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Abstract

The synthesis and characterization (1H and 13C NMR) of a partially substituted lower rim p-tert-butylcalix(4)arene, namely, (5,11,17,23-tetra-tert-butylcalix(4)arene, namely, (5,11,17,23-tetra-tert-butyl-calix[4]arene, 1) were reported. The solution thermodynamics of the ligand in a variety of solvents at 298.15 K was investigated through solubility (hence standard Gibbs energy) measurements while the calorimetric technique was used to derive the standard solution enthalpy. These data were used to calculate the standard entropy of solution. An enthalpy-entropy compensation effect is shown and as a result, slight variations are observed in the transfer Gibbs energies from the reference to other solvents.

Keywords: lower rim p-tert-butylcalix(4)arene; 1H NMR, Extraction of Cations From Water.

Introduction

Calixarenes1 have received wide recognition in chemistry to the extent that several books have been published in a relative short period of time2,3. Particular emphasis has been placed on the cyclic tetramer and mainly on its lower rim derivatives4, in their ‘cone’ conformation. The single most significant feature of these macrocycles is the different nature of their two cavities. As far as the hydrophilic cavity is concerned, donor atoms such as oxygen (hard Lewis base)5 interact with Lewis acid cations. On the other hand, sulphur and phosphorus are typical soft donor atoms and as such these are likely to interact with soft metal cations6.

Calixarene derivatives containing sulphur, oxygen and phosphorus donor atoms in their lower rim pendant arms have been synthesised and used as ion selective electrodes7,8.

In this paper we report:

The synthesis, 1H and 13C and thermodynamic characterization of 1 and its interaction with metal cations (Pb2+, Cd2+, Hg2+, Cu2+ and Zn2+) in acetonitrile. In doing so, 1H NMR, conductance and calorimetric measurements were carried out.

The extraction of metal cations (Pb2+ and Cd2+) as perchlorates from the aqueous to the non-aqueous phase. In doing so, distribution experiments in the absence and in the presence of the ligand were performed.

Experimental Part

Chemicals.

p-tert-Butylcalix[4]arene, bromoacetonitrile, potassium carbonate and potassium hydrogen carbonate were purchased from Aldrich. Lithium aluminium tetrahydroxide, 18-crown-6 (18-C6), diethyl chlorophosphate, Tetra-n-butylammonium perchlorate (TBAP) and teta-n-butyl ammonium bromide purchased from Fluka were used without further purification. Metal-cation (lithium, sodium, potassium, rubidium, lead, cadmium, zinc, copper and mercury) perchlorates were purchased from Aldrich. These were dried over P2O5 under vacuum for several days before use.

Acetonitrile11 (HPLC grade, Hayman Limited, high purity reagent), THF (tetrahydrofuran), methanol (Fisher reagent, 99%) ethanol (HPLC grade, Fisher) dichloromethane (Fisher), N,N-dimethylformamide, (Fisher, AR), hexane (HPLC grade), 1-butanol (Fisher), dimethylsulphoxide (Fisher, AR) were used without further purification.


5,11,17,23-tetra-tert-butyl, 25,27 bis[(aminomethyl)oxy]ethoxy, 26,28 dihydroxy calix[4]arene, (1), was synthesized following the technique described by Zhang and Huang.2 Thus in a three-necked round bottomed flask (250 ml) equipped with an ice-bath, L (4.887 g, 6.65 mmol), potassium carbonate (1.369 g, 9.91 mmol) and potassium hydrogen carbonate (1.77 g, 17.73 mmol), were suspended in dry dichloromethane (100 ml). The mixture was left under continuous stirring for a period of half an hour. This was followed by drop wise addition of diethyl chlorophosphate (1 ml, 7.94 mmol). The reaction mixture was left at room temperature for 48 hours under vigorous stirring. The course of reaction was monitored by TLC using hexane: ethyl acetate (8:2) mixture as the developing solvent system.

The solvent was removed under reduced pressure and a white solid was afforded. The solid was recrystallized from methanol-acetonitrile. The mixture was left overnight at room temperature and the crystals furnished were left in a piston drier at 60°C. The product was obtained in 70 % yield, mp: 179 – 180°C. Elemental analysis carried out at the University of Surrey, calculated % C 66.78, H 8.41, N 2.78; found % C 66.49, H 8.62, N 2.82.

1H NMR (300 MHz), (CDCl3): δ (ppm) J (Hz): 8.57 (s, 2H, Ar-OH), 7.93 (s, 8H, Ar-H), 5.20 (d, 2H, J=1.10, -CH2-NH), 4.34 (d, 4H, J=13.20, Ar-C=CH2-Ar), 4.13 (m, 12H, -O=CH-CH2-CH2-O=CH-CH2-), 3.86 (m, 4H, -CH2-CH2-NH), 3.37 (d, 4H, J=1291, Ar-C=CH2-CH2-Ar), 1.36 (m, 12H, -O=CH-CH2-CH2-O=CH-CH2-), 1.21 (m, 36H, -C-CH3).}

13C NMR (300 MHz) (CDCl3): δ ppm: 149.67, 148.87, 148.24, 142.86, 133.76, 127.96, 126.13, 125.65 (Ar), 77.16 (OCH3,CH2,NH), 62.56, 62.49 [OCH2,CH3], 42.09 (OCH2,CH3,CH2).
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 CH₂Cl₂, CHCl₃ and DMSO, solvate formation was observed when 1 was exposed to a saturated atmosphere of the solvent.

### 1H NMR Studies

1H NMR measurements were recorded at 298 K using a Bruker AC-300E pulsed Fourier transform NMR spectrometer. Typical operating conditions for routine proton measurements involved "pulse" or flip angle of 30°, spectral resolution (SF) of 300.135 MHz, delay time of 1.60 s, acquisition time (AQ) of 1.819 s, and line broadening of 0.55 Hz. Samples of the ligand (~5 ml, 6.0x10⁻¹⁰ mol dm⁻³) were prepared in CD₂CN and placed in 5 mm NMR tubes using TMS (tetramethylsilane) as the chemical reference.

Then stepwise addition of the metal cation salt dissolved in CD₂CN (~ 3.0x10⁻² mol dm⁻³) were made until no further chemical shift changes were observed.

### Conductance Measurements

For these measurements the Wayne Kerr B642 Autobalance was used. For the determination of the constant of the conductivity cell, the method previously described was used.

The stoichiometry of the complexation process was assessed from conductance measurements. Thus fresh solutions of the metal-ion salt and the ligand in the appropriate solvent were prepared for each run. The cell was cleaned; dried and an accurately weighed solution of the metal-ion salt (~ 25 cm³, 3.0x10⁻¹⁰ mol dm⁻³) was added. The conductance was measured once thermal equilibrium was attained. This was followed by the addition of a solution of the ligand in the same solvent (~ 1.0 cm³, 1.0x10⁻¹⁰ mol dm⁻³). All measurements were taken at 298.15 K.

Conductance measurements were also used to assess the range of concentrations at which the free and the complex salts are predominately in their ionic forms in solution.

### Calorimetric Measurements

Calorimetric titrations were carried out with the aim of determining the stability constant (expressed as log K) and the enthalpy of complexation, ΔH. For this purpose the Tronac 450 calorimeter was used as an isoperibol titration calorimeter. The reproducibility of the apparatus was checked by chemical calibration using the protonation reaction of tris(hydroxy methyl)amino methane, THAM, with HCl to form the standard solution Gibbs energies, ΔG°, enthalpies, ΔH°, and entropies, ΔS° of this ligand in non aqueous media.

Taking acetonitrile, MeCN, as the reference solvent, transfer thermodynamic parameters (ΔG°, ΔH° and ΔS°) of 1 to other solvents were calculated. The data show that ΔG° values from acetonitrile to dipolar aprotic (N, N-dimethylformamide, DMF; tetrahydrofuran, THF) and to protic (MeOH, EtOH, BuOH) solvents are slightly negative (favourable transfer). This is indeed not the case for hexane (inert solvent). While the ΔG° values of 1 from MeCN to other solvents do not significantly differ, large variation are observed in the transfer enthalpies and entropies of this ligand to other solvents. This is due to the presence of the phenol hydrogen atoms.

Determination of enthalpies of solution

Enthalpies of solution were measured with the Tronac 450 calorimeter. To check the reliability of the solution calorimeter, the standard enthalpy of solution of THAM in an aqueous solution of 0.1 M of HCl was determined. The value obtained (ΔH° = -29.62 ± 0.11 kJ mol⁻¹) is in agreement with the value reported by Irving and Wadsö (~ -29.71 kJ mol⁻¹).

Distribution studies in the absence and in the presence of 1

Before carrying out the distribution studies, both solvents were mutually saturated to avoid volume changes during the experiments. For partition experiments carried out in the absence of ligand, equal volumes (10 cm³) of the aqueous phase containing different concentrations of metal-ion perchlorate in the aqueous phase (2.0x10⁻⁴ – 2.0x10⁻¹ mol dm⁻³) were mixed with water saturated dichloromethane. The mixtures were shaken for a period of 30 minutes, and then these were left overnight in an isothermal bath at 298.15 K.

### Results and Discussion

Solution thermodynamics of 1- transfer parameters

The results from 1H NMR studies involving this ligand show that 1 is in a 'cone' conformation in solution. This statement is corroborated by the two pairs of doublets at 3.37 and 4.34 ppm observed for the methylene bridge protons. In order to proceed with solution studies of 1, knowledge on the solubility of this ligand in various solvents is required.

Thus solubility data for 1 in a variety of solvents at 298.15 K are reported in Table 1. Also included in this Table are the standard solution Gibbs energies, ΔG°, enthalpies, ΔH° (derived from calorimetric measurements) and entropies, ΔS° of this ligand in non aqueous media.

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transfer of 1 from MeCN to the alcohols is concerned, this process is entropically controlled since the $\Delta H^0$ does not contribute favourably to the transfer of the ligand from a less (acetonitrile) to a more structured solvent (alcohol). Indeed disruption of the solvent structure requires energy (endothermic process) and leads to an entropy increase. Having established the solution properties of 1, we proceeded with $^1$H NMR studies with the aim of assessing the interaction of this ligand with metal cations and this is now discussed.

**Table 1**: Solubilities and derived standard Gibbs energies of solution, enthalpies and entropies of 1 in various solvents at 298.15 K. Transfer data from acetonitrile.

<table>
<thead>
<tr>
<th>Solv.</th>
<th>Solublity</th>
<th>$\Delta G^0$</th>
<th>$\Delta H^0$</th>
<th>$\Delta S^0$</th>
<th>$\Delta G^\circ$</th>
<th>$\Delta H^\circ$</th>
<th>$\Delta S^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeCN</td>
<td>(6.60±0.10)$\times 10^{-3}$</td>
<td>12.4±0.2</td>
<td>26.9±0.7</td>
<td>48</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>DMF</td>
<td>(7.95±0.09)$\times 10^{-2}$</td>
<td>6.3±0.2</td>
<td>24.4±0.6</td>
<td>61</td>
<td>-6.17</td>
<td>-2.50</td>
<td></td>
</tr>
<tr>
<td>THF</td>
<td>(5.01±0.08)$\times 10^{-2}$</td>
<td>7.4±0.2</td>
<td>32.4±0.6</td>
<td>151</td>
<td>-5.02</td>
<td>25.50</td>
<td></td>
</tr>
<tr>
<td>EtOH</td>
<td>(4.23±0.05)$\times 10^{-2}$</td>
<td>7.8±0.2</td>
<td>37.7±0.8</td>
<td>100</td>
<td>-4.61</td>
<td>10.80</td>
<td></td>
</tr>
<tr>
<td>BuOH</td>
<td>(4.10±0.10)$\times 10^{-2}$</td>
<td>7.9±0.2</td>
<td>50.9±0.2</td>
<td>144</td>
<td>-4.51</td>
<td>24.00</td>
<td></td>
</tr>
<tr>
<td>Hex</td>
<td>(8.40±0.03)$\times 10^{-1}$</td>
<td>17.6±0.3</td>
<td>83.0±0.7</td>
<td>220</td>
<td>5.11</td>
<td>56.10</td>
<td></td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>very soluble</td>
<td>solvate formation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMSO</td>
<td>very soluble</td>
<td>solvate formation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>very soluble</td>
<td>solvate formation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Abbreviations used for solvents; MeCN, acetonitrile; DMF, N,N-dimethylformamide; THF, tetrahydrofuran; MeOH, methanol; EtOH, ethanol; BuOH, 1-butanol; Hex, hexane; CH$_2$Cl$_2$, dichloromethane; DMSO, dimethylsulphoxide; CHCl$_3$, chloroform.

**Fig. 1**: Plot of standard enthalpy of transfer against standard entropy of transfer from acetonitrile to other solvents at 298.15 K

$^1$H NMR studies

Results from $^1$H NMR titrations of 1 with Pb$^{2+}$, Cd$^{2+}$, Hg$^{2+}$ and Zn$^{2+}$ in CD$_3$CN, (Table 2) show that as complexations proceeds, the chemical shift changes observed for the t-butyl and the aromatic protons are not significant. Deshielding effects are observed for the equatorial protons (6), the methylene protons adjacent to the O (7 and 10) and nitrogen (8) and the proton (9) of the NH group indicating that the metal cations interact with the O and the N donor atoms. Shielding effects are observed for the axial (5) and the phenolic protons (12).

The differences between the chemical shifts of the methylene bridge (axial and equatorial) protons relative to the that for the free ligand indicate that the complex adopts a flattened ‘cone’ conformation.$^{2,3,4}$

An indication that the two pendant arms containing the donor atoms participate in the complexation process is...
reflected in the significant chemical shift changes observed for protons 5, 7, 9 and 10.

**Conductimetric titrations**

The titrations were carried out with the aim of establishing the stoichiometry of the metal-ion complexes in acetonitrile. As far as the alkali-metal cations are concerned, there is no indication of a change of slope at any given mol ratio in this solvent. This is in accord with the results obtained from 

\[
\text{H}^n\text{NMR in which no chemical changes were observed by the addition of the appropriate alkali-metal salt to the ligand in acetonitrile. Representative examples are the conductimetric titration curves for lead, cadmium and mercury cations shown in Fig. 2. In all cases, 1:1 complexes of moderate stability are formed.}
\]

For all the systems considered, \( A_m \) values decrease upon complex formation due to a size increase in moving from the free (small) to the complex (large) cation.

**Table 2**: Chemical shift changes (\( \Delta\delta \) ppm) in the \( ^1\text{H} \) NMR spectra of 1 with metal cations (Pb\(^{2+}\), Cd\(^{2+}\), Hg\(^{2+}\) and Zn\(^{2+}\)) in CD\(_3\)CN 298 K.

<table>
<thead>
<tr>
<th>Protons</th>
<th>Free</th>
<th>Pb(^{2+})</th>
<th>Cd(^{2+})</th>
<th>Hg(^{2+})</th>
<th>Zn(^{2+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.21</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>1.16</td>
<td>0.01</td>
<td>0.01</td>
<td>0.00</td>
<td>0.01</td>
</tr>
<tr>
<td>3</td>
<td>7.26</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>4</td>
<td>7.21</td>
<td>0.03</td>
<td>0.02</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>5</td>
<td>3.45</td>
<td>0.04</td>
<td>0.05</td>
<td>0.04</td>
<td>0.05</td>
</tr>
<tr>
<td>6</td>
<td>4.31</td>
<td>-0.13</td>
<td>-0.12</td>
<td>-0.09</td>
<td>-0.14</td>
</tr>
<tr>
<td>7</td>
<td>4.08</td>
<td>0.10</td>
<td>0.09</td>
<td>0.06</td>
<td>0.11</td>
</tr>
<tr>
<td>8</td>
<td>3.52</td>
<td>0.06</td>
<td>0.04</td>
<td>0.06</td>
<td>0.05</td>
</tr>
<tr>
<td>9</td>
<td>5.19</td>
<td>0.09</td>
<td>0.03</td>
<td>overlap</td>
<td>0.14</td>
</tr>
<tr>
<td>10</td>
<td>4.08</td>
<td>0.10</td>
<td>0.08</td>
<td>0.05</td>
<td>0.10</td>
</tr>
<tr>
<td>11</td>
<td>1.29</td>
<td>0.06</td>
<td>0.05</td>
<td>0.05</td>
<td>0.07</td>
</tr>
<tr>
<td>12</td>
<td>8.55</td>
<td>-0.11</td>
<td>-0.11</td>
<td>-0.11</td>
<td>-0.14</td>
</tr>
</tbody>
</table>

**Fig. 2**: Conductimetric titration curve for lead, cadmium and mercury cations, (as perchlorates) with 1 in acetonitrile at 298.15 K

**Table 3**: Shows log \( K_s \) values and derived standard Gibbs energies, enthalpies, and entropies of complexation of 1 and metal cations (Pb\(^{2+}\), Cd\(^{2+}\), Hg\(^{2+}\), Cu\(^{2+}\) and Zn\(^{2+}\)) in acetonitrile at 298.15 K. These were derived from classical titration calorimetry and are referred to the process.

\[
\text{M}^{\text{2+}}(\text{MeCN}) + \text{1}(\text{MeCN}) \xrightarrow{K_s} \text{M}^{\text{3+}}(\text{MeCN})
\]

In eq. 1, \( \text{M}^{\text{2+}} \) and \( \text{M}^{\text{3+}} \) are predominantly as ionic species in solution. The results in Table 3 show that there are not significant differences in the \( \Delta G^\circ \) values for the different cations, except for Zn\(^{2+}\). There is a remarkable enthalpy-entropy compensation effect. This is shown in Fig. 3, which is a plot of \( \Delta H^\circ \) against \( \Delta S^\circ \) for the various cations and this ligand in acetonitrile. It should be noted that in previous papers\(^{17}\) we demonstrated that this effect upon complexation is often a reflection of the compensation between enthalpy and entropy already shown by the host or the guest species. The results shown in this paper corroborate further this statement, as demonstrated in Fig 3.

In an attempt to analyse the effect of binding and cation desolvation on the enthalpies of complexation of 1 and these cations, the \( \Delta H^\circ \) values are plotted against the hydration thermodynamic of complexation

\[
\text{THERMODYNAMIC OF COMPLEXATION}
\]

The titrations were carried out with the aim of establishing the stoichiometry of the metal-ion complexes in acetonitrile. As far as the alkali-metal cations are concerned, there is no indication of a change of slope at any given mol ratio in this solvent. This is in accord with the results obtained from \( ^1\text{H} \) NMR in which no chemical changes were observed by the addition of the appropriate alkali-metal salt to the ligand in acetonitrile. Representative examples are the conductimetric titration curves for lead, cadmium and mercury cations shown in Fig. 2. In all cases, 1:1 complexes of moderate stability are formed.

For all the systems considered, \( A_m \) values decrease upon complex formation due to a size increase in moving from the free (small) to the complex (large) cation.
enthalpies, $\Delta H^o$ of these cations\(^\text{18}\) (Fig.4). Due to the additional factors besides the electrostatic ones that need to be considered when dealing with the first transition metal cations (highly polarisable), the latter parameter rather than the ionic radii of the cations is selected\(^\text{19}\). The choice of $\Delta H^o$ rather than $\Delta_{\text{solv}} H^o$ is based on i) the few data available for the $\Delta_t H^o$ of these cations from water to acetonitrile and ii) the magnitudes of the $\Delta_t H^o (\text{H}_2\text{O} \rightarrow \text{MeCN})$ are small relative to their hydration enthalpies \(^{19}\) and therefore, the sequence in the $\Delta_h H^o$ is not altered. Fig. 4 shows that as the $\Delta_h H^o$ for the cation increases (become more negative), the stability of complex formation (endothermic) decreases. This may be attributed to the desolvation process (endothermic), which predominates over the binding process (exothermic), except for Cu\(^{2+}\). For this cation, the energy associated with the binding process appears to predominate and an increase in enthalpic stability is observed for this cation and 1 in acetonitrile. Enthalpy values are compensated by entropy values and as a result, the latter becomes more favourable in moving from Pb\(^{2+}\) to Zn\(^{2+}\). In fact for the latter, the complexation process is entropically controlled. Given that there are several factors besides complexation which contribute to the overall extraction of cations by macrocycles from the aqueous to the non-aqueous phase, we proceeded with distribution experiments in the absence and in the presence of the macrocycle in the water-dichloromethane solvent system and this is now discussed.

**Table 3: Stability constants ($\log K_s$) and derived standard Gibbs energies, enthalpies and entropies of 1 with metal cations in acetonitrile 298.15 K.**

<table>
<thead>
<tr>
<th>Cation</th>
<th>$\log K_s$</th>
<th>$\Delta_G^o$</th>
<th>$\Delta_H^o$</th>
<th>$\Delta_S^o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(^{2+})</td>
<td>3.80±0.10</td>
<td>-21.70±0.40</td>
<td>-61.90±0.30</td>
<td>-136</td>
</tr>
<tr>
<td>Cd(^{2+})</td>
<td>3.80±0.10</td>
<td>-21.70±0.40</td>
<td>-61.60±0.20</td>
<td>1</td>
</tr>
<tr>
<td>Hg(^{2+})</td>
<td>3.40±0.10</td>
<td>-19.40±0.40</td>
<td>-12.00±0.40</td>
<td>25</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>3.80±0.10</td>
<td>-21.70±0.40</td>
<td>-6.10±0.50</td>
<td>52</td>
</tr>
<tr>
<td>Zn(^{2+})</td>
<td>2.80±0.10</td>
<td>-16.00±0.40</td>
<td>26.90±0.10</td>
<td>144</td>
</tr>
</tbody>
</table>

**Fig. 3:** Plot of standard enthalpy of complexation against standard entropy of complexation in acetonitrile at 298.15 K

**Fig. 4:** Plot of standard enthalpy of complexation against enthalpy of hydration of cations at 298.15 K

**Phase transfer involving bivalent cations.**

The extraction of univalent cations from the aqueous to the organic phase in the absence and in the presence of a neutral macrocycle has been previously discussed by us\(^{20,21}\). In this paper we formulate a treatment for the derivation of the partition, $K_p$ and the ion-par formation, $K_a$ constants for the
process represented in eqs. 2 and 4 involving a 2:1 metal-ion salt.

\[ \text{M}^2\text{(H}_2\text{O}) + 2 \text{X(H}_2\text{O}) \xrightarrow{K_p} \text{M}^2\text{(s)} + 2 \text{X(s)} \]  \hspace{1cm} (2)

where \( K_p \) expressed in terms of concentrations may be defined as.

\[ K_p = \frac{[\text{M}^2]}{[\text{M}^2]_{\text{H}_2\text{O}}}[\text{X}]^{1/2}_{\text{H}_2\text{O}} \]  \hspace{1cm} (3)

and \( K_d \) is referred to the process given in eq. 4

\[ \text{M}^2\text{(s)} + 2 \text{X(s)} \xrightarrow{K_d} \text{MX}_2\text{(s)} \]  \hspace{1cm} (4)

Therefore,

\[ K_d = \frac{[\text{MX}_2]}{[\text{M}^2]_{\text{H}_2\text{O}}}[\text{X}]^{1/2}_{\text{H}_2\text{O}} \]  \hspace{1cm} (5)

Combination of (2) and (4) leads to eq. 6

\[ \text{M}^2\text{(H}_2\text{O}) + 2 \text{X(H}_2\text{O}) \xrightarrow{K_d} \text{MX}_2\text{(s)} \]  \hspace{1cm} (6)

Thus the distribution constant, \( K_d \) may be expressed as

\[ K_d = \frac{[\text{MX}_2]_{\text{H}_2\text{O}}}{[\text{M}^2]_{\text{H}_2\text{O}}}[\text{X}]^{1/2}_{\text{H}_2\text{O}} \]  \hspace{1cm} (7)

\( K_p \) and \( K_d \) are referred to the mutually saturated solvents and \( K_d \) to the water saturated organic phase. From distribution experiments on the assumption that \( \text{M}^2\text{a} \) and \( \text{MX}_2 \) are the predominant species in the organic phase (saturated with water), the distribution ratio, \( D_m \) can be defined.

\[ D_m = \frac{[\text{M}^2]}{[\text{M}^2]_{\text{H}_2\text{O}}} = \frac{[\text{M}^2]_{\text{H}_2\text{O}} + [\text{MX}_2]_{\text{H}_2\text{O}}}{[\text{M}^2]_{\text{H}_2\text{O}}} \]  \hspace{1cm} (8)

Based on mass balance and electroneutrality and combining equations 3, 5 and 8, it follows that.

\[ D_m = K_p^{1/3} + 4K_d \]  \hspace{1cm} (9)

Then a plot of \( D_m \) against \( [\text{M}^2]_{\text{H}_2\text{O}} \) should give a straight line of slope equal to \( 4K_d \) and an intercept equal to \( K_p^{1/3} \).

Distribution ratios for \( \text{Cd(ClO}_4)_2 \) and \( \text{Pb(ClO}_4)_2 \) were carried out at 298.15 K in the water-dichloromethane (mutually saturated) solvent system. Thus plots of \( D_m \) values against \([\text{Cd}^{2+}]_{\text{H}_2\text{O}}\) and \([\text{Pb}^{2+}]_{\text{H}_2\text{O}}\) respectively are shown in Fig. 5.

The lineal relationships observed in both cases led to the calculation of \( K_p \), \( K_d \) and \( K_d \) and these data are shown in Table 4.

The data show that for the system involving \( \text{Cd}^{2+} \), \( K_p \) although small makes a favourable contribution to \( K_d \) values. This is not case for \( \text{Pb}^{2+} \).

However the high \( K_p \) values observed for these systems are mostly due to the high degree of ion-pair formation of the metal-ion salts in the water-dichloromethane solvent system.

\section*{Distribution data in the presence of 1 in the organic phase.}

A general equation for the process taking place when a bivalent cation is extracted from water by the presence of a neutral macrocycle in the organic phase may be written as follows,

\[ \text{M}^2\text{(H}_2\text{O}) + 2 \text{X(H}_2\text{O}) + \text{L(s)} \xrightarrow{K_{sa}} \text{MLX}_2\text{(s)} \]  \hspace{1cm} (10)

The extraction constant, \( K_{sa} \) can be defined as.

\[ K_{sa} = \frac{[\text{MLX}_2]_{\text{H}_2\text{O}}}{[\text{M}^2]_{\text{H}_2\text{O}}}[\text{X}]^{1/2}_{\text{H}_2\text{O}}[\text{L}]_{\text{s}} \]  \hspace{1cm} (11)

Taking into account eqs. 7, 8 and 11 it follows that

\[ D_m = 4K_d + 4K_{sa}[\text{L}]_{\text{s}} \]  \hspace{1cm} (12)

Therefore a plot of \( D_m/[\text{M}^2]^2\text{(H}_2\text{O}) \) against \([\text{L}]_{\text{s}}\) should give a straight line of slope \( = 4K_d \) and intercept equal to \( 4K_{sa} \).

Distribution data (carried out in the presence of the ligand \( \text{L} \) in the organic phase) against \([\text{L}]_{\text{s}}\) for \( \text{Cd}^{2+} \) and \( \text{Pb}^{2+} \) as perchlorates in the water-dichloromethane system are shown in Fig. 6.

\( K_{sa} \) and \( K_{sa} \) values are reported in Table 5. Excellent agreement is found between the \( K_p \) values obtained from distribution data in the absence and in the presence of the ligand.

The interesting aspect of the data is that \( \text{Pb}^{2+} \) is better extracted than \( \text{Cd}^{2+} \) by a factor of 2.5. In an attempt to analyse the individual processes that are likely to contribute to the extraction of bivalent cations from the aqueous phase by the presence of \( \text{L} \) in the organic phase, the following schemes are considered.

\section*{Table 4: Partition, distribution and extraction constants in the water-dichloromethane solvent system and association constants in water saturated dichloromethane at 298.15 K.}

<table>
<thead>
<tr>
<th>Cation</th>
<th>( K_p )</th>
<th>( K_a )</th>
<th>( K_d )</th>
<th>( K_{sa} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cd}^{2+} )</td>
<td>2.38a</td>
<td>1.80 x 10^{6a}</td>
<td>4.29 x 10^{4a}</td>
<td></td>
</tr>
<tr>
<td>( \text{Pb}^{2+} )</td>
<td>0.86a</td>
<td>6.42 x 10^{4a}</td>
<td>5.54 x 10^{4a}</td>
<td></td>
</tr>
<tr>
<td>( \text{Cd}^{2+} )</td>
<td></td>
<td></td>
<td>4.30 x 10^{4b}</td>
<td>1.00 x 10^{8b}</td>
</tr>
<tr>
<td>( \text{Pb}^{2+} )</td>
<td></td>
<td></td>
<td>5.70 x 10^{4b}</td>
<td>2.50 x 10^{8b}</td>
</tr>
</tbody>
</table>

\( ^a \)From distribution data in the absence of \( \text{L} \), eq. 9, see text.

\( ^b \)From distribution data in the absence of \( \text{L} \), eq. 12, see text.
Table 5: Individual processes contributing to the overall extraction of cadmium and lead cations by 1 in the water-dichloromethane solvent system at 298.15 K.

<table>
<thead>
<tr>
<th>Cation</th>
<th>$K_d$</th>
<th>$K_{assn}$</th>
<th>$K_sK'_a$</th>
<th>$K_{ex}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd$^{2+}$</td>
<td>$4.29 \times 10^4$</td>
<td>$2.40 \times 10^3$</td>
<td>$4.20 \times 10^7$</td>
<td>$1.00 \times 10^8$</td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>$5.54 \times 10^4$</td>
<td>$4.40 \times 10^3$</td>
<td>$2.90 \times 10^8$</td>
<td>$2.50 \times 10^8$</td>
</tr>
</tbody>
</table>

Fig. 5: Distribution data of cadmium and lead cations, (as perchlorates) in the water-dichloromethane solvent system at 298.15 K.

Scheme 1

Under this scheme, two individual processes are considered. The distribution of the 2:1 metal-ion salt with ionic species predominantly in the aqueous phase and ion-pairs in the organic phase (eq. 6)

The interaction of the ion pairs with the ligand in the organic phase (eq. 13)

$$MX_2(s) + L(s) \xrightarrow{K_{assn}} MLX_2$$  \hspace{1cm} (13)

Thus combination of equations 6 and 13 leads to the process described in eq. 10 Therefore

$$K_{ex} = K_d K_{assn}$$  \hspace{1cm} (14)

The extraction process (eq.10) can be split into three individual contributions.

Scheme 2

Partition of the dissociated electrolyte in the water-dichloromethane solvent system (eq.2)

Complexation of 1 with the metal cation (eq. 1)

Ion-pair formation between the complex cation and the anion (eq. 15).

Thus,

$$K_{ex} = K_p K_{xK'_a}$$

Data for the individual processes involved in these two schemes are given in Table 5. $K_p$ and $K_d$ are parameters inherent of the system (in the absence of the macrocycle) while $K_{assn}$ (Scheme 1) or $K_xK'_a$ (Scheme 2) result from the presence of the ligand in the organic phase. Therefore $K_{assn}$ (Scheme 1) or $K_xK'_a$ (Scheme 2) are the parameters to be
considered to determine which of the two schemes is likely to take place. Given that $K_a$/$K_c$ values are greater than $K_{cm}$, leads to the suggestion that Scheme 2 is more likely to take place.

**Final Conclusions.**

From the above discussion it is concluded that:

1. $\text{Pb}^{2+}$ is able to interact with bivalent cations ($\text{Pb}^{2+}$, $\text{Cd}^{2+}$, $\text{Hg}^{2+}$, $\text{Cu}^{2+}$, $\text{Zn}^{2+}$) in acetonitrile giving 1:1 complexes of moderate stability. No significant variations are found in the stability constants of these cations and 1 in this solvent as a result of a remarkable enthalpy-entropy compensation effect.

Although the degree of selectivity of 1 for these bivalent cations is not significant (as reflected in the log $K_a$ values) in the water-dichloromethane solvent system, $\text{Pb}^{2+}$ is better extracted than $\text{Cd}^{2+}$ by a factor 2.5. This is attributed to the various individual processes which contribute to the overall extraction of cations from water to the organic phase in the presence of a non-water soluble ligand.

**Acknowledgment**

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**References**


**DIAGRAM**

![Diagram of Calixarenes](image_url)