The Medium Effect on the Selective Complexation of Mercury (II) and Silver (I) by a Fully Substituted Lower Rim Calix[4]arene Receptor

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Abstract:

Mercury has been recognized as a highly dangerous element by the Environmental Protection Agency (EPA) due to its accumulative and persistent character in the environment and biota. In the Latin American region several countries are affected by the extremely high contents of mercury in the environmental and consequently in water, therefore the aim of this research is to synthesize receptors able to interact selectively with mercury species.

This paper reports the synthesis of a novel lower rim calix[4]arene derivative with pendent arms containing oxygen, phosphorus and sulphur as donor atoms, (**1**). Spectrometric (^{1}H NMR) measurements were performed to determine the actives site of complexation of this ligand and the mercury (II) and silver (I) cations in solution. Conductance data provide information regarding the composition of the metal-ion complex in acetonitrile and methanol. The stability constant of the mercury (II) and silver (I) complex was derived from direct potentiometric titration. The latter technique was also used to characterize the thermochemical character of the binding process

Key words: Mercury, *p-tert*-Butylcalix[4]arene, Binding, potentiometry, conductometry, Protons, selectivity

INTRODUCTION

Among the synthetic macrocycles, calixarenes have attracted a great deal of attention as reflected by the number of papers and books published in this area[1-6]. Interest has been mainly centered the cyclic tetramer and its upper and lower rim derivatives. It has been demonstrated that complexing agents containing nitrogen, oxygen and mainly sulphur donor atoms are able to interact with transition and heavy metal cations.

Representative examples dithiazone[7], dithia-crown ethers[8], hexathia-18-crown-6-tetraone[9] and 2-mercapto benzimidazole[10] which have been used as potential complexing agents for transition metal cations. More recently 1, 3 -amino diethylthiophosphorus[11] and 1,3 diethyl thioether[12] have been reported as very selective ionophores for mercury (II).

Functionalisation of calix(n)arenes has produced derivatives with different pendant arms in the lower rim containing hard, soft and mixed donor atoms to target cations, anions and neutral species[13-15]. We report here the synthesis and characterisation of a fully substituted lower rim *p-tert*-butyl calix(4)arene, namely 5, 11, 17, 23-tetra-tert-butylcalix[4]arene, tetra diethylthiophosphate, **1** and its interactions with metal cations. In doing so spectrometric (^{1}H NMR), electrochemical (conductance measurements) and calorimetric measurements were performed. Solvents selected for this study are acetonitrile (dipolar aprotic) and methanol (protic). The medium effect on the complexation process is discussed.

MATERIALS AND METHODS

Chemicals: *p-tert*-Butylcalix[4]arene *p-tert*-Butylcalix[4]arene, diethyl chlorothiophosphate were purchased from Aldrich, Tetra-*n*-butylammonium bromide and tetra-*n*-butylammonium perchlorate, both from Fluka were used without further purification. Metal cation salts as perchlorates (Li$^+$, Na$^+$, K$^+$, Cs$^+$, Ag$^+$, Cd^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, Hg^{2+}) purchased from Aldrich, were dried over P$_4$O$_{10}$ under vacuum for several days before use. Magnesium sulphate and sodium hydroxide were purchased from Fisher Scientific.

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Acetonitrile (HPLC grade, Hayman Limited, high purity reagent), methanol and ethanol (HPLC grade) and dichloromethane, from Fisher were used without further purification,

Synthesis of 5, 11, 17, 23-tetra-*tert*-butylcalix[4]arene, tetra diethyl thiophosphate: In a three-necked round bottomed flask (250 ml), *p-tert*-butyl calix[4]arene (1.0 g, 1.54 mmol), tetra-n-butylammonium bromide (0.1 g, 0.31 mmol) and diethylchlorothiophosphate (5.0 ml g, 39.7 mmol) were suspended in dry dichloromethane (100 ml). This was followed by dropwise addition of a solution of NaOH (50 %). The course of the reaction was monitored by TLC (thin layer chromatography) using a dichloromethane: Methanol (9:1) mixture as the developing solvent system. Then the mixture was cooled down and the organic phase was separated and washed with brine. It was then dried with magnesium sulphate and evaporated under reduced pressure. The oil residue was treated with hot methanol and left to cool down. White crystals were isolated. The product was obtained in 85% yield, melting point 263-264°C and was characterised by elemental analysis (Calculated % C, 57.31; H, 7.37; found % C, 57.13; H, 7.59) ^{1}H and ^{13}C NMR spectroscopy:

^{1}H NMR (300 MHz, in CDCl$_3$); δ (ppm), J (Hz); 8.90 (s, 8H, Ar-**H**), 4.85 (d, 4H, J = 14.10, Ar-**CH$_2$ax**-Ar), 4.29 (m, 16H, -O-**CH$_2$**-CH$_3$), 3.24 (d, 4H, J = 13.80, Ar-**CH$_2$eq**-Ar), 1.34 (t, 24H, O-CH$_2$-**CH$_3$**), 1.07 (s, 36H, -C-(**CH$_3$**)$_3$)

^{13}C NMR (300MHz) (CDCl$_3$) δ$_C$ ppm; 146.78, 143.24, 134.32, 125.92 (**Ar**), 65.52 (O**CH$_2$**CH$_3$), 34.36 (**C**(CH$_3$)$_3$, 32.41 (Ar**CH$_2$**Ar), 31.80 (C(**CH$_3$**)$_3$ and 16.44 (OCH$_2$**CH$_3$**)

Solubility measurements: Saturated solutions were prepared by adding an excess of **1** to the solvent. The mixtures were left in a thermostated bath at 298.15 K for several days until equilibrium was attained.

Samples of the saturated solutions were withdrawn and placed in different porcelain crucibles, (which had been previously dried and accurately weighed). The solvent was carefully evaporated until constant weight. Blank experiments showed no impurities in the solvent. Analysis was done at least by duplicate on the same equilibrium mixture.
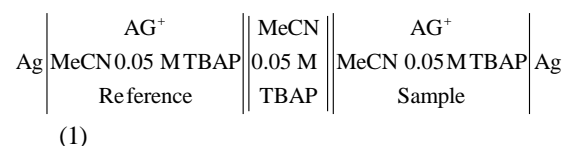
In dichloromethane, chloroform, tetrahydrofuran, dimethyl sulphoxide and N,N-dimethyl formamide, solvate formation was observed when 1 was exposed to a saturated atmosphere of the solvent. Therefore these data were not used for the calculation of the standard Gibbs energies of solution of this macrocycle in this solvent.

Conductometric measurements: The Wayne- Kerr B642 Bridge was used. For the determination of the constant of the conductivity cell, an aqueous solution of KCl (0.10 mol dm^{-3}) was dropwise added to deionised water placed in the cell. The cell was kept in a thermostated bath at 298.15 K. The conductance of water was measured in advance and subtracted from each conductance change recorded during the course of the experiment. The corresponding molar conductance (S. cm^2 mol^{-1}) was calculated using the Lind, Zwolenik and Fuoss[16]. equation as detailed elsewhere[17].

For conductometric titrations fresh solutions of both, the metal-ion salt and the ligand under investigation were made up for each experimental run. A solution of the metal-ion salt of known concentration was placed in the conductimetric cell and left to reach thermal equilibrium. It was then titrated with a solution of the ligand in the same solvent. Conductance changes during the course of the titration were recorded.
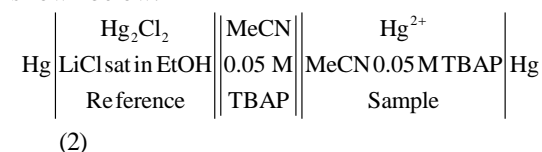
Potentiometric measurements: The stability constant of **1** and mercury (II) and silver (I) cations in acetonitrile and methanol at 298.15 K were measured by potentiometry using the appropriate electrodes as described below.

A digital micro-processor pH/mV-meter HANNA model pH 213 Microprocessor pH- Meter, was used to measure the potential changes during the course of the titration. For the determination of the stability constant of silver (I) in acetonitrile and methanol the following electrochemical cell was used:

$$\left| \begin{array}{c} AG^+ \\ Ag \, | \, MeCN \, 0.05\,M\,TBAP \\ Reference \end{array} \right|\left|\begin{array}{c} MeCN \\ 0.05\,M \\ TBAP \end{array}\right|\left|\begin{array}{c} AG^+ \\ MeCN \, 0.05\,M\,TBAP \, | \, Ag \\ Sample \end{array}\right|$$

(1)

Experimental details have been described elsewhere[19].

As far as mercury (II) is concerned for the determination of the stability constant of this metal cation and **1**, the electrochemical cell use is that shown below:

$$\left|\begin{array}{c} Hg_2Cl_2 \\ Hg \, | \, LiCl\,sat\,in\,EtOH \\ Reference \end{array}\right|\left|\begin{array}{c} MeCN \\ 0.05\,M \\ TBAP \end{array}\right|\left|\begin{array}{c} Hg^{2+} \\ MeCN\,0.05\,M\,TBAP \, | \, Hg \\ Sample \end{array}\right|$$

(2)

Thus the reference and indicator electrodes were connected to an automatic titrator- processor Metrohm 716 DMS Titrino. All titrations were carried out under a nitrogen atmosphere. For the calibration experiments, the vessel was filled with a

solution of TBAP in the appropriate solvent (20 mL, 0.05 mol dm^{-3}), while the burette was filled with a solution of $Hg(ClO_4)_2$ (~3×10^{-3} mol dm^{-3}). After thermal equilibrium was reached, the automatic addition of titrant proceeded. Data were collected by a Hyperaccess data system. The Nernstian behaviour of the electrode was evaluated from the slope of a plot of potential against-log [Hg^{2+}].

For the determination of the stability constant, the ligand solution (~1×10^{-3} mol dm^{-3}) was prepared in a TBAP solution (0.05 mol dm^{-3}) and placed in the burette. The vessel solution containing a known concentration of Hg^{2+} was titrated with the ligand allowing the formation of the 1:1 mercury calixarenate complex. Data were collected by a Hyperaccess System and used for the calculation of the stability constant.

Calorimetric measurements: For calorimetric titrations, the Tronac 450 calorimeter was used as an isoperibol titration calorimeter[18]. It is equipped with a 2 cm^3 burette connected by a silicone tube to the reaction vessel. The reproducibility of the apparatus was checked by (i) calibrating the burette[19] and (ii) chemical calibration using the standard reaction of protonation of an aqueous solution of Tris(Hydroxymethyl)Aminomethane (THAM) in hydrochloric acid (HCl, 0.1N) at 298.15 K. Therefore, an aqueous solution of THAM was placed in the burette and incrementally titrated into the reaction vessel containing the solution of HCl (50 mL). The value determined -47.63±0.19 kJ. mol^{-1} is in agreement with the one reported by Öjelund and Wadsö (-47.49 kJ. mol^{-1}) using an LKB reaction calorimeter.[20] Direct titrations were carried out when log Ks < 6. Thus a solution of the metal ion salt (concentration range 2.0×10^{-2}-5.0×10^{-2} mol dm^{-3}) was prepared in acetonitrile or methanol, placed in the burette and titrated into the vessel containing a solution of 1 (50 cm^3, concentration range 6.0×10^{-4}-1.5×10^{-3} mol dm^{-3}) in the same solvent.

RESULTS AND DISCUSSION

Synthesis of 1: The synthetic route used for the preparation of **1** is that shown in Fig. 1.

^{1}H NMR studies: As far as the ligand is concerned the two pairs the doublets found at 3.24 and 4.85 ppm observed in the ^{1}H NMR spectrum in $CDCl_3$ corresponding to the equatorial and the axial protons respectively with $\Delta\delta_{ax-eq}$ = 1.61 ppm, indicate that this ligand adopts a distorted 'cone' conformation in this solvent at 298 K.

Except for Ag(I) and Hg(II) the addition of any other metal cation (alkali, alkaline-earth, transition heavy metal cations) salt (perchlorate as counter-ion) to a solution of 1 in CD_3CN did not lead to any significant chemical shift changes. Thus Table 1 reports the changes in the ^{1}H NMR signals of 1 with Ag^+ and Hg^{2+} relative to those for the free ligand in this solvent. It is evident from Table 1 that the most significant chemical shift changes are observed in the axial (H-3, deshielded) and the equatorial (H-4)protons. As a result shift differences between the pair of doublets decreases from the free (1.54 ppm) to the complex ligand (~0.99 ppm). Thus Fig. 2 shows a plot of $\Delta\delta_{ax-eq}$ against the metal cation:ligand ratio for Ag^+ and Hg^{2+}. The decrease in the $\Delta\delta_{ax-eq}$ values in moving from the free to the complex ligand is indicative that the
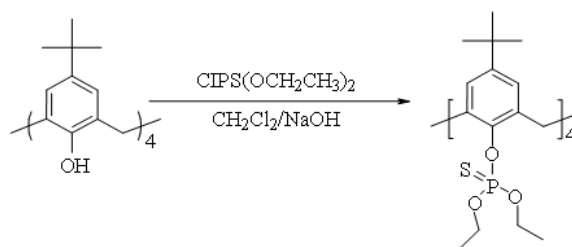
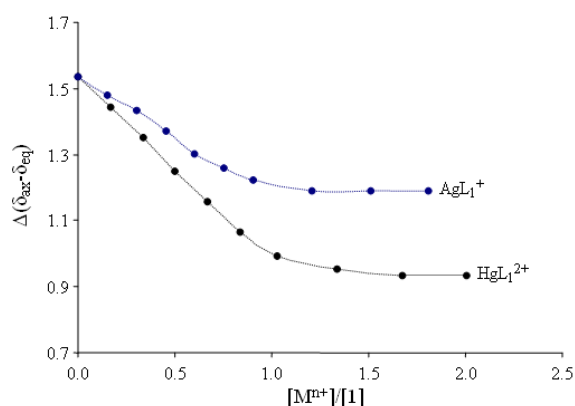

Fig. 1: Synthetic route used for the preparation of **1**

Fig. 2: Plot variation of $\Delta(\delta_{ax}-\delta_{eq})$ ppm against $[M^{n+}]/[1]$ molar ratio for the complexes of **1** with Hg^{2+} and Ag^+ (as perchlorates) in CD_3CN at 298 K

Table 1: Chemical shift changes ($\Delta\delta$ ppm) in the ^{1}H NMR spectra of 1 by the addition of metal-ion (as perchorate) in CD_3CN 298 K

Protons	1	2	3(ax)	4(eq)	5	6
L(free)	1.185	7.258	4.861	3.326	4.252	1.323
Cd^{2+}	0.000	0.000	0.000	0.000	0.01	0.010
Pb^{2+}	0.000	0.000	0.000	0.000	0.01	0.010
Hg^{2+}	-0.040	-0.040	-0.300	0.210	0.07	0.010
Zn^{2+}	0.000	0.000	0.000	0.000	0.01	0.010
Ag^+	-0.010	-0.010	-0.200	0.130	-0.05	-0.050

aromatic rings of the hydrophobic cavity are adopting a more flattened 'cone' conformation while the pendant arms of the ligand are moving closer together to provide the sites of coordination for the metal cation. Chemical changes are more pronounced for Hg^{2+} than for Ag^+ in CD_3CN. Fig. 1 also shows that chemical shifts changes in the methylene protons are observed until the 1:1 complex stoichiometry is achieved and then $\Delta\delta_{ax-eq}$ values remain constant.

In order to further corroborate the complex composition in acetonitrile and to assess the medium effect on the interaction of these cations and **1**, conductometric titrations were carried out and these are now discussed.

Conductometric titrations: The addition of 1 to solutions of silver and mercury salts (as perchlorates) in acetonitrile led to significant changes in conductance. Plots of molar conductance, Λ_m against ligand: metal cation ratios for the titration of mercury and silver cations with 1 in acetonitrile are shown in Fig. 3a and b respectively. It is observed that the break point observed at the 1:1 stoichiometry is sharper for Hg^{2+} than for Ag^+. This is concomitant with the results obtained from ^1HNMR studies. It should also noted that the molar conductances observed at $1:M^{n+} = 0$ corresponding to the free metal cation salts (prior addition of **1**) are well within the conductance values expected for these electrolytes in acetonitrile[21].
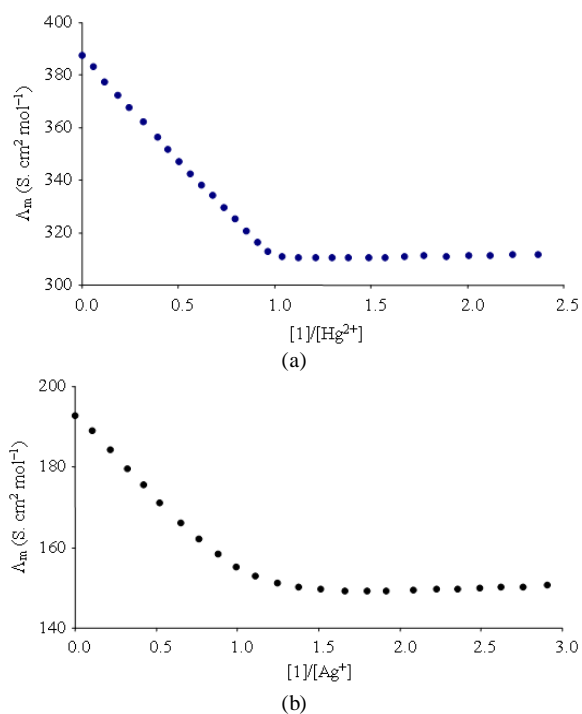

Fig. 3: Conductimetric titration curves for mercury (a) and for silver (b) cations, (as perchlorates) with 1 in acetonitrile at 298.15 K

No changes in conductance were observed by addition of alkali and alkaline-earth metal and other heavy metal cations in acetonitrile. Representative examples for Na^+, Ba^{2+} and Cd^{2+} in acetonitrile are shown in Fig. 4.
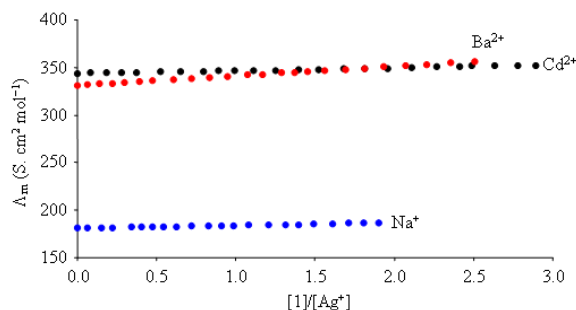

Fig. 4: Conductimetric titration curves for barium, cadmium and sodium cations, (as perchlorates) with 1 in acetonitrile at 298.15 K

Previous study carried out by us[22] demonstrated that the composition of metal ion complexes involving calix[4]arene derivatives may be altered in moving from one solvent to another. Therefore we proceeded with conductance studies involving the same cations (Ag^+ and Hg^{2+}) in methanol.
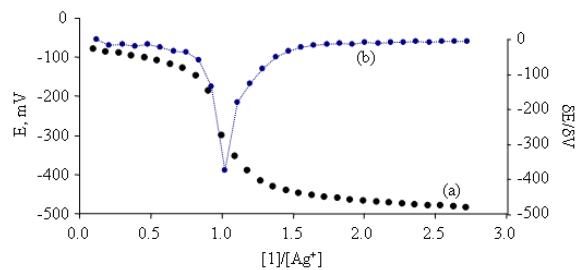

Fig. 5: Potentiometric titration curve for the titration (a) and the first derivative to indicate the end point (b) of the potentiometric titration of silver(I) (as perchlorate) with 1 in methanol at 298.15 K

Thus conductometric curves for the titration of these cations and 1 in these solvent were carried out. These are shown in Fig. 5. As far as Ag^+ is concerned the conductometric curve shows a similar pattern to that observed in acetonitrile in that a decrease in conductance is observed upon complexation with the ligand. However the increase in conductance observed in the titration of Hg^{2+} with **1** in methanol may be attributed to a slight association of the free metal-ion salt in this solvent. Thus addition of **1** to form the metal-ion complex will lead to an increase in the Λ_m value given that

the metal-ion complex (large cation) salt is likely to be more dissociated than the free metal ion salt. Unlike in acetonitrile the shape of the conductometric titration curves for these cations strongly suggests that the stability of the silver complex is likely to be greater than that of the mercury complex. To corroborate these striking results we proceeded with thermodynamic studies involving **1** and these cations in these solvents. These are discussed in thermodynamics of complexation.
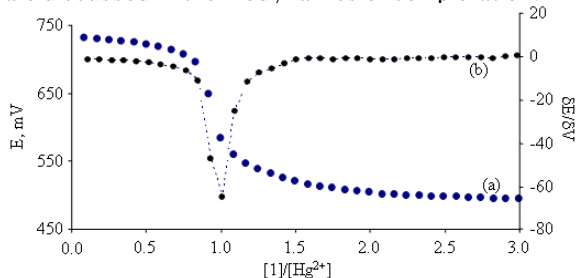

Fig. 6: Potentiometric curve for the titration (a) and the first derivative to indicate the end point (b) of the potentiometric titration of mercury(II) (as perchlorate) with 1 in acetonitrile at 298.15 K.
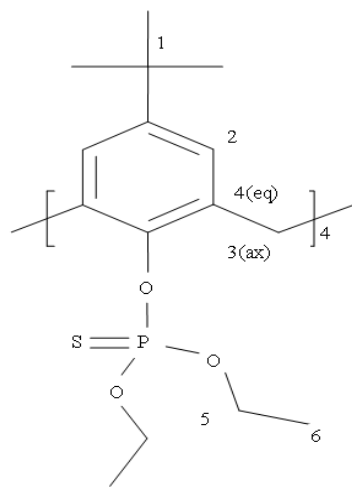

Fig. 7: *p-tert*-butylcalix(4)arene, namely 5, 11, 17, 23-*tetra-tert*-butylcalix[4]arene, tetra diethylthiophosphate, **1**

Thermodynamics of complexation: Having established the composition of the metal-ion complexes of silver and mercury(II) with **1** in acetonitrile and methanol through conductance measurements we proceeded with the determination of their stability constants in these solvents by potentiometry. A typical potentiometric titration curve for Ag^+ and **1** in methanol is shown in Fig. 5. Figure 5 corroborates the conductometric data in that the composition of the silver complex is 1:1 (ligand: Metal cation). As far as mercury and **1** in acetonitrile is concerned potential changes during the course of

the titration are plotted against the ligand:metal cation ratio, (Fig. 6). Again these data corroborate further the 1:1 (metal cation:ligand) stoichiometry of the mercury (II) complex. In both cases Nernstian behavior was found with slopes of 29.86 mV for mercury (II) and 60.01 mV for silver (I).

Table 2: Stability constants (log K_s) and derived standard Gibbs energies, enthalpies and entropies of 1 with silver and mercury metal cations in acetonitrile and methanol at 298.15 K

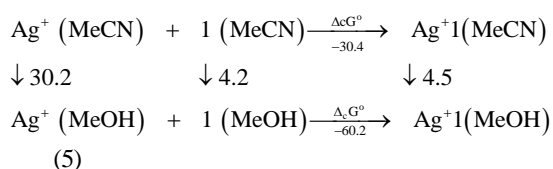| Metal cation	log K_s	$\Delta_c G^o$ (kJ mol^{-1})	$\Delta_c H^o$ (kJ mol^{-1})	$\Delta_c S^o$ (J K^{-1} mol^{-1})
Acetonitrile				
Ag^+	5.33±0.03[c]	-30.40±0.10	-11.4±0.3[b]	64
Hg^{2+}	11.31±0.01[b]	-64.51±0.06	-41.9±0.4[b]	76
Methanol				
Ag^+	10.54±0.01[b]	-60.20±0.30	-51.5±0.2[a]	29
Hg^{2+}	7.14±0.02[b]	-40.80±0.10	-38.5±0.6[a]	8

[a]: Macrocalorimetric data, [b]: Potentiometric data, [c]: Average value

The enthalpy of complexation, $\Delta_c H^o$, associated with these processes was derived from calorimetric data. Combination of Gibbs energy and enthalpy data yields the entropy of complexation, $\Delta_c S^o$ for these systems. Thus stability constants (expressed as log K_s), $\Delta_c G^o$, $\Delta_c H^o$ and $\Delta_c S^o$ values are reported in Table 2. The data are striking in that the selective behavior of **1** towards these cations is reversed in moving from one solvent to another. Indeed while in acetonitrile the selectivity of **1** for mercury (II) is 9.5×10^5 greater than that for silver, the opposite is true in methanol. In the latter solvent the ligand is able to recognize selectively Ag^+ by a factor of 2.5×10^3 relative to Hg^{2+}. This remarkable change in selectivity resulting from the medium effect on the complexation process must be attributed to the salvation changes that the reactants and the product undergo in these solvents and will be discussed in the solubilities and standard Gibbs energies of solution and transfer section. In all cases these processes are favorable in terms of enthalpy (negative) and entropy (positive). However the complexation of Ag^+ and **1** in acetonitrile is entropically controlled while in methanol, the enthalpy rather than the entropy contribute favorably to the stability of complex formation. The latter applies to the complexation of Hg^{2+} and **1** in both solvents. In an attempt to investigate the factors contributing to the higher stability of Ag^+ and **1** in methanol relative to acetonitrile the transfer Gibbs energies of reactants and product were considered and these are now discussed. Attempts to obtain corresponding data for mercury (II) failed. The reason is that mercury salts undergo solvate formation when exposed to a saturated atmosphere of these solvents.

Solubilities and standard Gibbs energies of solution and transfer: The solubility of **1** in acetonitrile and methanol were found to be

$(6.59\pm0.08)\times10^{-3}$ and $(1.21\pm0.02)\times10^{-3}$ mol dm^{-3} respectively. These are the result of three analytical measurements carried out on the same saturated solution. Solvate formation was checked by exposing the ligand to a saturated atmosphere of the appropriate solvent. These tests indicated that **1** does not undergo solvation in these solvents. Thus the standard Gibbs energies of solution, $\Delta_s G^o$, referred to the standard state of 1 mol dm^{-3} are 12.45 ± 0.03 kJ mol^{-1} in acetonitrile and 16.65 ± 0.02 kJ mol^{-1} in methanol at 298.15 K. Therefore the transfer standard Gibbs energy of this ligand from acetonitrile to methanol, $\Delta_t G^o$ is 4.2 kJ mol^{-1}. By inserting this value together with that for the transfer of the silver cation from MeCN to MeOH reported in the literature[23] (data based on the Ph$_4$AsPh$_4$B)[24] and complexation data (Table 2) in the following thermodynamic cycle (expressed in terms of Gibbs energies in kJ mol^{-1}), transfer data for Ag1$^+$ from MeCN to MeOH is calculated:

$$Ag^+\,(MeCN)\ +\ 1\,(MeCN)\xrightarrow[-30.4]{\Delta_c G^o} Ag^+1\,(MeCN)$$
$$\downarrow 30.2\qquad\qquad \downarrow 4.2\qquad\qquad \downarrow 4.5$$
$$Ag^+\,(MeOH)\ +\ 1\,(MeOH)\xrightarrow[-60.2]{\Delta_c G^o} Ag^+1\,(MeOH)$$
$$(5)$$

Taking into account eq.6 (rearrangement of Eq. 5),

$$\Delta_c G^o\,(MeOH)- \Delta_c G^o\,(MeCN) = \Delta_t G^o Ag^+1(MeCN \rightarrow MeOH)$$
$$-\Delta_t G^o 1(MeCN \rightarrow MeOH)$$
$$-\Delta_t G^o Ag^+\,(MeCN \rightarrow MeOH)$$
$$(6)$$

It follows that the higher stability of the complex in methanol relative to acetonitrile is mainly attributed to the lower solvation of the free cation in the former relative to the latter solvent. To a much lesser extent the ligand also contribute favorably to complexation in methanol. However this is almost fully compensated by the unfavorable contribution of the metal-ion complex which is slightly better solvated in acetonitrile than in methanol.

Although we were unable to obtain data for the transfer of Hg^{2+} from MeCN to MeOH, it is well established that acetonitrile is a poorer solvator for the cations than methanol and therefore it is likely that again it is the lower salvation of the free cation in MeCN relative to MeOH which contribute favorably to the higher stability of the complex in the former relative to the latter solvent.

CONCLUSION

Based on the above discussion the following conclusions are drawn:

- A new calix(4)arene derivative able to interact with soft metal cations (Ag$^+$ and Hg^{2+}) in methanol and acetonitrile has been synthesized and characterized.

- Standard Gibbs of complexation of **1** and these metal cations in these solvents reflect that the selectivity of the ligand for these cations is reversed as a result of the medium effect. Thus while in acetonitrile the ligand is able to selectively recognize Hg^{2+} relative to Ag$^+$ by a factor of 9.5×10^5 this is dramatically altered in methanol. This is attributed to the solvation changes that the free cations undergo in these solvents

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