag^+{}_{(DMF)}$ + $\mathbf{2}_{(DMF)}$ $\longrightarrow$ $Ag\mathbf{2}^+{}_{(DMF)}$

$\Delta_cG° = -26.5$ kJ mol^{-1}
$\Delta_cH° = -48.0$ kJ mol^{-1}
$\Delta_cS° = -71$ J K^{-1} mol^{-1}

SCHEME 3

MeCN-MeOH

$\Delta_cH° = -74$ kJ mol^{-1}

$Hg^{2+}{}_{(MeCN)}$ + $\mathbf{1}_{(MeCN)}$ $\longrightarrow$ $Hg\mathbf{1}^{2+}{}_{(MeCN)}$

$\Delta_tH° = -19.5$ kJ mol^{-1} $\Delta_tH° = -4.7$ kJ mol^{-1} $\Delta_tH° = 30.71$ kJ mol^{-1}

$Hg^{2+}{}_{(MeOH)}$ + $\mathbf{1}_{(MeOH)}$ $\longrightarrow$ $Hg\mathbf{1}^{2+}{}_{(MeOH)}$

$\Delta_cH° = -19.70$ kJ mol^{-1}

$\Delta_cH° = -83.5$ kJ mol^{-1}

$Hg^{2+}{}_{(MeCN)}$ + $\mathbf{2}_{(MeCN)}$ $\longrightarrow$ $Hg\mathbf{2}^{2+}{}_{(MeCN)}$

$\Delta_tH° = -19.5$ kJ mol^{-1} $\Delta_tH° = 9.8$ kJ mol^{-1} $\Delta_tH° = 2.0$ kJ mol^{-1}

$Hg^{2+}{}_{(MeOH)}$ + $\mathbf{2}_{(MeOH)}$ $\longrightarrow$ $Hg\mathbf{2}^{2+}{}_{(MeOH)}$

$\Delta_cH° = -72.0$ kJ mol^{-1}

same applies for the perchlorate anion.[18] The $\Delta_tG°$ values for Ag$\mathbf{1}^+$ and Ag$\mathbf{2}^+$ from MeCN to MeOH and to DMF were calculated from corresponding data for the cation, the ligand, and the Gibbs energies of complexation of this cation and the appropriate ligand in the reference and the receiving medium. Indeed, the sum of all the processes involved in the thermodynamic cycle should be equal to zero.

As far as Ag$^+$ and **1** in the MeCN−MeOH solvent system are concerned, in terms of Gibbs energies, the more favorable stability in MeOH relative to MeCN, is mainly due to the favorable contribution of the cation (strongly solvated in MeCN) and to a much lesser extent to that of the ligand (better solvated in MeCN) which overcomes the unfavorable contribution of the metal−ion complex in MeOH (less solvated) with respect to MeCN (more solvated).

For the MeCN−DMF solvent system, the stability observed for Ag$^+$ with **1** in MeCN and DMF is similar, indicating that these solvents do not offer a differentiating solvating media for these species in solution. This is evident from the relatively small values of $\Delta_tG°$ for the ligand, the free, and the complexed cations in going from MeCN to DMF. However, the contribution of the ligand, though small, still does not favor the complexation in DMF. Therefore, the small difference observed in the stability for this system in DMF with respect to MeCN is attributed to both the slightly higher solvation of the metal−ion complex in DMF and the lower solvation of the free cation in this solvent relative to MeCN.

As far as enthalpies are concerned, in MeCN−MeOH, the higher enthalpic stability observed in the complexation of Ag$^+$ with **1** in MeOH relative to MeCN is due to the favorable contribution of both the free (poorly solvated in MeOH) and the complexed cation (better solvated in MeOH). The free ligand being enthalpically more stable in MeOH than in MeCN does not contribute favorably to the enthalpy of complexation, $\Delta_cH°$, in the former relative to the latter solvent.

On the other hand, for MeCN−DMF, with the ligand being enthalpically more stable in DMF than in MeCN, it contributes unfavorably to the enthalpy for complexation in DMF relative to MeCN. However, this unfavorable contribution from the free ligand and the small value for the transfer enthalpy of the free
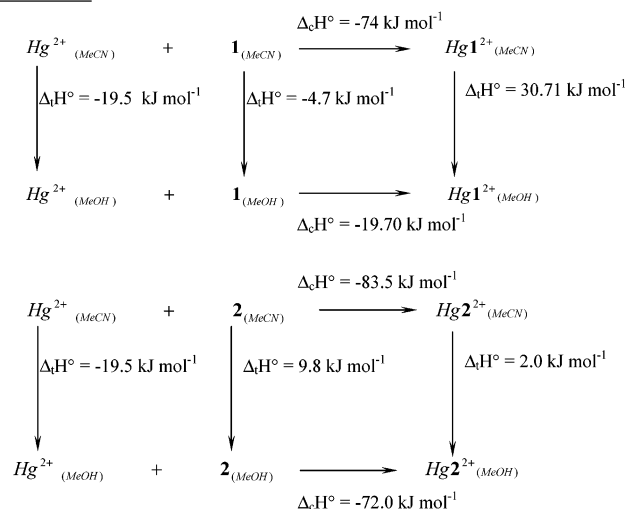
metal cation are overcome by the favorable $\Delta_tH°$ of the metal−ion complex (negative value) from MeCN to DMF, and therefore, the complexation process is enthalpically more stable in DMF than in MeCN.

The greater loss in entropy (unfavorable) in transfers to MeOH and DMF relative to MeCN is mainly attributed to the negative values of transfer entropies, $\Delta_tS°$, of the metal−ion complex in moving from MeCN to these solvents that overcome those of the ligand and the metal cation.
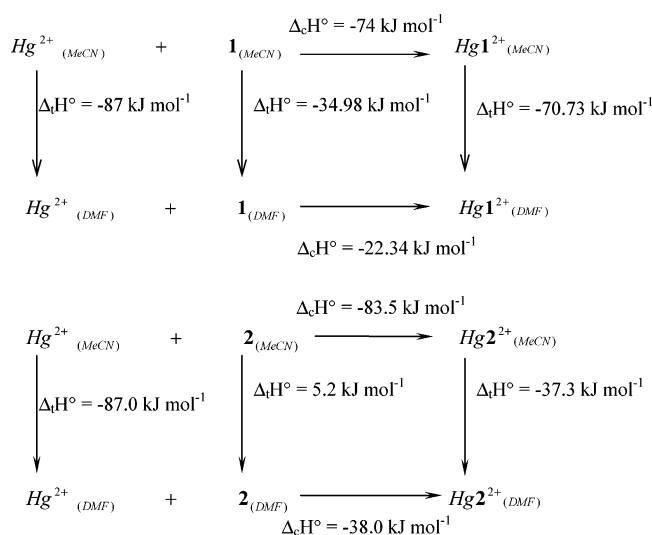
As far as mercury(II) is concerned, there are no data available on the single-ion Gibbs energies of transfer for this cation among these solvents. This is not surprising given the complexities involved in the derivation of solution Gibbs energies for 2:1 electrolytes in nonaqueous solvents. In addition mercury(II) complex salts are mostly solvated in these solvents. Therefore, these complex salts would be only discussed in terms of enthalpy data. Thus for Hg$\mathbf{1}^{2+}$ and Hg$\mathbf{2}^{2+}$ in the MeCN−MeOH and in the MeCN−DMF solvent systems, the single-ion $\Delta_tH°$ values were calculated from the standard enthalpies of solution of the mercuy(II) perchlorate salts in these solvents (Table 4) and the $\Delta_tH°$ value for the ClO$_4^-$ anion from MeCN to MeOH and DMF based on the PhAsPhB convention reported in the literature.[1] The $\Delta_tH°$ values from MeCN to the appropriate solvents for **1** and **2** are those reported in Table 3. Complexation data for these ligands and Hg^{2+} in these solvents are those previously reported by us.[14,15] By inserting the appropriate quantities in the thermodynamic cycle for these solvent systems and the two ligands, **1** and **2**, it follows from eq 1 that in the MeCN−MeOH (Scheme 3) solvent system, the most favorable $\Delta_cH°$ value for Hg^{2+} and **1** in MeCN results from the contribution of the lower stabilities of the reactants and the higher stability of the product (in enthalpic terms) in this solvent relative to MeOH.

On the other hand, in the MeCN−DMF (Scheme 4) solvent system although the complexation process of Hg^{2+} with **1** is more favorable in the reference solvent than in DMF, the metal−ion complex does not contribute favorably to complexation in MeCN (Hg$\mathbf{1}^{2+}$ is enthalpically more stable in DMF than in MeCN).

However, this is overcome by the favorable contribution of the reactants (both enthalpically more stable in DMF and therefore more reluctant to enter complexation in DMF than in MeCN).

As far as **2** is concerned, in the MeCN−MeOH solvent system, the complex stability in enthalpic terms is higher in

SCHEME 4

$$Hg^{2+}_{(MeCN)} \quad + \quad \mathbf{1}_{(MeCN)} \xrightarrow{\Delta_c H^\circ = -74 \text{ kJ mol}^{-1}} Hg\mathbf{1}^{2+}_{(MeCN)}$$

$\Delta_t H^\circ = -87 \text{ kJ mol}^{-1}$ $\Delta_t H^\circ = -34.98 \text{ kJ mol}^{-1}$ $\Delta_t H^\circ = -70.73 \text{ kJ mol}^{-1}$

$$Hg^{2+}_{(DMF)} \quad + \quad \mathbf{1}_{(DMF)} \longrightarrow Hg\mathbf{1}^{2+}_{(DMF)}$$

$$\Delta_c H^\circ = -22.34 \text{ kJ mol}^{-1}$$

$$Hg^{2+}_{(MeCN)} \quad + \quad \mathbf{2}_{(MeCN)} \xrightarrow{\Delta_c H^\circ = -83.5 \text{ kJ mol}^{-1}} Hg\mathbf{2}^{2+}_{(MeCN)}$$

$\Delta_t H^\circ = -87.0 \text{ kJ mol}^{-1}$ $\Delta_t H^\circ = 5.2 \text{ kJ mol}^{-1}$ $\Delta_t H^\circ = -37.3 \text{ kJ mol}^{-1}$

$$Hg^{2+}_{(DMF)} \quad + \quad \mathbf{2}_{(DMF)} \longrightarrow Hg\mathbf{2}^{2+}_{(DMF)}$$

$$\Delta_c H^\circ = -38.0 \text{ kJ mol}^{-1}$$

the former relative to the latter solvent. This is attributed to the lower cation−solvent interaction in MeCN relative to MeOH, which overcomes the unfavorable contribution of the ligand. It seems that the medium effect for the transfer of the complex cation from MeCN to MeOH is negligible. On the other hand, in the MeCN−DMF solvent system, although both the ligand and particularly the metal−ion complex contribute favorably to complexation in DMF, the strength of interaction between Hg^{2+} and DMF is relatively high. As a result, the complexation process is enthalpically more favored in MeCN relative to DMF.

The above examples illustrate that the extent of complexation of these ligands with metal cations in different media is not only controlled by the solvation changes that the free cation undergoes in the various solvents but also controlled by the solvation of the ligand and the metal−ion complex in these solvents.

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