

## Complexation Studies of a Calix[4](aza)crown and the Crystal Structure of its Magnesium Complex

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(Received: 6 May 2003; in final form: 4 September 2003)

**Key words:** calix[4]arenes, calix[4](aza)crowns, alkaline-earth cations, transition metals, complexation

### Abstract

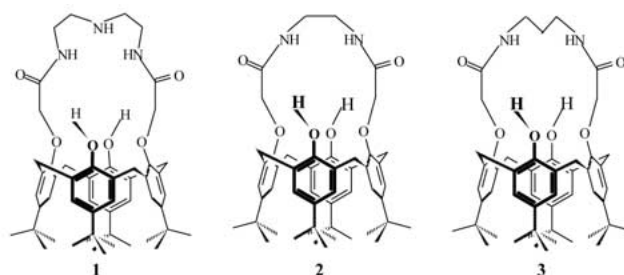
A systematic study of extraction properties and complexation behaviour of the calix[4](aza)crown **1** towards alkaline earth ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ) and transition metal ( $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ) cations is presented. The binding behaviour of **1** was also investigated by <sup>1</sup>H-NMR and the crystal structure of the 1:1 complex with  $\text{Mg}^{2+}$  is described.

### Introduction

During the past decades, as a major activity in supramolecular chemistry, chemists have synthesized many types of receptors for complexing cations and anions [1]. Since the first reports of Reinhoudt, Ungaro and co-workers [2, 3] reporting the selective binding of potassium ions (relative to sodium or lithium) by calix[4]crown-5 ligands, the use of crown ethers covalently bound to calix[4]arenes to selectively complex cations has been studied extensively [4]. Such calixcrown studies have expanded to include calix[4]arene in modified crown-like structures. Among them, the family of *calix[4](aza)crowns* involves molecules combining calix[4]arene elements and polyaminoalkylene chains attached to the phenolic oxygen atoms of the calixarene via acetamido functions which may also serve as linking functions and chelating groups [5–13]. In spite of a quite large number of publications [5–13], only two reports describe the cation-complexing properties of calix[4](aza)crowns. Calix(aza)crowns **2** and **3** show low affinity for divalent ( $\text{Be}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ) and trivalent ( $\text{Sc}^{3+}$ ,  $\text{Y}^{3+}$ ,  $\text{In}^{3+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Bi}^{3+}$ ) metal cations detected as  $[\text{L} + \text{M}]^+$  species by FAB-mass spectrometry [5]. Preliminary two-phase extraction studies of solid  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  picrates by **1** dissolved in  $\text{CDCl}_3$  led to the conclusion that no metal-extraction occurs whereas picric acid is extracted in a 1:1 complex [13].

We present in this paper a systematic study of the extraction properties from water into dichloromethane and complexation in acetonitrile of calix[4](aza)crown **1** towards alkaline earth ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ) and transition metal cations ( $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ). The complexation of some cations was also ascertained by <sup>1</sup>H-NMR spectro-

metry. The crystal structure of the 1:1 complex of **1** with  $\text{Mg}^{2+}$  has been solved.



### Experimental

Calixarene ligand **1** was prepared as described previously [12].

**Extractions.** Metal picrates were produced by stirring dilute picric acid solution ( $\sim 10^{-2}$  M) with freshly precipitated metal hydroxides, the acid being added until complete dissolution just occurred. Reduction in volume of these solutions resulted in the deposition of yellow crystals in all cases. These were collected, washed with ethanol/ether, then ether, and dried under vacuum for 24 hours. Dichloromethane (Chemi-Pharma) was used without purification. The extent of extraction (%E) of metal picrates ( $2.5 \times 10^{-4}$  M) from water to dichloromethane containing the ligand ( $2.5 \times 10^{-4}$  M) was determined at 20 °C as previously described [14].

### Complexation studies

Acetonitrile for HPLC (Siegfried Handel 99%) was used without further purification. The metallic (alkaline earth

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Table 1. Ratio values of end of complexation.

Compound	Metal cation						
	Mg <sup>2+</sup>	Sr <sup>2+</sup>	Ba <sup>2+</sup>	Co <sup>2+</sup>	Ni <sup>2+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>
1	1	0.5	50	0.5	5	12	0.5

and transition metal) salts were perchlorates (Fluka, *purum*) dried under vacuum before use and assumed to be anhydrous. The supporting electrolyte Et<sub>4</sub>NClO<sub>4</sub> (Fluka, *purum*) was first recrystallised from water and washed with acetone and ether, then dried under vacuum for 24 hours. The stability constants in acetonitrile were determined by UV absorption spectrophotometry at 20 °C (PERKIN ELMER Lambda 10). The procedure consisted in adding increasing amounts of alkaline earth and transition metal perchlorate solutions to a solution of the ligand ( $C_L = 1.67 \times 10^{-5}$  M). The resulting spectral changes were analysed by the program Letagrop Spefo [15] to provide the stoichiometry of the complexes and their stability constants  $\beta_{ij}$  as well as their calculated individual electronic spectra. Log  $\beta_{ij}$  values, which are given in Tables 1 and 2, correspond to the arithmetic means of at least two independent experiments. Theoretically, the presence in solution of the species ML<sub>2</sub> or M<sub>2</sub>L shows the coexistence of ML species. However, when low quantities of ML (<3%) coexist with higher quantities of ML<sub>2</sub> or M<sub>2</sub>L, the program Letagrop takes only into account the species ML<sub>2</sub> or M<sub>2</sub>L.

<sup>1</sup>H-NMR spectrometry. The <sup>1</sup>H-NMR spectra were recorded at 200 MHz on a Bruker SY 200 nuclear magnetic resonance spectrometer. A solution  $1.0 \times 10^{-3}$  M of **1** was prepared in 1:1 mixture CD<sub>3</sub>CN:CDCl<sub>3</sub>. To 0.20 mL of this solution in NMR tube were added 0.0–9.0 equiv. of solid Sr(ClO<sub>4</sub>)<sub>2</sub>. Once the strontium perchlorate had dissolved, the spectra were recorded every 24 hours until the complexation reached equilibrium. The result of the experiment was a plot of displacement in chemical shift as a function of the ratio  $R_{M/L} = C_{Metal}/C_{Ligand}$ . <sup>1</sup>H-NMR spectrum was recorded after 4 weeks reaction between solid ZnPic<sub>2</sub> and a  $10^{-2}$  M CDCl<sub>3</sub> solution of ligand **1**.

Crystallography. The data were collected at 100(2) K on a Nonius Kappa-CCD area detector diffractometer [16] using graphite-monochromated Mo-K $\alpha$  radiation (0.71073 Å). The crystal was introduced in a glass capillary with a protecting “Paratone” oil (Exxon Chemical Ltd.) coating. The data were processed with DENZO-SMN [17]. The structure was solved by direct methods with SHELXS-97 [18] and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on  $F^2$  with SHELXL-97 [18]. The absorption effects were empirically corrected with the program DELABS from PLATON [19]. Three *tert*-butyl groups were found disordered over two positions each, which were refined with occupancy factors constrained to sum to unity. The protons bound to phenolic oxygen and amine nitrogen atoms were introduced as found on the Fourier-difference

maps whereas all other hydrogen atoms, except those of the water molecules and those in the disordered parts, were introduced at calculated positions. All hydrogen atoms were treated as riding atoms with a displacement parameter equal to 1.2 (OH, NH, CH, CH<sub>2</sub>) or 1.5 (CH<sub>3</sub>) times that of the parent atom. All non-hydrogen atoms were refined anisotropically, except the disordered ones. Refinement of 885 parameters on 12190 independent reflections out of 34153 measured reflections ( $R_{int} = 0.091$ ) led to  $R_1 = 0.111$ ,  $wR_2 = 0.294$ ,  $S = 1.130$ ,  $\Delta\rho_{max} = 1.22 \text{ e } \text{Å}^{-3}$ . The rather low quality of the refinement, which is due to the low quality of the Crystals themselves, does not prevent the structure to be unambiguously determined. The molecular plot was drawn with SHELXTL [20]. Crystal data: C<sub>64</sub>H<sub>106</sub>Cl<sub>3</sub>MgN<sub>5</sub>O<sub>25</sub>,  $M = 1476.20$ , monoclinic, space group  $P2_1/n$ ,  $a = 12.6505(15)$ ,  $b = 48.3019(17)$ ,  $c = 12.8818(16)$  Å,  $\beta = 103.853(6)^\circ$ ,  $V = 7642.4(13)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.283 \text{ g cm}^{-3}$ ,  $\mu = 0.205 \text{ mm}^{-1}$ ,  $F(000) = 3152$ . CCDC reference number 202108.

Extraction of divalent metal picrates. Solvent extraction of alkaline earth and transition metal picrates dissolved in water by **1** into dichloromethane at 20 °C under neutral conditions leads to the following extend values: Mg<sup>2+</sup> (12%), Ca<sup>2+</sup> (9%), Sr<sup>2+</sup> (12%), Ba<sup>2+</sup> (9%), Co<sup>2+</sup> (7%), Ni<sup>2+</sup> (11%), Cu<sup>2+</sup> (19%) and Zn<sup>2+</sup> (9%). Although commonly chosen as substrates for extraction studies, metal picrates are an inappropriate choice in systems such as the present. Under the specific conditions presently employed, it can be said that extraction of picrate occurs to an extent which is dependent on the metal ion, but whether a metal ion or a proton (or both) accompanies the picrate is unknown. We have shown elsewhere for a similar case that exclusive extraction of picric acid may occur and thus it would be unwise to attempt any interpretation of the present results in terms of any differences between the metal ions [13]. However the E% values of extraction ranging from 7% to 19% (triple value) let us conclude that not only the picrate is extracted. We therefore investigated further complexation studies by other techniques to ensure the results.

Complexation of divalent metal cations. Upon the addition of metal perchlorates to a solution of **1**, the observed UV spectral changes suggest a single reaction equilibrium in every case. With Mg<sup>2+</sup>, the spectral changes correspond to an increase of absorbance between 310 nm and 290 nm and between 289 nm and 281 nm, and a decrease of absorbance between 290 nm and 289 nm and between 281 nm and 264 nm, drawing thus four isobestic points at 264 nm, 281 nm, 289 nm and 290 nm wave lengths. Ratios of end of complexation are shown in Table 1. The values of the ratios are a preliminary indication of the complexation behaviour of **1**. Complexation is ended at M/L = 0.5 for Sr<sup>2+</sup>, Co<sup>2+</sup> and Zn<sup>2+</sup>, probably due to the formation of 2:1 complexes, whereas M/L = 1 for Mg<sup>2+</sup>, which suggests a 1:1 complex. M/L ranges from 5 to 50 for Ni<sup>2+</sup>, Cu<sup>2+</sup> and Ba<sup>2+</sup>, probably due to formation of weak complexes.

Table 2. Stability constant ( $\log \beta_{ij}$ ) values for alkaline earth and transition metal complexes of **1** in acetonitrile.  $C_L = 1.67 \times 10^{-5}$  M,  $I = 10^{-2}$  M ( $\text{Et}_4\text{NClO}_4$ ),  $T = 293$  K.

M:L	$\log \beta$						
	$\text{Mg}^{2+}$	$\text{Sr}^{2+}$	$\text{Ba}^{2+}$	$\text{Co}^{2+}$	$\text{Ni}^{2+}$	$\text{Cu}^{2+}$	$\text{Zn}^{2+}$
1:1	5.13 ± 0.26		3.03 ± 0.12				
1:2		10.04 ± 0.18		10.30 ± 0.09	11.01 ± 0.05		11.04 ± 0.09
2:1						7.63 ± 0.25	

Constant stability values of alkaline earth and transition metal complexes shown in Table 2 indicate that **1** forms mononuclear complexes (ML) with  $\text{Mg}^{2+}$  and  $\text{Ba}^{2+}$ , which stabilities range from 3.03 to 5.13 log units. Additionally  $\text{ML}_2$  complexes with  $\text{Sr}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  which stabilities vary from 10.04 to 11.04 log units.  $\text{M}_2\text{L}$  complex was detected only with  $\text{Cu}^{2+}$  ( $\log \beta_{21} = 7.63$ ).

In addition to UV spectroscopy study,  $^1\text{H}$  NMR experiments were conducted to study either the titration of  $\text{Sr}^{2+}$  or the solid-liquid extraction of  $\text{Zn}^{2+}$ .

$^1\text{H-NMR}$  studies. Changes in the  $^1\text{H-NMR}$  spectrum of **1** in 1:1  $\text{CD}_3\text{CN}:\text{CDCl}_3$  induced by the stepwise addition of  $\text{Sr}(\text{ClO}_4)_2$  are summarised in Figure 1.

The signal of  $\text{CH}_2\text{NHCH}_2$  protons are the most affected by the presence of the metal. Signals of  $\text{CONH}$  and  $\text{CONHCH}_2$  protons move toward high magnetic fields until the ratio  $R_{\text{M/L}} = 0.5$ . After this value, signals of  $\text{CONH}$  move toward low magnetic fields, and those of  $\text{CONHCH}_2$  stop. Furthermore, signals of  $\text{ArOH}$ ,  $\text{CH}_2\text{NHCH}_2$  and  $\text{ArOCH}_2$ -amide move toward low magnetic fields and begin to stabilize from the ratio  $R_{\text{M/L}} = 0.5$ . These spectroscopic changes confirm  $\text{ML}_2$  stoichiometry determined in acetonitrile (Table 2).  $^1\text{H}$  RMN spectrum of  $[\text{1}_2.\text{Sr}]^{2+}$  (Figure 2b) shows the signals of each aromatic proton, supporting azacrown chain, and *t*Bu protons to become closer ( $\Delta\delta_{\text{H}_{\text{meta}}}$  and  $\Delta\delta_{\text{C}(\text{CH}_3)_3}$  negative) giving rise to a more symmetrical cone conformation.

The same observations were made by recording  $^1\text{H-NMR}$  spectrum after a 4 weeks reaction between solid  $\text{ZnPic}_2$  and a  $\text{CDCl}_3$  solution of the free ligand **1** (Figure 3). The recorded spectrum shows and is compatible with the formation of 1:2 ( $\text{ML}_2$ ) complex, thus confirming the observed stoichiometry in acetonitrile. In this case the stoichiometry was determined by the ratio of picrate extracted as calculated from the integration ratio between the picrate singlet and the  $\text{CONH}$  triplet of the calixarene **1**.

### Crystal structure of the $\text{Mg}^{2+}:\mathbf{1}$ complex

The reaction of **1** with  $\text{Mg}(\text{ClO}_4)_2$  in a 1:1 mixture of  $\text{CH}_3\text{CN}:\text{Et}_2\text{O}$  gave the complex  $\text{Mg}(\text{H}_2\text{O})_4(\text{H1})(\text{ClO}_4)_3 \cdot 2(\text{CH}_3\text{CH}_2)_2\text{O} \cdot 2\text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$   $1.\text{Mg}^{2+}$ , which is represented in Figure 4. The magnesium ion is not complexed in an “internal” way by the calix(aza)crown and is not bound to any of the nitrogen atoms. The cation coordination sphere is of octahedral geometry and, as is commonly observed

for this metal ion, largely occupied by water molecules (possibly arising from the use of undried solvents in the crystallisation process). The four water molecules are in fact mutually *cis*, with two *trans* sites occupied by carbonyl-O atoms from different calixarene entities, so that in the solid state, the complex is actually a coordination polymer, with **1** acting as a *bis*(unidentate) bridging ligand, and with alternately “up” and “down” calix(aza)crowns along the chain. The magnesium ion coordination sphere is a rather regular octahedron [mean value of  $\text{Mg}-\text{O}_{\text{calyx}}$  and  $\text{Mg}-\text{O}_{\text{water}}$  bond lengths 2.052 and 2.064 Å, respectively, in agreement with literature values]. The central amine group of the calix(aza)crown is protonated, which counterbalances the charge of the third perchlorate ion. The conformation of the calixarene is the usual *cone* one, with dihedral angles between the mean plane defined by the four carbon atoms of the methylene bridges and the four aromatic rings of 66.2(2), 55.3(2), 66.3(2) and 55.5(2)°, indicating that the two diametrically located rings bearing the chain are farther from the mean plane than the two other ones. The distances between diametrically located oxygen atoms are  $\text{O}(1) \cdots \text{O}(4)$  4.548(6) and  $\text{O}(5) \cdots \text{O}(6)$  3.488(6) Å. This conformation is close to that observed in the related calixarene with a  $-\text{NH}-(\text{CH}_2)_2-\text{NH}-$  [6] central unit. The phenol- and phenolic-O atoms, along with the amide- and amine-N atoms are involved in complicated proton-coordination (hydrogen bonding) networks, in preference to any direct interaction with the metal ion. The phenolic protons are thus bound to the ether oxygen atoms and those of N(1) and N(3) with ether or phenolic oxygen atoms. One of the protons of N(2) is involved in an intermolecular hydrogen bond with a water molecule, which is itself possibly hydrogen bonded to oxygen atoms of a diethylether molecule, a perchlorate anion, and a coordinated water molecule. An intricate hydrogen bonding pattern further links the various water molecules, anions and solvents. An acetonitrile molecule is included in the calixarene cavity, which is a usual feature.

### Discussion

Although the presence of true amine-N donors within ligand **1** might be expected to enhance the binding of transition metal ions, it must be noted that secondary N donors such as are present in this molecule is generally a rather poor binding group, unless part of a chelating unit. Depending upon the ligand conformation and N-donor configuration,

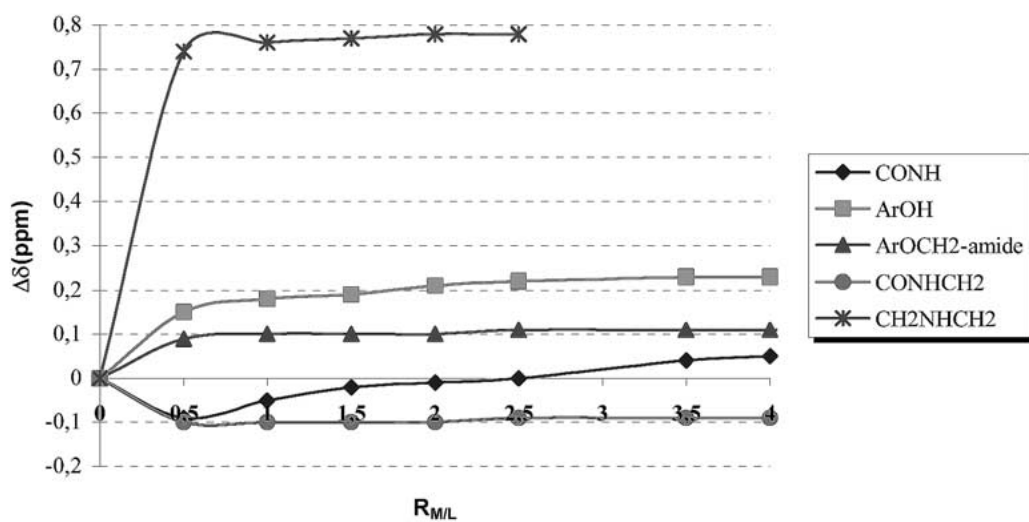


Figure 1. Changes in  $^1\text{H}$  chemical shifts upon titration of **1** by  $\text{Sr}(\text{ClO}_4)_2$  in a mixture 1:1  $\text{CD}_3\text{CN}:\text{CDCl}_3$  at  $20^\circ\text{C}$ ,  $C_L = 10^{-3}$  M.

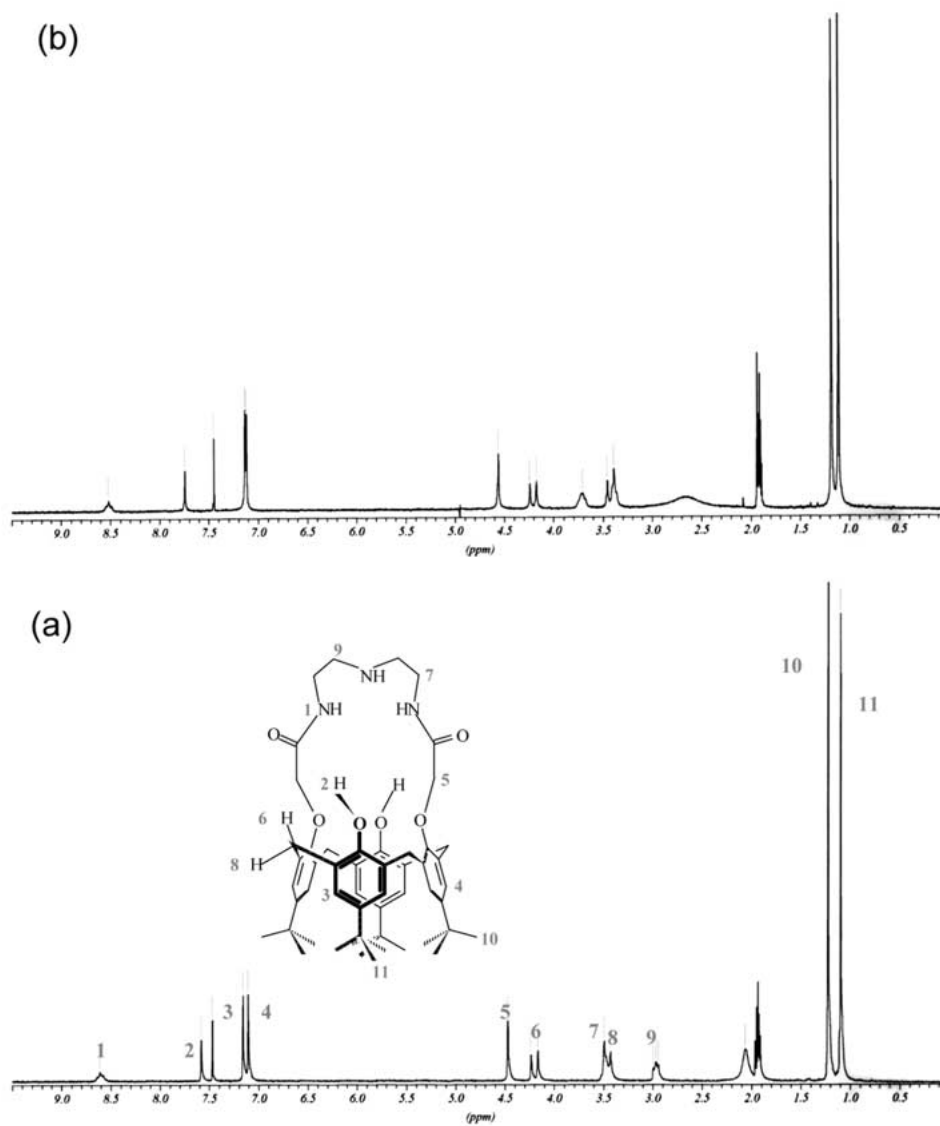


Figure 2.  $^1\text{H}$  NMR spectra (200 MHz) in 1:1  $\text{CD}_3\text{CN}:\text{CDCl}_3$  of (a) **1** and (b)  $[\text{12.Sr}]^{2+}$  complex.

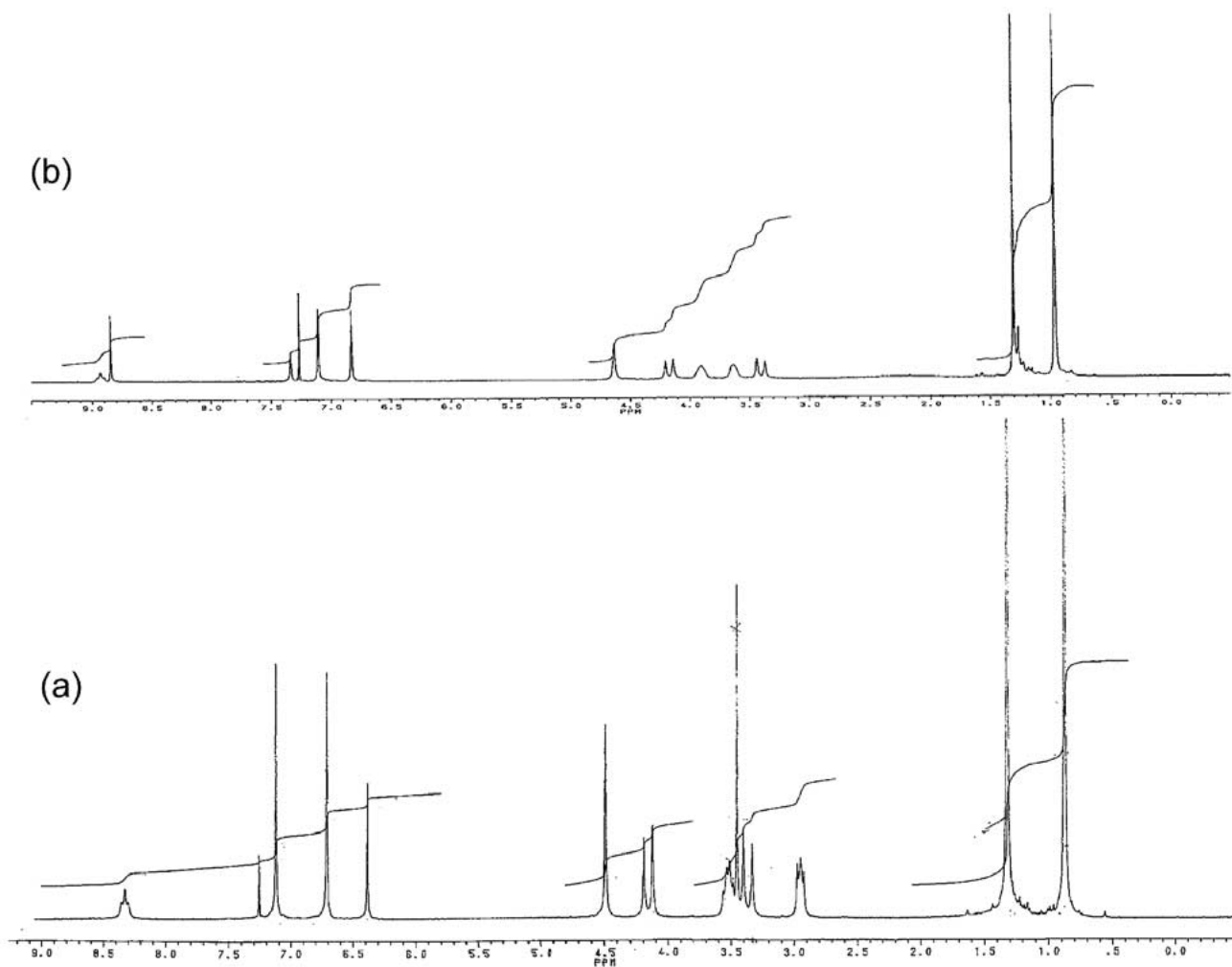


Figure 3.  $^1\text{H}$  NMR spectra (200 MHz) in  $\text{CDCl}_3$  of (a) **1** and (b)  $[\text{1}_2\text{.Zn}]^{2+}$  complex.

N,O chelation is certainly possible in **1** but structural studies were considered desirable to precisely define its actual coordination mode. In the case of  $1.\text{Mg}^{2+}$ , it would not be expected that the coordination polymer would persist in a coordinating solvent such as acetonitrile, and thus this structure indicates that **1** may act as no more than a simple unidentate ligand in solution. **1** interacts weakly with  $\text{Ba}^{2+}$  to form a ML complex ( $\log \beta_{11} = 3.03$ ) 130 times less stable than the  $\text{Mg}^{2+}$  complex. This stability decrease can be assigned to the double size of  $\text{Ba}^{2+}$  and/or to its higher coordination number. However, with  $\text{Sr}^{2+}$ , the metal cation is further stabilized by N-donor binding site of each calixarene unit ( $^1\text{H}$ -NMR data).

The crystal structure of the picric acid complex of **1**, crystallized from acetonitrile, has been reported previously [13]. In this case, one of the carbonyl oxygens is directed towards the centre of the crown cavity and involved in a hydrogen bond with a phenolic proton. A second intramolecular hydrogen bond links the other phenolic group to an ether oxygen atom, whereas several intermolecular bonds are formed between the calix(aza)crown, one of its symmetry equivalents, a water molecule, and picric acid. It is of course unsure that this solid state structure gives

any precise information on the behaviour of **1** in solution. However, the presence of intramolecular hydrogen bonds similar to those in the picric acid or the  $\text{Mg}^{2+}$  complexes is probable. It may thus be assumed that coordination of  $\text{Mg}^{2+}$  or  $\text{Ba}^{2+}$  in the cavity would require rupture of these bonds with possibly a contribution of the amine nitrogen atom in the case of the larger  $\text{Ba}^{2+}$  cation.

On the other hand, exocyclic cation coordination, as evidenced by the crystal structure, only involves carbonyl oxygen atoms. Intramolecular hydrogen bonds, albeit different from those in the picric acid complex, are still present, which is likely to favour exocyclic coordination. It may be noted that such intermolecular hydrogen bonds in calixcrowns containing ether oxygen atoms only are much less important, being reduced to those uniting the phenolic groups to the proximal ether groups.

Exocyclic complexation promotes the formation of polymeric species or of complexes involving more than one ligand for each cation. Hence, the observation of  $\text{ML}_2$  species with the  $\text{Sr}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  cations can be considered as indicative of exocyclic complexation. The  $\text{Sr}^{2+}$  complex appears less stable than the transition metal

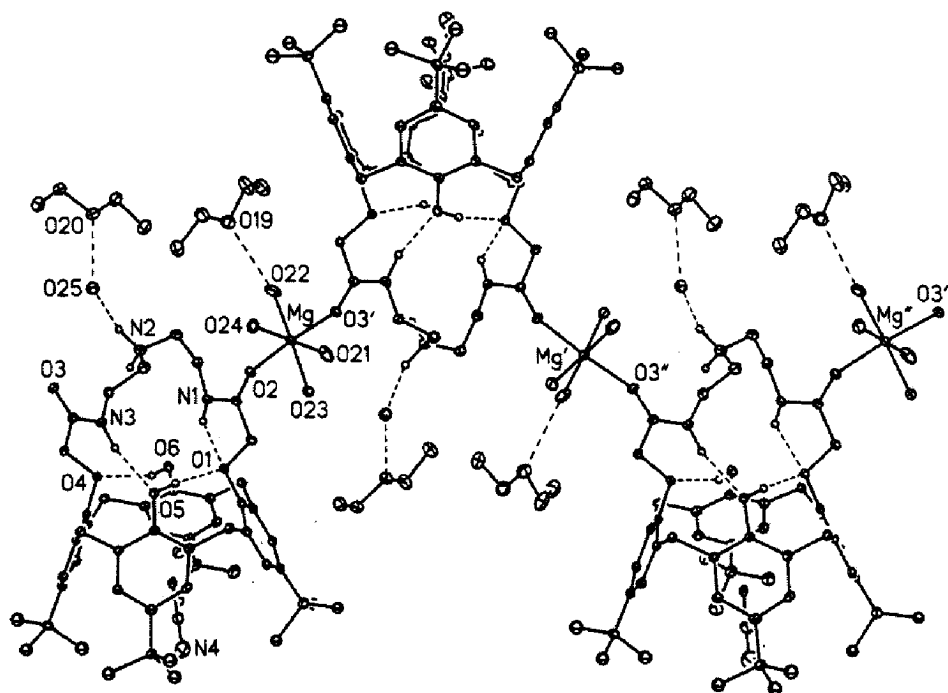


Figure 4. View of the coordination polymer in compound  $\text{Mg}^{2+}:1$ . Hydrogen bonds represented as dashed lines. Hydrogen atoms not involved in hydrogen bonding and perchlorate anions omitted for clarity. Only one position of the disordered *tert*-butyl groups is represented. Displacement ellipsoids drawn at the 10% probability level. Protons of phenolic and amine groups represented as small spheres of arbitrary radii. Selected bond lengths (Å): Mg-O2 2.060(5), Mg-O3' 2.043(5), Mg-O21 2.023(6), Mg-O22 2.102(7), Mg-O23 2.082(6), Mg-O24 2.047(6). Symmetry codes: ' =  $0.5 + x, 0.5 - y, z - 0.5$ ; '' =  $1 + x, y, z - 1$ ; ''' =  $1.5 + x, 0.5 - y, z - 1.5$ .

complexes, which may be indicative of some differences in the coordination mode.

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