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ORIGINAL ARTICLE

Synthesis, ^{1}H-NMR conformational analysis and complexation studies of two di-imidazolyl acetamido *p-tert*-butylcalix[4]arenes

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Abstract The synthesis of a new di-imidazolyl-di-methoxy acetamido *p-tert*-butylcalix[4]arene **4** is reported. **4** has been prepared by reacting the corresponding di-methyl ester di-methoxy derivative with histamine in 1:1 mixture of methanol: toluene. The binding properties of **4** towards alkali, alkaline earth, transition (Zn^{2+}, Co^{2+}) and heavy (Pb^{2+}, Cd^{2+}) metals have been investigated along with the complexes stoichiometries. The ^{1}H-NMR spectra of complexes show the location of cations in receptor **4**. Partial cone conformation is observed only with strontium and calcium whereas the cone conformation is detected with most of the cations. Comparison of the complexation results with those obtained for di-imidazolyl acetamido *p-tert*-butylcalix[4]arene **3** missing the methyl groups is also reported.

Keywords Calix[4]arenes · Di-amido · Imidazolyl · Cation complexation

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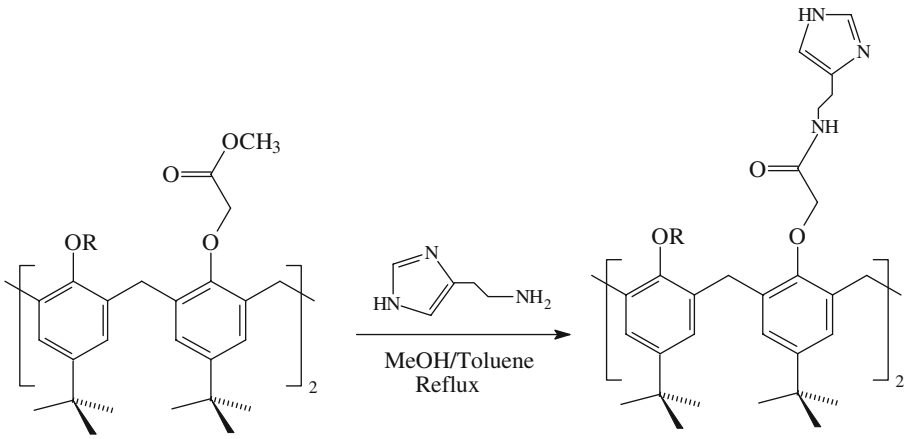
Introduction

The calixarenes and their analogues are very efficient and versatile metal binding agents [1]. Their binding properties depend on the specific substituents at the lower, upper rim and on the conformation of the host. In particular calix[4]arene amides can selectively bind alkali, alkaline earth, silver and lanthanide ions [2–4]. There is also great interest in the synthesis of receptors containing hydrogen bond, such as N–H groups, as ligands for anions [5–9].

In recent years, we have started the synthesis of calix[4]arene amides and the study of their binding properties. These ditopic receptors can bind metal cations [10–15] and anions [16–19] as well. In the present work, we report the synthesis, the conformational and the complexing properties of calixarene **4**. Related di-amidocalix[4]arene **3** without the methyl groups is also reported for comparison with **4**. These ligands contain two binding sites: the first delineates a cavity comprised of two carbonyl units and four phenolic oxygens which may complex hard cations such us alkali metals; the second cavity is delineated by the attachment of two 'imidazolyl' moieties via the amido functional groups which are able to complex soft cations by the N–H and C–H atoms. The binding properties of these compounds towards alkali, alkaline earth, transition (Zn^{2+}, Co^{2+}) and heavy (Pb^{2+}, Cd^{2+}) metals have been established by extraction study of solid metal picrates to $CDCl_3$-ligand solutions. This study has been followed by ^{1}H-NMR spectroscopy and completed by the determination of the stability constants of the complexes in methanol using the UV spectrophotometry technique.



1-2 **1-3** R = H **3-4**
2-4 R = CH_3

Experimental section

General

The melting points (Mps) were determined on an electrothermal apparatus in sealed capillary tubes under nitrogen. ^{1}H-NMR spectra were recorded with Bruker SY 300 spectrometer (300 MHz). Chemical shifts δ are expressed in ppm from TMS as an internal standard and $CDCl_3$ as solvent at 7.27 ppm. Coupling constants J are given in Hz. Elemental analyses were performed at the Service de Microanalyse of the Institut de Chimie de Strasbourg. Histamine, methyl bromo acetate and the solvents were commercial reagents and were used without further purification. 1,3-Dimethyl ester- and 1,3-dimethyl ester-dimethoxy *p-tert*-butyl calix[4]arenes were prepared as described in the literature [28]. All the reactions were carried out under nitrogen.

Syntheses

*Preparation of 5,11,17,23-tetra (tert-butyl)-25,27-di(4-ethyl imidazole acetamide) calix[4]arene (**3**)*

A mixture of 1,3-dimethyl ester calix[4]arene (**1**) (1.03 g, 1.30 mmol) and histamine (0.291 g, 2.60 mmol) in 16 mL of a 1:1 mixture of methanol: toluene was refluxed for 4 days. The solvents were removed by evaporation under reduced pressure. The residue was dissolved in dichloromethane and washed with water. The organic layer was dried over Na_2SO_4. The residue was precipitated with diethyl ether to give pure **3** (0.75 g, 68%) as a white solid. Mp 154–155 °C. ^{1}H-NMR ($CDCl_3$): 9.11 (broad t, 2H, N*H* amide), 7.84 (s, 2H, O*H*), 7.46 (s, 2H, C*H* imidazolyl-*Ha*), 7.08 (s, 4H, Ar*H*), 6.95 (s, 4H, Ar*H*), 6.77 (s, 2H, C*H* imidazolyl-*Hb*), 4.58 (s, 4H, ArOCH_2), 4.13 (d, 4H, J = 13.3 Hz, AB system, ArCH_2Ar), 3.69 (q, 4H, J = 7.7 Hz, NHCH_2CH_2-imidazole), 3.45 (d, 4H, J = 13.3 Hz, AB system, ArCH_2Ar), 2.94 (t, 4H, J = 7.7 Hz, CH_2-imidazole), 1.28 (s, 18H, *tert*-butyl), 1.07 (s, 18H, *tert*-butyl). Anal.calcd. For $C_{58}H_{74}O_6N_6$, CH_3OH: C, 72.05; H, 8.00; N, 8.55. Found: C, 72.43; H, 7.74; N, 8.75.

*Preparation of 5,11,17,23-tetra (tert-butyl)-25,27-di(4-ethyl imidazole acetamide-26,28-di-methoxy calix[4]arene (**4**)*

A mixture of 1,3-dimethyl ester-dimethoxy calix[4]arene (**2**) (0.850 g, 1.03 mmol) and histamine (0.461 g, 4.0 mmol) in 15 mL of a 1:1 mixture of methanol: toluene was refluxed for 4 days. The solvents were removed by evaporation under reduced pressure. The residue was dissolved in dichloromethane and washed with water. The organic layer was dried over Na_2SO_4. The residue was precipitated with hexane to give pure **4** (0.407 g, 40 %) as a white solid. Mp 167–169 ° C. ^{1}H-NMR ($CDCl_3$): 7.53 (s, 2H, C*H*-imidazole *Hb*), 7.26- 7.06 (m, 8H, Ar*H*), 6.89 (s, 2H, *CH*-imidazole *Ha*), 2.94- 4.39 (m, 26H, ArOCH_2, ArCH_2Ar, CH_2-imidazole and ArOCH_3), 1.28 (s, 18H, *tert*-butyl), 1.03 (s, 18H, *tert*-butyl). Anal.calcd. For $C_{60}H_{78}O_6N_6$: C, 73.57; H, 8.03; N, 8.59. Found: C, 73.35; H, 7.89; N, 8.35.

^{1}H-NMR study of the complexation of metal picrates and conformational analysis

$CDCl_3$-solutions of **3**–**4** (10^{-2} M) were reacted with different solid metal picrates: M^+Pic^- with $M^+ = Li^+$, Na^+, K^+, Rb^+ and Cs^+, and M^{2+} $(Pic^-)_2$ with $M^{2+} = Mg^{2+}$, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+} and Co^{2+}. The ratio of the extracted cation to ligand in the solution was estimated

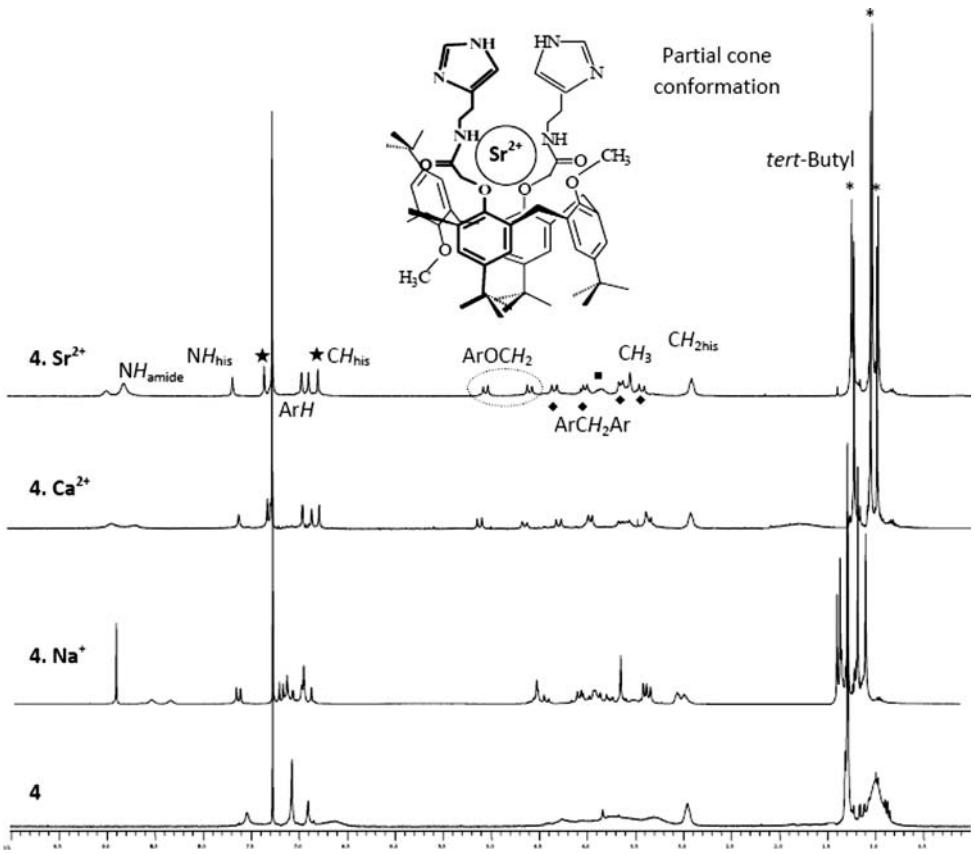


Fig. 1 ^{1}H-NMR spectra (300 MHz, room temperature) of ligand **4** upon addition of metal picrates

by calculating the integration ratio of the picrate protons vs the aromatic protons of the calix unit.

The ^{1}H-NMR spectra of alkali cations with ligand **3** shows the non complexation of these cations. The complexation of alkaline earth cations shows the formation of biligand complexes with Mg^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+} and Zn^{2+}, mononuclear complexe with Ca^{2+}, Pb^{2+} and cone conformation is observed [23].

The ^{1}H-NMR spectra of alkali cations with ligand **4** show that only Na^+ can rigidify the calixarene. The complexation of alkaline earth cations shows the formation of mononuclear complexes with Sr^{2+} and Ca^{2+} and partiel cone conformation is observed.

The coalescence of NMR spectra corresponding to the complexation of Zn^{2+}, Pb^{2+}, Cd^{2+} and Co^{2+} leads to a difficult interpretation and attribution of the different signals. This coalescence shows also the complexation of these cations.

4. $Na^+(Pic)^-$

8.93 (s, 2H, picrate), 8.34 (sl, 1H, CON*H*), 8.14 (sl, 1H, CON*H*), 7.63 (s, 1H, C*H*-imidazole), 7.58 (s, 1H, C*H*-imidazole), 7.19–6.85 (m, 12H, Ar*H*, C*H*-imidazole, N*H*-imidazole), 4.46- 4.396 (m, 4H, ArOCH_2), 4.06- 3.27 (m, 18H, ArCH_2Ar, OCH_3, NHCH_2CH$_2$-imidazole), 2.99–2.89 (m, 4H, CH$_2$-imidazole), 1.31 (s, *tert*-butyl), 1.27 (s, *tert*-butyl), 1.19 (s, *tert*-butyl), 1.08 (s, *tert*-butyl), 1.00 (s, *tert*-butyl).

4. $Sr^{2+}(Pic)_2^-$

8.99 (s, 4H, *H* pic), 8.79 (broad t, 2H, N*H* amide), 7.67 (s, 2H, N*H* imidazole),7.35 (s, 2H, C*H* imidazolyl-*Ha*), 6.96 (s, 4H, Ar*H*), 6.89 (s, 4H, Ar*H*), 6.79 (s, 2H, C*H* imidazolyl-*Hb*), 5.05 (d, 2H, $J = 15.0$ Hz, AB system, ArOCH_2), 4.60 (d, 2H, $J = 15.0$ Hz, AB system, ArOCH_2), 4.35 (d, 2H, $J = 13.0$ Hz, AB system, ArCH_2Ar), 3.66 (d, 2H, $J = 13.0$ Hz, AB system, ArCH_2Ar), 4.03 (d, 2H, $J = 15.0$ Hz, A′B′ system, ArCH_2Ar), 3.45 (d, 2H, $J = 15.0$ Hz, A′B′ system, ArCH_2Ar), 3.87 (m, 4H, NHCH_2CH$_2$-imidazole), 3.57 (s, 6H, ArOCH_3), 2.92 (broad t, 4H, CH_2-imidazole), 1.28 (s, 9H, *tert*-butyl), 1.07 (s, 18H, *tert*-butyl), 1.01 (s, 9H, *tert*-butyl).

4. $Ca^{2+}(Pic)_2^-$

8.91 (s, 4H, *H* pic), 8.69 (broad t, 2H, N*H* amide), 7.61 (s, 2H, N*H* imidazole), 7.31(s, 2H, C*H* imidazolyl-*Ha*), 6.95 (s, 4H,

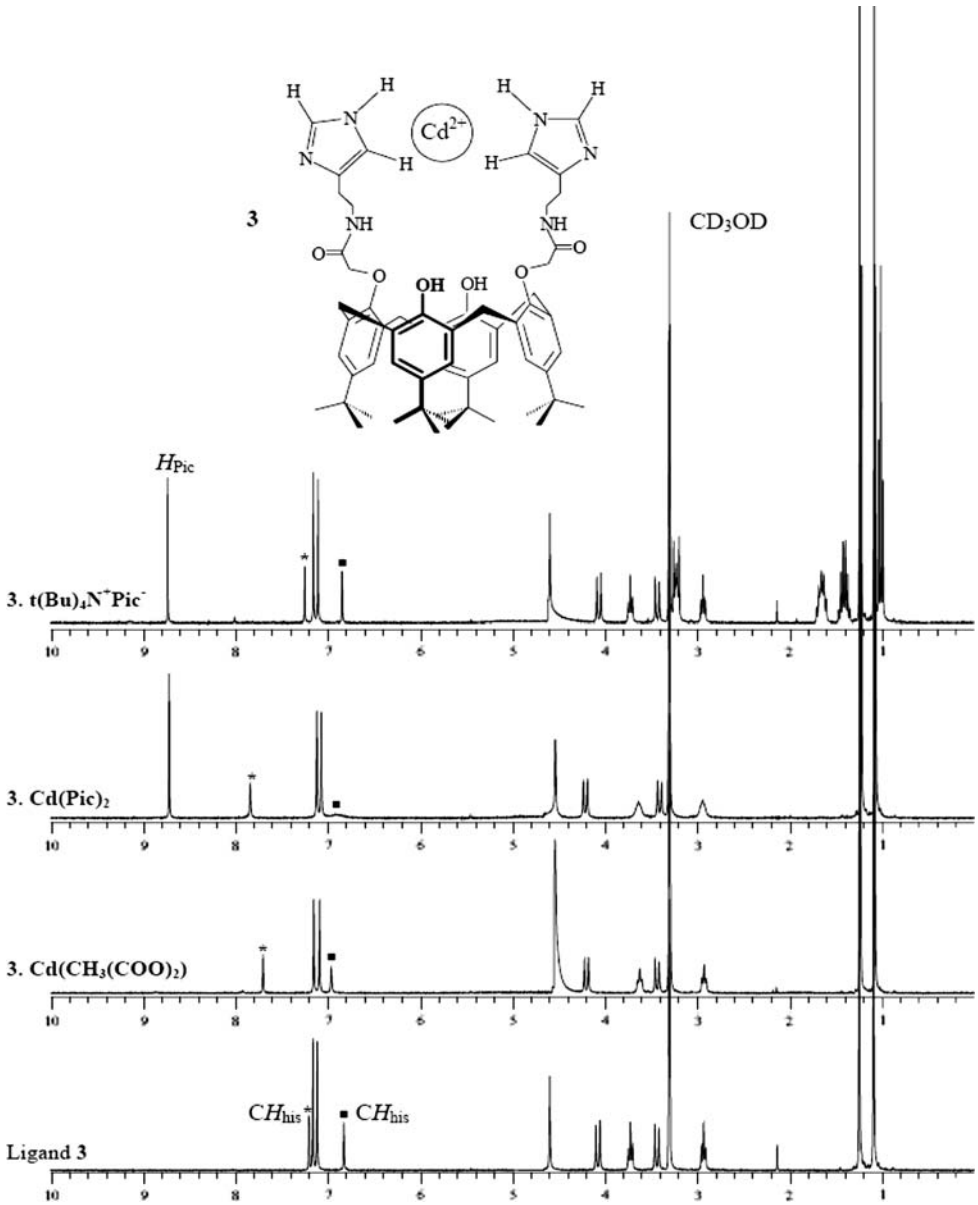


Fig. 2 ^{1}H-NMR spectra (300 MHz, room temperature) of ligand **3** upon addition of ($Cd(CH_3COO)_2$), ($Cd(Pic)_2$) and $(Bu)_4\ N^+Pic^-$

Ar*H*), 6.86 (s, 4H, Ar*H*), 6.78 (s, 2H, C*H* imidazolyl-*Hb*), 5.12 (d, 2H, $J = 15.0$ Hz, AB system, $ArOCH_2$), 4.65 (d, 2H, $J = 15.0$ Hz, AB system, $ArOCH_2$), 4.30 (d, 2H, $J = 13.0$ Hz, AB system, $ArCH_2Ar$), 3.69–3.54 (m, 6H, AB system, $ArCH_2Ar$ and $NHCH_2CH_2$-imidazole), 3.98 (d, 2H, $J = 15.0$ Hz, A′B′ system, $ArCH_2Ar$), 3.40 (d, 2H, $J = 15.0$ Hz, A′B′ system, $ArCH_2Ar$), 3.41 (s, 6H, $ArOCH_3$), 2.94 (broad t, 4H, CH_2-imidazole), 1.26 (s, 9H, *tert*-butyl), 1.09 (s, 18H, *tert*-butyl), 1.02 (s, 9H, *tert*-butyl).

Result and discussion

Calixarenes derivatives **3** and **4** were prepared by amidation of the methyl ester functions of **1** and **2** by histamine in 1:1 mixture of methanol: toluene. The crude mixtures were respectively precipitated with diethyl ether to give **3** in 61% and with hexane to give **4** in 40%.

The conformation of **3** was deduced to be cone from its ^{1}H-NMR spectrum presenting characteristic AB systems for the $ArCH_2Ar$ methylene protons of the calix macroring. The coalescence of ^{1}H-NMR spectrum of **4** can be explained by the rotation of the methoxy (OCH_3) units through the ring of macrocycle and shows that this ligand does not have a well-defined conformation.

Soli–liquid extractions of alkali and alkaline-earth picrates by ligands **3** and **4**, monitored by ^{1}H-NMR spectroscopy, shows that the cations are probably localised in the amido cavity. Indeed, this assumption is supported first by Pearson classification concerning Hard and Soft

Acids and Bases (HSAB model: hard acids prefer to interact with hard bases and soft acids with soft bases) [20], and second by several crystalline related structures in which alkali and alkaline-earth cations are generally in interaction with oxygens [3, 21, 22].

The ^{1}H-NMR spectra corresponding to Na^+ and K^+ extraction do not show any affinity between this type of cation and ligand **3**. Nonetheless, the substitution of two hydrogens by two methyl groups introduces an important change in the ligand properties. Effectively, ligand **4** extracts and complexes Na^+ in two different conformations since the majority of ^{1}H-NMR signals have been duplicated and five singlets corresponding to *tert*-butyl protons appear. However this multiplicity is not sufficiently clear to allow the identification of those two conformers.

Otherwise, ^{1}H-NMR spectra obtained after the extraction of alkaline earth cations by ligand **3**, shows the formation of biligand complexes with Mg^{2+}, Sr^{2+} and Ba^{2+} and mononuclear complex with Ca^{2+} [23]. Partial cone conformations are observed with Sr^{2+} and Ca^{2+} and ligand **4**. The partial cone conformation is deduced from the ^{1}H-NMR spectra. Only one AB system corresponding to the $ArOCH_2$, two AB systems corresponding to the $ArCH_2Ar$ methylene protons and three singlets corresponding to the *tert*-butyl groups were detected (Fig. 1).

The extraction of transition and heavy metals (soft cations) shows that these cations are probably located in the 'histamine' site. To confirm our suggestion, we have followed the extraction of cadmium acetate ($Cd(CH_3CO_2)_2$) and cadmium picrate ($Cd(Pic)_2$) and the extraction of tetrabutylammonium picrate $(Bu)_4\ N^+Pic^-$ by ligand **3**. The ^{1}H-NMR spectrum corresponding to the extraction of cadmium picrate and acetate showed that only the CH_{his} signals are shifted. This was interpreted by a chelation of the cadmium with histamine due to the presence of nitrogen soft atoms. No NMR-signal changes were observed in the case of tetrabutylammonium picrate probably due to the large size of the tetrabutyl ammonium cation and the picrate anion. This study showed that neither the cation nor anion are included (Fig. 2). These results are also in agreement with similar studies elaborated by the team of Reinaud and colleague which show that these metals are located in this site as also confirmed by crystalline structures [24–26].

Table 1 reports the $\Delta\delta$ values as ($\delta_{free\ ligand} - \delta_{complex}$). Large $\Delta\delta$ values of $CH_{histamine}$ signals were assumed to be indicative of the location of cation near the histamine site.

Study of the complexing properties by UV-visible spectrophotometry

The stability constants β of complexes formed with ligands **3** and **4** with alkali, alkaline-earth, transition and heavy metals, have been determined at 25 °C in methanol (Merck, Uvasol) by spectrophotometry in the wavelength range 240–320 nm. The concentration of the ligand solutions is about 10^{-4} M. The ionic strength (0.01 M) was provided by *Et_4NCl* (Fluka, purum > 98%) and the used salts were chlorides.

Table 1 $\Delta\delta$ (ppm) value for the complexes of **3** with $Cd(CH_3COO)_2$), $(Cd(Pic)_2)$ and $(Bu)_4\ N^+Pic^-$

	$CH_{histamine}$	$CH_{histamine}$
Ligand **3**	7.21	6.82
3. $Cd(CH_3(COO)_2)$	7.72	6.98
$\Delta\delta$	**−0.51**	**−0.16**
3. $Cd(Pic)_2$	7.83	6.96
$\Delta\delta$	**−0.62**	**−0.14**
3. $(Bu)_4\ N^+Pic^-$	7.23	6.82
$\Delta\delta$	*	*

*$\Delta\delta \leq 0.05$

The procedure has been described in detail and consisted of adding increasing amounts of metallic chlorides to a solution of **3**, **4** (Figs. 3, 4). The resulting changes of UV absorption spectra were analysed by the program Letagrop-Spefo [27].

The values of the corresponding stability constants (as $\log\beta_{ij}$) are given in Table 2 along with the assumed stoichiometries of the complexes.

Table 2 shows that there is no complexation of Na^+ and K^+ by ligand **3**. In the case of bivalent cations the affinity of this ligand became significant and the stability constants of formed mononuclear species are ranged between $10^{3.76}$ and $10^{5.83}$. The best affinity is for Sr^{2+} with a selectivity $S_{Sr/Mg} \approx 10^2$.

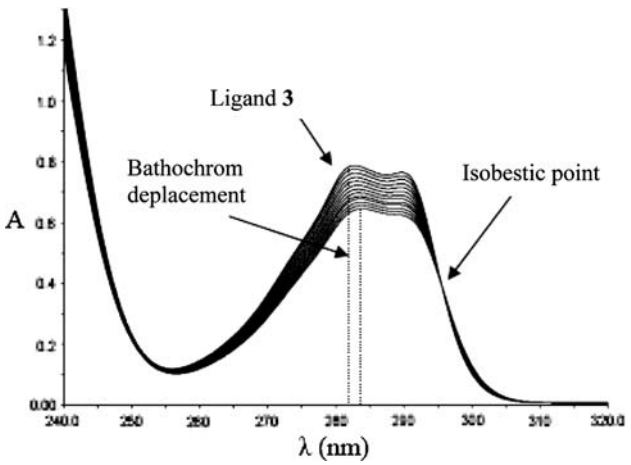


Fig. 3 Changes in the UV absorption spectrum of ligand **3** upon addition of $ZnCl_2$ in methanol; concentration of ligand: 10^{-4} M, $0 \leq R \leq 1.4$; concentration of $NEt_4Cl = 0.01$ M; cuvettes of 1 cm path length

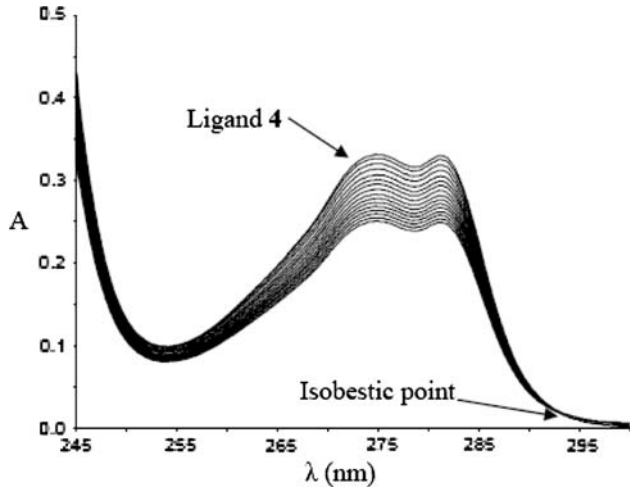


Fig. 4 Changes in the UV absorption spectrum of ligand **4** upon addition of $MgCl_2$ in methanol; concentration of ligand: 2.10^{-4} M, $0 \leq R \leq 1$; concentration of $NEt_4Cl = 0.01$ M; cuvettes of 1 cm path length

Table 2 Logarithm of stability constants corresponding to alkali, alkaline-earth transition and heavy metal complexes

Cations	Metal: ligand **3** stoichiometries	logβ_{ij} of **3**	Metal: ligand **4** stoichiometries	logβ_{ij} of **4**
Na^+	a	a	1:1	3.85 ± 0.10
K^+	a	a	1:1	3.61 ± 0.09
Mg^{2+}	1:1	3.78 ± 0.06	1:1	6.49 ± 0.02
Ca^{2+}	1:1	4.20 ± 0.02	2:1	7.63 ± 0.06
Sr^{2+}	1:1	5.83 ± 0.07	2:1	8.28 ± 0.03
Ba^{2+}	1:1	4.15 ± 0.08	1:1	3.38 ± 0.03
Zn^{2+}	1:1	4.84 ± 0.01	1:1	5.62 ± 0.03
Co^{2+}	1:1	3.79 ± 0.06	1:1	4.97 ± 0.05
Pb^{2+}	1:1	3.76 ± 0.05	1:1	6.83 ± 0.01
Cd^{2+}	1:1	4.70 ± 0.08	1:1	3.89 ± 0.01

a: no change in the spectrum

$C_{L3} = 10^{-4}$ mol L^{-1}, $C_{L4} = 2.10^{-4}$ mol L^{-1} [*Et₄NCl*] $= 10^{-2}$ mol L^{-1}

The substitution of hydrogen by methyl groups improves the complexing properties with all cations, particularly with alkali. For ligand **4**, we observed the formation of mononuclear species with almost all cations and binuclear complexes with calcium and strontium.

This substitution induces a stability enhancement. A significant enhancement is observed for magnesium and lead complexes which are respectively $10^{2.7}$ and 10^3 times more stable with ligand **4** than with ligand **3**. The difference of the affinity between the two ligands could result from hydrogen bonds established with the oxygen cavity of ligand **3**, leading to unavailable oxygen atoms for coordination and/or maybe due to a decrease of the size of the oxygen cavity. This suggestion explains the absence of alkali complexation observed with ligand **3** and the amelioration of complexing properties by introducing the methyl groups. However, we noted that the calculated stability constants of the barium and cadmium complexes have decreased with ligand **4**. These results can be supported by:

– the steric effect of methyl groups which can make difficult the inclusion of a large cation as barium or
– the no-contribution of oxygen atoms in the coordination of cadmium cation as suggested by NMR study.

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