

An overview on the solution thermodynamics of lower rim functionalised calixarene derivatives and metal cations. New derivatives containing amino and thioalkyl functional groups

Angela F. Danil de Namor,* Robert G. Hutcherson, Felix J. Sueros Velarde, Mariel L. Zapata-Ormachea, Lupe E. Pulcha Salazar, Ibrahim Al Jammaz and Nawar Al Rawi.

Laboratory of Thermochemistry, Department of Chemistry, University of Surrey, Guildford, Surrey, GU2 5XH, UK

ABSTRACT

This article is concerned with the solution thermodynamics of lower rim functionalised calixarenes and metal cations. The coverage is selective focussing on the solution thermodynamics of ligands and their metal-ion complexes. Its scope is not only to report what was done on the thermodynamics of complexation but to discuss aspects which need to be addressed. An account on recent developments involving new lower functionalised calixarenes containing mixed pendant arms and their interactions with metal cations is given.

INTRODUCTION

Undoubtedly the remarkable growth of the field of calixarene chemistry (ref. 1) has been greatly motivated by the interest in finding derivatives able to enter selective complexation with neutral or ionic species. Given that selectivity is a crucial issue in calixarene chemistry (and in macrocyclic chemistry) the role of experimental thermodynamics for understanding the factors contributing to their selective behaviour for one species relative to others is too important to be undermined. From molecular dynamic studies of calixarene derivatives and their metal-ion complexes, the influence of solvation on structures and stabilities (ref. 2) has been discussed. However, in order to test the relevance of such studies, accurate thermodynamic data are required. Thermodynamic aspects of calixarene chemistry are discussed in this paper covering calixarene derivatives and their metal-ion complexes and cation complexation processes.

Since the thermodynamics of cation complexation ($\Delta_c P^\circ = \Delta_c G^\circ, \Delta_c H^\circ, \Delta_c S^\circ$) in two solvents (s_1, s_2) is dependent on the transfer thermodynamics ($\Delta_t P^\circ$) of the metal cation, M^{n+} ; the ligand, L; and the metal-ion complex, M^+L (eq. 1) (refs. 3-7),

$$\Delta_c P^\circ_{(s_2)} - \Delta_c P^\circ_{(s_1)} = \Delta_t P^\circ(M^+L)_{(s_1 \rightarrow s_2)} - \Delta_t P^\circ(M^+)_{(s_1 \rightarrow s_2)} - \Delta_t P^\circ(L)_{(s_1 \rightarrow s_2)} \quad (1)$$

the solution thermodynamics of calixarene derivatives and their metal-ion complexes is first discussed.

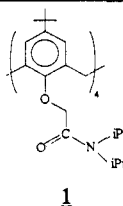
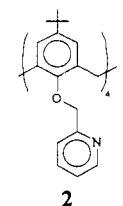
SOLUTION THERMODYNAMICS OF LOWER RIM CALIXARENE DERIVATIVES AND THEIR METAL-ION COMPLEXES.

Solution Gibbs energies, $\Delta_s G^\circ$, enthalpies, $\Delta_s H^\circ$ and entropies, $\Delta_s S^\circ$ of parent calixarenes and ester derivatives in various solvents have been previously discussed by Danil de Namor and coworkers (refs. 8-11). These data have been used to derive the thermodynamic parameters of transfer ($\Delta_t G^\circ, \Delta_t H^\circ, \Delta_t S^\circ$) of these ligands from one solvent (s_1) to another (s_2) (eq. 2)



As previously reported these data provide a quantitative measure of the solvation changes of the solute in its transfer from one medium to another and therefore, transfer parameters are instructive, particularly in calixarene chemistry where the presence of hydrophilic and hydrophobic regions provides unusual properties to these molecules to the extent that specific solute-solvent interactions often occur. These may have profound implications on many processes (ref. 11). With the aim of illustrating the significance of these parameters, solution data for an amide 1 and amino 2 derivative are listed in Table 1.

TABLE 1. Solution thermodynamics of lower rim functionalised calixarenes in various solvents at 298.15 K

Ligand	Solvent ^a	$\Delta_r G^\circ$ kJ mol ⁻¹	$\Delta_r H^\circ$ kJ mol ⁻¹	$\Delta_r S^\circ$ J K ⁻¹ mol ⁻¹	$\Delta_r G^\circ$ kJ mol ⁻¹
 <u>1</u>	MeCN	14.72			0
	1-BuOH	10.90	15.41 ^d	15.1	-3.82
	1-BuOH satd H ₂ O	11.61	0.76 ^d	-36.4	-3.11
	Me ₂ CO	10.22			-4.50
	DMF	13.38			-1.34
	THF	4.67			-10.05
	1,2 DCE ^b				
 <u>2</u>	MeCN	19.35			0
	MeOH	16.59			-2.76
	EtOH	12.80			-6.55
	1-ProOH	9.39			-9.96
	1-BuOH	8.15	8.97 ^d	2.7	-11.20
	PhCN	11.30	9.17 ^d	-7.10	-8.05
	PhCN satd H ₂ O	-	5.86 ^d		-
	CH ₂ Cl ₂ ^b	-			-
	PhNO ₂	14.77			-4.58
	DMF	15.56			-3.79
	PC	19.77			-0.42

^aAcetonitrile, MeCN; methanol, MeOH; ethanol, EtOH; propan-1-ol, 1-ProOH; butan-1-ol, 1-BuOH; acetone, Me₂CO, N,N dimethylformamide, DMF; Tetrahydrofuran, THF; 1,2 dichloroethane, 1,2 DCE; benzonitrile, PhCN, propylene carbonate, PC. ^bSolvate formation ^cDerived from solubility data ^dCalorimetric data

Gibbs energies for these ligands (non-electrolytes) show that the transfer from one solvent to another can be quite selective. Indeed, differences of up to 10 to 13 kJ mol⁻¹ are observed in the $\Delta_r G^\circ$ values of 1 and 2; respectively.

There are important points to stress regarding the data in Table 1

1) The fact that these ligands undergo solvate formation in some solvents underlines the possibility that the use of these solvents for crystallisation purposes may lead to the isolation of their complexes rather than the pure ligands

2) It has been implied that the solvation of calixarene derivatives may be related to the Gutman's donor numbers of the solvent (ref. 12). However, the fact that parent calixarenes are highly solvated in low donor solvents (1,2 DCE, DN=0; PhNO₂, DN=4.4; PhCN, DN=11.9) (ref. 7) provides experimental evidence that this is not a suitable parameter to predict the solvation of these ligands and therefore, any suggestion regarding this type of correlations should be taken with caution.

3) Much of the current interest in calixarene chemistry is the use of these ligands as extracting agents for metal cations from water to the organic phase (ref. 13) where the two solvents involved are mutually saturated. Within this context, the thermodynamic parameters of solution shown in the table for 1 in 1-BuOH and water saturated 1-BuOH are immediately striking.

Indeed, the observed decrease in entropy and the concomitant increase in enthalpic stability in moving from the pure to the water saturated solvent was attributed to specific water-ligand

interactions. Quite clearly the data show that the system is seriously perturbed by the presence of water in the non-aqueous phase. The outcome is a complete enthalpy-entropy compensation effect since hardly any changes are observed in the $\Delta_t G^\circ$ value for this system from the pure to the water saturated solvent. In fact, these findings provide further support to the interesting formalism (solvent reorganisation associated with chemical and physical processes and enthalpy and entropy compensation effect) recently developed by Grunwald and Steel (ref. 14) in that $\Delta_t G^\circ \cong 0 \text{ kJ mol}^{-1}$ for **1** from 1-BuOH to water saturated 1-BuOH and consequently, $\Delta_t H^\circ \cong T\Delta_t S^\circ$. These results provide a sharp illustration that misleading conclusions can be drawn from data based solely on Gibbs energies. Furthermore, the presence of water in the organic phase, particularly in the H₂O-1-BuOH solvent system where the mutual solubility of the solvents involved is high, seriously alters the strength of complexation of this ligand with metal cations (ref. 13). A direct implication of this statement is that in reporting the thermodynamics of complex formation in non-aqueous media, the water content of the solvent should be specified. As far as transfer data for metal-ion complexed salts are concerned, the only data available are those for the lithium and sodium perchlorate complexes of the tetraethyl ester derivative (ref. 10). For this system data have been reported in methanol, MeCN and PhCN and these are discussed below. More recently, thermochemical data for the sodium and potassium tetraphenylborate salts of the hexaethyl derivative have been reported (ref. 15). In the following section, the significance of the solution thermodynamics of reactants and product in the interpretation of the complexation process is discussed.

SIGNIFICANCE OF SOLUTION THERMODYNAMICS OF REACTANTS AND PRODUCT IN THE INTERPRETATION OF COMPLEXATION DATA.

There are concepts in the literature that deserve some comments. Thus, McKerverey *et al.* (ref. 16) under the heading of stability constants and association constants, the authors only define the stability constant. Within the context of this paper, it is important to define carefully the parameters relating to the complexation process. Thus for the formation of a 1:1 cation:ligand complex (eq. 3),

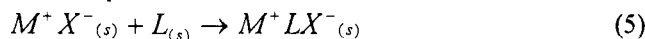


where M^{n+} , L and $M^{n+}L$ denote cation, ligand and metal-ion complex respectively, the thermodynamic stability constant, K_s (molar scale) refers to the process in which reactants and product are in their standard state (units of K_s are cancelled) is defined by

$$K_s = \frac{a_{ML^{n+}}}{a_{M^{n+}} \cdot a_L} = \frac{[ML^{n+}]\gamma_{\pm}}{[M^{n+}]\gamma_{M^{n+}} [L]\gamma_L} \cong \frac{[ML^{n+}]}{[M^{n+}][L]} \quad (4)$$

In eq. 4, a and γ_{\pm} denote activity and mean activity coefficient respectively. The inequality of eq. 4 holds provided that the solutions are relatively dilute in which case $\gamma_L \cong 1$ and $\gamma_{\pm M^{n+}L} \cong \gamma_{\pm M^{n+}}$. For processes involving charged ligands, particularly multicharged ligands, it may be necessary to consider explicitly the activity coefficients of the species concerned in the equilibria.

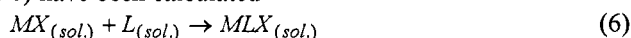
In solvents of low dielectric constants, such as chloroform or water (D₂O) saturated chloroform, whose ion association becomes important, it is common to define an 'association' constant, K_{ass} , which refers to the process



involving ion-pairs rather than free ions. It is important not to confuse K_{ass} with K_s as these refer to two different processes. The discussion which follows concerns complexation processes in ionising media (eq. 3) involving neutral ligands.

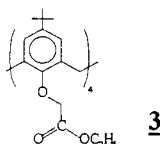
As far as calixarene derivatives and alkali-metal cations are concerned, the most detailed thermodynamic information is that involving the esters (refs. 9-10). This statement is based on the following facts

- i) Stability constants for these systems have been determined by several methods; particularly, for lithium and sodium derivatives in MeCN and PhCN.
- ii) Enthalpies of complexation have been measured by classical titration calorimetry and checked by the most sensitive microcalorimetric technique
- iii) For the interpretation of the complexation process, the solution thermodynamics of the free and the complexed cation salts as well as the ligand was considered
- iv) Enthalpies of coordination, $\Delta_{\text{coord}}H^\circ$ referred to the process in which reactants and product are in their solid state (eq. 6) have been calculated



For a given system, $\Delta_{\text{coord}}H^\circ$ should be the same, independently of the solvent from which this is derived. Therefore, in addition to the information that can be obtained from these data, its calculation provides an useful way of checking the reliability of the data. These statements are corroborated by the data shown in Table 2 for ethyl *p*-*tert*-butylcalix(4)arene, EtCalix(4), **3**, and lithium and sodium cations (refs. 9-10).

TABLE 2. Solution thermodynamics of the free and complexed electrolytes and the ligand. Complexation of ethyl *p*-*tert*-butylcalix(4)arene tetraethanoate and lithium and sodium in acetonitrile and benzonitrile. Coordination data in the solid state at 298.15 K (refs. 9-10).^a



NaClO ₄	EtCalix(4)	[NaEtCalix(4)]ClO ₄	Na ⁺ +EtCalix(4) (solution)	NaClO ₄ +EtCalix(4) (solid)
$\Delta_{\text{f}}G^\circ / \text{kJ mol}^{-1}$	$\Delta_{\text{f}}G^\circ / \text{kJ mol}^{-1}$	$\Delta_{\text{f}}G^\circ / \text{kJ mol}^{-1}$	$\Delta_{\text{c}}G^\circ / \text{kJ mol}^{-1}$	$\Delta_{\text{coord}}G^\circ / \text{kJ mol}^{-1}$
Acetonitrile				
2.51	11.14	16.11	-43.81	-46.27
$\Delta_{\text{f}}H^\circ / \text{kJ mol}^{-1}$	$\Delta_{\text{f}}H^\circ / \text{kJ mol}^{-1}$	$\Delta_{\text{f}}H^\circ / \text{kJ mol}^{-1}$	$\Delta_{\text{c}}H^\circ / \text{kJ mol}^{-1}$	$\Delta_{\text{coord}}H^\circ / \text{kJ mol}^{-1}$
Acetonitrile				
-17.28	22.67	-34.62	-69.20	-29.19
Benzonitrile				
-10.42	14.03	-12.70	-50.70	-34.39
} -31.80				
$\Delta_{\text{f}}S^\circ / \text{J K}^{-1} \text{mol}^{-1}$	$\Delta_{\text{f}}S^\circ / \text{J K}^{-1} \text{mol}^{-1}$	$\Delta_{\text{f}}S^\circ / \text{J K}^{-1} \text{mol}^{-1}$	$\Delta_{\text{c}}S^\circ / \text{J K}^{-1} \text{mol}^{-1}$	$\Delta_{\text{coord}}S^\circ / \text{J K}^{-1} \text{mol}^{-1}$
Acetonitrile				
-66.4	38.7	-170.2	-85.2	-48.5
LiClO ₄	EtCalix(4)	[LiEtCalix(4)]ClO ₄	Li ⁺ +EtCalix(4) (solution)	LiClO ₄ +EtCalix(4) (solid)
$\Delta_{\text{f}}H^\circ / \text{kJ mol}^{-1}$	$\Delta_{\text{f}}H^\circ / \text{kJ mol}^{-1}$	$\Delta_{\text{f}}H^\circ / \text{kJ mol}^{-1}$	$\Delta_{\text{c}}H^\circ / \text{kJ mol}^{-1}$	$\Delta_{\text{coord}}H^\circ / \text{kJ mol}^{-1}$
Acetonitrile				
-43.26	22.67	-9.17	-48.78	-60.20
Benzonitrile				
-27.32	14.03	-10.42	-57.20	-60.07
} -60.13				

As far as the system involving sodium is concerned, $\Delta_{\text{coord}}G^\circ$ does not differ significantly from the complexation data, although these two parameters are not strictly comparable since the former involves the electrostatic interaction between cation and anion which may be quite significant if the cation is not fully shielded by the ligand although this is unlikely to be the case for the sodium calixarene perchlorate complex. The availability of coordination data for sodium

perchlorate and cryptand 222 ($\Delta_{\text{coord}}G^\circ = -67.4 \text{ kJ mol}^{-1}$) leads to the conclusion that the stability of NaEtCalix(4)ClO_4 in the solid state is lower by about 21 kJ mol^{-1} from that of sodium cryptate. In terms of enthalpy, through analysis of the data in Table 2 it was demonstrated that the increase in exothermic behaviour of sodium and EtCalix(4) in MeCN relative to PhCN ($\cong -19 \text{ kJ mol}^{-1}$) is almost entirely due to the higher enthalpic stability of the NaEtCalix(4)ClO_4 in the former ($-34.62 \text{ kJ mol}^{-1}$) relative to the latter ($-12.70 \text{ kJ mol}^{-1}$) solvent. This statement is further corroborated by the greater loss of entropy observed for the complexation of Na^+ and EtCalix(4) in MeCN relative to the same process in PhCN.

Enthalpy data for lithium were found to contrast with those for sodium, in that the transfer enthalpy of the complexed cation from MeCN to PhCN (data based on the $\text{Ph}_4\text{AsPh}_4\text{B}$ convention) is cancelled by that of the ligand and therefore, the differences in the $\Delta_c H^\circ$ values in these solvents were attributed to the changes in the enthalpic stability of lithium in these media. This statement is partially corroborated by the gain in entropy observed for this cation upon complexation with EtCalix(4) in MeCN relative to PhCN as shown in Table 2. Comparison of enthalpies of coordination of LiEtCalix(4)ClO_4 and NaEtCalix(4)ClO_4 with corresponding data for cryptands demonstrated that the stability in enthalpic terms in the solid state is lower for the complex which shows the higher stability in solution. This was explained on the basis of a possible correlation between stability and the effectiveness of the ligand to shield the cation so that the electrostatic interaction of the latter with the anion becomes weaker when greater is the stability of the complex. The positive entropy of coordination observed for EtCalix(4) and NaClO_4 also observed for cryptand 222 and this salt was attributed to a weaker cation-anion interaction in the sodium macrocyclic salt relative to the stronger cation-anion interaction in the ionic solid (ref. 10). Further studies on these systems are required in order to corroborate these statements. More recently, similar studies were carried out with the hexaester derivatives and metal cations in PhCN (ref. 15). Stability constants show a 'peak' selectivity with a monotonic increase in stability from lithium to potassium followed by a decrease from the latter to rubidium. In terms of enthalpy, a linear relationship was obtained when $\Delta_c H^\circ$ values were plotted against the stability ($\log K_s$) of the metal-ion complexes. Therefore, these complexes are enthalpy stabilised. In terms of entropy, the destabilising effect was found to be at its maximum for potassium. The results were analysed in terms of solute-solvent interactions reflected on the solution thermodynamics of the free and complexed salts and the ligand in PhCN.

A few representative examples which clearly demonstrate the importance of considering the relevant thermodynamic parameters of the free and complexed ligand as well as those for the free metal cations in the interpretation of the complexation process are now given.

Table 3. Thermodynamic parameters of complexation of alkali-metal cations and calixarene amides in MeOH and MeOH at 298.15 K (ref. 12).

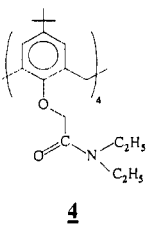
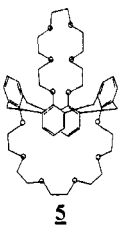
Ligand	Cation	Log K_s	$\Delta_c G^\circ/\text{kJ mol}^{-1}$	$\Delta_c H^\circ/\text{kJ mol}^{-1}$	$\Delta_c S^\circ/\text{J K}^{-1} \text{mol}^{-1}$
 4	Methanol				
	Li^+	4.1	-22.1	-7	50
	Na^+	7.9	-45.0	-50.6	-20
	K^+	5.8	-33.1	-42.4	-31
	Rb^+	3.8	-21.6	-17.5	13
	Cs^+	2.5	-14.0	-9.0	17
	Acetonitrile				
	Li^+	≥ 8.5	-	-55.0	≥ -22
	Na^+	> 8.5	-	-79.0	≥ -103
	K^+	≥ 8.5	-	-64.0	≥ 52
Rb^+	5.7	-32.5	-37.2	-17	
Cs^+	3.5	-19.9	-26	-20	

Table 3 reports thermodynamic data for a calix(4)arene amide derivative **4** in MeOH and in MeCN at 298 K (ref. 12).

As observed for the esters, the complexation enthalpies for the alkali-metal cations display more exothermic complexation enthalpies in MeCN than in MeOH. Using transfer activity coefficients of the alkali-metal cations from MeCN to MeOH it was pointed out by Arnaud *et al.* that the lithium and sodium cations are better solvated in MeOH than in MeCN. Neglecting some discrepancy found in the literature as to whether the Gibbs energies of transfer (related to the transfer activity coefficients γ by $\Delta G^\circ = -R T \ln \gamma$) from MeCN to MeOH are exogonic or endogonic, **it should be stressed that in assessing enthalpies of complexation, the relevant parameter to consider are the enthalpies of transfer, $\Delta_c H^\circ$ of these cations from MeCN to MeOH.** In fact, transfer enthalpies of K^+ , Rb^+ and Cs^+ from MeCN to MeOH (data based on the Ph_4AsPh_4B convention) are consistently endothermic reflecting that the stabilities in enthalpic terms are higher in MeCN than in MeOH. As $\Delta_c H^\circ$ values for these cations are more exothermic in MeCN than in MeOH, it follows that the relevant parameter for the cation is not the dominant factor affecting the relative $\Delta_c H^\circ$ values in the two solvents, the enthalpy of transfer of the free and complex ligand must be considered.

Another example which illustrates the relevance of characterising thermodynamically the ligand and the derived metal-ion complex salt is that involving the complexation of calix(4) bis crowns and alkali-metal cations in MeOH and MeCN (ref. 17). Thermodynamic data for a representative ligand **5** and K^+ , Rb^+ and Cs^+ cations in MeOH and MeCN at 298 K are listed in Table 4.

Table 4. Thermodynamic parameters of complexation of a calix(4)-bis-crown ligand and alkali-metal cations (K^+ , Rb^+ , Cs^+) in methanol and acetonitrile at 298 K (ref. 17).

Ligand	Cation	Solvent	$\log K_s$	$\Delta_c G^\circ$ kJ mol ⁻¹	$\Delta_c H^\circ$ kJ mol ⁻¹	$\Delta_c S^\circ$ J K ⁻¹ mol ⁻¹
 5	K^+	MeOH	4.1	-23.4	-31.7	-28
		MeCN	4.12	-23.5	-17	23
	Rb^+	MeOH	4.3	-24.5	-52	-92
		MeCN	4.41	-25.1	-25.2	0
	Cs^+	MeOH	4.8	-27	-56.2	-98
		MeCN	4.9	-27.9	-29.7	-6

The most notable feature of these data is the decrease in enthalpic stability and the entropy gain observed in the complexation of ligands containing six oxygens in the crown moiety and alkali-metal cations in MeCN relative to MeOH. These were attributed to the different states of solvation of alkali-metal cations and to the possibility that these ligands may be better solvated in MeCN than in MeOH. Although omitted by the authors, it should be noted that there is considerable evidence in the literature regarding specific interactions between 18-crown-6 and MeCN in the solid state and in solution (refs. 18-19). In fact the trend in enthalpies and entropies observed with the calix-bis-crowns and metal cations in MeCN is very similar to that observed for 18-crown-6 and these cations in this solvent, although for the latter ligand more dramatic effects are found in this solvent (ref. 20). Molecular Dynamics and Free Energy Perturbation studies carried out by Varnek and Wipff predict that **5** interacts with acetonitrile (ref. 2).

A more refined insight into ligand and metal-ion complex solvation is needed to decide what are the predominant factors contributing to the thermodynamics of complexation of these systems in solution.

NEW DERIVATIVES

Lower rim *p-tert*-butylcalix(4)arenes recently synthesised by our group are shown in Fig. 1. Except for **6b** which have been previously reported (ref. 21), these are new derivatives.

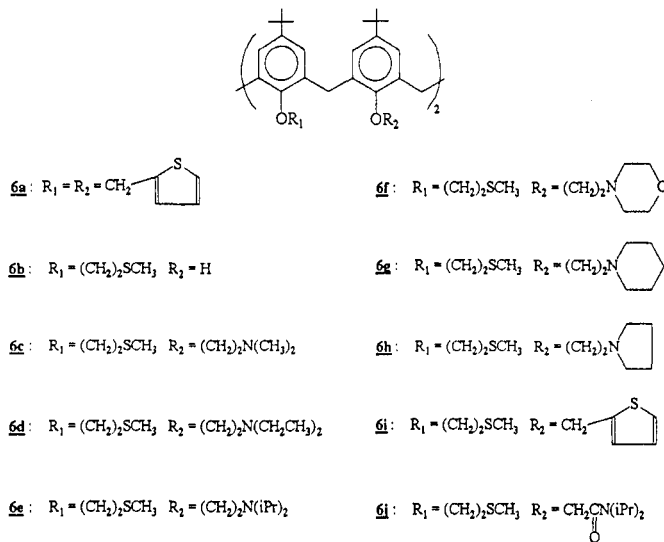


Fig. 1. Structure of *p-tert*-butylcalix(4)arenes containing thiophenoethoxy and mixed pendant arms.

methylethio ethoxy substituents adopt a flattened conformation. It is found that the two amino nitrogen atoms in this macrocycle are 8.678 Å apart while the two sulphur atoms are separated by 5.231 Å. Information regarding the conformation of these compounds in solution was obtained from NMR studies in Cl_3CD and in CD_3OD at 298 K. As far as the ^1H NMR is concerned, non-equivalence was found between the axial and equatorial protons of the methylene bridge reflected in the pair of doublets, indicating that these compounds also adopt 'cone' conformations in solution (ref. 23). Further evidence was obtained from the ^{13}C NMR spectra where the C signal connecting two adjacent phenyl moieties is found at 31 ppm (ref. 24). Since this paper is concerned with thermodynamic aspects of calixarene chemistry, the discussion is focussed on the thermodynamics of **6d** and metal cations in CD_3OD .

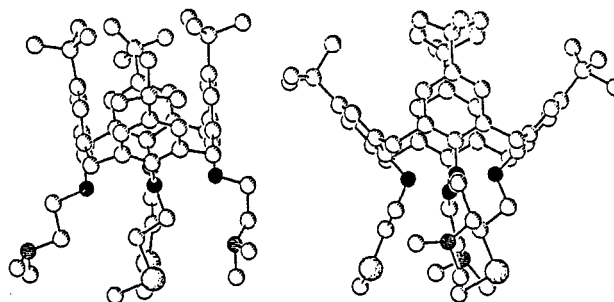


Fig. 2. Side views showing the cone conformation of 5,11,17,23-tetrakis-(1,1-dimethylethyl)-25,27-bis(methylthioethoxy)-26,28-bis[(dimethylamine)ethoxy] calix(4)arene.

COMPLEXATION STUDIES

Ligand **6d** is able to complex selectively Hg^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} and Cu^{2+} as assessed from ^1H NMR titrations. Both, NMR and conductimetric titrations indicate that while the complex stoichiometry is 1:1 for silver, lead, cadmium and copper, this ligand is able to host two mercury (II) cations per calixarene unit. These findings were also corroborated by titration

microcalorimetry. Since enough thermodynamic information is available on the interaction of **6d** with silver in various solvents, this system is now discussed.

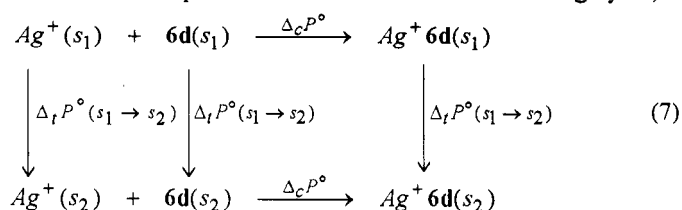
THERMODYNAMICS OF COMPLEXATION

The process of complexation of **6d** and silver in a variety of solvents (methanol, MeOH; ethanol, EtOH; propan-1-ol, 1-Pr; N,N dimethylformamide, DMF; acetonitrile, MeCN and benzonitrile, PhCN) at 298.15 K has been thermodynamically characterised. Thus, log K_s and derived standard Gibbs energies, enthalpy and entropy values for **6d** and Ag^+ in MeOH, MeCN and PhCN are listed in Table 5.

Table 5. Thermodynamic parameters of complexation of **6d** and Ag^+ in various solvents at 298.15 K.

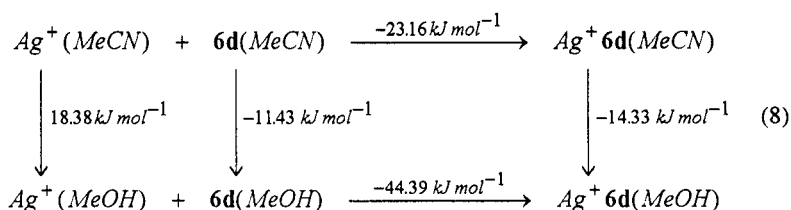
Solvent	log K_s	$\Delta_c G^\circ / \text{kJ mol}^{-1}$	$\Delta_c H^\circ / \text{kJ mol}^{-1}$	$\Delta_c S^\circ / \text{J K}^{-1} \text{mol}^{-1}$
MeOH	5.92±0.09	-33.79±0.51	-44.39±1.12	-35.5
MeCN	3.46±0.16	-19.77±0.91	-23.16±1.65	-11.4
PhCN	4.00±0.04	-22.84±0.23	-44.85±0.73	-73.8

In all solvents, the process is enthalpy controlled. However, the higher stability in MeOH relative to PhCN results from a more favourable entropy in the former relative to the latter solvent given that in these solvents, $\Delta_c H^\circ$ values are about the same. However, availability of enthalpy data for the ligand, free and metal cation salts in five different solvents allows the calculation of the enthalpies of coordination ($\Delta_{\text{coord}}H^\circ$) referred to the process in the solid state (eq. 6). The $\Delta_{\text{coord}}H^\circ$ values for this system is $-71.38 \pm 1.20 \text{ kJ mol}^{-1}$. This is the average of values derived from five different solvents (from MeOH, $\Delta_{\text{coord}}H^\circ = -72.02 \text{ kJ mol}^{-1}$; from EtOH, $\Delta_{\text{coord}}H^\circ = -72.61 \text{ kJ mol}^{-1}$; from 1-PrOH, $\Delta_{\text{coord}}H^\circ = -69.90 \text{ kJ mol}^{-1}$; from MeCN, $\Delta_{\text{coord}}H^\circ = -72.07 \text{ kJ mol}^{-1}$; from PhCN; $\Delta_{\text{coord}}H^\circ = -70.28 \text{ kJ mol}^{-1}$). Since $\Delta_{\text{coord}}H^\circ$ should be the same independently of the solvent from which these are derived, the agreement found among these values unambiguously demonstrates the reliability of complexation and solution data. In order to assess the contribution of ligand, free and complex cations to the differences observed in the thermodynamics of complexation of silver and the ligand in two solvents, eq. 1 is used. The processes involved in each term of eq. 1 are best illustrated in the following cycle,

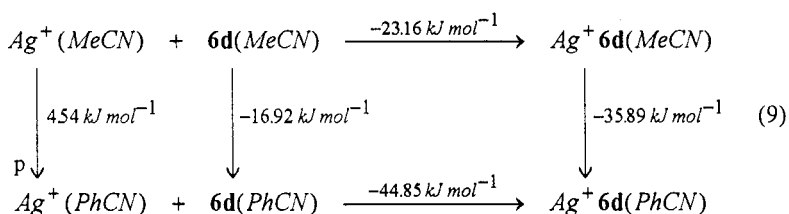


For the calculation of transfer data, $\Delta_t P^\circ$, MeCN is chosen as reference solvent. Single-ion values for Ag^+ and $\text{Ag}^+ \mathbf{6d}$ cations are based on the $\text{Ph}_4\text{AsPh}_4\text{B}$ convention (ref. 25), although it should be emphasised that the difference between $\Delta_c P^\circ$ in the two solvents is independent of any extrathermodynamic convention since the anion constituent of the free and complex cation salts is the same.

Analysis of enthalpy data in the MeCN-MeOH solvent system can be made by inserting the appropriate quantities into eq. 7



A direct implication of eq. 1 is that if the complex cation is more stabilised (in enthalpic terms) in s_2 (MeOH) than in s_1 (MeCN), and if both, the free metal-ion and the ligand (or indeed the balance between the $\Delta_c H^\circ$ values of reactants) show the opposite enthalpy trend, the complexation process will be enthalpically more stable in s_2 than in s_1 . Inspection of data in eq.6 unambiguously demonstrate that the higher complex stability (in enthalpic terms) in MeOH relative to MeCN ($\Delta\Delta_c H^\circ \cong -21 \text{ kJ mol}^{-1}$) results from the favourable contribution of both, free and complex cations, since the contribution of the ligand is unfavourable. Similar analysis in the MeCN-PhCN solvent system,



show quite dramatic changes with respect to the MeCN-MeOH system. Although the transfer enthalpies of the free and complex cations contribute to the higher complexation enthalpy in PhCN relative to MeCN, the contribution of the free cation is relatively small with respect to that of the complex cation.

We therefore conclude that (i) in both systems, the ligand contributes unfavourably to the higher stabilities of complex formation reflected in the almost identical $\Delta_c H^\circ$ values observed in MeOH and in PhCN. However, the extent of contribution of free and complex cation (favourable) to the $\Delta_c H^\circ$ values in MeOH differ significantly from that in PhCN. Similar studies are being conducted in terms of Gibbs energies and entropies. We are now proceeding with the thermodynamic characterisation of these ligands and different metal cations in a variety of solvents.

Acknowledgements: The authors thanks the EPSRC (GP/K28510) and the EU (DGI) (ARG/B7-3011/94/25B) for the financial support provided for this work.

REFERENCES

1. a) C. D. Gutsche, in *Monographs in Supramolecular Chemistry*, ed. J. F. Stoddart, Royal Society of Chemistry: London, 1989. b) 'Calixarenes. A Versatile Class of Macrocyclic Compounds', Ed. Vicens, J., Böhmer V., Kluwer Academic Publishers, 1991. c) *Calixarenes 50th Anniversary: Commemorative Volume*, Ed. Vicens, J.; Asfari, Z.; Harrowfield, J. M.; Kluwer Academic Publishers, 1994.
2. A. Varnek and G. Wipff; *J. Mol. Structure (Theochem.)*; **363**, 67 (1996) and references therein.
3. A. F. Danil de Namor and L. Ghossein; *J. Chem. Soc.; Faraday Trans.*; **81**, 781 (1985).
4. A. F. Danil de Namor; *J. Chem. Soc.; Faraday Trans.*; **84**, 3539 (1988).
5. A. F. Danil de Namor; *Pure & Appl. Chem.*; **62**, 2121 (1990).

6. A. F. Danil de Namor and D. Kowalska, *J. Phys. Chem.*; **101**, 1643 (1997).
7. B. G. Cox and H. Schneider in 'Coordination and Transport Properties of Macrocyclic Compounds in Solution', Elsevier, 1992.
8. A. F. Danil de Namor; *Pure & Appl. Chem.*; **65**, 193, (1993).
9. A. F. Danil de Namor; E. Gil; M. A. Llosa Tanco; D. A. Pacheco Tanaka; L. E. Pulcha Salazar; R. A. Schulz and J. Wang; *J. Phys. Chem.*, **99**, 16776 (1995),
10. A. F. Danil de Namor; E. Gil; M. A. Llosa Tanco; D. A. Pacheco Tanaka; L. E. Pulcha Salazar; R. A. Schulz and J. Wang; *J. Phys. Chem.*, **99**, 16781 (1995).
11. A. F. Danil de Namor; J. Wang; I. Gomez Orellana; F. J. Sueros Velarde and D. A. Pacheco Tanaka, *J. Inclusion Phenom. Mol. Recognit. Chem.*; **19**, 371 (1994) and references therein.
12. F. Arnaud-Neu; G. Barrett; S. Fanni; D. Marrs; W. McGregor; M. A. McKerver; M. J. Schwing-Weill; V. Vetrogon and S. Wechsler, *J. Chem. Soc., Perkin Trans. 2*, 453 (1995) and references therein.
13. A. F. Danil de Namor; F. J. Sueros Velarde; A. R. Casal; A. Pugliese; M. T. Goitia; M. Montero and F. Fraga López, *J. Chem. Soc., Faraday Trans.*; 1997 (in the press).
14. E. Grunwald; C. Steel; *J. Am. Chem. Soc.*, **117**, 5687 (1995).
15. A. F. Danil de Namor; M. L. Zapata-Ormachea; O. Jafou and N. Al Rawi; *J. Phys. Chem.*, (1997) (in the press).
16. M. A. McKerver; M. J. Schwing-Weill and F. Arnaud-Neu in *Comprehensive Supramolecular Chemistry*; ed. Gokel G.W., Elsevier: Oxford, 1996, Vol.1, 537 and references therein.
17. F. Arnaud-Neu; Z. Asfari; B. Souley and J. Vincens; *New J. Chem.*; **20**, 453 (1996).
18. R. L. Garrell; J. C. Smyth; F. R. Fronczek; R. D. Gandour; *J. Inclusion Phenom. Mol. Recognit. Chem.*; **6**, 73 (1988).
19. K. Ozutsumi; M. Natsuhara; H. Ohtaki; *Bull. Chem. Soc. Jpn.*; **62**, 2807 (1989)
20. K. Ohtsu; T. Kawashima and K. Ozutsumi *J. Chem. Soc.; Faraday Trans.*, **91**, 4375 (1995) and references therein.
21. a) P. L. M. Cobben; R. J. M. Egberink; J. G. Bomer; P. Bergveld; W. Verboom; D. N. Reinhoudt; *J. Am. Chem. Soc.*, **114**, 10573 (1992). b) P. D. Beer; J. P. Martin; M. G. B. Drew; *Tetrahedron*, **48**, 9917 (1992).
22. A. F. Danil de Namor; R. G. Hutcherson; F. J. Sueros Velarde; J. I. Bullock, J. L. Briansó and M. A. Alvarez García (1997) submitted for publication.
23. C. D. Gutsche, *Aldrichimica Acta*, **28**, Nro. 1, 3 (1995)
24. J. C. Mendoza; P. Prados; P. M. Nieto; C. Sanchez; *J. Org. Chem.*, **56**, 3372 (1991).
25. L. Ghouseini, PhD thesis, University of Surrey, 1984.