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# New Complexes of Ditopic Ligands with "d" and/or "s" Metal Ions

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**The asymmetric compartmental macrocycles containing one $N_2O_2$ or $N_3O_2$ Schiff base and one $O_2O_3$ or $O_2O_4$ crown-ether like chamber, have been obtained by condensation reaction of the formyl precursors 3,3′-(3-oxapentane-1,5-diyldioxy) bis (2-hydroxybenzaldehyde) or 3,3′-(3,6-dioxaoctane-1,8-diyldioxy)-bis(2-hydroxybenzaldehyde) with ethylenediamine ($H_2L_A$, $H_2L_C$) or 1,5-diamino-3-azamethylpentane($H_2L_B$, $H_2L_D$), also in the presence of metal ions as templating agents. These ditopic ligands, with dissimilar coordination sites, have been designed and used for the selective complexation of "d" and/or "s" metal ions, respectively into the Schiff base and the crown ether chamber. The selectivity of these processes strongly depends on the size and on the donor atom sets of the sites. The possibility to obtain mononuclear $M(L) \cdot nH_2O$ ($M = Ni^{2+}, Cu^{2+}, Co^{2+}$), $Mn(L)(CH_3COO) \cdot nH_2O$ or Na(L) and hetero-dinuclear $MNa(L)(CH_3COO)$ ($M = Ni^{2+}, Cu^{2+}, Co^{2+}$) and $MnNa(L)(CH_3COO)_2 \cdot nH_2O$ complexes has been successfully tested. The ligands and complexes have been characterized by ir, nmr, mass spectrometry and magnetic susceptibility measurements.**

**Two of the ligands used for the preparation of the solid samples, *i.e.*, to $H_2L_A$ and $H_2L_B$, have been employed to study complexation reactions of Co(II) and Na(I) in solution. In order to obtain information on the ligand preorganization effect toward the complex stabilities, a simpler open chain parent compound of $H_2L_B$ ($H_2L_E$) has been also prepared and studied. FT-IR spectra show that $H_2L_A$ is unable to complex $Na^+$ in DMSO while the complexation reactions of $Na^+$ by $H_2L_B$ and of $Co^{2+}$ by $H_2L_A$ take place with slow kinetics. Therefore, thermodynamic data have been obtained only for the systems $Co^{2+}/H_2L_B$ and $Co^{2+}/H_2L_E$. The thermodynamic parameters obtained for the complexation reactions show that the pre-organization of the donor atoms in $H_2L_B$ does not add a significant contribution to the stabilities of the complexes. Both $H_2L_B$ and $H_2L_E$ form in DMSO 1:1, 1:2 and 1:3 = M:L complexes with very similar stabilities and almost equal enthalpies of formation. Physico-chemical studies suggest besides that the slow reaction of $Na^+$ with $H_2L_B$ is probably due to the formation of a 1:1 complex where the metal cation, initially occupying the $O_3$ cage of the ligand, slowly binds also the oxygens of the phenolic moieties. Spectral and calorimetric data on solutions containing $H_2L_B$ and different $Co^{2+}$: $Na^+$ ratios evidence that in DMSO no stable heterodinuclear complexes form when the neutral ligand is considered.**

*Keywords*: Heteroditopic ligands; Complexes Ni(II); Cu(II); Co(II); Mn(III); Na(I); Schiff Base

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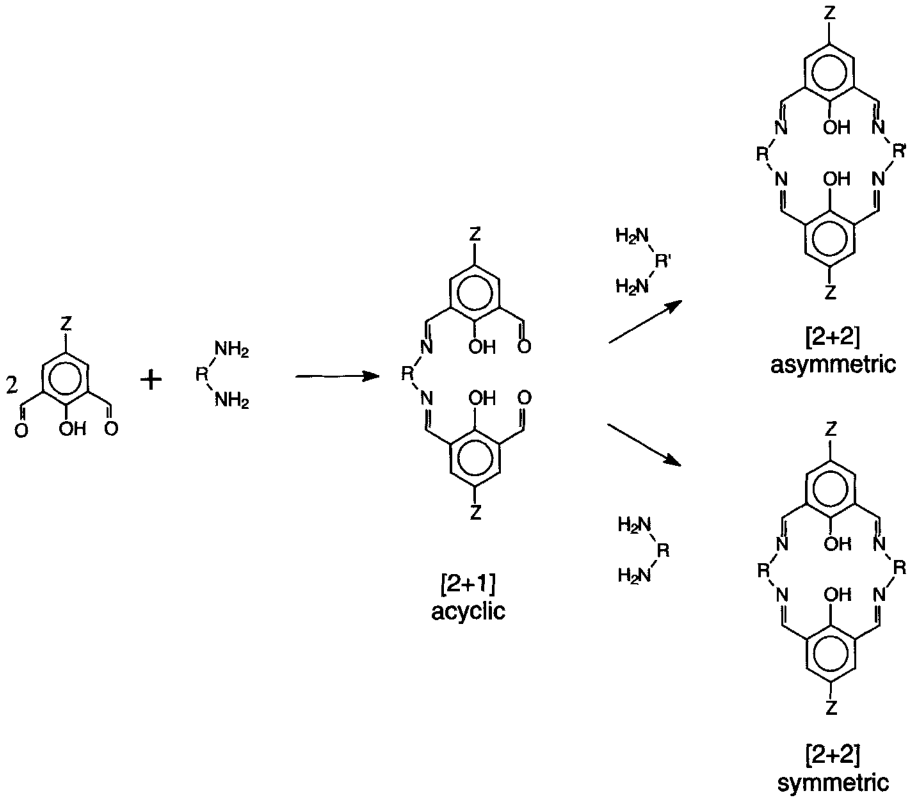
## 1. INTRODUCTION

In the last years the design and synthesis of asymmetric compartmental macrocyclic ligands have received particular attention owing to the ability of these systems to form hetero-dinuclear complexes with suitable metal ions [1,2]. In these studies [2+2] asymmetric tetraimine macrocycles derived by the condensation of 2,6-diformyl-4-substituted phenol (head unit) and appropriate polyamines (lateral unit), have been primarily used [3-6].

Many papers and several review articles have been published on the physico-chemical properties of these systems, on their magneto-structural correlation together with their possible use as molecular devices, as unconventional precursors in the synthesis of new materials, as new catalysts, *etc.* [7-11]. For the synthesis of these asymmetric macrocycles a step by step pathway has been employed in order to avoid the easy formation of the corresponding [2+2] symmetric macrocycles (Scheme 1) which, owing to the easy accessibility of the two identical adjacent sites, give rise to homodinuclear-instead of heterodinuclear-complexation. Nevertheless, heterodinuclear complexes with symmetric macrocycles have been prepared, using particular experimental procedures. It was verified that the reaction of [2+2] symmetric macrocycles with metal salts results in the formation of heterodinuclear complexes especially when the nitrogen atoms of one chamber are protonated. This can be realised when the coordination of the first metal ion to the neutral ligand favours the formation of phenolate groups with the consequent migration of protons from the phenolic oxygens to the iminic nitrogens. Owing to this process, the two coordination chambers are no longer equal and can give rise to two subsequent recognition processes, hence the formation of heterodinuclear complexes [12].

Alternatively heterodinuclear complexes can be prepared using the [2+1] macroacyclic ligands that, owing to the two adjacent dissimilar coordination chambers (one $N_2O_2$ and one $O_2O_2$), can undergo two subsequent and different complexation processes. In the first step a mononuclear acyclic complex is formed which in a second step can react with a second different metal ion originating the corresponding hetero-dinuclear complex. This last complex can be subsequently cyclized by condensation with an appropriate amount of the same polyamine. However, once prepared these heterodinuclear species, the possibility of scrambling reactions with the consequent formation of mixture of homo-dinuclear complexes is highly probable. Consequently the use of asymmetric systems for the preparation of heterodinuclear complexes is strongly recommended. Quite often a template procedure can be used in the preparation of these asymmetric macrocycles as the presence of appropriate metal salts may strongly favour the attainment of the designed intermediate compound in high yield and purity. Successive reaction with the desired polyamine converts the free acyclic [2+1] Schiff base (or its metal complex) into the [2+2] asymmetric cyclic derivative. The asymmetry in these cyclic systems is represented by the two lateral units (R, R′ in Scheme 1) which contain a different number of carbon atoms, aromatic and aliphatic chains and different donor groups. However these two chambers are often not different enough to give rise to two well-defined, stable and different recognition processes at the two sites. In fact, complexes of this kind may undergo further reactions as transmetallation, migration, demetallation, *etc.*, which significantly modify their physico-chemical properties making crucial or questionable their use in the preparation of molecular devices based on a well-defined distance and stereochemistry of the two different metal ions [13].

More recently acyclic and cyclic functionalized ligands containing Schiff base and crown-ether sites have been proposed with the hope that the fusion of these two quite different moieties may originate interesting selectivity in subsequent recognition processes [6,14-20]. The availability of two, equally accessible, chambers can offer an



SCHEME 1 Formation of the acyclic [2 + 1] and [2 + 2] asymmetric and symmetric cyclic Schiff bases.

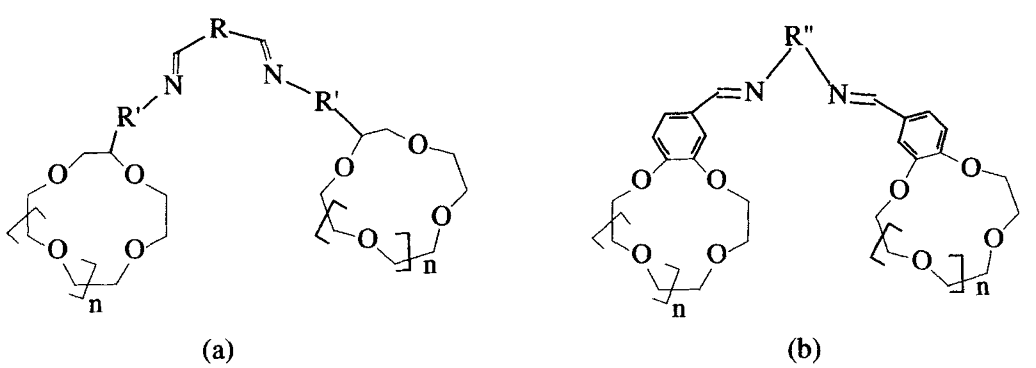
interesting and valuable possibility to estimate the selectivity of these sites towards different "soft" and "hard" metal ions (Scheme 2).

These systems have been prepared by condensation of appropriate formyl (*i.e.*, substituted salicylaldehyde, formyl pyridine, *etc.*) or diformyl derivatives (2,6-diformyl-4 substituted phenols, 2,6-diformyl-pyridine, 2,5-diformyl pyrrole, 2,5-diformyl furan, 2,5-diformyl-thiophene, *etc.*) with the appropriate amino methyl- or amino phenyl-crown ether (Scheme 2a). Alternatively 4-formyl-benzo-crown ethers can react with $H_2N$-R-$NH_2$ or $[NH_2(CH_2)_n]_3N$ to form the corresponding Schiff bases (Scheme 2b).

In these systems the two different coordination moieties can be very far each other, owing to the free rotation about the simple C–C bonds, and/or to the presence of aliphatic or aromatic spacers. Thus as an extension of these investigations cyclic compounds as $H_2L_A$-$H_2L_D$ (Scheme 3) have been designed and successfully tested in multiple selective recognition processes [17–21].

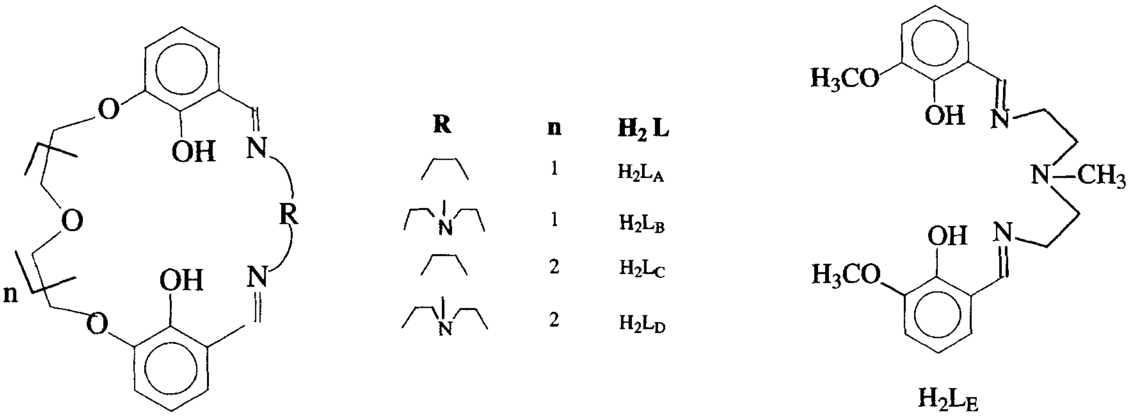
These ligands contain one $N_2O_2$ and $N_3O_2$ Schiff base and one $O_2O_n$ crown ether-like coordination site and can hence give rise to specific recognition when reacted with different metal ions. With the present work we verified that they coordinate preferentially alkali metal ions (*i.e.*, sodium) in the $O_2O_n$ chamber and d- (*i.e.*, copper(II), nickel(II), cobalt(II), manganese(III)) metal ions in the Schiff base moiety as confirmed by ir, nmr and mass spectrometry. Also the formation of heterodinuclear complexes containing sodium and a "d" metal ion was ascertained.

As no studies have been reported on the solution thermodynamics of heteropolytopic Schiff base complexes, even though many of these complexes have been prepared and



(a) (b)

SCHEME 2 Schematic representation of acyclic and cyclic compartmental ligands containing crown-ether moieties.



SCHEME 3 Prepared ligands.

studied in the solid state, preliminary measurements intended to characterize peculiar aspects of the solution chemistry of some of these systems have also been performed.

The solution chemistry of the [2 + 1] acyclic ligand $H_2L_E$ was also investigated in order to compare the chemical behaviour toward different metal ions of similar cyclic and acyclic compartmental Schiff bases.

## 2. EXPERIMENTAL

### 2.1. Materials

The cobalt(II) acetate tetrahydrate, copper(II) acetate monohydrate, nickel(II) acetate tetrahydrate and manganese(III) acetate dihydrate, sodium hydroxyde, diethylene glycol ditosylate, triethylene glycol ditosylate, ethylenediamine, 1,5-diamino-3-azamethylpentane and the other reagents were commercial products used as received by Aldrich. Dimethylsulfoxide (DMSO) was purified by standard methods [22], while the other solvents were reagent grade, used as received. The diformyl precursors 3,3'-(3-oxapentane-1,5-diyldioxy)bis(2-hydroxybenzaldehyde) ($H_2L^I$) and 3,3'-(3,6-dioxaoctane-1,8-diyldioxy)bis(2-hydroxybenzaldehyde) ($H_2L^{II}$) were prepared by literature method [21].

The acyclic complexes $Ba(H_2L^I)(ClO_4)_2$ and $Ba(H_2L^{II})(ClO_4)_2$ used as precursors in the synthesis of the related macrocyclic barium complexes were prepared following a literature procedure [20], by reaction of the appropriate diformyl precursor with an ethanolic solution of $Ba(ClO_4)_2 \cdot 2H_2O$ in a 1 : 1 molar ratio, by collecting the residue, washing it with chloroform and tetrahydrofuran and drying in vacuo.

The macrocyclic complexes $Ba(H_2L)(ClO_4)_2$ ($H_2L = H_2L_B$; $H_2L_D$) were prepared by reaction of the appropriate precursors in the presence of $Ba(ClO_4)_2$ (60–70% yield) or by condensation in methanol of the desired acyclic barium diperchlorate complex $Ba(H_2L^{I,II})(ClO_4)_2$ with the appropriate diamine (30–40% yield) [20].

The ligands $H_2L_A$, $H_2L_B$, $H_2L_C$ and $H_2L_D$ were prepared according to literature procedure [20] by self condensation of the appropriate precursors or by demetallation of the appropriate barium diperchlorate macrocyclic complex $Ba(H_2L)(ClO_4)_2$ with guanidinium sulphate.

DMSO for solution studies (Aldrich, water content < 0.005%), was degassed by a pumping-freezing procedure and stored over 4 Å molecular sieves. Tetraethylammonium perchlorate (Fluka 99%) was purified by crystallization from $CH_3OH$ following the published procedure [23]. The wet salt so obtained, was then dried by heating at 110° C under high vacuum for 24 hours. $NaClO_4$ (Aldrich 99.9%) was re-crystallized from water and dried under vacuum for a week at 100° C.

$Co(ClO_4)_2(DMSO)_6$ and $Co(ClO_4)_2(DMSO\text{-}d_6)_6$ were prepared by precipitation from an almost saturated solution of $Co(ClO_4)_2(H_2O)_6$ (Aldrich 98%) in DMSO or DMSO-$d_6$ with abundant acetone. The precipitate was filtered off and washed with cold acetone followed by cold ether. The cobalt adducts were later re-crystallized by a similar procedure (DMSO/Acetone), dried under vacuum at a mild temperature (~40° C) and stored under controlled atmosphere being hygroscopic. The compounds were characterized as $Co(ClO_4)_2(DMSO)_x$ ($x = 6.0$ both for DMSO and DMSO-$d_6$) by elemental analysis (C,H,S) and by titration of the Co(II) content with EDTA [24].

The preparation and the manipulation of the cobalt(II) complexes have been carried out in dry boxes or under nitrogen atmosphere.

*Caution* Although during these experiments no accidents have occurred, extreme care should be taken when perchlorates are handled, because they may explode spontaneously and may be sensitive to shock. The perchlorates should only be prepared in small quantities.

TABLE I Elemental analyses of the prepared ligands and related complexes

| | Calcd. | | | Found | | |
|---|---|---|---|---|---|---|
| Compound | C | H | N | C | H | N |
| $H_2L_A \cdot 1.5H_2O$ | 60.45 | 6.34 | 7.05 | 60.92 | 5.67 | 7.23 |
| $Co(L_A) \cdot H_2O$ | 53.94 | 4.98 | 6.29 | 53.38 | 5.18 | 5.69 |
| $Mn(L_A)(CH_3COO) \cdot 2H_2O$ | 50.98 | 5.25 | 5.40 | 51.22 | 4.85 | 5.19 |
| $Ni(L_A) \cdot H_2O$ | 53.97 | 4.98 | 6.29 | 53.39 | 4.88 | 6.70 |
| $CoNa(L_A)(CH_3COO) \cdot 2H_2O$ | 48.45 | 4.99 | 5.14 | 48.89 | 4.96 | 4.61 |
| $MnNa(L_A)(CH_3COO)_2 \cdot 2H_2O$ | 49.50 | 4.85 | 4.81 | 49.28 | 4.93 | 5.52 |
| $H_2L_B \cdot H_2O$ | 62.01 | 7.01 | 9.43 | 62.71 | 6.73 | 9.28 |
| $Ni(L_B) \cdot H_2O$ | 53.11 | 6.01 | 8.08 | 52.38 | 6.38 | 7.38 |
| $Co(H_2L_B)(CH_3COO)_2 \cdot H_2O$ | 50.63 | 6.14 | 6.56 | 50.84 | 6.17 | 6.48 |
| $NiNa(L_B)(CH_3COO) \cdot H_2O$ | 51.40 | 5.52 | 7.19 | 51.49 | 5.87 | 6.78 |
| $CoNa(L_B)(CH_3COO) \cdot H_2O$ | 51.38 | 5.52 | 7.19 | 51.34 | 5.61 | 6.48 |
| $H_2L_C$ | 63.76 | 6.32 | 6.76 | 62.29 | 6.64 | 6.69 |

TABLE I (Continued)

| | Calcd. | | | Found | | |
|---|---|---|---|---|---|---|
| Compound | C | H | N | C | H | N |
| $Co(L_C) \cdot 2H_2O$ | 52.08 | 5.56 | 5.52 | 52.46 | 5.45 | 4.96 |
| $Mn(L_C)(CH_3COO)$ | 54.76 | 5.17 | 5.32 | 54.33 | 5.48 | 4.87 |
| $Ni(L_C) \cdot 0.5H_2O$ | 55.04 | 5.25 | 5.83 | 54.82 | 5.01 | 5.62 |
| $Cu(L_C) \cdot H_2O$ | 53.49 | 5.31 | 5.67 | 53.49 | 5.71 | 6.28 |
| $CoNa(L_C)(CH_3COO) \cdot H_2O$ | 48.91 | 5.30 | 4.75 | 49.29 | 4.96 | 4.47 |
| $MnNa(L_C)(CH_3COO)_2$ | 51.33 | 4.97 | 4.60 | 51.77 | 5.11 | 4.42 |
| $NiNa(L_C)(CH_3COO)$ | 52.28 | 5.46 | 4.94 | 52.11 | 4.92 | 5.06 |
| $CuNa(L_C)(CH_3COO)$ | 51.66 | 4.88 | 5.02 | 52.34 | 5.59 | 5.17 |
| $H_2L_D$ | 63.68 | 7.05 | 8.91 | 62.77 | 6.88 | 8.45 |
| $Co(L_D) \cdot 4H_2O$ | 50.00 | 6.55 | 7.00 | 49.78 | 5.80 | 7.69 |
| $Mn(L_D)(CH_3COO)$ | 55.58 | 5.87 | 7.20 | 54.80 | 6.40 | 7.92 |
| $H_2L_E$ | 65.44 | 7.06 | 10.90 | 64.98 | 7.12 | 10.45 |

The elemental analyses of the prepared ligands and complexes are reported in Table I.

### 2.2. $H_2L_E$

$H_2L_E$ was prepared for condensation of 1,5-diamino-3-azamethylpentane (1 mmol) with 3-methoxy-2-hydroxybenzaldehyde (2 mmol) in methanol (200 ml). The crude dark brown oil, separated after addition of ether, was purified by repeatedly dissolving in methanol, separating with ether and drying under vacuum (yield 50%).

### 2.3. $M(L) \cdot nH_2O$ ($M = Cu^{2+}, Ni^{2+}, Co^{2+}$) and $Mn(L)(CH_3COO) \cdot nH_2O$ ($L = L_A - L_D$)($n = 0-2$)

To a methanolic solution (60 ml) of the diformyl precursor (1 mmol), ethylenediamine (1 mmol) in methanol (10 ml) was added dropwise. To the resulting yellow solution the appropriate $M(CH_3COO)_2 \cdot nH_2O$ (1 mmol) in methanol (30 ml) was added and the resulting solution, red for Co(II), brown for Mn(III), orange for Ni(II) or green for Cu(II) was refluxed for 2h, then evaporated to dryness. The residue was dissolved in EtOH (20 ml); the precipitate obtained by addition of diethylether was washed with an ethanol/diethylether solution and dried in vacuo (30–40% yield).

### 2.4. $MNa(L)(CH_3COO) \cdot nH_2O$ and $MnNa(L)(CH_3COO)(OH)$ ($M = Ni^{2+}, Cu^{2+}, Co^{2+}$; $L = L_A, L_B, L_C$; $n = 1, 2$)

A hot yellow methanolic solution (50 ml) of the appropriate macrocyclic Schiff base (1 mmol) was reacted with $M(CH_3COO)_x \cdot nH_2O$ (1 mmol) in 10 ml of methanol. The solution was stirred for 15 min, then NaOH (2 mmol) in methanol (15 ml) was added. The resulting solution, red for Co(II), brown for Mn(III), red or green for Ni(II) and brown for Cu(II) was refluxed for 2h, then evaporated to dryness under reduced pressure. The residue was dissolved in $CHCl_3$ and the solution was clarified by filtration and evaporated to dryness. The residue was dissolved in ethanol (15 ml). The precipitate obtained by addition of diethylether (30 ml) was filtered, washed with an ethanol/diethylether solution and dried in vacuo.

Alternatively the chloroform solution, by addition of diethyl ether, separated a precipitate, which was collected by filtration, washed with diethylether and dried in vacuo.

## 2.5. Solution Studies

The cobalt adducts were used for preparing by weight stock solutions of the metal ion ($[Co^{2+}] \sim 50\,mM$) in DMSO. Working solutions of $Co^{2+}$ were prepared by appropriate dilution of the cobalt stock with 0.1 mM tetraethylammonium perchlorate.

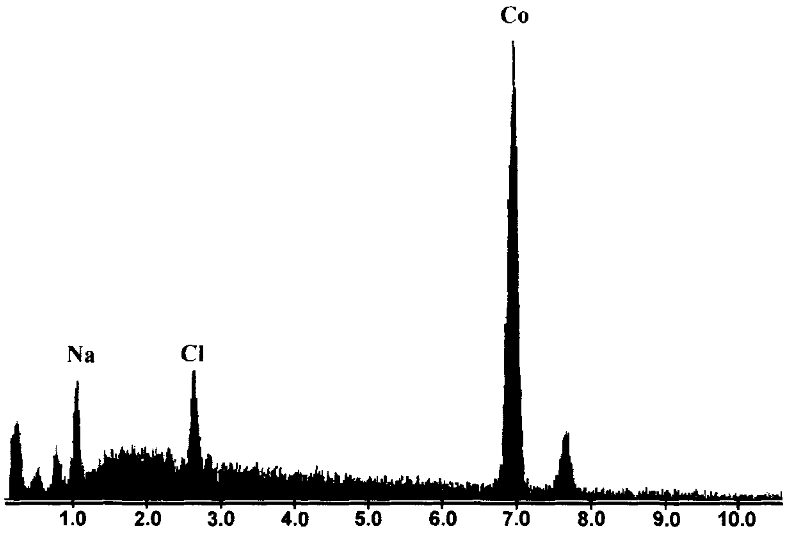
Extreme care was taken to obtain and maintain the lowest water and oxygen content in the systems throughout the experiments carried out to characterize the solution chemistry of heteropolytopic ligands. All solutions were prepared and stored in a controlled atmosphere chamber (Braun model MB 150B-G-I) filled with dry nitrogen ($O_2 < 2\,ppm$ and $H_2O < 1\,ppm$). Before being introduced into the chamber, the apparatus and nonvolatile samples were degassed in a transport that was evacuated and purged with dry nitrogen. All the experiments were conducted at $25.0 \pm 0.1°C$ and in an ionic medium of perchlorate 0.1 mM. To create this ionic medium anhydrous tetraethylammonium perchlorate was used.

A Tronac precision titration calorimeter, Model 87-558, equipped with a 25 ml titration vessel, was used. The cover of the titration vessel and its connection to the calorimeter were modified in order to make a gasproof closure possible. Both the vessel and the piston burette were filled inside the controlled atmosphere chamber, joined together, taken out of the chamber, and connected to the calorimeter for measurements. For each titration run, $n$ experimental values of the total heat produced in the reaction vessel ($Q_{ex,j}$, $j = 1$ to $n$) were calculated as a function of the volume of the added titrant. These values were corrected only for the heat of dilution of the titrant ($Q_{dil,j}$), which was determined separately, because the heat of dilution of the titrate was found to be negligible in the ligand concentration range used. The net reaction heat at the $j$-th point ($Q_{r,j}$) was obtained from the difference: $Q_{r,j} = Q_{ex,j} - Q_{dil,j}$. The quantity $\Delta h_v$ was then calculated by dividing the net reaction heat with the number of moles of metal in the calorimeter vessel. The formation constants of the identified complexes, the enthalpy and entropy changes of the complexation were calculated by using a FORTRAN program MQF90 [25] with $\Delta h_v$ as the error-carrying variable.

## 2.6. Physico-chemical Measurements

IR spectra were recorded as KBr pellets on a Mattson 5000 FT-IR spectrometer. The same instrument, connected to a Quantum microscope equipped with a MCT detector, was used to collect the spectral data directly on the samples and eliminate the risk of metathetic processes with KBr matrix.

FT-IR spectroscopy was also used to study the interactions between metal ions and $H_2L_A$, $H_2L_B$ and $H_2L_E$ in DMSO. The IR spectra in the range $4000-850\,cm^{-1}$ were recorded under dry-air purge at $25 \pm 1°C$ on a Nicolet Magna FT-IR spectrometer with $2\,cm^{-1}$ resolution and 256 scans. Cells with barium fluoride windows (optical path $\sim 28\,\mu m$) were used. The cells were filled with sample solutions in the controlled atmosphere chamber, tightly closed, and quickly transferred into the spectrometer. The spectra of DMSO and the sample solutions were recorded separately, ratioed against background and converted to absorbance units. Successively, the DMSO spectrum was numerically subtracted from sample solution spectra to obtain the difference spectra. Due to the high molar absorbance of DMSO, six spectral regions of the solvent spectrum, in the range $4000-850\,cm^{-1}$ (3020-2980, 2930-2895, 1450-1400, 1340-1300, 1075-995, $970-920\,cm^{-1}$), resulted almost blind (see Fig. 1 of supplementary material). As a result, besides difficult, the spectral subtraction in these zones is meaningless. Therefore, the values



| Element | Wt% | At% |
|---|---|---|
| NaK | 26.00 | 46.01 |
| ClK | 6.34 | 7.28 |
| CoK | 67.65 | 46.71 |
| Total | 100.00 | 100.00 |

FIGURE 1 SEM-EDS of $[CoNa(L_A)(CH_3COO)] \cdot 2H_2O$ evidencing the Na : Co = 1 : 1 ratio (a) and the homogeneity of the sample (b). The presence of chlorine is due to chlorinated solvents used for the purification of the sample.

of absorbance in the above regions were not reported in the spectra given as supplementary materials.

Spectra in the UV-VIS region were collected with a standard 0.1 cm quartz cell and a Cary 5E spectrometer. Also in this case all preliminary operations were carried out in controlled atmosphere chamber in order to avoid the contact of the solutions with atmosphere.

$^1H$, $^{13}C$ and $^{23}Na$ NMR spectra were recorded at 300.13 MHz on a Bruker AMX300 spectrometer at room temperature. Some of the signals were assigned by the spin decoupling technique. All the samples examined were dissolved in deuterated methanol or DMSO used also as internal references. The morphology, homogeneity and the metal:sodium ratio 1 : 1 in the complexes were checked by using a Philips XL40 model scanning electron microscopy equipped with an EDAX DX PRIME X-ray energy dispersive spectrometer [26].

The water content in the prepared samples was evaluated by thermal analysis curves using a Netzsch STA 429 thermoanalytical equipment. The tests were performed in a nitrogen atmosphere (flux rate 250 ml/min; heating rate $5° C\,min^{-1}$) and in air under the same conditions. Neutral alumina (Carlo Erba product) was used as reference material.

All mass spectrometric measurements were performed on a VG ZAB 2F instrument (VG analytical Ltd.) operating in fast atom bombardment (FAB) conditions (8 KeV Xe atom bombarding a nitrobenzylalcohol solution of the sample) [27]. Also ESI-MS spectra have been recorded by using a LCQ mass spectrometry (Finnigam) and methanol solutions of the samples ($10^{-5}$ M).

Magnetic susceptibilities were determined by the Faraday method at room temperature, the apparatus (Oxford Instruments) being calibrated with $HgCo(NCS)_4$ [28]. Diamagnetic corrections were performed [29].

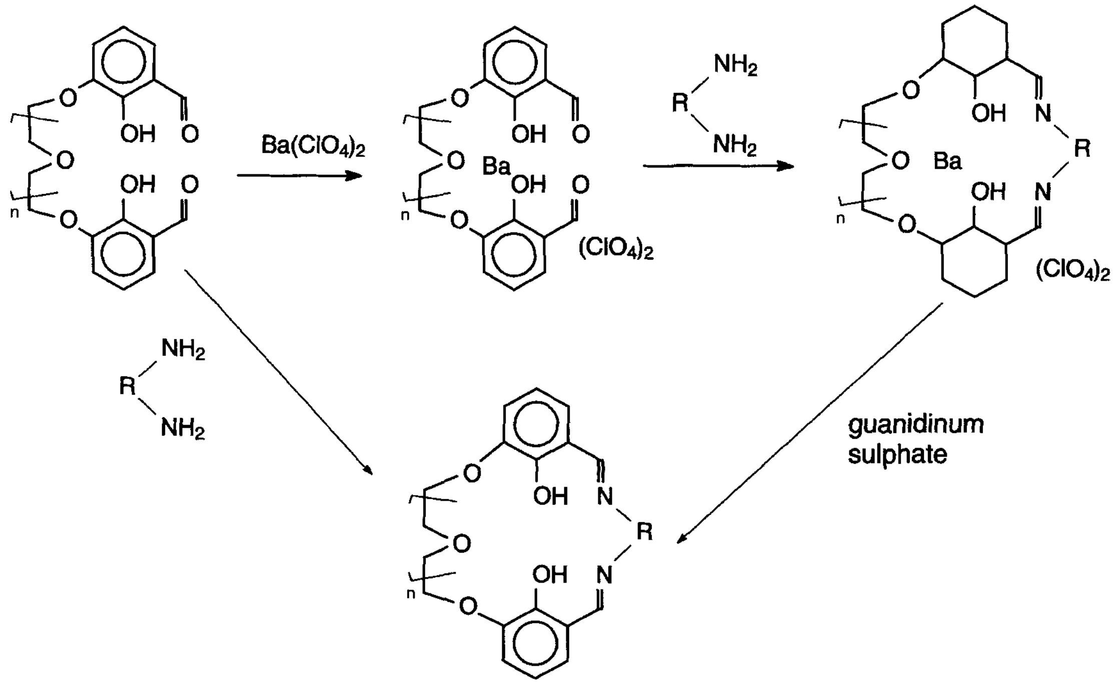
## 3. RESULTS AND DISCUSSION

### 3.1. Preparation of the Ligands and Complexes

The diformyl precursors $H_2L^I$ and $H_2L^{II}$, where $H_2L^I$ is 3,3′-(3-oxapentane-1,5-diyldioxy)bis(2-hydroxybenzaldehyde) and $H_2L^{II}$ is 3,3′-(3,6-dioxaoctane-1,8-diyldioxy)bis(2-hydroxybenzaldehyde), obtained by reaction of the appropriate ditosylate derivative and 2,3-dihydroxybenzaldehyde in the presence of NaH [20, 21] react in acetonitrile or methanol with an equimolar amount of polyamine (1,5-diamino-3-azamethylpentane or ethylenediamine) to form the corresponding [1 + 1] asymmetric cyclic compartmental Schiff bases $H_2L_A - H_2L_D$ (Scheme 4). Alternatively $H_2L_B$ and $H_2L_D$ have been prepared by demetallation with guanidinium sulphate of the macrocyclic barium complex, $Ba(H_2L)(ClO_4)_2$ ($H_2L = H_2L_B$, $H_2L_D$) followed by the extraction of the residue with $CHCl_3$ [21, 22]. The macrocyclic barium complexes have been synthesised by condensation of the appropriate acyclic complexes, $Ba(H_2L^I)(ClO_4)_2$ or $Ba(H_2L^{II})(ClO_4)_2$, derived by reaction in ethanol of $H_2L^I$ or $H_2L^{II}$ with equimolar amount of $Ba(ClO_4)_2 \cdot nH_2O$, with 1,5-diamino-3-azapentane or ethylenediamine (Scheme 4).

As the self condensation pathway may give, as by products, the larger [2 + 2] or [3 + 3] macrocycles or $[1 + 1]_n$ polymers and the metallation–demetallation processes give the desired macrocycle in a poor yield, the macrocyclic ligands $H_2L_A - H_2L_D$ have been obtained in high yield and in pure form by using high dilution techniques in methanol-diethyl ether solution. Further purification of these products by chromatography on allumina, using $CHCl_3$ as eluant, gave very pure samples of $H_2L_A$ and $H_2L_B$, suitable for solution measurements [30].

The prepared Schiff bases are yellow solids, stable in air, very soluble in $CHCl_3$ and lightly soluble in DMSO. A strong ir band at



SCHEME 4 Formation of the asymmetric cyclic ligands $H_2L_A - H_2L_D$.

$1635-1630\,cm^{-1}$, due to $\nu$ C=N and the contemporary absence of bands attributable to $\nu$ C=O or $\nu$ $NH_2$ support the formation of the cyclic species.

$H_2L_E$, obtained by condensation of 3-methoxy-2-phenoxybenzaldehyde with 1-5,diamino-3-azamethylpentane is a brown-yellow oil soluble in common organic solvents. Its IR spectrum shows a strong band at $1631\,cm^{-1}$, due to $\nu$ C=N while $^1H$ nmr spectrum in $CDCl_3$ shows a broad singlet at 13.95 ppm (phenolic protons), a singlet at 8.25 ppm due iminic protons, a doublet of doublets at 6.88 ppm and a multiplet at 6.73 ppm, attributed to aromatic protons, and peaks at 3.89 ppm (singlet, $OCH_3$), 3.66 ppm (triplet, $CH_2N{=}C$), 2.77 ppm (triplet, $CH_2N$) and 2.36 ppm (singlet, $CH_3$).

$H_2L_A-H_2L_D$ react with $M(CH_3COO)_2 \cdot nH_2O$ ($M = Cu^{2+}$, $Ni^{2+}$, $Co^{2+}$) or $Mn(CH_3COO)_3 \cdot 2H_2O$ in refluxing alcoholic solution and in a 1:1 molar ratio to form respectively $M(L) \cdot nH_2O$ and $Mn(L)(CH_3COO) \cdot nH_2O$. The same copper(II) and nickel(II) complexes have been obtained also by template procedure.

For cobalt (II) a nitrogen atmosphere was used to eliminate possible oxidation processes. It was qualitatively verified that the oxidation of cobalt(II) to cobalt(III) is not very fast: the colour of a solution of the complex, dissolved in dimethylsulphoxide or dimethylformamide and allowed to stand in air, change (from red-brown to green-dark brown) only after some hours. However a vigorous stirring of the solution produces significant variation of the colour about after one hour.

The ir spectra of the complexes show a strong peak at $1640-1616\,cm^{-1}$, due to $\nu$ C=N. Additional bands at $1552\,cm^{-1}$ ($\nu_{asym}$ COO) and at $1318-1392\,cm^{-1}$ ($\nu_{sym}$ COO), due to the acetate group possible acting as monodentate are clearly detectable in the ir spectra of the manganese(III) complexes $Mn(L)(CH_3COO) \cdot nH_2O$. The absence of these bands in the spectra of the complexes of the bivalent metal ions rules out the possible presence of acetate groups and confirm the $M(L) \cdot nH_2O$ stoichiometry suggested by elemental analyses.

Using different experimental conditions (*i.e.*, no or a very gentle reflux), cobalt(II) complexes of the type $Co(H_2L)(CH_3COO)_2 \cdot nH_2O$ have been obtained. For these complexes the infrared spectra evidence strong peaks, due to acetate groups. For instance for the complex $Co(H_2L_B)(CH_3COO)_2$ strong absorption at $1606\,cm^{-1}$ and at $1450\,cm^{-1}$, respectively due to the antisymmetric and symmetric $\nu$ COO have been detected.

Magnetic and electronic data suggest that the nickel(II), cobalt(II) and copper(II) metal ions in the complexes $M(L_A) \cdot nH_2O$ and $M(L_C) \cdot nH_2O$ are in an approximately square planar environment. The copper(II) complexes show a magnetic moment of 1.7-1.8 BM. The nickel(II) complexes are almost diamagnetic (0.6 BM) while the magnetic moment for the cobalt(II) complexes is 2.1 BM; these magnetic values are typical of a square planar configuration about the central metal ion. Electronic spectra in chloroform of nickel(II) and copper(II) complexes showing a band at ≅565 nm (Ni) and at 561 nm (Cu) give further evidence about this coordination mode of both metal ions in related complexes.

The square planar configuration of the nickel(II) complexes with $L_A^{2-}$ and $L_C^{2-}$ and hence their diamagnetism, allowed an nmr investigation. Thus the $^1H$ nmr spectrum of $Ni(L_C) \cdot 0.5H_2O$ in $CDCl_3$ showed the presence of a singlet at 7.24 ppm due to imine protons, two doublets of doublets at 6.59-6.33 ppm due to four aromatic protons and a triplet at 6.25-6.18 ppm due to the remaining two aromatic protons. Moreover two triplets lie at 3.99-3.95 ppm, due to eight protons belonging to the etheric chain, and two singlets lie at 3.82 and 3.42 ppm, due to four protons of the etheric chain and to the methylenic groups bound to the iminic group. A lowering of the resonance of the imine protons from 8.25 in ($H_2L_C$) to 7.24 ppm reflects the Schiff base occupancy.

An ESI-MS electrospray mass spectrometry for $Co(L_C)\cdot nH_2O$ evidences peaks due to $[CoL_CH]^+$, $[CoL_CNa]^+$ and $[CoNaL_C(CH_3OH)]^+$ at 471, 494 and 525 m/z respectively with the fragmentation pattern reported in Scheme 5.

In the $Mn(L_A)(CH_3COO)$ and $Mn(L_C)(CH_3COO)$ a magnetic moment of 5.0 and 5.5 BM was found in agreement with the presence of a manganese(III) which, on the basis of ir data may be in a pentacoordinate or octahedral environment.

Finally, the magnetic moment of 3.1 – 3.2 BM found for the cobalt(II) complexes $Co(H_2L)(CH_3COO)_2\cdot nH_2O$ ($H_2L = H_2L_A - H_2L_D$) suggests a severe distortion from the planarity toward a tetrahedral or octahedral configuration. In agreement with such a configuration, their electronic spectra show a band at $\cong 610$ nm.

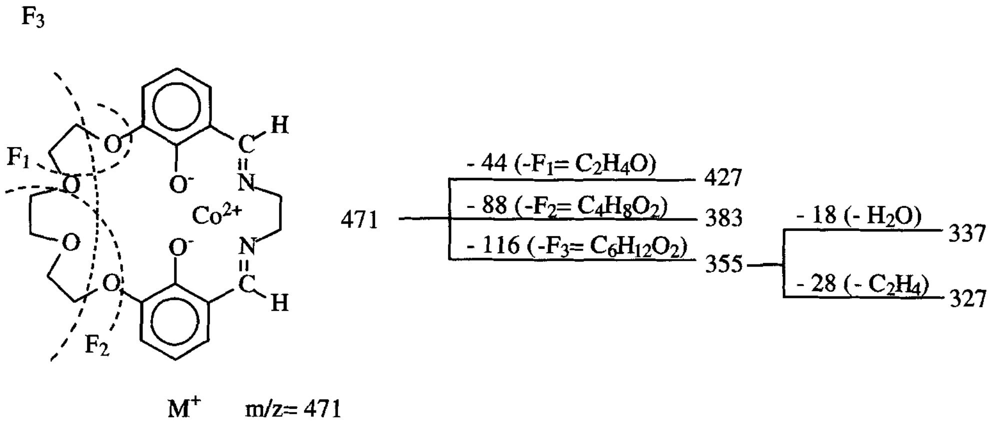
Thus, according to the above reported physico-chemical data, the transition metal ion invariantly occupies the Schiff base site in the mononuclear cyclic complexes. These complexes in turn contain a free and adjustable "crown-ether-like" coordination chamber and can be used as "ligands" towards appropriate hard metal ions giving rise to pure positional isomers.

It is well known, for example, the ability of crown-ethers to bind selectively alkali ions strongly depending on the dimension and on the denticity of the coordination moiety [31, 32]. Moreover, it has been recently observed that also lanthanide(III) ions, when reacted with the macrocyclic Schiff bases $H_2L_A - H_2L_D$, invariantly prefers the $O_2O_n$ chamber [16, 17].

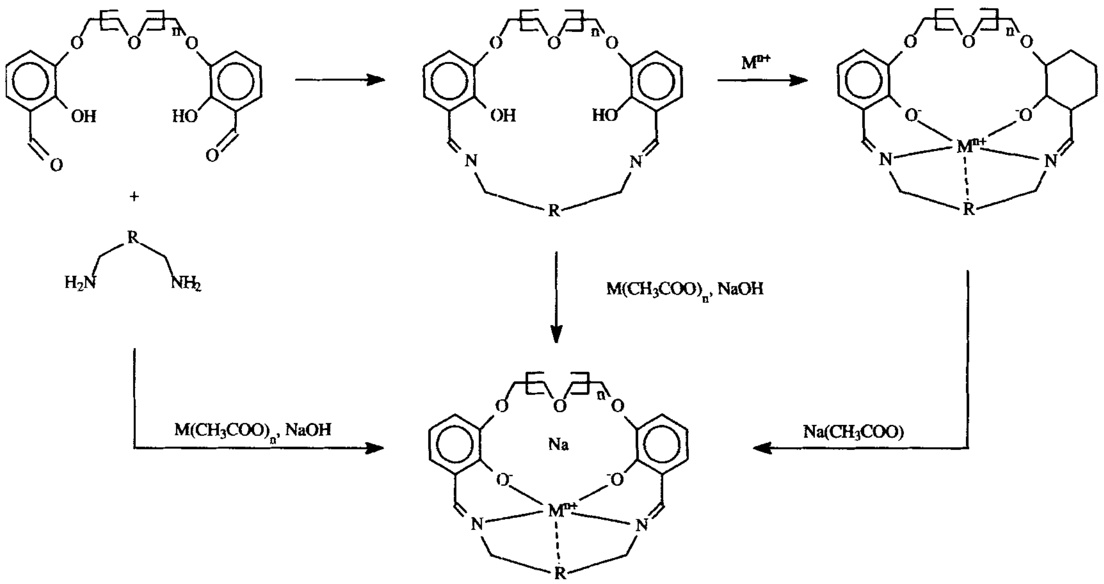
In agreement with this behaviour, the high selectivity of the two chambers towards different metal ions allowed an *in situ* preparation of heterodinuclear complexes of the type $MNa(L)(CH_3COO)\cdot nH_2O$ and $MnNa(L)(CH_3COO)_2\cdot nH_2O$. They were prepared by reaction of the appropriate Schiff base ($H_2L$) with the desired metal acetate in the presence of NaOH. The homogeneity of the complexes and the correct M : Na ratio are well evidenced in Figure 1 where the results of a SEM analysis on the complex $[CoNa(L_A)(CH_3COO)]\cdot 2H_2O$ are reported as an example of hetero-dinuclear complexation.

The overall synthetic pathway for the preparation of mononuclear and heterodinuclear complexes is reported in Scheme 6.

The ir spectra of the heterodinuclear complexes show strong bands at 1619 – 1639 $cm^{-1}$, due to $\nu$ C=N and at 1580 – 1604 $cm^{-1}$ and at 1313 – 1406 $cm^{-1}$, due to the asymmetric and symmetric stretching of the acetate groups. Magnetic data suggest a square planar coordination about the central metal ion in the complexes $MNa(L_A)(CH_3COO)$ and $MNa(L_C)(CH_3COO)$ ($M = Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$). The nickel(II)



SCHEME 5 Fragmentation pattern of $Co(L_C)\cdot nH_2O$ complex.



SCHEME 6 Preparation of mononuclear and heterodinuclear complexes.

complexes are diamagnetic (≅0.4 BM), the cobalt(II) complexes have a magnetic moment 2.2–2.8 in line with a square planar coordination. The electronic spectra parallel those of the mononuclear analogues. The $^1$H-nmr spectra of $NiNa(L_C)(CH_3COO)$ in $CD_3OD$ shows a peak at 7.55 ppm (iminic protons), at 6.88–6.38 ppm (aromatic protons), 4.28, 3.88 and 3.74 ppm (ethylenic $OCH_2CH_2O$ protons) and at 3.44 ppm (ethylenic $NCH_2CH_2N$ protons).

In $NiNa(L_B)(CH_3COO)$ and $NiNa(L_D)(CH_3COO)$ the magnetic moment of ≅3.5 BM suggest an octrahedral environment about the central metal ion.

### 3.2. Solution Studies

The aim of these investigations was to acquire information about the nature of the complexes in solution and to obtain a set of comparable formation constants and reaction enthalpies. To achieve this aim, various solvent systems were examined. Unfortunately, ligands $H_2L_A$–$H_2L_D$ are almost insoluble in many solvents commonly used to study complexation reactions (water, methanol, ethanol) and only slightly soluble in acetonitrile (AN) and dimethylsulfoxide (DMSO). Thus, preliminary measurements were performed in AN and DMSO to find the best experimental technique to carry out thermodynamic studies. For various reasons, spectrophotometry and potentiometry, which could allow determination of the formation constants, were discarded.[1] Calorimetry seemed to be the most promising technique as, in certain circumstances, it allows simultaneous evaluation of formation constants and reaction enthalpies. In particular, as already observed [33], calorimetry may profitably be used if formation constants are not too high. In this case while enthalpies may be accurately calculated, it is impossible to obtain reliable values for formation constants. This eventuality was estimated as highly probable in AN, which has a low Gutmann donor

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[1] Spectrophotometry was discarded, as the low solubility of the ligands (see below) and the very low absorption coefficient of the metal ion made it impossible to create opportune experimental conditions to show complexation. Potentiometry was not used either, since it was impossible to find selective metal ion electrodes that worked appropriately in nonaqueous solutions.

number [34] and dielectric constant (DN = 14.1, $\varepsilon = 35.94$), so that the more solvating DMSO (DN = 29.8, $\varepsilon = 46.45$) was used.

Studies were limited to the complexation of cobalt(II) and sodium(I) with $H_2L_A$ and $H_2L_B$. These two ligands were chosen in order to show the effects of the different number and nature of the basic sites on the kinetics and thermodynamics of complexation. Cobalt(II) was selected, as the present study was starting-point of more general research on the preparation and investigation of new synthetic systems for transport and activation of dioxygen, and $Co^{2+}$ due to its well-known ability to bind molecular dioxygen [35], seemed to be an ideal candidate for basic studies of this kind. Lastly, sodium ion was chosen as heteroatom, both for its known ability to complex cyclic polyethers in DMSO [36] and for the intrinsic interest which stable hetero-bimetallic complexes of Na(I) and Co(II) may have when employed as dioxygen probes in $^{23}$Na-NMR experiments. With the purpose of elucidating the role of ligand preorganization on the stability of the complexes in solution, we prepared a simpler open chain compound ($H_2L_E$) having the same Schiff base moiety as $H_2L_B$.

To provide insights into the nature of the metal/ligand systems, FT-IR and UV-Vis experiments were carried out before calorimetric measurements. FT-IR measurements were performed to follow changes in the vibrational spectra of the Schiff bases upon coordination. In UV-Vis measurements, changes in intensity of bands in the region where $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions occur were followed.

The FT-IR subtraction spectra of $H_2L_A$, $H_2L_B$ and $H_2L_E$ were very similar (see Fig. 2, suppl. mat.). In particular, there were three intense bands in the region 1760 - 1100 $cm^{-1}$: the band at 1630 $cm^{-1}$, attributable to C=N stretching [37], two intense bands at 1273 and 1254 $cm^{-1}$ in the region of Ar-O-$CH_2$ and Ar-OH stretchings [37], and one near 1470 $cm^{-1}$, which may be a multicomponent band, as many vibrations characteristic of particular groups of the molecules appear in this region: O-$CH_2$ deformation bands of ethers, C=C stretchings of aromatic groups, in-plane C-H bend bands, and those due to $CH_3$ and $CH_2$ groups [37]. The less intense band at 1135 $cm^{-1}$, not visible in the $H_2L_E$ spectrum, could confidently be assigned to C-O-C stretching; the vibration at 2799 $cm^{-1}$, not appearing in the $H_2L_A$ spectrum, was safely assigned to $CH_3N$ stretching. Lastly, it should be noted that the bands intensities due to stretchings of the OH groups (3400 - 3600 $cm^{-1}$) decreased in the molecule lacking in conformational restraints ($H_2L_E$).

The UV-Vis absorption spectra (280 nm < ) of the ligands were also similar (Fig. 3 suppl. mat.). They consisted of a relatively intense band centered at 318 nm, involving $\pi \rightarrow \pi^*$ transitions [38] and a low intensity feature in the 380 - 450 nm region, responsible for the yellow color of the ligands and complexes in solution, and presumably involving $n \rightarrow \pi^*$ excitation [38].

### 3.2.1. *System Co(II)/$H_2L_B$*

Formation of Co/$H_2L_B$ complexes was followed by collecting the FT-IR spectra of a series of solutions of $H_2L_B$ (50 mM) and $Co^{2+}$ with different ligand/metal ratios ranging from 10/1 to 1/1, as well as the spectrum of the ligand alone. Complexation implied an immediate change in the $H_2L_B$ spectrum in the region assigned to C=N stretching and in those ascribed to Ar-O and $NCH_3$ (Fig. 4 suppl. mat.). In the region near 1630 $cm^{-1}$, the ligand band showed a very limited red shift (from 1630 to 1632 $cm^{-1}$), whereas the two weak bands at 1600 $cm^{-1}$ and 1586 $cm^{-1}$ became evident with increasing metal ion concentration. At the same time, a new vibration at 1213 $cm^{-1}$ originated and the band ascribed to $NCH_3$ stretching (2799 $cm^{-1}$) (Fig. 5, suppl. mat.) progressively decreased, disappearing at $H_2L_B$ / $Co^{2+} \leq 3$.

No significant differences between the spectra of the solutions containing 3/1, 2/1, and 1/1

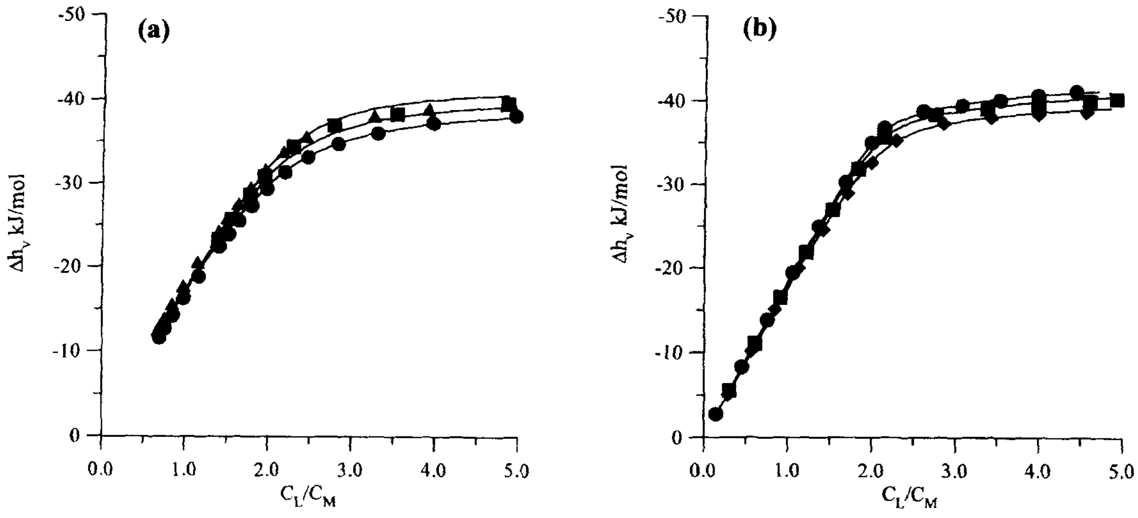

FIGURE 2 $Co^{2+}-H_2L_B$ (a) and $Co^{2+}-H_2L_E$ (b) systems in DMSO. $\Delta h_v$ as a function of the ligand to metal ratio $C_L/C_M$. (a) $C^o_{H_2L_B}$, $C^o_M$: 5.20, 50.0 mM (●); 8.60, 50.0 mM (▲); 17.10, 50.0 mM (■). (b) $C^o_M$, $C^o_{H_2L_E}$: 2.50, 80.8 mM (▼); 6.25, 217.0 mM (■); 12.5, 217.0 mM (●).

$H_2L_B/Co^{2+}$ ratio were observed, and the spectra were not time-dependent.

UV-Vis spectra of solutions $H_2L_B$ 2 mM and concentrations of $Co^{2+}$ increasing from 0.2 to 2 mM (Fig. 6, suppl. mat.) showed that complexation involved decrease of the ligand band at 430 nm and the formation of a shoulder at about 370 nm, near the principal absorption band of the ligand at 330 nm. Here too the spectra did not change with time.

The disappearance of the peak at 2799 cm$^{-1}$ from the FT-IR spectra when the metal to ligand ratio is $\geq 1/3$ suggested involvement of the amino nitrogen of the ligand, at least with the formation of a strong complex with 1 : 3 M : L stoichiometry. This result was rather surprising, as the formation of cobalt(II) complexes higher than ML was never observed in preparative works, most probably because preparative procedures were especially designed in order to obtain stable 1 : 1 complexes, in which the ligands had lost one or both their acid phenol protons. Evidently, in the experimental conditions adopted to carry out FT-IR measurements, the acid protons of the ligand are less prone to release and this facilitates the formation of higher complexes of $Co^{2+}$.

The FT-IR difference spectra of solutions containing $[Co^{2+}] = 50$ mM and increasing concentrations of $H_2L_E$, from 50 to 250 mM, have peaks of shape, relative intensity and spectral position very similar if not equal to those observed in the $Co^{2+}/H_2L_B$ system (Fig. 7, suppl. mat.). Also in this case, the characteristic band of $NCH_3$ stretching which appeared at 2799 cm$^{-1}$ only when the $C_L/C_M$ ratio was higher than 3 is noteworthy.

More information on the nature and relative stability of $H_2L_B$ and $H_2L_E$ complexes in solution were obtained from calorimetric measurements. The heats of formation of $Co^{2+}$ complexes with $H_2L_B$ were determined by adding a metal solution of concentration $C^o_M$ at a constant rate ($\sim$0.2 mL min$^{-1}$) to a ligand solution of concentration $C^0_{H_2L_B}$. $C^0_{H_2L_B}$ was in the range of 5 to 18 mM and $C^o_M$ was $\sim$50 mM. The formation of $H_2L_E$ complexes was followed by adding ligand solutions, of concentration $C^0_{H_2L_E}$ (from 80 to 220 mM), to the metal solutions of concentration $C^o_M$ (from 2.5 to 12.5 mM).

$\Delta h_v$ *vs.* $C_L/C_M$ data, obtained under a carefully controlled nitrogen atmosphere for the $Co^{2+}/H_2L_B$ and $Co^{2+}/H_2L_E$ systems, are shown in Figure 2a and b, respectively.

For both systems, almost equal plots of the overall enthalpies per mole of metal were obtained. Figure 2 shows that the $\Delta h_v$ values increase, overlapping almost linearly up to $C_L/C_M = 2$, and differentiate for higher values of the metal/ligand ratio. This is typical when the formation of two strong complexes with similar stepwise constants and similar enthalpies is followed by the formation of a third weaker complex.

The high stability of the first two complexes is probably due to the large co-operative effect between the nitrogen atoms of the ligand. Involvement in the cobalt(II) coordination of the imino nitrogens of the ligand, in addition to tertiary amino nitrogen, is strongly supported by the following experimental evidence: (a) it has already been observed that tertiary monoamines show scarce affinity for cobalt(II) in solution [36], and it would be rather surprising if the ligands act as monodentate in this case; (b) the UV-Vis spectra of DMSO solutions containing different ratios (from 1 : 0 to 1 : 1, 1 : 2, and 1 : 5) of $Co^{2+}$/N-methylpiperidine (the most basic and soluble in DMSO tertiary amine we could find) did not show any change in the range 300–900 nm and, similarly, no changes in the FT-IR difference spectra of the N-methylpiperidine were observed upon addition of $Co^{2+}$; (c) no heat changes were observed when N-methylpiperidine $\approx 1$ M was added to a DMSO solution $\approx 50$ mM in $Co^{2+}$; (d) the high stability of the Co(II) complexes of $H_2L_B$ and $H_2L_E$ is largely due to the favourable enthalpies of reaction which, in DMSO, can only be the result of multiple ligand-metal bonding.

The processing of calorimetric data for $Co^{2+}/H_2L_E$ gave quite accurate values for the formation constants and the relative enthalpies of reaction. Conversely, for the $Co^{2+}/H_2L_B$, system, probably due to the larger constraints associated with the study of this system, only much less accurate values could be obtained.

Table II lists the values obtained from data processing. The full line plots of Figure 2 were obtained with these values, and reproduce the experimental data well or sufficiently well. Notwithstanding the large approximation of some of the thermodynamic parameters, note the close similarity of the values obtained for the $H_2L_B/Co^{2+}$ and $H_2L_E/Co^{2+}$ systems (reflected in the similarity of the experimental plots), we may draw the conclusion that, in both systems, the same donor atoms are involved in the cobalt coordination. Moreover, the high values of stepwise $\log K_1$, $\log K_2$, $\Delta H_1$ and $\Delta H_2$ strongly support the hypothesis that, in the first two complexes, all the nitrogens of the ligands are involved in coordination. The fact that C=N stretching absorption is only insignificantly shifted ($2\,cm^{-1}$) upon complexation is not unusual. It may be explained by admitting substitution of the primitive hydrogen bond H(phenol)-N(imine) in the free ligand, by interaction of the imino nitrogen with cobalt(II) in the complex. Evidently, the above two interactions exert very similar effects on C=N stretching. In addition, the lowering of Ar–O–C absorption to $1213\,cm^{-1}$ indicates that the break of the H(phenol)-N(imine) hydrogen bond is probably followed by the formation of a similar interaction between phenol hydrogens and ether oxygens.

The third complex stepwise formation constant is one order of magnitude smaller than those of the first two and, at the same time, the corresponding enthalpy change is reduced to about one-third. Due to the inability (see above) of single tertiary amino nitrogen to bind $Co^{2+}$ in DMSO to form stable complexes, it is reasonable that $ML_3$ is octahedral, with each ligand bound to the metal ion by chelate rings involving the amine and one of the imine nitrogen atoms.

Lastly, note the similarity between the thermodynamic data of the complexes formed by $H_2L_B$ and $H_2L_E$ with cobalt(II), *indicating that*

TABLE II Thermodynamic data for $Co^{2+}/H_2L_B$ and $Co^{2+}/H_2L_E$ systems

| | | $H_2L_B$ | | $H_2L_E$ | |
|---|---|---|---|---|---|
| Reaction | j | $\log K_j$ $mol^{-1}$ | $-\Delta H_j$ kJ/mol | $\log K_j$ $mol^{-1}$ | $-\Delta H_j$ kJ/mol |
| $Co^{2+} + H_2L \rightarrow [Co(H_2L)]^{2+}$ | 1 | 3.7 ± 0.2 | 18.2 ± 1.2 | 3.86 ± 0.08 | 17.6 ± 0.6 |
| $[Co(H_2L)]^{2+} + H_2L \rightarrow [Co(H_2L)_2]^{2+}$ | 2 | 3.6 ± 0.4 | 19.3 ± 3.0 | 4.05 ± 0.23 | 19.8 ± 1.5 |
| $[Co(H_2L)_2]^{2+} + H_2L \rightarrow [Co(H_2L)_3]^{2+}$ | 3 | 2.5 ± 0.3 | 7.3 ± 3.6 | 2.12 ± 0.24 | 5.4 ± 2.7 |

pre-organization of donor atoms in $H_2L_B$ does not add any significant contribution to the stability of the complexes in solution.

### 3.2.2. *System $Na^+/H_2L_B$*

$Na^+$ forms complexes with $H_2L_B$ slowly and with erratic kinetics which are difficult to control. In fact, the time required to reach equilibrium (*i.e.*, invariance of FT-IR spectra) in two identical experiments, repeated on different occasions, was quite different. This phenomenon was not investigated further, due to our main interest in determination of the stability constants of the complexes.

After a sufficient wait, the subtracted spectra of solutions of $H_2L_B/Na^+ = 100/100$ mM (Figs. 8 and 9, suppl. mat.), showed the following features:

(i) an increase in intensity and a blue shift of the C=N stretching band;
(ii) a corresponding red shift of the band at $1253\,cm^{-1}$ (Ar–O stretching);
(iii) a robust increment in band absorbances at about 1540 and $1520\,cm^{-1}$ and a decrease in the band at $1470\,cm^{-1}$ (zone of C–C skeletal and O–H phenol stretching vibrations)

Time changes of the spectra of solutions having different $Na^+/H_2L_B$ ratios (from 2/1 to 1/2) also suggest that the reaction rate is in some way influenced by the concentration of $Na^+$. However, after a sufficient amount of time, all the spectra did not differ from each other.

These spectral changes are compatible with the slow formation of a 1 : 1 complex between $Na^+$ and $H_2L_B$ in which the metal ion is initially located in the ligand $O_3$ cage and progressively extends its coordination to the phenol oxygens, leading to the probable break of the hydrogen bond H(phenol)-N(imine).

In order to verify the coordination ability of $Na^+$ toward the crown-ether-like chamber, $^1H$ 300 MHz nmr spectra were collected of a solution containing $H_2L_B/Na^+ = 100/100$ mM in DMSO-$d_6$. The measurements were carried out periodically for a long period of time (≅5 days) to allow the completeness of the reaction. The comparison of these spectra (Tab. III) with that of a solution 100 mM of $H_2L_B$ in DMSO-$d_6$, evidences:

- no variation of the resonance due to methyl and methylenic protons bound to aminic nitrogen;
- an increased multiplicity of the resonances of the methylenic protons of the crown-ether-like site;
- a downfield shift and a contemporary splitting in two signals of the phenolic protons;
- a splitting into two peaks with no relevant shift of the iminic protons.

These data suggest that $Na^+$, when coordinated to the etheric oxygens, restricts the

TABLE III Comparison of $^1H$ nmr spectra in DMSO-$d_6$ of $H_2L_B$ and $[Na(H_2L_B)]^+$

| proton | $H_2L_B$<br>ppm, int, (mult) | $[Na(H_2L_B)]^+$<br>ppm, int, (mult) |
|---|---|---|
| $-C\underline{H}{=}N-$ | 8.37,2, (s) | 8.49,1, (s)–8.48,1, (s) |
| $-CH_2C\underline{H}_2O-Ar$ | 4.05,4, (t) | 4.07,4, (m) |
| $-OC\underline{H}_2CH_2-$ | 3.76,4, (t) | 3.87,4, (m) |
| $=NC\underline{H}_2CH_2-$ | 3.59,4, (t) | 3.79,4, (t) |
| $-C\underline{H}_2N(CH_3)-$ | 2.64,4, (t) | 2.66,4, (t) |
| $-C\underline{H}_3$ | 2.23,3, (s) | 2.26,3, (s) |
| $p\underline{H}-Ar$ | 6.61,2, (t) | 6.40,2, (t) |
| $m\underline{H}-Ar$ | 6.92,2, (d)–6.84,2, (d) | 6.86,4, (d) |
| $-O\underline{H}$ | 13.87,2, (b) | 14.05,2, (mb) |

polyetheric chain motion and hence increases the methylenic peaks multiplicity due to the growing of geminal resonances. Accordingly, the iminic nitrogens are not involved in the coordination and the signals of surrounding protons are almost unaltered. Moreover, the splitting of the peaks due to phenolic and iminic protons, together with their low downfield shift, indicates that $Na^+$ is engaged at least in the coordination of one of the phenol oxygens. This makes the corresponding OH group less prone to give hydrogen bond with the neighbouring imine nitrogen that, therefore, is a bit different from the other imine nitrogen, still engaged in $-OH \cdots N=$ bonding.

Thus, according to the "hard" character of sodium ion, the spectral data show that it occupies the polyether moiety of the macrocycle which still has an $N_3$ moiety capable of coordinating $Co^{2+}$ easily. In order to verify if the formation of heterodinuclear $Na^+-Co^{2+}$ complexes can occur, the addition of $Co^{2+}$ to solutions of the $[Na(H_2L_B)]^+$ complex was periodically followed with a parallel series of FT-IR and UV-Vis measurements.

The introduction of cobalt(II) in the system generated an initial marked variation in both IR and UV-Vis, followed by a slow evolution finally leading to spectral plots which did not differ from those recorded for the $Co^{2+}/H_2L_B$ system. This spectral similarity also reveals that, in excess of cobalt, sodium ion is outside the polyether cage and suggests that the formation of cobalt(II) complexes causes the contemporaneous removal of sodium(I) from the ligand. A similar conclusion may be drawn from the results of calorimetric titration carried out by adding $Na^+ \approx$ 100 mM to a preformed $[Co(H_2L_B)]^{2+}$ complex. As expected, sodium ion cannot enter in the polyether cage of the cobalt complex, and no appreciable thermal effects were observed in this case. According with these results, formation of heterobimetallic complexes of the neutral $H_2L_B$ ligand in DMSO solution seems to be excluded.

However nmr spectroscopy suggests that, even unstable, hetero-binuclear complexes can form in DMSO solution. The isotropic paramagnetic shift of the $^{23}Na$ resonance due to the influence of the paramagnetic $Co^{2+}$ ion, was particularly indicative at this purpose. The evolution of the reaction $[Na(H_2L_B)]^+$ (100 mM) + $Co^{2+}$ (100 mM) in DMSO, monitored by means $^{23}Na$ 79.353 MHz nmr spectroscopy, showed that the behaviour of the reaction for the first four hours agreed with the existence of species where $Na^+$ approaches to $Co^{2+}$, possibly in a hetero-bimetallic complex. The system further (25 hrs) evolved giving rise to species that resemble the behaviour of a sodium ion farther from the paramagnetic centre. Finally, after a long period (60 hrs), the $^{23}Na$ paramagnetic shift of the system was similar to that of the $[Co(H_2L_B)]^{2+}/Na^+$ mixture indicating that no hetero-bimetallic complexation is maintained at all.

### 3.2.3. *System $Co^{2+}/H_2L_A$*

FT-IR and UV-Vis experiments clearly showed that the formation of complexes between $Co^{2+}$ and $H_2L_A$ was quite slow. As in the case of $H_2L_B$, metal coordination reflected large changes in spectral regions at 1630, 1470 and 1250 cm$^{-1}$ (Fig. 10, suppl. mat.). These changes evolved with time, and only after about 40′ from solution preparation could the final spectra be recorded. Missing spectral features for some bands indicating complex formation did not allow any conclusion about the stoichiometry of the complexes formed to be drawn. However, the similarity of the spectra obtained for complexation of cobalt(II) with $H_2L_A$ and $H_2L_B$ suggests that, also in this case, the metal is bound to the iminic nitrogen and that rearrangement of the hydrogen bonding in the ligand is induced.

### 3.2.4. *System $Na^+/H_2L_A$*

All experimental evidence collected for this system unequivocally indicates that $H_2L_A$ is unable to bind sodium ion in DMSO solution. The spectra of the free ligand and of a solution in which the $Na^+/L$ ratio was 1/1, collected after 5 days, were almost identical, with the only exception of the strong band at $1103\,cm^{-1}$ due to the introduction of sodium perchlorate in solution (Fig. 11, suppl. mat.). Moreover, no changes in the UV-Vis spectra of the free ligand (2 mM) were observed with increasing concentrations of $Na^+$ in solution, nor was any heat evolution observed at calorimetric titration of $H_2L_A$ 25 mM with a 100 mM $NaClO_4$ solution.

## 4. CONCLUSIONS

The availability of a series of [1 + 1] macrocyclic asymmetric Schiff bases allows study of the recognition processes occurring at the two adjacent different coordination sites. The soft transition metal ions (*i.e.*, nickel(II), copper(II), cobalt(II), manganese(III)) invariantly occupy the $N_2O_2$ or $N_3O_2$ Schiff base site, whereas sodium is incorporated in the crown-ether-like $O_2O_3$ or $O_2O_4$ chamber.

These different selective coordination processes at the same ligand allow the formation of heterodinuclear *d*-metal ion-sodium complexes in alcohol solution in one pot. Complexes $[MNa(L)(CH_3COO)_n] \cdot xH_2O$ can be prepared by reaction of the appropriate formyl and amine precursors in the presence of $M(CH_3COO)_n \cdot xH_2O$ and NaOH.

Recent studies have unequivocally shown that also lanthanide(III) ions, when reacted with the same ligand, strongly prefer the crown-ether chamber. Again this behaviour, together with the observations reported in the present paper about the preference of the *d*-transition metal ions toward the Schiff base donor set, offers the possibility to synthesise hetero-dinuclear complexes containing d- and f- metal ions $[MLn(L)(X)_3] \cdot nH_2O$ in a single reaction step without the formation of positional isomers by scrambling, migration, transmetallation processes [39].

A common characteristic of these receptors is their insolubility in water and in most usual solvents, with the exception of DMSO, in which they are slightly soluble. When both formation of Co(II) and Na(I) complexes are considered, FT-IR and UV-Vis studies in this medium have shown that the decreased basicity of the ligands and/or their lower flexibility imparted by the absence of the amino group in the Schiff base moiety, results at least in a greatly reduced reaction rate if not also of their thermodynamic stability.

Moreover, it is to be emphasized that the great similarity between the stability of the complexes formed by $H_2L_B$ and $H_2L_E$ with cobalt indicates that pre-organization of the donor atoms in $H_2L_B$, obtained with ring closure with an ether unit, does not add any significant contribution to the stability of the complexes.

In $[Co(H_2L)_2]^{2+}$ ($H_2L = H_2L_B$ or $H_2L_E$), an octahedral $M_6$ environment about the central metal ion may occur in which each ligand coordinates only through the nitrogens. In $[Co(H_2L)_3]^{2+}$, it is likely that the ligands coordinate with the amine nitrogen and only one of the imine donors forming, three chelate rings. In any case, our data exclude involvement of the neutral phenol oxygen in coordination.

Unlike the results yielded by preparative procedures, no formation of heterodinuclear cobalt(II)-sodium(I) species was observed in DMSO solution. The experimental conditions used did not allow deprotonation of phenol groups; consequently they could not be engaged in dinuclear complexation, being unable to work as bridging groups.

Evidences exist that heterodinuclear $Co^{2+}-Na^+$ species are formed in DMSO, although they evolve toward the formation of mononuclear $Co^{2+}$ complexes with the progressive expulsion of $Na^+$ from the macrocyclic moiety.

The possibility of obtaining stable heterodinuclear complexes with the above macrocycles was proved in alcohol. Our current efforts are addressed to modify the ligands in order to make them more soluble in alcohol or acetonitrile solutions and/or to use preformed mononuclear complexes like Co(L) or Na(HL) as starting "ligands" for further hetero-complexation experiments.

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