

Complexing Properties of Calix[4]arene Amide Derivatives

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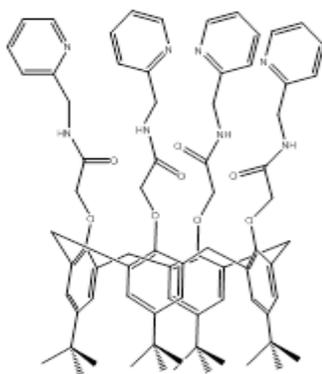
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ABSTRACT: The complexing properties of some pyridine amide calix[4]arenes have been carried out in acetonitrile and monitored by UV spectrophotometry. Their considered targets were several heavy metals (Hg^{2+} , Cd^{2+} and Pb^{2+}) and trivalent lanthanide cations (La^{3+} , Nd^{3+} , Eu^{3+} , Gd^{3+} and Yb^{3+}). The three derivatives (1, 2 and 3) form mononuclear complexes with heavy metal and lanthanide cations, except in the case of calixarene 2, which formed simultaneously mononuclear and binuclear species with Pb^{2+} . The results show that the complexation is the main factor affecting the extraction with the tetra-substituted ligands (1, 2), in contrast with the di-substituted ligand 3.

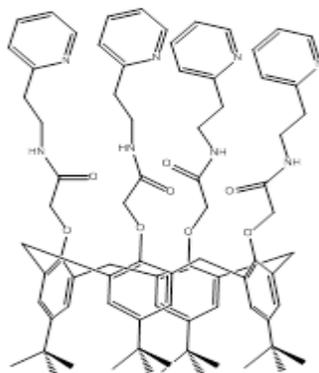
Keywords: Calixarene; Complexation; Stability constant; Extraction; Host-guest chemistry.

INTRODUCTION: Calixarenes have been widely used as building blocks in the design and synthesis of new materials for molecular recognition and supramolecular chemistry¹. They form an important class of supramolecules used for the detection of main pollutants due to their ability to be preorganized and tuned to complex metal ion². Calix[4]arene derivatives³ & ⁴ can take four conformation: cone, partial cone, 1,2-alternate and 1,3-alternate. Their complexing behaviours have been proved to be depended on the conformation of the calixarene moiety. Much attention has been paid to calix[4]arenes in the cone conformation, O-substituted with amide, ester or ketone groups, while their complexing properties towards metal cations have been recently reviewed⁵.

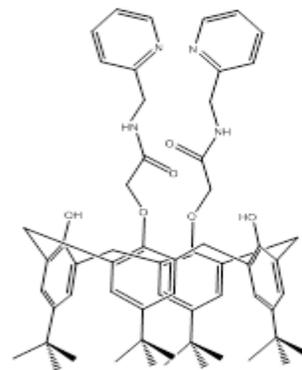
The present paper deals with an experimental study on the complexation of heavy metals (Hg^{2+} , Cd^{2+} and Pb^{2+}) and lanthanide metal cations (La^{3+} , Nd^{3+} , Eu^{3+} , Gd^{3+} and Yb^{3+}), as well as the liquid-liquid extraction of heavy metals (Cd^{2+} and Pb^{2+}) and some lanthanide metal (La^{3+} and Yb^{3+}) cations by tetra(2-pyridylmethyl)amide calix[4]arene **1**, le tetra(2-pyridylethyl)amide calix[4]arene **2** and di(2-pyridylmethyl)amide calix[4]arene **3**. The assessment of the complexation equilibria were based on the use of UV spectrophotometry, although conductimetric measurements were also used to obtain preliminary estimations of the stoichiometry of the formed complexes.



1



2



3

MATERIAL AND METHODS:

Experimental setup: UV spectra were recorded on a Perkin Elmer Lambda 11 spectrophotometer. The

conductance was measured by a Meter Lab CDM210 conductimeter having cell constant $k = 0.90$ cm. Acetonitrile (SDS for HPLC, 0.03% water content) was

commercial and used without further purification. The supporting electrolyte used in the stability constant determination was Et_4NClO_4 (Acros Organics).⁹ The metal salts chosen were perchlorates (Fluka, purum). The picrate salts employed in the extraction were prepared as described elsewhere⁶.

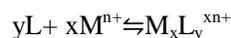
Extraction study: The experimental extraction of metal picrates from water into dichloromethane was performed according to the literature procedure^{7 & 8}. Equal volumes (5 mL) of neutral aqueous solutions of metal picrate ($2.5 \times 10^{-4} \text{ mol L}^{-1}$) and CH_2Cl_2 solution (5 mL) of calixarene derivatives ($2.5 \times 10^{-4} \text{ mol L}^{-1}$) 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 of extraction (%E) was obtained by the following expression:

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

Where; A_0 is the absorbance of the aqueous solution of a blank experiment without calixarene.

Conductivity study: As the complexation by a neutral ligand is not expected to dramatically alter the molar conductivity of a cationic species, the differences can usually be detected. Thus, the measurement of the conductance of a ligand solution into which a metal ion is added can be a useful rapid means of establishing the stoichiometry of a complex ions species. Hence, such procedure was followed to obtain preliminary estimations of the metal/ligand ratio in the formed complexes by the three calixarenes.¹¹

RESULTS AND DISCUSSION: The stability constants β_{xy} are the concentration ratios $[\text{M}_x\text{L}_y^{\text{xn}+}]/[\text{M}^{\text{n}+}]^x[\text{L}]^y$ following the general equilibrium:



Where; $\text{M}^{\text{n}+}$: metal ion, L: ligand

They have been determined in acetonitrile by UV/vis spectrophotometry at 25°C, with the ionic strength maintained at 0.01 mol.L^{-1} using Et_4NClO_4 . The spectra of ligand solutions ($5 \times 10^{-5} \text{ mol L}^{-1}$) and increasing the metal ion has been recorded between 220 and 320 nm (see Tables 1 and 2). Figure 1 indicates the complexation of Cd^{2+} with ligand 2. Generally the metal ion to ligand ratio R at the end of the titration did not exceed 20 and the equilibrium was quasi instantaneous for all systems. Adding the metal salts to the ligand has induced large spectra changes which were enough to allow the analysis of the resulting data using the program "Letagrop"¹⁰. The β_{xy} values given in tables 1 and 2 correspond to the arithmetic means of at least three independent experiments.

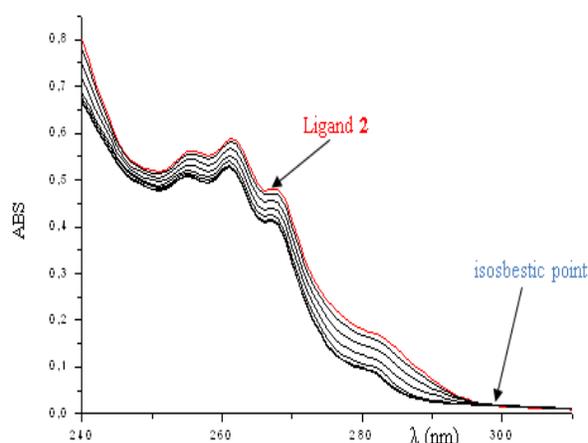


Figure 1: UV absorption spectra on complexation of cadmium perchlorate.

Metal cations complexation in acetonitrile: The logarithms of the stability constants $\log\beta_{xy}$ and the stoichiometries for the different formed complexes by ligands 1, 2 and 3 with heavy metals and some lanthanide cations in acetonitrile are given in tables 1 and 2.

Table 1: Stability constant of the complexes of heavy metal cations by ligands 1-3 in acetonitrile ($C_L = 4.9 \times 10^{-5} \text{ mol.L}^{-1}$, 25 °C).

Cations	Ligand 1		Ligand 2		Ligand 3	
	M:L	$\log\beta_{xy}$	M:L	$\log\beta_{xy}$	M:L	$\log\beta_{xy}$
Cd^{2+}	1:1	5.62 ± 0.04	1:1	5.69 ± 0.09	1:1	5.75 ± 0.08
Hg^{2+}	1:1	5.00 ± 0.06	1:1	5.10 ± 0.07	1:1	4.54 ± 0.09
Pb^{2+}	1:1	5.80 ± 0.08	1:1	6.34 ± 0.01	1:1	4.91 ± 0.09
			2:1	7.85 ± 0.1		

Table 2: Stability constant of the complexes of lanthanides cations by ligands 1-3 in acetonitrile ($C_L = 4.9 \times 10^{-5} \text{ mol L}^{-1}$, 25 °C).

Cations	Ligand 1		Ligand 2		Ligand 3	
	M:L	$\log\beta_{xy}$	M:L	$\log\beta_{xy}$	M:L	$\log\beta_{xy}$
La^{3+}	1:1	5.41 ± 0.06	1:1	4.87 ± 0.09	1:1	7.36 ± 0.06
	2:1	---	2:1	---	2:1	11.18 ± 0.08
Nd^{3+}	1:1	5.15 ± 0.07	1:1	4.66 ± 0.07	1:1	7.04 ± 0.08
	2:1	---	2:1	---	2:1	12.39 ± 0.06
Eu^{3+}	1:1	7.61 ± 0.09	1:1	5.09 ± 0.07	1:1	5.63 ± 0.03
	2:1	10.30 ± 0.04	2:1	9.50 ± 0.04	2:1	11.39 ± 0.05
Gd^{3+}	1:1	5.43 ± 0.10	1:1	5.31 ± 0.04	1:1	6.45 ± 0.01
	2:1	---	2:1	9.94 ± 0.03	2:1	12.21 ± 0.07
Yb^{3+}	1:1	5.45 ± 0.09	1:1	5.63 ± 0.04	1:1	6.32 ± 0.05
	2:1	9.08 ± 0.08	2:1	10.51 ± 0.07	2:1	11.41 ± 0.06

Table 1 lists the stability constant ($\log\beta_{xy}$) data for the heavy metal complexes. The data are consistent with the formation of mononuclear species by the three ligands, except for Pb^{2+} which forms complexes of two mononuclear and binuclear stoichiometry species with ligand 2.

The order of mononuclear complexes stability is similar for both ligands 2 and 3. The Derivative 3 has a

slight affinity for cations lower than its two equivalent heavy metals. This close stability shows that the introduction of two arms or also the intercalation of pyridine amide of a second carbon between the amide function and the pyridine unit improves the affinity ligand for Pb^{2+} cation without affecting the complexation of cations Cd^{2+} and Hg^{2+} .

The affinities to remember are those of the ligand **2** for Pb^{2+} and the derivative **3** for Cd^{2+} . For the latter we can suggest that because of the existence of hydrogen bonding between the amide nitrogen and the phenol as well as the presence of only two arms amido pyridine hydrogen, **3** disubstituted derivative complexing cations prefer the less voluminous series as Cd^{2+} (Table 1).

Regarding the stability of mononuclear species, we can note that the complexes with ligands **1** and **3** are more stable than those of the ligand **2**. The mononuclear complexes of La^{3+} and Nd^{3+} with the ligand **2** are 10 times less stable than those formed with the ligand **1** and 300 times less stable than the ligand **3**. In general, the mononuclear species formed by the ligand **3** are the most stable.

The comparison of the of stability profiles corresponding to the disubstituted derivative and its tetrasubstituted equivalent shows that the stability of the latter increases significantly for Eu^{3+} till it becomes constant for Gd^{3+} and Yb^{3+} while for the disubstituted derivative, the stability decreases for Eu^{3+} till it becomes constant for Gd^{3+} and Yb^{3+} .

The effect of the intercalation of carbon atom between the amide function and the pyridine unit responsible for the stability increases of the species ML. This may be explained by the involvement of the pyridine nitrogen in coordinating of the cation for the ligands **1** and **3** or by high repulsion pyridine units in the case of the ligand **2**.

The complex biligands (ML_2) formed by **3** has an affinity for the complex Nd^{3+} and low stability lanthanide with a selectivity $S_{Nd^{3+}/La^{3+}} = 16$, taking into account the fact that the lanthanide cations have a hard acid character, they prefer interacting with hard bases such as oxygen atoms. Furthermore, the stoichiometries of complexes with **1**, **2** and **3** were confirmed by conductometric studies (Figure 2).

The study of the conductometric titration confirmed mainly stoichiometries of the complexes formed in solution with ligands **1-3** determined by the UV spectrophotometry.

Extraction of metal picrates: Extraction percentages (%E) of heavy metals (Cd^{2+} and Pb^{2+}) and lanthanides (La^{3+} and Yb^{3+}) cations by ligands **1**, **2** and **3** from water into dichloromethane are given in Table 3 & Figure 3.

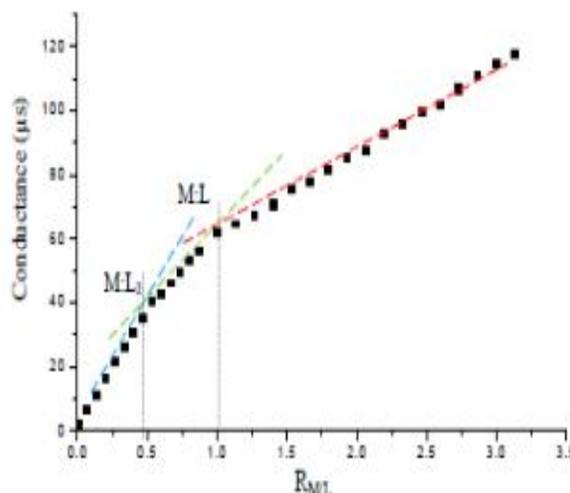


Figure 2: Conductimetric titration in the case of ligand **3** with Yb^{3+} .

Table 3: Extraction percentages (%E) of heavy metals and lanthanides picrates from water into dichloromethane by ligands **1**, **2** and **3**, at 25°C ($C_L = C_M = 2.5 \cdot 10^{-4} \text{ mol L}^{-1}$).

Cations	Ligand		
	1	2	3
Cd^{2+}	12.94	7.61	<1
Pb^{2+}	11.45	4.34	<1
La^{3+}	11.66	2.79	<1
Yb^{3+}	13.59	13.86	<1

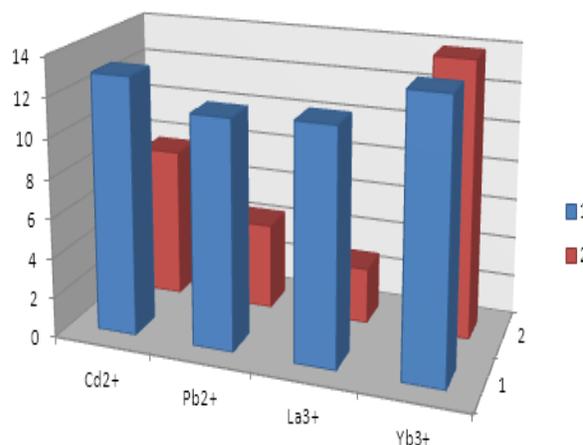


Figure 3: Trends of the extraction percentages (%E) for salt metal picrates from water into dichloromethane.

The extraction study shows that the studied cations are generally poorly extracted by the pyridine amide calixarenes **1-3**. However, Cd^{2+} is slightly better extracted than Pb^{2+} ($1 < \Delta E\% < 3$), while as for studied lanthanides, the Yb^{3+} cation is better extracted than the

La³⁺ cation using both ligands **1** and **2** ($2 < \Delta E\% < 11$). We can suggest that the dipyridine methyl amide calix[4]arene **3** does not have any extractant power with respect to the studied cations, it is then enough to substitute two phenolic hydrogen by two new arms pyridine methyl amide in order to improve the percentages of extraction. The intercalation of carbon between the pyridine unit and the amide function leads to a decrease in new extraction percentages. Hence, we may suggest that the pyridine unit contributes to the trapping of the cation to be extracted.

CONCLUSION: The complex formation using ligands **1-3** with heavy metals and lanthanides cations has been established. The conductometric titration confirmed mainly stoichiometry of the formed complexes in solution determined by the UV spectrophotometric study. However, the ligand **3** didn't reveal the extraction affinity for picrate metals. The ligands **1** and **2** extract the majority of the studied cations with an average extraction between 2 and 14%. Compared to the ligand **2**, ligand **1** is nevertheless can be considered as the best extractant.

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