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ARTICLE *in* JOURNAL OF INCLUSION PHENOMENA AND MACROCYCLIC CHEMISTRY · AUGUST 2012

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Cation binding by thiacalixthianthrenes

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Received: 8 February 2011 / Accepted: 10 August 2011
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Abstract The complexing properties of a thiacalix[2]thianthrene **1** and its disulfoxide derivative **2** toward alkali metal, alkaline earth metal, some transition metal and some heavy metal cations have been investigated in acetonitrile by means of UV spectrophotometry. At the concentrations suited to this technique, complexation of the alkali metal cations by the sulfoxide but not the thiacalixthianthrene was detectable, whereas the converse was true for both transition metal and lanthanide cations. Complexation of the alkaline earth cations was not detectable. The strongest binding observed was that of Hg(II) to ligand **1** but in no case was complexation sufficiently strong for either ligand to function as a useful metal ion extractant.

Keywords Thiacalixthianthrenes ·
Complexation · Extraction · Transition metal ·
Heavy metal

Introduction

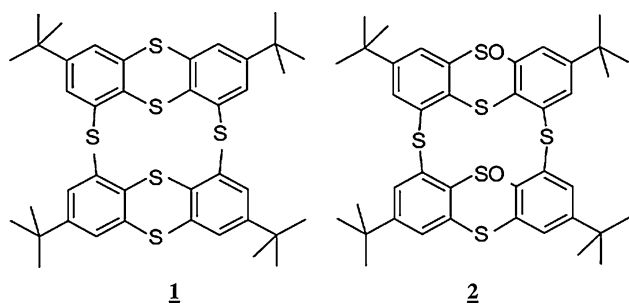
The chemistry of calixarenes [1] is a well-developed field [2–5], with applications to metal ion complexation and extraction being of particular importance. Thiacalixarenes, in which a sulfur bridge replaces the methylene link of calixarenes themselves, have but recently become accessible [6] although there has now been a decade of active research concerning their use for similar applications [7–12]. Particular interest in thiacalixarenes has arisen for specific applications in optical materials technology and coordination chemistry due to the unique properties and strong coordinating ability of these macrocycles [13–18]. Recently, the synthesis of a new, related class of macrocycles, the thiacalixthianthrenes [19, 20], has been reported. The fusion of thianthrene and calixarene chemistry is of considerable promise in areas of supramolecular and solid state chemistry such as the synthesis of non-linear optical materials, of electrochromic and luminescent devices, and of switchable receptors in molecular recognition. The resulting functionalized macrocycles provide new molecular platforms with numerous novel properties.

We present in this paper experimental studies on the complexation of alkali metal, alkaline-earth metal, some transition metal (Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} and Hg^{2+}) and some lanthanide metal (Nd^{3+} and Eu^{3+}) cations, and the liquid–liquid extraction of alkali metal and some transition metal (Co^{2+} , Cu^{2+} , Zn^{2+} and Cd^{2+}) cations by 5,11,17,23-*tetra-tert*-butylthiacalix[2]thianthrene (**1**) and 5,11,17,23-*tetra-tert*-butylthiacalix[2]thianthrene-2,27-disulfoxide (**2**). Efforts to quantify the complexation equilibria were based on the use of UV spectrophotometry, although conductimetric measurements were also used to obtain preliminary estimates of the stoichiometry of any complexes formed.

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Experimental

Instrument and analysis

UV spectra were recorded on a Perkin Elmer Lambda 11 spectrophotometer. Conductance measurements were recorded on a MeterLab CDM210 conductimeter with cell constant $k = 0.93$ cm. Acetonitrile (SDS for HPLC, 0.03% water content) was commercial and used without further purification. The supporting electrolyte used in the stability constant determinations was Et_4NClO_4 (Acros Organics). The metal salts chosen were perchlorates (Fluka, purum). The picrate salts employed in extraction were prepared as described elsewhere [21].

Extraction studies

The extraction experiments of alkali metal picrates from water into dichloromethane were performed according to a literature procedure [22, 23]. Equal volumes (5 mL) of neutral aqueous solutions of alkali metal picrate (2.5×10^{-4} mol L^{-1}) and CH_2Cl_2 solution (5 mL) of thiacalix[2]thianthrene derivatives (2.5×10^{-4} mol L^{-1}) were mixed under magnetic agitation for 24 h and then left standing for 1 h in order to obtain a complete separation of the two phases.

The concentration of metal picrate remaining in the aqueous phase was determined from the absorbance A at 355 nm. The percentage extraction (%E) was derived from

the following expression in which A_0 is the absorbance of the aqueous solution of a blank experiment without calixarene:

$$\%E = 100(A_0 - A)/A_0$$

Conductimetric studies

While complexation by a neutral ligand is not expected to dramatically alter the molar conductivity of a cationic species, the differences can usually be detected and so the measurement of conductance of a solution of a ligand into which a metal ion is added can be a useful rapid means of establishing the stoichiometry of a complex ion species. Thus, this procedure was followed to obtain preliminary estimates of the metal:ligand ratio in the complexes formed by the two thiacalixthianthrenes.

Stability constant measurements

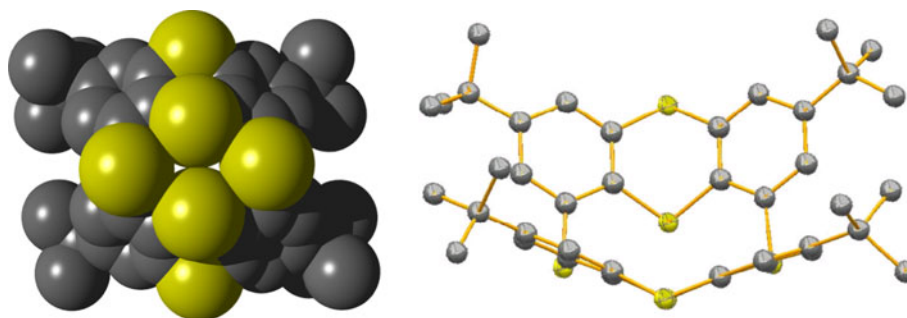
Stability constant values were determined by fitting to the changes in absorbance resulting when solutions of the ligands initially at concentrations between 2×10^{-5} and 7×10^{-6} mol L^{-1} were titrated with solutions of the various metal ions up to a final M:L ratio of 20. All measurements were made at 25 °C using acetonitrile as solvent, with the ionic strength maintained at 0.01 mol L^{-1} using $[\text{Et}_4\text{N}][\text{ClO}_4]$. Significant changes in absorbance were found in the wavelength range 220–320 nm in most cases and were suitable for analysis using the program “Letagrop” [24]. In principle, multi-step equilibria could have been involved in these reactions but in all cases where the effects of complexation could be detected, a simple 1:1 model provided a satisfactory fit.

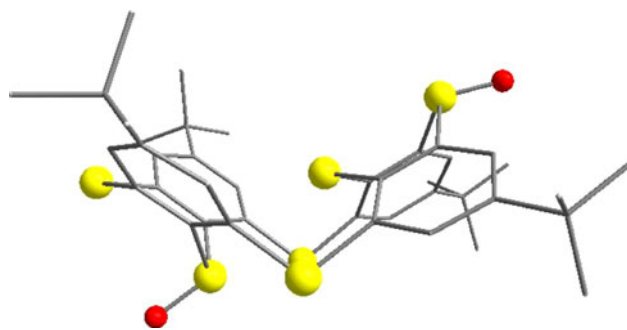
Results and discussion

Synthesis of the thiacalixthianthrenes

The molecular structures of the two thiacalixthianthrenes **1** and **2** are shown in respectively Structures 1 and 2 [19, 20]. Compound **1** adopts a cone conformation while compound

Structure 1 Solid state structures of **1** showing the coplanarity between the four inner sulfur atoms and the cavity formed by the cone conformation





Structure 2 Solid state structure of **2** in the “1,2-alternate” conformation

2 is isolated in the 1,2-alternate conformation in the solid state. This may have an important impact on the capabilities for selective cation complexation.

Complexation of metal cations in acetonitrile

The logarithms of the stability constants $\log \beta$ and the stoichiometries for the different complexes formed by ligands **1** and **2** with alkali metal, alkaline-earth metal, some transition metal and some lanthanide metal cations in acetonitrile are given in Tables 1, 2, 3, 4.

A limitation of spectrophotometry as a method of stability constant measurement is that changes in absorbance values must be measureable, most desirably, precisely,

Table 1 Stability constants ($\log \beta \pm \sigma_n - 1$) for alkali metal cation complexes of ligands **1** and **2** in acetonitrile at 25 °C, $I = 10^{-2}$ M

	1		2	
	ML	Log β	ML	Log β
Li ⁺	a	a	1:1	4.20 ± 0.04
Na ⁺	a	a	1:1	4.76 ± 0.11
K ⁺	a	a	1:1	4.28 ± 0.01
Rb ⁺	a	a	1:1	4.80 ± 0.05
Cs ⁺	a	a	1:1	4.28 ± 0.09

^a Absorbance changes too small to enable satisfactory fitting

Table 2 Stability constants ($\log \beta \pm \sigma_n - 1$) for alkaline earth metal cation complexes of ligands **1** and **2** in acetonitrile at 25 °C, $I = 10^{-2}$ M

	1		2	
	ML	Log β	ML	Log β
Mg ²⁺	a	a	a	a
Ca ²⁺	a	a	a	a
Sr ²⁺	a	a	a	a
Ba ²⁺	a	a	a	a

^a Absorbance changes too small to enable satisfactory fitting

Table 3 Stability constants ($\log \beta \pm \sigma_n - 1$) for transition metal cation complexes of ligands **1** and **2** in acetonitrile at 25 °C, $I = 10^{-2}$ M

	1		2	
	ML	Log β	ML	Log β
Co ²⁺	1:1	4.63 ± 0.09	a	a
Ni ²⁺	1:1	5.02 ± 0.03	a	a
Cu ²⁺	1:1	5.21 ± 0.11	a	a
Zn ²⁺	1:1	4.87 ± 0.07	a	a
Ag ⁺	a	a	a	a
Cd ²⁺	1:1	4.85 ± 0.06	a	a
Hg ²⁺	1:1	5.46 ± 0.01	a	a

^a Absorbance changes too small to enable satisfactory fitting

Table 4 Stability constants ($\log \beta \pm \sigma_n - 1$) for lanthanide metal cation complexes of ligands **1** and **2** in acetonitrile at 25 °C, $I = 10^{-2}$ M

	1		2	
	ML	Log β	ML	Log β
Nd ³⁺	1:1	4.82 ± 0.01	a	a
Eu ³⁺	1:1	5.36 ± 0.01	a	a

^a Absorbance changes too small to enable satisfactory fitting

meaning that for strongly absorbing ligands such as **1** and **2**, very dilute solutions or very short path lengths must be used. Thus, there is a practical limit to the value that may be estimated (roughly, the reciprocal of the ligand concentration), and it is possible that in many of the present cases the complexes may have been too weak for their stability constants to be reliably estimated. For the alkali metal cations, ligand **1** displays no detectable binding in acetonitrile, whereas ligand **2** appears to form complexes of moderate stability. The binding of ligand **2** to Li(I) is characterized by small decreases in absorbance (Fig. 1). Surprisingly, despite the higher charge and greater polarising power of the alkaline earth cations, there is no spectroscopic evidence of their interaction with either ligand, a fact which may indicate that exceedingly small absorbance changes are simply indicative of a very minor difference in absorption by the free and bound ligand and not necessarily of a small stability constant value. This, of course, is a well-known problem with main group cations when compared to transition metal and some lanthanide ion species.

The transition metal ions, interestingly, display behaviour opposite to that of the alkali metal ions in that they appear to interact significantly with ligand **1** but not with ligand **2**. The binding of ligand **1** to Hg(II), in particular, is characterised by marked spectral changes involving two well-defined isosbestic points (Fig. 2), nicely consistent

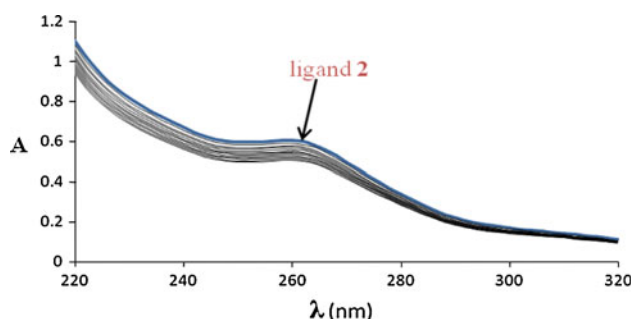


Fig. 1 UV absorption spectra on complexation of lithium perchlorate (LiClO_4) with ligand **2** in acetonitrile ($0 \leq R_{M/L} \leq 5$) and 25°C , $C_L = 1.74 \times 10^{-5} \text{ mol L}^{-1}$

with a 1:1 binding equilibrium. Formally, ligand **1** is an S-donor ligand whereas ligand **2** is an S,O species, so that preferential binding of Hg(II) to **1** might be considered as an illustration of the thiophilicity of this cation, though clearly this does not lead to a remarkably enhanced value of the formation constant compared to those of other transition metal ions (Table 3). A theoretical investigation of complex formation by Zn(II) , Cd(II) and Hg(II) with ligand **1** was recently reported [25]. Formation of 1:1 complexes was predicted, as indeed found in the present work. However, the prediction of strong selectivity for Zn(II) is not supported by the experimental results, probably indicating the importance of solvent effects not included in the theoretical calculations.

Although only two of the lanthanide metal ions have been studied, both Nd and Eu show an unexpected similarity to the transition metal cations, rather than the alkali metal cations, in appearing to interact more significantly with ligand **1** than ligand **2**. Again, however, it is possible that only very small spectral changes may be associated with lanthanide ion binding. With **1**, the significant difference in the stability constant values for two relatively close members of the lanthanide series such as Nd and Eu

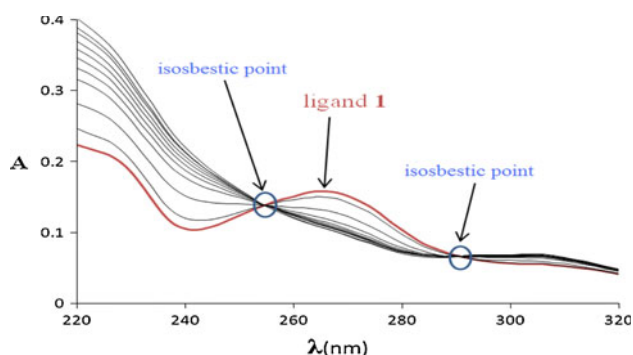


Fig. 2 UV absorption spectral changes during the complexation of mercury(II) perchlorate ($(\text{Hg}(\text{ClO}_4)_2)$) with ligand **1** in acetonitrile ($0 \leq R_{M/L} \leq 4$) and 25°C , $C_L = 4.74 \times 10^{-6} \text{ mol L}^{-1}$

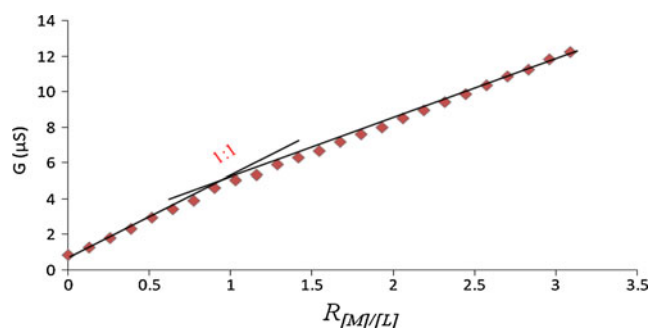


Fig. 3 Conductometric titration in the case of ligand **1** with Hg^{2+} ($C_L = 6.9 \times 10^{-6} \text{ mol L}^{-1}$)

indicates that the ligand might have some potential in lanthanide ion separation.

The 1:1 stoichiometry of the complexes with ligands **1** and **2** were confirmed by conductimetric studies (Fig. 3).

An important feature of the present results is the quite remarkable changes in complexing properties which result from the partial oxidation of ligand **1** to give ligand **2**. As the exact form of the bound ligand is unknown in both cases and it is possible that there may be differences in denticity as well as in the donor atoms involved, it is difficult to offer any interpretation but since the ligands should have rather different solvation energies, especially in H-bonding solvents, it may be interesting to examine solvent effects on the stability constant values.

Extraction of metal picrates

Extraction percentages (%E) of alkali and transition metal cations by ligands **1** and **2** are given in Table 5. In fact, neither ligand proved to have any significant extraction affinity for the studied metal ions under the conditions used. Here, therefore, partial oxidation of the sulfur sites seems to have no effect.

Table 5 Extraction percentages (%E) of alkali and transition metal picrates from water into dichloromethane by ligands **1** and **2**, at 25°C ($C_L = C_M = 2.5 \times 10^{-4} \text{ mol L}^{-1}$)

		Ligands	
		1	2
%E	Alkali cations	Li^+	<1
		Na^+	<1
		K^+	<1
		Rb^+	<1
		Cs^+	<1
		Co^{2+}	<1
		Cu^{2+}	2.9
	Transition metals cations	Zn^{2+}	3.2
		Cd^{2+}	<1
			<1

Conclusions

The ligands tetra-*tert*-butylthiacalix[2]thianthrene **1** and tetra-*tert*-butylthiacalix[2]thianthrene disulfoxide **2** show some interesting differences in their complexation ability towards different metal groups, the alkali metal cations, in particular, showing a preference for the ligand **2** in which some O-donor atoms are present, while the transition metal ions appear to prefer the ligand **1**, which is an exclusively S-donor species. This is consistent with differences between such metal ions in terms of hard–soft acid behaviour, though the hard alkaline earth metal ions seem anomalous in appearing not to interact significantly with either ligand. In no case does the stability of the complexes result in significant extraction ability of the ligands.

Acknowledgment Special thanks go to Professor Jack Harrowfield and Professor Jacques Vicens (CNRS-Strasbourg) and Professor Rym Abidi (FSB-Tunisia) for their invaluable support.

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