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Transition Metal Cation Binding Properties By [2+2'] *p-tert*-Butyl Calix[4]Arene Derivatives

Corresponding Author

Lassaad Baklouti[1,2], Jacques Vicens[2]
[1]Facultés des Sciences de Bizerte,
7021 Zarzouna-Bizerte (TUNISIA)
[2]ECPM, Université Louis Pasteur,
Associé au CNRS, 25 rue Becquerel
F-67087, Strasbourg (FRANCE)
E-mail: bakloutilassaad@yahoo.fr

Co-Authors

Besma Mellah[1], Mouna Mahouachi[1,2], Amel Ben Othman[1,2], Rym Abidi[1]
[1]Facultés des Sciences de Bizerte, 7021 Zarzouna-Bizerte (TUNISIA)
[2]ECPM, Université Louis Pasteur, associé au CNRS, 25 rue Becquerel
F-67087, Strasbourg (FRANCE)

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ABSTRACT

We report the metal binding properties of [2+2'] *p-tert*-butyl calix[4]arene derivatives **(1-13)** towards transition metal cations (Co^{2+}, Ni^{2+} and Zn^{2+}) The formation of ML and M_2L species is observed. The formation of M_2L species is detected with tetrasubstituted ligands, the most stable complexes being observed for ligand bearing at least two ethyl ester functions.

KEYWORDS

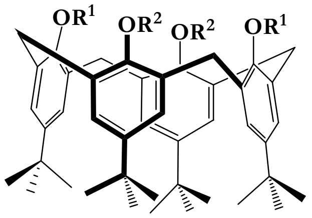
Calixarenes;
[2+2']Functionalisation;
Binding properties;
Transition metal.

INTRODUCTION

The importance of calixarenes as host macrocyclic molecules in host-guest chemistry is now well established[1-3]. In this context, much work has been devoted to the synthesis of calixarenes chemically modified on the upper (*para* position)[2-4] and lower (phenolic oxygens) rims[1-10]. Several functions have been introduced at the lower rim such as ethers[5], ketones[8] and esters[8, 10]. *p-tert*-Butylcalix[4]arene O-tetrasubstituted by ethyl ester functions shows a high affinity for sodium and potassium in methanol the cations being located in the cavity delineated by the oxygen atoms[11].

In order to understand the behaviour of the functionalities and the combination of these functionalities involved in the complexation of O-tetrasubstituted *p-tert*-butyl calix[4]arenes to find new selectivities in series of metals, we have previously reported studies on the binding properties O-tetrasubstituted *p-tert*-butyl calix[4]arenes **(1-13)** in which **(1-3)** are *homogeneously* O-tetrasubstituted by methoxy groups, glycol groups and ethyl acetate and **(4-13)** are [2+2'] *p-tert*-butyl calix[4]arene derivatives[10,12-18]. The complexation of calixarenes **(1-8)** towards alkali and alkaline earth metal cations in acetonitrile by means of UV spectrophotometry and ^{1}HNMR spectroscopy[13] show the formation of mononuclear ML and/or bilgand ML_2 species.

In this paper, we enlarge these studies to transition metal cations (Co^{2+}, Ni^{2+} and Zn^{2+}).



1	$R^1 = R^2 = CH_3$	
2	$R^1 = R^2 = CH_2CH_2OMe$	
3	$R^1 = R^2 = CH_2CO_2Et$	
4	$R^1 = CH_2CH_2OMe$	$R^2 = CH_3$
5	$R^1 = CH_2CH_2OMe$	$R^2 = CH_2CO_2Et$
6	$R^1 = CH_2CH_2OMe$	$R^2 = CH_2C_6H_5$
7	$R^1 = CH_2C_6H_5$	$R^2 = CH_3$
8	$R^1 = CH_2C_6H_5$	$R^2 = CH_2CO_2Et$
9	$R^1 = H$	$R^2 = CH(CO_2Et)_2$
10	$R^1 = H$	$R^2 = C(CH_3)(CO_2Et)_2$
11	$R^1 = CH_2CO_2Et$	$R^2 = CH(CO_2Et)_2$
12	$R^1 = CH_2CO_2Et$	$R^2 = C(CH_3)(CO_2Et)_2$
13	$R^1 = H$	$R^2 = CH_2CO_2Et$

EXPERIMENTAL

Instrument and analysis

^{1}HNMR spectra was recorded on a Bruker SY300 spectrometer and FAB mass spectrum was run on a VG-Analytical ZAB HF instrument. The UV spectra were recorded on a Perkin Elmer Lambda 11 spectrophotometer.

Materials

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 perchlorates (Fluka, purum).

5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetramethoxy calix[4]arene **(1)**[8].

5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetra(2-methoxyethoxy)calix[4]arene **(2)**[13].

5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetraoxyethyl acetatecalix[4]arene **(3)**[11].

5,11,17,23-tetra*tert*-butyl-25,27-dimethoxy-26,28-di (2-methoxyethoxy)calix[4]arene **(4)**[13].

5,11,17,23-tetra-*tert*-butyl-25,27-di(2-methoxy ethoxy)-26,28-dioxyethylacetatecalix[4]arene **(5)**[16].

5,11,17,23-tetra-*tert*-butyl-25,27-di(phenylmethoxy)-26,28-di(2-methoxyethoxy)calix[4]arene **(6)**[14].

5,11,17,23-tetra-*tert*-butyl-25,27-dimethoxy-26,28-diphenylmethoxycalix[4]arene **(7)**[13].

5,11,17,23-tetra-*tert*-butyl-25,27-dioxyethylacetate-26,28-diphenylmethoxycalix[4]arene **(8)**[13].

5,11,17,23-tetra-*tert*-butyl-25,27-dihydroxy-26,28-dioxyethylmalonatecalix[4]arene **(9)**[10].

5,11,17,23-tetra-*tert*-butyl-25,27-dihydroxy-26,28-dioxy(2-methylethylmalonate)calix[4]arene **(10)**[10].

5,11,17,23-tetra-*tert*-butyl-25,27-dioxyethylacetate-26,28-dioxyethylmalonatecalix[4]arene **(11)**[10].

5,11,17,23-tetra-*tert*-butyl-25,27-dioxyethylacetate-26,28-dioxy(2-methylethylmalonate)calix[4]arene **(12)**[10].

5,11,17,23-tetra-*tert*-butyl-25,27-dihydroxy -26,28-dioxyethylacetatecalix[4]arene **(13)**[10].

Stability constant measurements

The stability constants β_{xy} being the concentration ratios $[M_xL_y^{xn+}]/[M^{n+}]^x[L]^y$ and corresponding to the general equilibrium:

$$\mathbf{yL + xM^{n+} \rightleftharpoons M_xL_y^{xn+}}$$

(where M^{n+} = metal ion, L = ligand) were determined in acetonitrile by UV-absorption spectrophotometry at 25° C. The ionic strength has been maintained at 0.01 M using Et_4NClO_4. The spectra of ligand solutions of concentrations ranging between 10^{-4} and 2×10^{-4} M and increasing concentration of metal ion were recorded between 250 nm and 350 nm. Generally the metal to ligand ratio R at the end of the titration did not exceed 20 and the equilibria were quasi-instantaneous for all the systems. Addition of the metal ion salts to the ligand induced in the spectra changes large enough to allow the analysis of the resulting data using the program "Letagrop"[19]. Best values for the formation constants β_{xy} of the various complex species and their molar absorptivity coefficients for various wavelengths, are deduced from the best fit between the experimental and calculated UV spectra. The best fit is reflected by the lowest value of U (the sum of U values for all lambda given) corresponding to the square sum of a differences between experimental and calculated absorbances ($U = \Sigma (A_{cal} - A_{exp})^2$). The β_{xy} values correspond to the arithmetic means of at least three independent experiments.

RESULTS AND DISCUSSION

Figures 1 and 2 illustrate the titration of ligand **(4)** by cobalt perchlorate and **(11)** by zinc perchlorate in acetonitrile at 25°C. Upon addition of the metal the absorbance recorded between 250 nm and 350 nm decreased with (figure 1) or without (figure 2) an isobestic point. The spectra changes are analysed using the program "Letagrop"[19] and allows the determination of the stability constants β_{xy} of the various complex species along with their stoichiometry. TABLE 1 gives the constants log β_{xy} corresponding to the arithmetic means of at least three independent experiments and figures 3 and 4 illustrate the trends of the stability constants log β_{11} and log β_{21} (determined in acetonitrile) for Co^{2+}, Ni^{2+} and Zn^{2+} with ligands **(1-13)**.

The dimethoxy diphenylmethoxy **(7)** did show any complexation as it was observed for the alkaline earth metals[13]. This is probably due to the absence of binding sites such as glycol $-OCH_2CH_2OCH_3$ groups or carbonyl C=O functions.

TABLE 1: Stability constants (log $\beta_{xy} \pm \sigma_{N-1}$) for their transition metal ion complexes of ligands (1-13) in acetonitrile at 25°C (I = 0.01 M, Et_4NClO_4).

Ligands	M:L	log β_{xy}		
		Co^{2+}	Ni^{2+}	Zn^{2+}
1	1:1	a	a	3.05 ± 0.07
2	2:1	5.25 ± 0.14	5.67 ± 0.13	5.63 ± 0.10
3	2:1	6.48 ± 0.10	6.50 ± 0.12	6.60 ± 0.07
4	1:1	2.68 ± 0.10	2.75 ± 0.15	2.65 ± 0.07
5	2:1	6.87 ± 0.15	6.39 ± 0.05	a
6	1:1	2.14 ± 0.01	2.37 ± 0.02	2.68 ± 0.05
7	-	a	a	a
8	2:1	5.23 ± 0.04	5.33 ± 0.15	5.60 ± 0.01
9	1:1	1.78 ± 0.10	2.78 ± 0.09	3.32 ± 0.10
10	1:1	3.79 ± 0.10	2.88 ± 0.10	3.97 ± 0.10
11	2:1	5.39 ± 0.10	5.67 ± 0.08	6.11 ± 0.01
12	2:1	5.44 ± 0.08	5.89 ± 0.09	6.03 ± 0.04
13	1:1	1.87 ± 0.10	3.40 ± 0.14	2.29 ± 0.08

(a) Small spectral variations.

Zn^{2+} is the only metal to be complexed by the tetramethoxy 1 while it is not complexed by diglycol diester 5.

Mononuclear ML species were found with the ligands **(1)** with no chelating group and ligands **(4, 6, 8-10)** and **(13)** with only two chelating groups. The

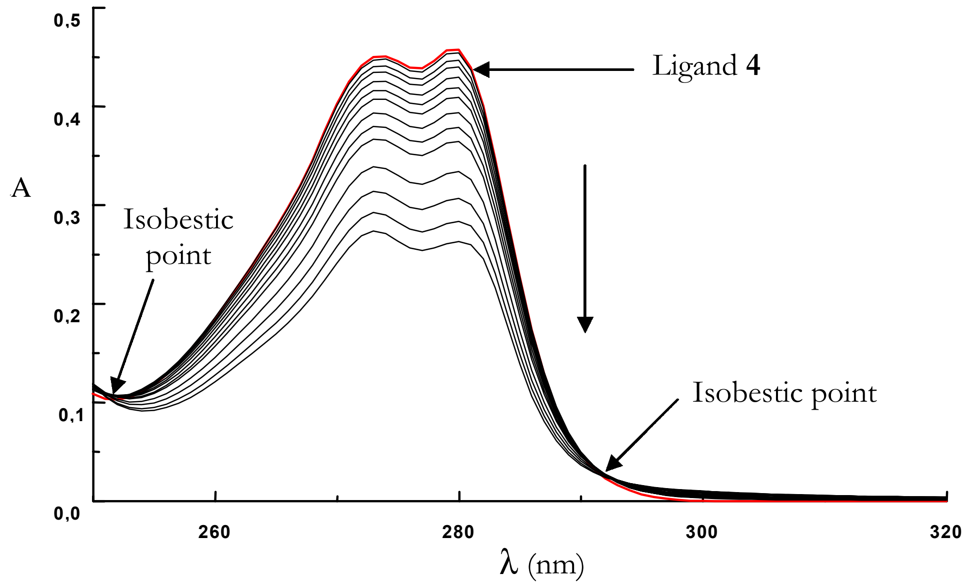


Figure 1: Changes of the UV spectrum of (4) upon addition of cobalt perchlorates in acetonitrile (C_L = 1.11 x 10^{-4} M, 0 = $R_{M/L}$ = 30, è = 25° C, [NEt_4ClO_4] = 0.01 M)

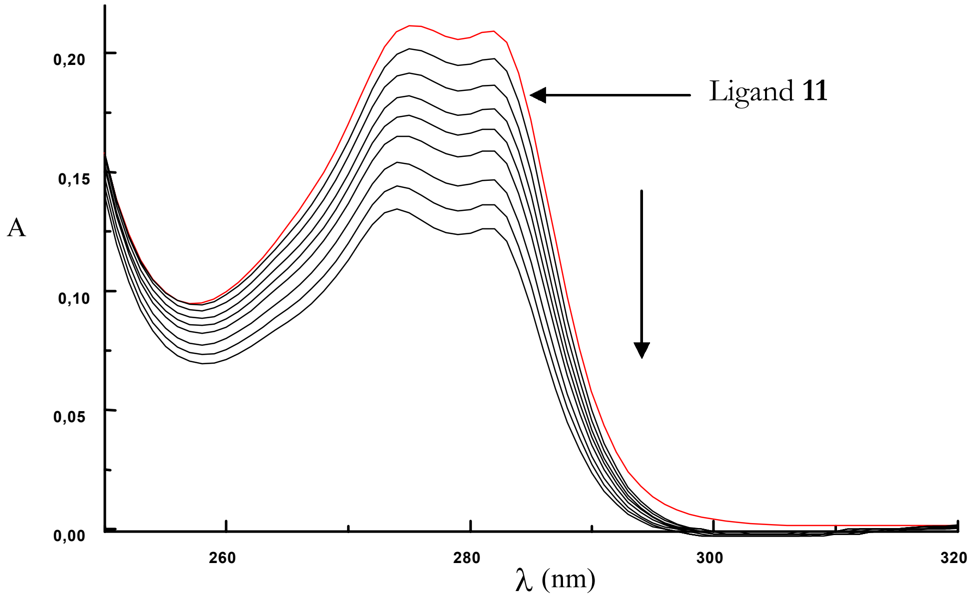


Figure 2: Changes of the UV spectrum of (11) upon addition of zinc perchlorates in acetonitrile (C_L = 1.05 x 10^{-4} M, 0 = $R_{M/L}$ = 30, θ = 25° C, [NEt_4ClO_4] = 0.01 M)

stability constants log β_{11} are lower (than for the alkaline and alkaline earth [12, 13]) varying from 1.78 for 9·Co^{2+} to 3.97 for 10·Zn^{2+}. The lower values can be due to the nature of the 'hard' donor oxygen atoms.

When the ligands contain four chelating groups one observes binuclear M_2L species. The stability constants log β_{21} are low varying from 5.23 for 8·$(Co^{2+})_2$ to 6.87 for 5·$(Co^{2+})_2$. For example diglycol diester **(5)** better complexes cobalt than tetragycol **(2)** to give 5·$(Co^{2+})_2$ which is a stronger complex (> 40 times) than 2·$(Co^{2+})_2$. This is explained by the replacement of two glycol by two ester groups. For the tetraethyl ester **(3)** complexes Co^{2+}, Ni^{2+} and Zn^{2+} with similar stability constants log β_{21}≈6.5 which is high because of the presence of four ester groups.

Ligand **(6)** behaves as ligand **(4)** to form mononuclear complexes with Co^{2+}, Ni^{2+} et Zn^{2+}, the logβ_{11} varying from 2.14 for 6·Co^{2+} to 2.68 for 6·Zn^{2+}which are in the range of the values of the stability constants of dimethoxy diglycol **(4)**. Although the introduction of additional ethyl ester groups ligands **(11)** and **(12)** are less complexing than the tetraethyl ester **(3)**.

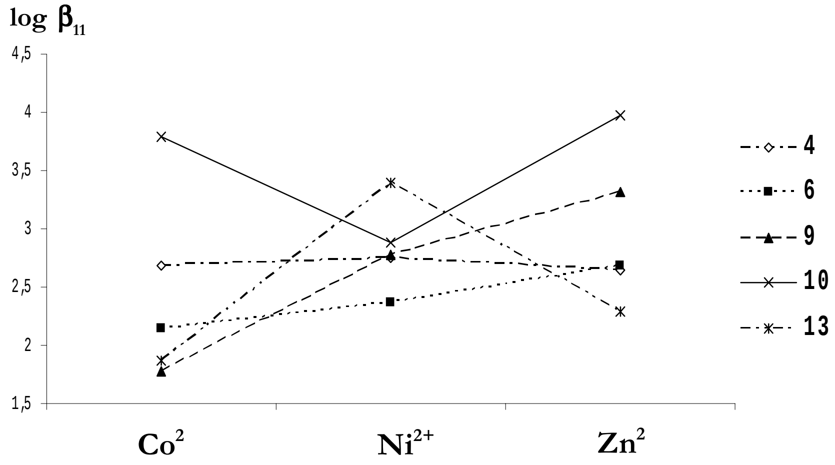


Figure 3: Trends of the stability constants log β_{11} (determined in acetonitrile) for Co^{2+}, Ni^{2+} and.Zn^{2+} with ligands (4), (6), (9), (10) and (13).

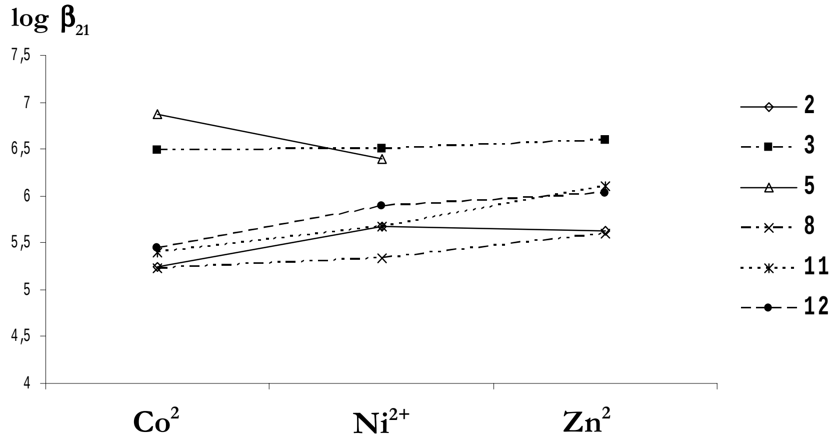


Figure 4: Trends of the stability constants log β_{21} (determined in acetonitrile) for Co^{2+}, Ni^{2+} and.Zn^{2+} with ligands (2), (3), (5), (8), (11) and (12).

In one case the formation of M_2L has been checked by FAB (positive) MS mass spectroscopy on a 10^{-3} M solution in acetonitrile of ligand **(5)** in the presence of an excess of $Ni(ClO_4)_2$. Mass-peaks have been detected at m/z = 959.4 for $(5 + Na)^+$, 994.4 for $(5 + Ni)^+$, and 1017.4 for $(5 + Na + Ni)^+$, The presence of a peak at 1017.4 indicates the possibility of **(5)** to form M_2L species. In this case one Ni^{2+} cation being replaced by a Na^+ cation leading to a more stable complex. This result is reminiscent of

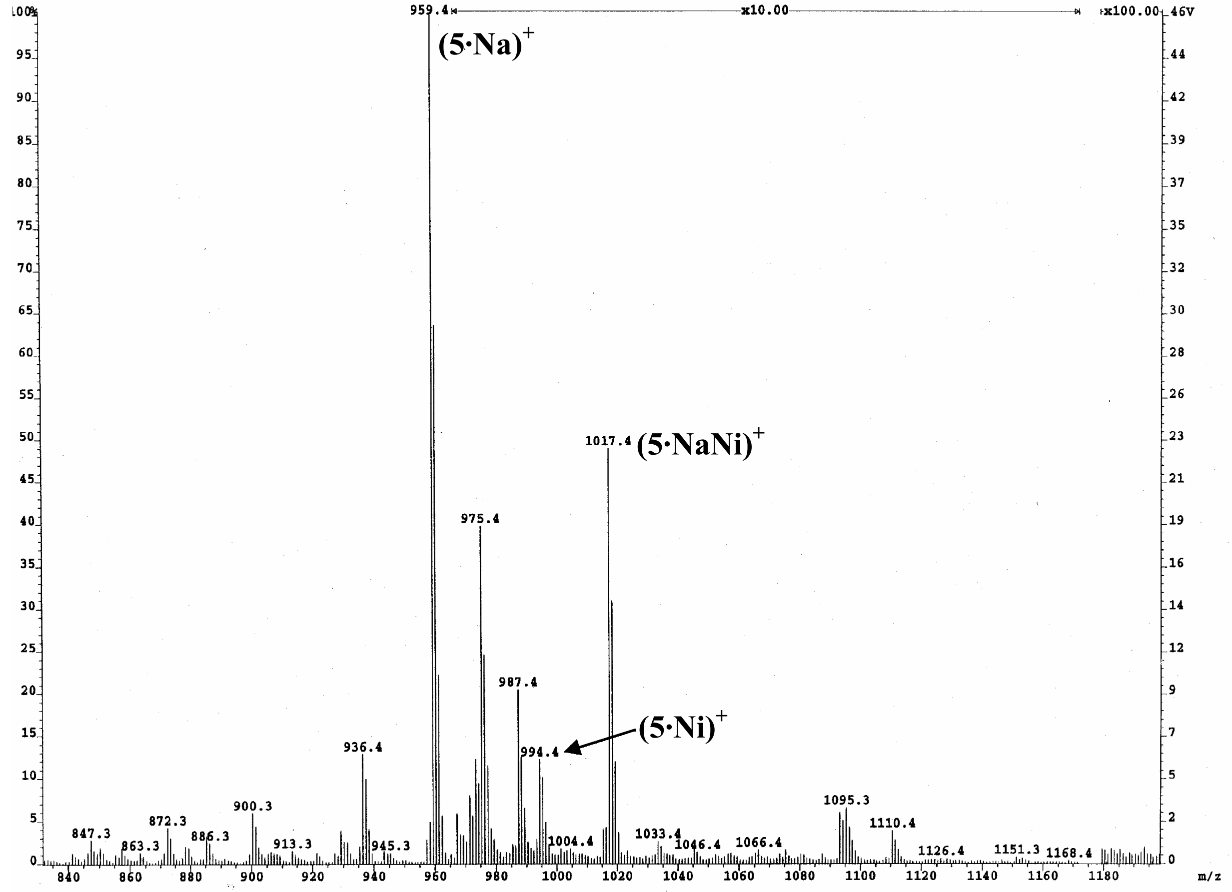


Figure 5: FAB+ MS spectrum for Ni^{2+} complex with (5) in acetonitrile.

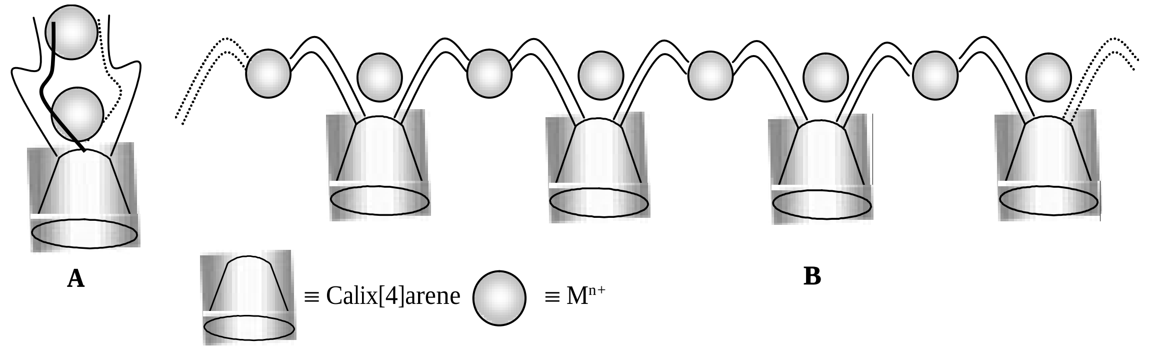


Figure 6: Schematic representations of M_2L.

the work of Shinkai and coll.[20] reporting the formation of different types of complexes with similar calixarenic receptors in the cone conformation and which are ditopic with $–OCH_2CONH(CH_2)_nSEt$. The authors described the kick out of a sodium cation from the amido cavity by cadmium reacting with the tetra-S atoms region by a mechanism of a 'template effect'. In our case the sodium cation is more attracted than nickel by the cavity delineated by the tetra ethyl esters.

To conclude in the present paper we have determined binding behaviour of ligands **(1-13)** towards transition metals. We have noted the formation of ML and M_2L species. The formation of M_2L species is detected with tetrasubstituted ligands. For the M_2L species the most stable complexes were observed for ligand bearing at least two ethyl ester functions.

By similarity with Shinkai and coll.[20] we can envisioned the complexes M_2L by different representations (figure 6). In representation A the two cations are included in the same calix unit and in representation B one cation is in the calix unit while a second cation is maintained outside between two calix units with possible formation of aggregates.

The introduction of ethyl malonate functions increases the number of the ethyl ester functions and decreases the stability constants, the tetraethyl ester ligand remaining the most efficient. This behaviour can be due to the presence of a large number of ethyl ester functions which cannot adapted the right disposition and steering of chelating functions towards the cavity.

As to compare with the published results on the complexation of alkali and alkaline earth metal cations, the complexes with transition metals remains less stable[12,13]. For example, ligand **(7)** complexes only Li^+ and Na^+. This probably due to a good fit between the hard-soft acidities because of the presence of the ethyl ester groups. This is also suggested by the observation that the combination of glycol, methyl and benzyl groups does not affect the binding properties of the ligands.

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