# [1+1] Asymmetric Compartmental Macrocycles Bearing a Pendant Arm and Related *s,f*-Heterodinuclear Complexes Containing Lanthanide(III) and Sodium Ions

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[1+1] Asymmetric compartmental macrocycles and/or related mononuclear, homodinuclear and sodium(I)-lanthanide(III) heterodinuclear complexes are reported and their properties investigated by SEM-EDS microscopy and $^{1}$H, $^{13}$C and $^{23}$Na NMR spectroscopy. These ligands bear a pendant arm, represented by a -$CH_2COOH$ ($H_3L_A$), -$CH_2C_5H_4N$ ($H_2L_B$) or -$CH_2C_6H_4OH$ ($H_3L_C$) group bonded to the aminic nitrogen, and contain an $O_2O_3$ crown-ether-like chamber and an $N_3XO_2$ (where X = O, N) Schiff-base chamber. It was found that the lanthanide(III) ion resides in the $N_3XO_2$ chamber while the sodium(I) ion fills the $O_2O_3$ crown-ether-like chamber, as ascertained for the complex [DyNa($L_C$)(PrOH)(Cl)] by a single-crystal X-ray structural investigation. The complex is monoclinic, space group $P2_1/c$, with $a$ = 9.601(2), $b$ = 12.927(2), $c$ = 26.638(4) Å, $\beta$ = 99.55(3)°. The dysprosium ion is seven-coordinate in the $N_3O_2$ site, showing a pentagonal-bipyramid-coordination polyhedron and bonded, in the axial positions, to a chlorine ion and to the oxygen of the pendant phenolic group of the ligand. The sodium ion is six-coordinate in the $O_3O_2$ site and bonded to the propyl alcohol oxygen. Furthermore, the potential use of these complexes as molecular probes for the selective recognition of specific metal ions has been tested. In particular, their ability to act as shift reagents towards $Na^+$ was investigated by $^{23}$Na NMR spectroscopy. The relationship between the structure of these complexes in the solid state and in solution is reported.


## Introduction

Macrocyclic compounds have attracted an increasing interest owing to their role in the understanding of the molecular processes that occur in different scientific fields, ranging from chemistry to biochemistry and medicine, from material science to hydrometallurgy.[1–9]

In the past, dinucleating macrocyclic systems attracted great interest. In particular, the physico-chemical properties arising from the proximity of two metal ions closely coordinated within an appropriate organic moiety were investigated. This molecular aggregation can mediate certain chemical reactions better (or in a different manner) than those in isolated centres. Moreover, it significantly contributes to the knowledge of cooperative effects in the activation, transport and separation of specific molecules with different complexity, in the selective recognition of neutral and charged species, in the design of probes and devices capable of operating at molecular level.[10–17]

Furthermore, dinucleating macrocyclic ligands have been used for the synthesis of compounds with specific spectroscopic and magnetic properties. It was demonstrated that complexes containing dinuclear (or polynuclear) magnetic entities at appropriate distances and/or with well-defined stereochemistry exhibit peculiar magnetic properties, arising from the nature and magnitude of the interactions between the metal ions within the molecular unit.[10,12]

In this field, a particular role was played by compartmental macrocyclic ligands, that is, systems with two adjacent coordination chambers capable of coordinating two metal ions, interacting through the appropriate bridging donor atoms of these ligands. This interaction can be tuned by changing the donor atoms of the two chambers, the flexibility of the ligands, the metal ions, the distance between the two chambers and/or the metal ions themselves.[10,12]

These compartmental ligands can be symmetric or asymmetric in nature, depending on the difference in the donor set and/or in the aliphatic or aromatic chains of the two adjacent coordination chambers; the symmetric ligating systems give rise almost exclusively to homo-dinuclear complexes. Only under specific, experimental conditions can they form mononuclear complexes, which, however, easily turn into the homo-dinuclear analogues.

Unsymmetrical modifications of these symmetric systems were designed in order to achieve a different recognition process at the two adjacent chambers and consequently to favour the formation of hetero-dinuclear complexes. The type and the extent of dissymmetry introduced in the coor-

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dination moiety can influence and modify considerably the coordination selectivity of the two sites, allowing the formation of pure hetero-dinuclear species, not otherwise accessible.[11,12,18]

Recently we have started a project aimed at the preparation of molecular probes for selective recognition of alkali or alkaline metal ions. In particular, we have prepared the [1+1] asymmetric cyclic ligands $H_2L_D$ and $H_2L_E$ by reaction of 3,3′-(3-oxapentane-1,5-diyldioxy)bis(2-hydroxybenzaldheyde) or 3,3′-(3,6-dioxaoctane-1,8-diyldioxy)bis(2-hydroxybenzaldheyde) with 1,5-diamino-3-azamethylpentane. They contain an $N_3O_2$ Schiff-base chamber and an $O_2O_n$ (where $n$ = 3, 4) crown-ether-like chamber and react with $LnCl_3{\cdot}nH_2O$ in alcoholic solution, giving rise to the related mononuclear complexes $[Ln(H_2L_D)(Cl)_3(H_2O)_4]$ or $[Ln(H_2L_E)(Cl)_3(H_2O)_4]$, where the lanthanide(III) ion invariantly occupies the $O_2O_n$ crown-ether-like chamber, as ascertained also by X-ray diffractometric investigations.[19,20] However, when this chamber is already occupied by a suitable metal ion [i.e. sodium(I) or calcium(II) ion] the lanthanide(III) ion is forced into the $N_3O_2$ Schiff-base chamber with the consequent formation of the hetero-dinuclear complexes $[Ln^{III}Na^{I}(L_D)(Cl)_2(CH_3OH)]$ or $[Ln^{III}Ca^{II}(L_D)(Cl)_3]$.[16,17]

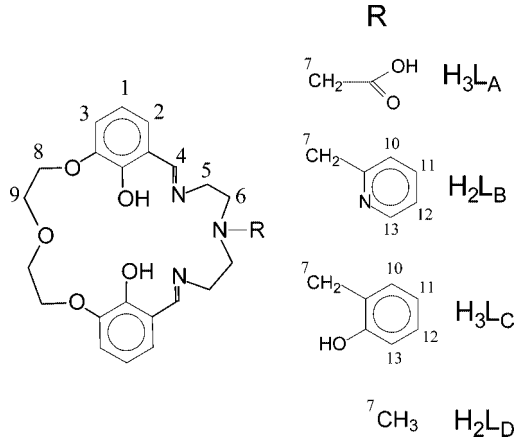
The alkali metal cations $Na^+$ and $K^+$ and the alkaline metal cations $Mg^{2+}$ and $Ca^{2+}$ are ubiquitous in living systems. The role of sodium and potassium stems essentially in their unequal distributions in the intra- and extracellular compartments and related transmembrane transport processes. The divalent magnesium and calcium cations possess a more marked binding ability towards macromolecules, polyelectrolytes and biological surfaces and thus their role is more differentiated. Under the form of aqua complexes, $Mg^{2+}$ is concentrated in the cells, whereas $Ca^{2+}$ is excluded. The distribution of alkaline and alkaline-earth ions in the inner- and outer-cell compartments is crucial to the viability of any organism. Thus, their qualitative and quantitative determination is essential, and NMR spectroscopy offers unique tools to reach this goal. The separation of the NMR signals from the two compartments is possible when their magnetic environments are made different by the presence of a paramagnetic agent, which selectively distributes in one compartment only. A successful separation of in- and out-signals is strongly dependent upon the interaction that the cation of interest is able to set up with the paramagnetic agent. In this context, compartmental ligands can be very useful. In fact, one may design systems containing a suitable lanthanide(III) ion endowed with a high magnetic moment and a non-*S* electronic configuration in one chamber, whereas the second chamber is available for coordination of an alkaline or alkaline-earth ion, possibly involved in an exchange process with the "bulk".

By this procedure quite interesting and powerful shift reagents (LIS reagents) have been proposed, in particular for $Na^+$.[21–23] The lanthanide(III) ions offer the unique possibility of progressively modifying their physical properties (and hence their ability to act as shift reagents), while maintaining the same chemical properties.

Most of the work was carried out on heterodinuclear lanthanide(III) complexes containing sodium(I).[24,25] More recently, some very encouraging results have been obtained with analogous complexes containing lithium(I), potassium(I) or calcium(II) ions instead of sodium(I).[26]

Unfortunately, these systems are sparingly soluble and not very stable in water. Consequently, in order to overcome these problems, we have functionalized the macrocyclic ligand by inserting pendant arms, which also bear additional donor groups. An additional, not negligible result of these functionalizations is that they further diversify the two coordination chambers, thus introducing more precise and selective recognition properties at the two chambers.

This paper deals with the design, synthesis and characterization of hetero-dinuclear sodium(I)-lanthanide(III) complexes with the ligands $H_3L_A$, $H_2L_B$,[27] $H_3L_C$, containing an $O_2O_3$ crown-ether-like chamber and an $N_3XO_2$ (X = O, N) Schiff-base chamber, where the pendant arm is represented by $-CH_2COOH$, $-CH_2C_5H_5N$, $-CH_2C_6H_4OH$, respectively, directly bound to the central aminic nitrogen as described in Scheme 1. The ligand $H_2L_D$ and related complexes have been already studied and are here included for comparison purposes only.




Scheme 1. The prepared ligands with the numbering scheme used to assign the peaks of the NMR spectra.

## Results and Discussion

### $H_3L_A$, $H_2L_B$, $H_3L_C$ and/or Related Sodium(I) Derivatives

While the macrocyclic ligand $H_3L_A$ was not obtained in acceptable quantities by condensation of the appropriate diformyl and polyamine precursors, the related trisodium derivative $Na_3L_A$ was synthesised in a considerable amount by treating the disodium diformyl precursor $Na_2L'$ with the functionalized polyamine *i*-DTMA·3 HCl in the presence of NaOH. The crude product can be purified by crystallization from *i*PrOH. Its IR spectrum shows a strong band at 1623 $cm^{-1}$ ($\upsilon_{C=N}$) and two intense bands at 1594 $cm^{-1}$ ($\upsilon_{asymm}$ COO) and at 1396 $cm^{-1}$ ($\upsilon_{symm}$ COO); two additional strong bands at 1213 and 1096 $cm^{-1}$ are due to the $\upsilon_{C-O}$ of the crown-ether groups. The $^1H$ NMR spectroscopic data

in $CD_3OD$ show a peak at δ = 8.41 ppm due to the formation of the CH=N group; the contemporary absence of the CH=O resonance at δ = 10 ppm proves that the condensation process is complete. As for the macrocycle $Na_3L_A$, the NMR spectroscopic data indicate that the $Na^+$ ion is not strongly coordinated to the etheric chamber and is bound only to phenolato groups. In fact, the molecules are very flexible in solution (fast exchange on the NMR timescale) and there is no evidence of geminal multiplets in the aliphatic region, due to the characteristic stereochemical rigidity of $Na^+$ when it is fully coordinated in the etheric site. The ESI-MS spectrum in MeOH shows a peak at *m*/*z* (%) = 473 (5) due to the free ligand $[H_4L_A]^+$, an intense peak at *m*/*z* (%) = 495 (100) due to the species $[NaH_2L_A]$ and two additional peaks at *m*/*z* (%) = 517 (20) $[Na_2HL_A]$ and *m*/*z* (%) = 538 (20) $[Na_3L_A]$.

Attempts to isolate the ligand $H_2L_B$ or its sodium derivative $Na_2L_B$ by self-condensation of the precursors, using different experimental conditions, failed. The ligand can only be obtained under template conditions, as mononuclear or dinuclear lanthanide(III) complexes as a result of the experimental conditions used, as reported in the subsequent paragraph.

The phenol-containing ligand $H_3L_C$ was obtained as the sodium derivatives $[Na_2(HL_C)]$ or $[Na(H_2L_C)]$ by treating the appropriate precursors in the presence of NaOH in two different synthetic ways: $[Na_2(HL_C)]$ was prepared by condensation of $Na_2L'$ and Moden·3HCl in methanol, whereas for $[Na(H_2L_C)]$, $H_2L'$, Moden·3HCl and NaOH were dissolved in a minimum amount of methanol, but the condensation reaction was conducted in diethyl ether. Once more, the completion of the condensation reaction is proved by the presence of the infrared $\upsilon_{C=N}$ band at 1624 $cm^{-1}$ for $[Na_2(HL_C)]$ and at 1639 $cm^{-1}$ for $[Na(H_2L_C)]$, which indicates, for the latter, that the $Na^+$ is not bound to the iminic nitrogen and quite probably resides in the crown-ether site. The ESI-MS spectrum of $[Na(H_2L_C)]$ in MeOH shows the parent peak at *m*/*z* (%) = 542 (55) due to $[Na(H_3L_c)]^+$. The $^1H$ NMR spectrum in $CD_3OD$ of both sodium derivatives, together with the bidimensional experiments COSY, NOESY and HMQC, allow us to correctly assign the observed proton and carbon peaks. The CH=N resonance at δ = 8.26 ppm proves that the condensation process has occurred, while 2D data demonstrate that the phenol pendant arm resonances at δ = 7.15 (10-H), 6.93 (12-H), 6.68 (11-H) and 6.30 (13-H) ppm are connected via the methylenic (7-H) resonance at δ = 3.81 ppm to the other methylenic groups of the Schiff base moiety at δ = 2.98 (6-H) and 3.88 (5-H) ppm and via the iminic resonance at δ = 8.26 (4-H) ppm to the phenolic protons.

## Mononuclear or Homodinuclear Lanthanide(III) Complexes

### *Complexes with $[L_A]^{3-}$*

Owing to the availability of $Na_3L_A$ and the difficulty in obtaining a suitable amount of $H_3L_A$, the complexation reactions were carried out using the tris-sodium derivative. $Na_3L_A$ reacts with the appropriate $LnCl_3{\cdot}nH_2O$ in methanol in a 1:1 molar ratio to yield, after a 2 h reflux, $[LnNa(NaL_A)(Cl)_2]{\cdot}nH_2O{\cdot}x$ NaCl (where $NaL_A$ indicates the diphenolate macrocycle with a sodium acetate group and Ln = Y, Lu, Yb) and, after a 12 h reflux, $[Ln_2(L_A)(Cl)_3]{\cdot}nH_2O{\cdot}x$ NaCl (where Ln = Y, Lu, Yb, Nd) (see Scheme 2). Attempts to isolate the LnNa heterodinuclear complexes by template synthesis failed. Furthermore, attempts to crystallize homo- and hetero-dinuclear complexes under a variety of experimental procedures failed. However, careful SEM-EDS investigations prove an Ln/Cl = 1:2 ratio together with well-detectable NaCl grains for the heterodinuclear LnNa and an Ln/Cl = 2:3 ratio for the homodinuclear LnLn complexes.

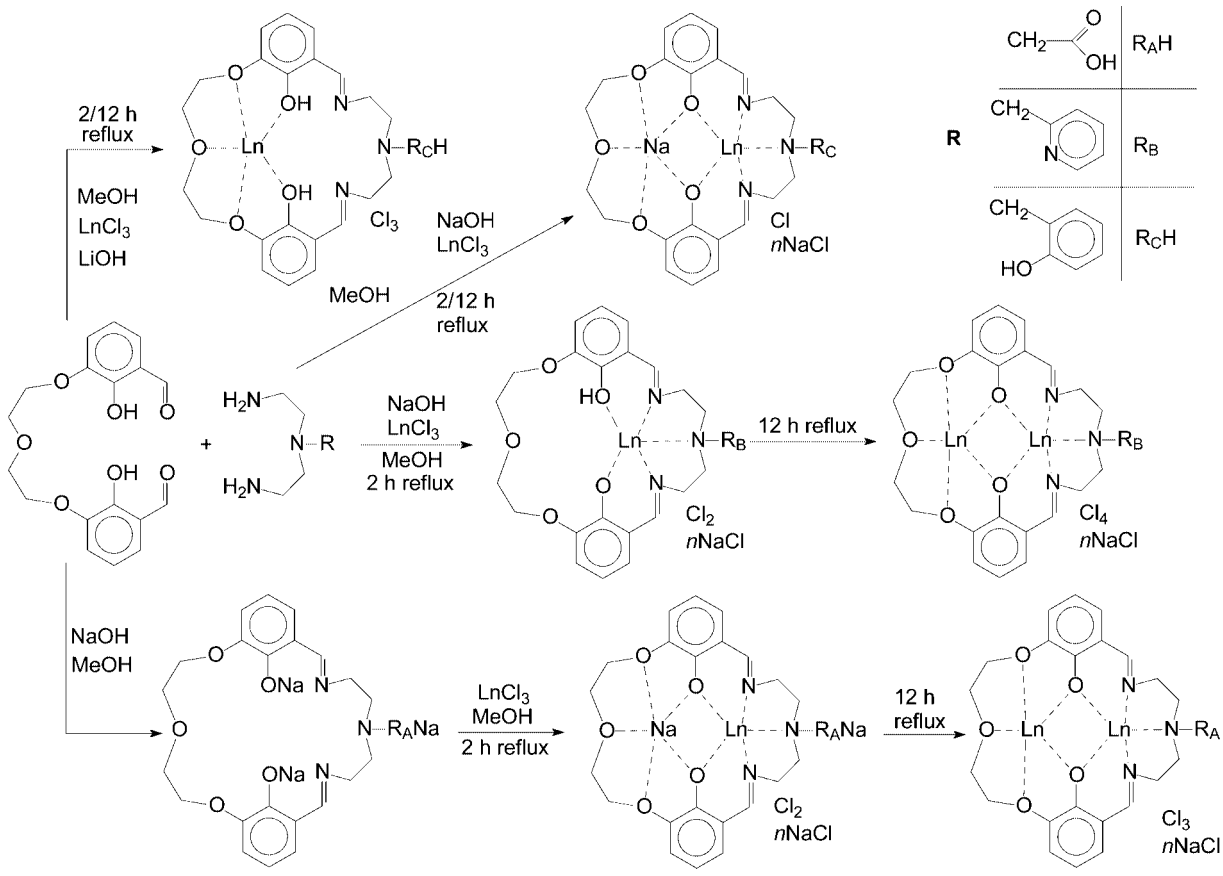
The properties of the Ln-Na complexes will be discussed in detail in the appropriate paragraph.

In the homodinuclear lanthanide(III) complexes, the $\upsilon_{C=N}$ is found at 1624–1654 $cm^{-1}$ and the stretchings of the etheric groups occur at 1230–1223 $cm^{-1}$ and at 1094–1090 $cm^{-1}$. Surprisingly, the $\upsilon_{C=N}$ of the homodinuclear complexes lies at higher wavelength in relation to the heterodinuclear Ln-Na analogues, where the same bands lie at 1625–1637 $cm^{-1}$. The long refluxing time required for the preparation of the homodinuclear complexes resulted in the loss of the sodium ion from the complex and consequent formation of NaCl, as shown by SEM and elemental analyses.

The carboxylate group quite probably participates in the coordination to the lanthanide ion as a monodentate group. The $\upsilon_{asymm}(COO)$ is found at1601–1618 $cm^{-1}$ whereas the $\upsilon_{symm}(COO)$ is at 1415–1459 and 1460–1500 $cm^{-1}$.

It may be suggested that, in the formation of the homodinuclear species, the first event to take place is the formation of the heterodinuclear LnNa complex with the lanthanide ion probably lying in the mean equatorial plane of the $N_3O_2$ donor set of the Schiff base, as already found for similar lanthanide complexes.[25] This is followed, as a consequence of the prolonged reflux and subsequent release of the $Na^+$ ion, by the coordination of a second lanthanide in the free $O_3O_2$ site, which is the favourite site of the lanthanide(III) ion, as already ascertained.[27] The macrocycle does not have the correct coordination shape to encapsulate both metal ions firmly into the mean equatorial plane. Consequently, the lanthanide ion coordinated to the Schiff-base site, owing to the steric hindrance caused by the incoming second lanthanide ion, is pushed away from the $N_3O_2$ mean plane toward the acetate group. This causes a coordination lowering of the iminic nitrogen to the central metal ion with the consequent shift of the $\upsilon_{C=N}$ toward higher wavelengths. The NMR spectroscopic data of $[Lu_2(L_A)(Cl)_3]{\cdot}0.3$ PrOH in $MeOD_4$ show that the compound is not stable in solution. The complexity of the aromatic and iminic region proves the presence of several species deriving from the demetalation reaction, with the formation of mononuclear complexes with different coordination sets. Another proof of this instability comes from the ESI-MS spectra of these complexes where no peak attributable to the homodinuclear specie was found.[28]




Scheme 2. Preparation of mononuclear and homo- or hetero-dinuclear complexes.

### *Complexes with $[L_B]^{2-}$*

As $H_2L_B$ or $Na_2L_B$ are not available, the pyridine-containing macrocycle was prepared by a template synthesis in the presence of the desired lanthanide(III) chloride hydrate in alcoholic solution. It was found that when the diformyl and amine precursor are condensed in the presence of NaOH and $LnCl_3 \cdot n H_2O$ in methanol (molar ratio 1:1:3:1), and the reaction mixture is allowed to reflux for 1–2 h, the mononuclear complexes $[Ln(HL_B)(Cl)_2] \cdot n NaCl \cdot m H_2O$ are obtained (Ln = Y, Yb, Lu, Tm, Tb, La, Ce); on the contrary, when the reflux is continued for 12 h, the homodinuclear complexes $[Ln_2(L_B)Cl_4] \cdot n NaCl \cdot m H_2O$ are collected (Ln = Y, Lu, Tb, La; see Scheme 2). Again, careful SEM-EDS investigations prove an Ln/Cl = 1:1 ratio for both complexes together with well-detectable NaCl grains.

The IR spectra of these mononuclear and dinuclear complexes are comparable to those obtained for the similar complexes with $Na_3L_A$. In particular, the mononuclear complexes show a strong $\upsilon_{C=N}$ absorption at 1617–1655 $cm^{-1}$. This band is generally higher in the dinuclear analogue; it lies for instance at 1625 $cm^{-1}$ in $[La(HL_B)(Cl)_2] \cdot 2.5 H_2O$ and at 1647 $cm^{-1}$ in $[La_2(L_B)(Cl)_4] \cdot 3.9 H_2O$.

The close proximity of the two metal ions in the dinuclear complexes, and the consequent steric hindrance, push a lanthanide ion partially out of its $N_4O_2$ coordination plane, causing a wavelength increase of the $\upsilon_{C=N}$ stretching band. A similar trend is observed in the related $^1H$ NMR spectrum in [D4]MeOH: the peak at $\delta$ = 8.15 ppm due to the iminic groups of the mononuclear complexes is shifted to $\delta$ = 8.60 ppm in the homodinuclear analogue.

The NMR experiments in the diamagnetic La, Y and Lu complexes also show that the impurities present in the mononuclear complexes are mainly the homodinuclear analogues. The NMR spectra of these dinuclear species, in fact, match perfectly those of the impurities present in the mononuclear complexes. The main differences in these spectra are localized in the Schiff-base protons. This confirms the above assumption that the Schiff-base site is only partially involved in the coordination. The solution instability of the dinuclear species represents a severe limitation to an exhaustive description of the behaviour of these complexes in solution.

In the mononuclear complexes, no evidence of $Na^+$ coordinated in the crown-ether moiety was found, probably because it may be more easily released than in the complexes with $Na_3L_A$, facilitating the formation of mononuclear lanthanide complexes. The lability of $Na^+$ in the crown-ether moiety, also verified by $^{23}Na$ NMR spectroscopy, is quite important in the determination of interesting LIS properties as reported above.

A study of the $^1H$, $^{13}C\{^1H\}$ and 2D COSY, NOESY, HMQC NMR spectra in [D4]MeOH allows a complete assignment and interpretation of the peaks occurring in the mononuclear $[Ln(HL_B)(Cl_2)]$ and dinuclear diamagnetic

and paramagnetic $[Ln_2(L_B)(Cl)_4]$ complexes (see Exp. Sect.).

The study of the weak paramagnetic complex $[Ce(HL_B)(Cl)_2]\cdot 7H_2O$ is particularly indicative of the lanthanide coordination. On the basis of 2D NOESY, acquired at several mixing times and HMQC experiments, it was possible to fully assign 13 resonances in the $^1H$ NMR spectrum. The very low-field 21.30 ppm shift of protons 4-H and the severe shift ( $\delta$ = 8.01 and –11.46 ppm) and broadening of methylenic protons of the Schiff-base moiety strongly support the thesis of lanthanide coordination in the Schiff-base site, also confirmed by the usual position of 8-H and 9-H resonances ($\delta$ = 3.66 and 4.77 ppm) of the $O_3O_2$ site. Furthermore, the downfield shift of pyridinic protons 13-H, 12-H, 11-H and 10-H ($\delta$ = 11.50, 8.62, 9.27, and 9.10 ppm) suggests that the pendant arm is involved in such coordination.

ESI-MS spectra of these samples show the presence of signals related to the sodium or lanthanide mononuclear complexes; this proves the real occurrence of the mononuclear lanthanide(III) complexes. Moreover, in a few cases the mononuclear lanthanide complexes encapsulate a methanol or chloride and/or water molecule.[28] As for the $L_A^{3-}$ ligand, no evidence of homodinuclear species was found.

### *Complexes with $[L_C]^{3-}$*

The mononuclear complexes $[Ln(H_3L_C)(Cl)_3]$ (where Ln = Lu, Eu, Tb, Y, La) were synthesised by [1+1] condensation of the triamine precursor (Moden·3HCl), neutralized with LiOH, with the diformyl precursor ($H_2L'$) in the presence of $LnCl_3\cdot n H_2O$. SEM-EDS data confirm the Ln/Cl = 1: 3 ratio (see Scheme 2). The key of this synthesis is the use of LiOH as a neutralizing agent of the aminic precursor instead of NaOH; $Li^+$ is not a suitable competitor of the lanthanide(III) ion for the hard site and hence it allows the coordination of the lanthanide ion to the crown-ether site. On the contrary, $Na^+$ strongly competes with the lanthanide(III) ion and makes the coordination of the 4f ion very problematic or impossible.

Long refluxing times do not yield homodinuclear species, as for the previous ligands $H_3L_A$ or $H_2L_B$. The complexes recovered after a 12 h reflux always produce the mononuclear or the heterodinuclear Ln-Na complexes when LiOH or NaOH, respectively, are used.

Quite interestingly, when a higher LiOH/ligand ratio is used, the coordination site of the lanthanide ion can be chosen. More precisely, under basic conditions (LiOH/Moden·3HCl/$H_2L'$/$LnCl_3$ = 6:1:1:1), complexes have been invariantly obtained where the NMR (iminic proton at higher field shifts and appearance of geminal peaks in the Schiff base methylenic region) and IR ($\upsilon_{C=N}$ at 1620–1625 $cm^{-1}$) spectra clearly indicate that the lanthanide ion resides in the Schiff-base site. Unfortunately, the compounds prepared always contain a low amount of mononuclear species with the lanthanide coordinated in the crown-ether moiety.

Less basic conditions (LiOH/Moden·3HCl/$H_2L'$/$LnCl_3$ = 3:1:1:1) always lead to pure mononuclear complexes in which the crown ether site is occupied by the lanthanide(III) ion. IR data corroborate the coordination in the $O_3O_2$ site: in fact, the $\upsilon_{C=N}$ IR band in these complexes lies between 1647 and 1653 $cm^{-1}$, which is higher than the analogue LnNa derivatives ($\upsilon_{C=N}$ at 1619–1626 $cm^{-1}$), where the lanthanide was found to reside in the Schiff-base site.

This hypothesis is in agreement with the study of the $^1H$ NMR spectrum of the paramagnetic $[Eu(H_3L_C)(Cl)_3]$ in $[D_4]$MeOH. In fact, the coordination of the $Eu^{III}$ ion in the crown ether moiety shifts and widens the peak at $\delta$ = 11.83 ppm related to aliphatic protons (8-H) and (9-H). On the other hand, protons of the pendant arm do not seem to be involved in the coordination of europium since they do not undergo any change in bandwidth or chemical shift [they are found at $\delta$ = 7.42 (10-H), 7.06 (12-H), 6.67 (11-H, 13-H) ppm; (see part a of Figure 1).

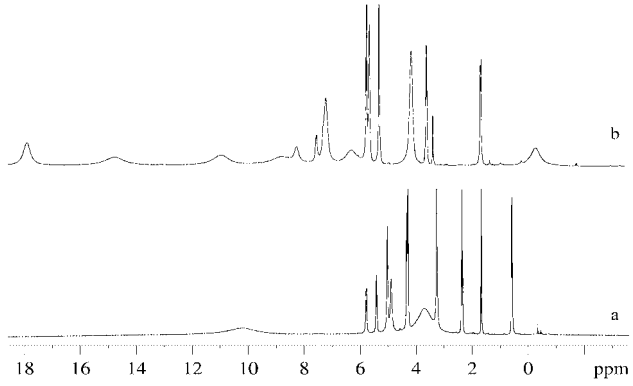



Figure 1. $^1H$ NMR spectra of $[Eu(H_3L_C)(Cl)_3]$ in $CD_3OD$ at 293 K (a) and 253 K (b).

The europium(III) coordination was further clarified by the NMR spectrum acquired at 253 K. The broad peak centered at $\delta$ = 11.83 ppm generated four peaks at 17.75, 14.53, 10.84 and –0.34 ppm assigned, on the basis of 2D NOESY acquired at several mixing times and HMQC experiments, to the geminal axial and equatorial 8-H and 9-H methylenic protons of the $O_3O_2$ site. At that temperature, the other broad resonance at $\delta$ = 5.33 ppm, assigned to the 5-H and 6-H methylenic protons of the $N_3O_3$ site, is shifted to 6.22 and 4.08 ppm but still unresolved (see part b of Figure 1).

## Heterodinuclear Lanthanide(III)–Sodium(I) Derivatives

### *Complexes with $[L_A]^{2-}$*

As reported above, the reaction of $Na_3L_A$ with the appropriate $LnCl_3\cdot n H_2O$ in methanol and in a 1:1 molar ratio, under a 2 h reflux, yields $[LnNa(NaL_A)(Cl)_2]\cdot n H_2O$, where it is likely that one sodium ion resides in the crown-ether chamber and the other is linked to the carboxylate group (see Scheme 2). These complexes always contain variable amounts of NaCl, clearly detected as grains by SEM-EDS microscopy. These measurements also prove that the complexes possess the right Na/Ln/Cl = 2:1:2 metal ratio (excluding NaCl crystals present in the sample).

The IR spectra of the LnNa complexes show a strong $\upsilon_{C=N}$ absorption at 1631–1619 $cm^{-1}$, supporting a complexation of the lanthanide(III) ion inside the Schiff-base site. The broadening of this band also suggests that the $\upsilon_{symm}(COO)$ occurs at these wavenumbers. Furthermore, strong bands at 1221–1217 $cm^{-1}$ and at 1093–1090 $cm^{-1}$, due to the stretching of the crown-ether C–O groups, have been observed, together with $\upsilon_{symm}(COO)$ absorption at 1410–1417 $cm^{-1}$.

NMR 2D data in $CD_3OD$ of the diamagnetic LuNa complex resemble those obtained for the $Na_3L_A$ precursor, allowing a complete assignment and interpretation of the peaks (see Exp. Sect.). Furthermore, the NMR spectroscopic data of the EuNa complex give a good indication of the site occupancy of the metal ions. In particular, the remarkable upfield shift of the iminic proton ($\delta$ = 28.28 ppm) and the presence of geminal methylenic protons between $\delta$ = –6.96 and –20.12 ppm indicate that the europium ion is coordinated to the Schiff-base site. Furthermore, geminal methylenic protons in the range $\delta$ = 2.33 to –0.36 ppm suggest that the etheric region of the macrocycle is rigidly coordinated to the sodium(I) ion. The peak at $\delta$ = 28.99 ppm of the remaining methylenic protons of the acetate pendant arm is very interesting and the considerable shift indicates that the acetate group is probably involved in the coordination of the paramagnetic ion. Moreover, the absence of methylenic geminal protons in the diamagnetic lutetium and lanthanum complexes suggests that the coordination proposed for the europium ion could be unrealistic for other LnNa complexes. The parent peaks at 644 and 666 *m*/*z* in the ESI-MS spectra of the europium and lutetium complexes, respectively, confirm the occurrence of a heterodinuclear $[(LnNaL_A)]^+$ species.

Surprisingly, the $^{23}Na$ NMR spectra in methanol of the paramagnetic complexes $[LnNa(Na_xL_A)(Cl)_{1+x}]$ (where Ln = Yb, Tm, Tb; $x$ = 0, 1) do not show any $^{23}Na$ shift, thus proving that no interaction between the two metal ions occurs. The reason for this failure is not easily explainable. Certainly it is due to a wrong Ln···Na alignment. It could also be due to the fact that the coordination observed in the NMR spectroscopic data of the europium complex is not maintained in other complexes and the acetate group is competing with the $O_3O_2$ site in coordinating the sodium ion, thus determining an incorrect stereochemistry for obtaining a relevant $^{23}Na$ shift. Alternatively, even if the lanthanide(III) ion were in the Schiff-base site, its displacement from the equatorial plane toward the carboxylate group would give rise to an incorrect alignment.

### *Complexes with $[L_B]^{2-}$*

Heterodinuclear Ln-Na complexes were not obtained with $L_B^{2-}$, but SEM-EDS measurements clearly prove the presence of NaCl in $[Yb(HL_B)(Cl)_2]\cdot 7\,NaCl\cdot 0.1\,H_2O\cdot 1.6\,EtOH$ and $[Tm(HL_B)(Cl)_2]\cdot 7.6\,NaCl\cdot EtOH$. As reported above, we have proved, by 2D NMR measurements on these paramagnetic complexes, that the lanthanide(III) ion, probably owing to the presence of a pyridinic pendant arm, prefers the Schiff-base site rather than the etheric one. Consequently, in methanolic solution, the sodium ion related to NaCl is partially coordinated to the Ln complex and this coordination causes a high isotropic $^{23}Na$ shift ($\delta$ = 330 ppm for the Tm complex at –20 °C). Furthermore, as expected, the $^{23}Na$ chemical shift linearly decreases with the increasing temperature. This behaviour is similar to that observed in the $[LnNa(L_D)(Cl)_2(MeOH)]$ complexes described in a previous paper,[25] where X-ray structural determinations show that the lanthanide(III) ion resides in the $N_3O_2$ Schiff-base chamber and the sodium(I) ion is in the crown-ether-like chamber. Thus we can reasonably suggest that heterodinuclear complexes are formed and that a site occupancy similar to that ascertained for $[LnNa(L_D)(Cl)_2(MeOH)]$ occurs, taking into account that the similar positional isomeric complexes with $H_2L_D$, where the lanthanide(III) ion resides in the $O_3O_2$ chamber and the sodium(I) ion in the crown-ether site, show a negligible $^{23}Na$ chemical shift.

The formation of an LnNa hetero-dinuclear coordination is also proved by the ESI-MS spectra in methanol of the complexes. The presence of peaks at 331.4 and 349.8 *m*/*z* (where $z$ = 2) of the La and Yb complexes, respectively, is convincing evidence of the formation of $[LnNa(L_B)]^{2+}$ species.

The lability of $Na^+$, mentioned above, is an interesting and useful feature in order to obtain powerful molecular shift devices as they need a quick complexation–decomplexation process of the species to be characterized.

### *Complexes with $[L_C]^{3-}$*

The heterodinuclear complexes $[LnNa(L_C)(Cl)]\cdot x\,NaCl$ (where Ln = Y, Yb, Lu, Tm, Tb, Dy, Eu, Er, La, Ce) were synthesised by condensation of the triamine precursor (Moden·3 HCl), with the diformyl precursor ($H_2L'$) in the presence of NaOH and the appropriate $LnCl_3\cdot n\,H_2O$ in a 1:1:5:1 ratio (see Scheme 2) in methanolic solution.

The IR spectra of the LnNa complexes show a strong $\upsilon_{C=N}$ absorption at 1626–1619 $cm^{-1}$, supporting a complexation of the lanthanide(III) ion inside the Schiff-base site. These complexes always contain variable amounts of NaCl, detected as grains by SEM-EDS electron microscopy. The ESI-MS spectra in MeOH for each complex clearly show the parent peak due to the appropriate $[LnNaL_C]^+$ molecule, bearing in mind that additional NaCl or solvent molecules present in the sample are not directly involved in the coordination. In agreement with the related systems containing $H_3L_A$ or $H_2L_D$ and with the literature,[25] the presence of $Na^+$, which preferentially fills the $O_2O_3$ site, forces the lanthanide(III) ion into the Schiff-base moiety; this coordination is strengthened by the further coordination of the phenolic group, as confirmed by X-ray diffractometry structural studies in the solid state and in solution by NMR spectroscopy.

The complexes are very soluble in methanol and sparingly soluble in water. Consequently, NMR spectra were carried out in $CD_3OD$. Moreover, the complexes are soluble and stable for a long period of time in a $CD_3OD/D_2O$ (1:1)

solution; the results in this solution completely parallel those obtained in $CD_3OD$.

In order to clarify the coordination in solution of the lanthanide ion, $^1H$ and $^{13}C$ NMR bidimensional studies were carried out on the paramagnetic complex [EuNa($L_C$)(Cl)]·6.5 NaCl in $CD_3OD$. On the basis of COSY, HMQC and several NOESY spectra with different mixing times and starting from the two doublets at δ = 0.52 ppm (d) and 1.98 ppm (d) (with identical $T_1$ = 450 ms), assigned respectively to protons 2-H and 3-H, we find the triplet related to proton 1-H at δ = 4.20 ppm (m), proton 4-H at δ = –29.90 ppm (s) (dipolar correlation with 2-H; see Figure 2, line a) and geminal proton 8e-H at δ = 2.63 ppm (t) [scalar coupled with 8a-H at δ = 4.42 ppm (m)] (dipolar correlation with 3-H). Geminal protons 9e-H at 3.95 (m) and 9a-H at δ = 5.67 ppm (m) are then assigned by scalar correlation with protons 8-H. Again, 2D NOESY spectra reveal the aliphatic geminal protons 5e-H, at δ = –9.57 ppm (s) (dipolar coupling with 4-H; see Figure 2, line b) and 5a-H, at δ = 4.22 ppm (m), and 6a-H, at δ = –1.00 ppm (s), and 6e-H, at δ = 19.46 ppm [(s); see Figure 2, line e]. Then proton 7-H lies at δ = –12.87 ppm [(s) dipolar correlation with 6a-H; see Figure 2, line c], which correlates with proton 10-H at δ = 4.20 ppm [(m); see Figure 2, line d]. Protons 11-H, 12-H and 13-H are found at δ = 5.67 (m), 5.31 (t) and 11.37 ppm (d), respectively.

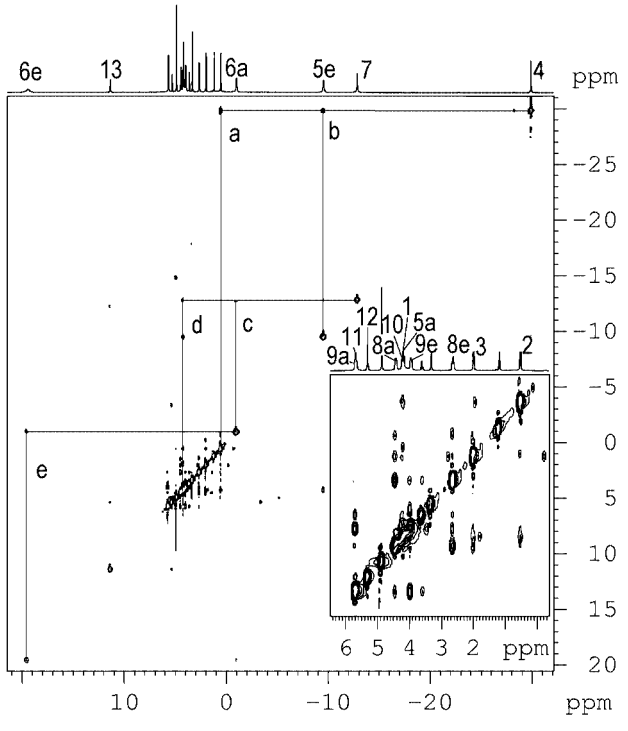



Figure 2. 2D $^1H$ NOESY NMR spectra of [EuNa($L_C$)(Cl)] in $CD_3OD$ at 293 K. Main window: mixing time = 60 ms; small window: mixing time = 220 ms.

NMR spectroscopy of paramagnetic Eu complexes is a powerful tool for a satisfactory understanding of the site occupancy of the lanthanide(III) ions. In contrast to [Eu($H_3L_C$)($Cl)_3$], where it was clearly demonstrated that the europium ion occupies the $O_3O_2$ site, in [EuNa($L_C$)(Cl)] the europium ion, due to the large shift of 5-H, 6-H (from δ = –9.57 to 19.46 ppm) and 4-H (δ = –29.90 ppm) resonances, lies in the $N_3O_3$ site. Furthermore, the pendant arm, owing to the large shift of the 10-H, 11-H, 12-H and 13-H resonances (from δ = 4.20 to 11.37 ppm), quite different from the diamagnetic one, is clearly coordinated to the europium(III) ion. Finally, the occurrence of a geminal resonance for each methylenic group proves that the complex is very rigid in solution and that both coordination sites are firmly occupied by a metal ion.

$^{23}Na$ NMR spectra of the [LnNa($L_C$)(Cl)] complexes (where Ln = Yb, Tm, Tb, Dy) show that complexes with $L_C^{3-}$ have the same behaviour as those with $L_B^{2-}$. The presence of a broad resonance with a large shift from the free-ion peak arises from the coordination of $Na^+$ in the $O_3O_2$ site of the complexes, resulting in a slow exchange at room temperature on the NMR timescale.

The slow exchange is confirmed by the peak at δ = 0 ppm corresponding to the free ion, which originates from the presence of NaCl in the sample. The observed isotropic shift is very large as far as the Tm, Dy and Tb complexes are concerned, whereas it is smaller for the Yb complex; numerical values of these shifts are: [TmNa($L_C$)(Cl)] +270 ppm (room temp.), +360 ppm (–20 °C); [DyNa($L_C$)(Cl)] –158 ppm (room temp.), –200 ppm (–20 °C); [TbNa($L_C$)(Cl)] –258 ppm (room temp.), –352 ppm (–20 °C); [YbNa($L_C$)(Cl)] +50 ppm (room temp.), +61 ppm (–20 °C; see Figure 3).

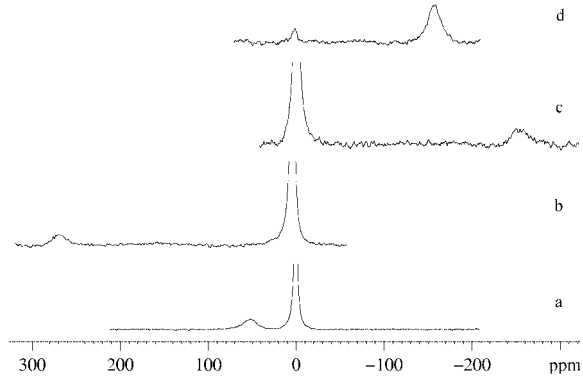



Figure 3. $^{23}Na$ NMR spectra at 293 K of [YbNa($L_C$)(Cl)] (a), [TmNa($L_C$)(Cl)] (b), [TbNa($L_C$)(Cl)] (c), [DyNa($L_C$)(Cl)] (d).

The $^{23}Na$ NMR spectroscopic data in $CD_3OD/D_2O$ (1:1) containing NaCl are comparable with those in $CD_3OD$ reported above; the most remarkable difference is a considerable broadening of the signal of the bound sodium ion due to the high $Na_{bound}/Na_{free}$ exchange.

## Crystal Structure

Crystals of [DyNa($L_C$)(PrOH)(Cl)] were obtained from slow evaporation of 1-propanol solutions. The ORTEP representation of the crystal-structure complex and coordination geometries are shown in Figure 4.

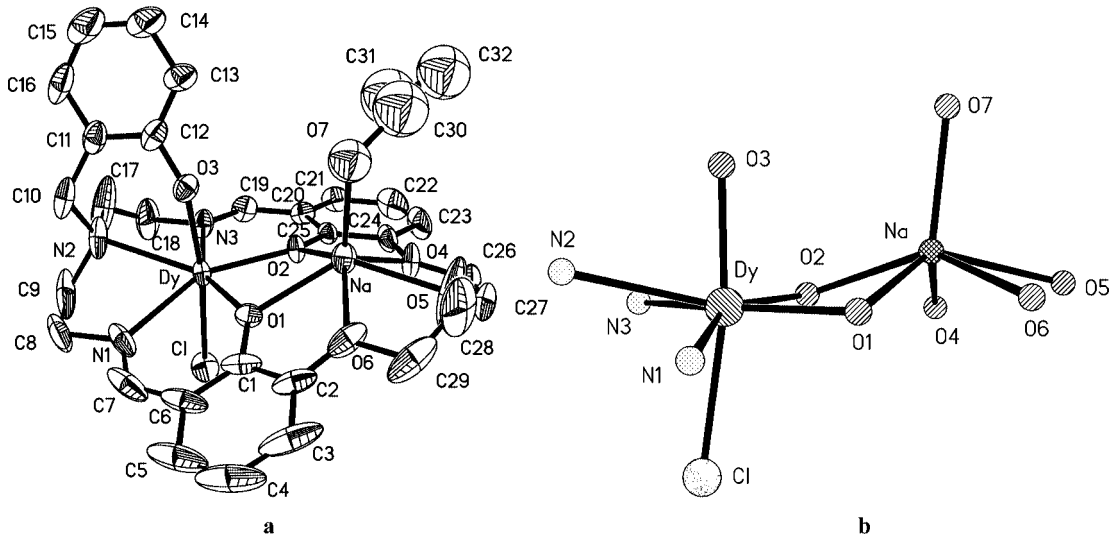



Figure 4. ORTEP representation of the (a) crystal structure of the complex [DyNa($L_C$)(PrOH)(Cl)] and (b) coordination geometries.

The sodium ion is located in the $O_2O_3$ crown-like site of the macrocyclic ligand and reaches the coordination number of six by bonding to five oxygen atoms from the ligand and one oxygen atom from the 1-propanol molecule. The oxygen atoms O(4), O(5) and O(6), are etheric, whereas O(1) and O(2) are phenolic. The coordination geometry around the sodium ion can be described as a distorted pentagonal pyramid with the 1-propanol oxygen atom as apex; the sodium atom is displaced by 0.765 Å from the basal mean plane. The seven-coordination of the dysprosium ion is achieved by three nitrogen atoms, two phenolic oxygens [O(1) and O(2)] that act as a bridge, the pendant phenolic oxygen of the ligand and one chlorine ion. The coordination polyhedron around the dysprosium ion is better depicted as a distorted pentagonal bipyramid with the chlorine ion and the phenolic pendant oxygen, O(3), as apices. The total four positive charges of the two metal ions are neutralized by the three, negatively charged phenyl oxygens and by the chlorine ion.

As for other similar complexes,[25] the molecule adopts a butterfly shape with the two benzene rings as wings that form a dihedral angle of 34.6°. The pendant system, beginning from N(2) and coordinated to Dy by the O(3) atom is placed on the convex part of the molecule and influences the conformation of the torsion angles involving the nitrogen atoms of the Schiff-base chamber.

The mean plane formed by the five, donor atoms [O(1), O(2), N(1), N(2), N(3)] bonded to the dysprosium atom includes this ion (displacement –0.0083 Å) while the displacements of the five atoms range between +0.416 and –0.456 Å. The mean plane formed by the five oxygen atoms bonded to the sodium ion [O(1), O(2), O(4), O(5), O(6)] is more planar; the displacements vary between +0.197 and –0.169 Å. The sodium ion is –0.7651 Å far from the plane.

The Dy–O distances are similar in the atoms involved in the bridge [O(1) 2.236(5) Å and O(2) 2.226(4) Å], while the Dy–O(3) bond is shorter, 2.185(6) Å [the O(3) atom is negatively charged and non-bridging]. Minor differences are present in the Dy–N distances; in fact the Dy–N(iminic) bonds are similar [Dy–N(1) 2.474(8) Å and Dy–N(3) 2.494(7) Å], while the Dy–N(2) (aminic) is 2.556(7) Å.

The Na–O(etheric) distances vary between 2.376(8) and 2.410(7) Å.

Owing to the interesting LIS data found for these complexes, structural data of the [DyNa($L_C$)(PrOH)(Cl] complex have been compared with the similar [LnNa($L_D$)-($Cl)_2$(MeOH)] (where Ln = Nd, Eu, Gd, Yb) complexes[25] that present a comparable $^{23}$Na NMR shift. All the complexes have shown that the sodium environment is always preserved with very similar coordination distances and angles, while some differences, as foreseen, are detected about the bond lengths around the lanthanide ions. These, in fact, follow the constant decreasing of the ionic radii along the lanthanide series with a decrease of the coordination bond lengths in going from Nd to Yb complexes. In the [LnNa($L_D$)($Cl)_2$(MeOH)] complexes, the conformation of the torsion angles N(1)–C(8)–C(9)–N(2) and N(2)–C(17)–C(18)–N(3) are $g^-$ and $g^+$, respectively, while they are $g^-$ (–47.6°) and $g^-$ (–42.6°) in [DyNa($L_C$)(PrOH)(Cl]. Other differences with the structure described here are present in the bond angles of coordinated atoms and are mainly due to the geometrical constrains of the pendant phenolate group. The contact distance Ln···Na of $L_D$ complexes has a mean value 3.55 Å compared to the 3.496(3) Å of Dy···Na found in the [DyNa($L_C$)(PrOH)(Cl] crystal.

## Conclusion

A series of heterodinuclear sodium-lanthanide complexes, together with the related mononuclear and/or homodinuclear lanthanide complexes with three different [1+1] asymmetric macrocyclic ligands, containing two adjacent cavities, an $O_3O_2$ crown-ether site and an $N_3XO_2$ Schiff-base site, where X is N or O of a pendant arm (-$CH_2$COOH for $H_3L_A$, -$CH_2C_5H_4$N for $H_2L_B$ and -$CH_2C_6H_4$OH for

$H_3L_C$) bonded to the aminic nitrogen, were synthesised by different routes, that is, self-condensation of the precursors followed by the reaction of the cyclic Schiff base with the appropriate lanthanide(III) ion or template synthesis [the lanthanide(III) ion used as templating agent]; both methods lead to the same products.

Remarkably, the use of NaOH as a base also introduces an $Na^+$ ion into the crown-ether cavity for both $L_A^{3-}$ and $L_C^{3-}$, but not for $L_B^{2-}$ (which generates only mononuclear and homodinuclear lanthanide complexes). Mononuclear lanthanide(III) complexes with $L_C^{3-}$ were synthesised only when NaOH was substituted by LiOH, as the $Li^+$ ion is not as tightly coordinated as $Na^+$ to the crown-ether moiety, thus it forces the lanthanide(III) ion to reside in the Schiff-base site, as confirmed by the X-ray structure of [DyNa-$(L_C)(Cl)(CH_3OH)$].

The refluxing time appears to be very important in determining the reaction pathway for complexes with $L_A^{3-}$ and $L_B^{2}$. Thus, when the appropriate reactants were refluxed for 2 h, the heterodinuclear LnNa (for $L_A^{3-}$) or the mononuclear Ln (for $L_B^{2-}$) complexes were obtained, whereas a prolonged reflux (12 h) led to the homodinuclear $Ln_2$ complexes of both ligands. Neither heterodinuclear LnNa complexes with $L_B^{2-}$, nor mononuclear Ln complexes with $L_A^{3-}$ were obtained. Under similar conditions, no homo-dinuclear lanthanide complexes were obtained with $L_C$; the hetero dinuclear NaLn or the mononuclear Ln complexes were invariantly obtained.

In all complexes, the presence of the lanthanide ion in the Schiff-base site is favoured only when the ligand is fully deprotonated. The formation of strong hydrogen bonds between phenolic hydrogen and iminic nitrogen or imine protonation probably prevent the coordination of the lanthanide in the $N_3O_2$ site.

There is not a clear explanation of the impossibility of obtaining the heterodinuclear LnNa complexes with $L_B^{2-}$. It must be stressed that this ligand, under particular conditions (i.e. a prolonged reflux in methanol), forms exclusively the dinuclear lanthanide(III) complexes. The partial occupancy of the crown-ether site by a lanthanide(III) ion may prevent a stable sodium encapsulation in the crown-ether moiety. The presence of a basic pendant arm may favour partial deprotonation of the phenolic oxygen and hence an easier formation of homodinuclear species, instead of heterodinuclear LnNa analogues. In any case, the coordination of sodium to the crown-ether moiety, whether it occurs, appears weak.

The introduction of a pendant arm containing a coordinating group in the macrocyclic system improves the solubility in relation to the complexes $[LnNa(L_D)(Cl)_2(MeOH)]$. Complexes with $L_C^{3-}$ show the best solubility in alcohol, but the heterodinuclear LnNa complexes are still insoluble in water (whereas mononuclear Ln complexes are slightly water-soluble). The solubility in $H_2O$/MeOH (1:1), however, is very good and the complexes are stable for many days. The stability of the LnNa complexes with the phenol pendant arm seems to increase significantly as well, though this is not a general trend with pendant arms.

The behaviour of $[LnNa(L_C)(Cl)]$ in solution was carefully studied especially by $^1H$ and $^{13}C$ NMR spectra. It was pointed out that in $[LnNa(L_C)(Cl)]$, the phenol pendant arm is tightly coordinated to the lanthanide ion. Evidence of a rigid system also comes from the quite simple $^1H$ NMR spectral pattern which denotes the presence of a symmetry plane perpendicular to the molecule and passing through the Ln-Na axis. These data show that the behaviour of these complexes in solution parallels that observed in the solid state.

While the $^{23}Na$ NMR spectra of the paramagnetic $[LnNa(L_A)(Cl)]$ (where Ln = Yb, Tm, Tb) do not show any $^{23}Na$ shift, probably for an incorrect alignment of $Ln^{3+}$ and Na, as already described, those of $[Ln(HL_B)(Cl)_2]\cdot n$NaCl (Ln = Yb, Tm) prove that the NaCl present in these complexes is partially coordinated to the crown-ether moiety, thereby causing a high isotropic $^{23}Na$ shift.

We have already observed that the mononuclear complexes $[Ln(HL_D)(Cl)_2(MeOH)]$,[25] where the lanthanide(III) resides in the $O_3O_2$ crown-ether chamber, do not strongly coordinate $Na^+$ in the $N_3O_2$ Schiff-base site (or in a correct way). In fact, only a negligible $^{23}Na$ shift was detected in these complexes. Thus, the mononuclear complexes with $L_B^{2-}$, on prolonged reflux, may prefer to coordinate a second lanthanide instead of an $Na^+$ ion. Moreover, $Na^+$ is not able to transmetallate the $Ln^{3+}$ from the crown-ether moiety. Nevertheless, the mononuclear complexes, once formed, when reacted with $Na^+$ in $[D_4]$MeOH, give rise to a significant $^{23}Na$ shift, which proves that a correct geometry is reached at least in solution with the $Na^+$ ion in the crown-ether moiety.

The coordination lability of $Na^+$, together with its relevant $^{23}Na$ shift, testifies that it could be an excellent molecular device for sodium detection in solution.

In the paramagnetic complexes $[LnNa(L_C)(Cl)]$ (where Ln = Yb, Tm, Tb, Dy), the $^{23}Na$ NMR resonance of the bound cation is markedly shifted from that of the free ion, and the shift itself is greater than that observed for $L_B^{2-}$ and for $L_D^{2-}$ complexes.

The formation of solution-stable LaNa complexes with $H_3L_C$ testifies also that the $N–CH_2–C_6H_4O^-$ arm, which forms a six-membered ring with the lanthanide(III) ion, is quite suitable to suppress molecular movements of the metal ions, assuring a correct stereochemistry that favours the interaction between the $Ln^{3+}$ ion and $Na^+$ that makes the paramagnetic complexes $[LnNa(L_C)(Cl)]$ the best $^{23}Na$ shift reagents prepared so far.

The $^{23}Na$ paramagnetic shift depends on the geometrical position of the sodium ion in relation to the magnetic symmetry axis of the complex and on the Ln–Na distance. Under the simplified hypothesis that the lanthanide complex is characterized by an effective axial symmetry (often a good approximation),[29] the magnitude of the shift is proportional to a term of the type $D_1(3\cos^2\theta - 1)/r^3$, where $\theta$ is the angle between the Ln–Na vector and the principal magnetic axis of the complex and $r$ is the Ln–Na distance. In the heterodinuclear $[LnNa(L_C)(Cl)]$ complexes, the distance $r$ is only 3.496(3) Å, shorter than that found in similar

$[LnNa(L_D)(Cl)_2(MeOH)]$ (Ln = Nd, Eu, Gd, Yb) complexes[25] (ca. 3.55 Å) and much shorter than that estimated for the corresponding polyaminopolycarboxylic (ca. 3.9 Å) and polyoxa tetraaza macrocyclic complexes (5.3 Å).[30] Furthermore, the negative sign of the hyperfine $^{23}Na$ shifts for the Tb and Dy complexes ($D_1 > 0$) and the positive sign of the Tm complex ($D_1 < 0$) suggests that the angle θ is close to 90° and thus that the principal magnetic susceptibility axis of the complex is orthogonal to the molecular plane. For the Yb complex ($D_1 > 0$) the sign of the $^{23}Na$ shift is positive (in contrast with the negative sign found in $[YbNa(L_D)(Cl)_2(MeOH)]$). In this case the principal magnetic susceptibility axis is parallel to the molecular plane (probably due to the fact that Yb has the smallest ionic radius) and this is supported by the $^1H$ NMR spectrum of the Yb complex (for which the dipolar contribution to the paramagnetic shift has the largest contribution), where the resonances have positive chemical shift values.

In conclusion, the introduction of suitable, coordinating pendant arms at the periphery of the coordination moiety of the [1+1] asymmetric compartmental macrocycles containing one $N_3O_2$ and one $O_3O_2$ adjacent coordination sites, increases the solubility and, for the complexes with $H_2L_B$ and $H_3L_C$, the $^{23}Na$ shift. Unfortunately, the three pendant arms do not confer enough solubility to the LnNa complexes to allow NMR spectroscopy experiments in water. The quite stimulating, preliminary results obtained in $CD_3OD/H_2O$ (1:1), however, force us to shift our efforts toward a deeper investigation of the complexes with $H_3L_C$ in water-containing solvents.

## Experimental Section

**Materials:** The solvents, the inorganic and organic compounds and the lanthanide chloride hydrates were commercial products, supplied by Aldrich, Riedel-de Haën, Carlo–Erba or Fluka. They were used as received, without further purification. Dimethyl sulfoxide, used in the preparation of the diformyl precursors, was purified according to the literature.[31]

**Physico-Chemical Measurements:** Elemental analyses were carried out using a Fison 1108 analyzer. IR spectra were recorded as KBr pellets on a Mattson FTIR spectrometer. All NMR spectra ($^1H$, $^{13}C$, $^{23}Na$) were recorded on a Bruker AMX300 spectrometer equipped with direct and inverse broad-band multinuclear probes and variable-temperature unit, with lanthanide(III) complexes dissolved in $CD_3OD$, used also as internal reference. The T1 longitudinal relaxation times and the mixing times of NOESY experiments of paramagnetic europium and cerium complexes were measured using the standard inversion recovery pulse sequence. All ESI-MS mass spectrometric measurements were performed using an LCQ mass spectrometry (Finnigam) and methanolic solutions of the samples ($10^{-5}$ M). The morphology, homogeneity and the Ln/Cl or Ln/Na/Cl ratio of the complexes were investigated using a Philips XL40 model scanning electron microscope equipped with an EDAXDXPRIME energy dispersive spectrometer.

**Diformyl and Amine Precursors:** The diformyl precursor 3,3′-(3-oxapentane-1,5-diyldioxy)bis(2-hydroxybenzaldheyde) ($H_2L'$) and its disodium derivative $Na_2L'$ were prepared according to the literature.[13,17] The diformyl precursor was purified by chromatography on silica gel using $CHCl_3$ as eluent. The amine precursors: 4-diethylenetriaminoacetic acid·3 HCl (i-DTMA·3 HCl), 1,7-bis-(aminoethyl)-2-(aminomethyl)pyridine·3 HCl (DETPY·3 HCl),*N*,*N*-bis(2-aminoethyl)-2-hydroxybenzylamine·3 HCl (Moden·3HCl) were prepared according to the literature.[32] Elemental analysis, ESI-MS, IR and NMR spectroscopic data agree with the proposed formulation.

**Macrocyclic Ligands**

**Preparation of $H_3L_A$:** *i*-DTMA·3 HCl ($0.10 \times 10^{-2}$ mol) and NaOH ($0.30 \times 10^{-2}$ mol) were added to a methanolic solution of the diformyl precursor $H_2L'$ ($0.10 \times 10^{-2}$ mol) and the solution was refluxed for 3 h. The solvent was then evaporated to dryness and the resulting solid was dissolved in $CH_2Cl_2$. The solution was clarified by filtration and the solvents evaporated to dryness. The yellow solid obtained was collected by filtration, dried in vacuo and recrystallised from a methanol/diethyl ether solution. Owing to the difficult purification, the ligand was obtained in very low yield (<5%). IR $\tilde{\nu}$ = 1646 (C=N) $cm^{-1}$. $C_{25}H_{36}N_3O_{9.5}$: calcd. C 56.60, H 6.84, N 7.92; found C 56.82, H 6.97, N 8.34. $^1H$ NMR ($CD_3OD$): δ = 8.42 (s, 2 H, 4-H), 6.96 (d, 2 H,3-H), 6.91 (d, 2 H, 2-H), 6.56 (t, 2 H, 1-H), 4.21 (m, 4 H, 8-H), 4.00 (m, 4 H, 9-H), 3.85 (m, 4 H, 5-H), 3.56 (s, 2 H, 6-H), 3.35 (m, 4 H, 7-H) ppm.

**Preparation of $Na_3L_A$:** *i*-DTMA·3 HCl ($0.10 \times 10^{-2}$ mol) was dissolved in methanol (30 mL) at a pH adjusted to ≈ 7 by NaOH. Then it was added to a methanolic solution of $Na_2L'$ ($0.30 \times 10^{-2}$ mol) and the resulting solution was refluxed for 2 h. The solvent was evaporated to dryness and the yellow solid obtained was dissolved in $CH_2Cl_2$. The solution, clarified by filtration, was evaporated to dryness. 2-Propanol was added to the residue and the mixture heated until a clear solution was obtained. The yellow product, crystallised by cooling the solution, was filtered and dried in vacuo. IR $\tilde{\nu}$ = 1623 (C=N) $cm^{-1}$. $C_{24.9}H_{31.2}N_3O_{8.7}Na_3 \cdot 1.4\,H_2O \cdot 0.3\,PrOH$: calcd. C 51.51, H 5.42, N 7.24; found C 51.44, H 5.07, N 6.47. $^1H$ NMR ($CD_3OD$): δ = 8.41 (s, 2 H, 4-H), 6.95 (d, 2 H, 3-H), 6.91 (d, 2 H, 2-H), 6.57 (t, 2 H, 1-H), 4.19 (m, 4 H, 8-H), 3.99 (m, 4 H, 9-H), 3.84 (m, 4 H, 5-H), 3.56 (s, 4 H, 6-H), 3.29 (m, 2 H, 7-H) ppm. $^{13}C$ NMR ($CD_3OD$): δ = 166.34 (C-4), 176.24 (C-13), 114.18 (C-2), 114.39 (1), 124.83 (3), 115.97 (C-10), 149.46 (C-11), 163.29 (C-12), 68.70 (C-8), 63.33 (C-9), 56.24 (C-5), 52.37 (C-6), 57.66 (C-7) ppm.

**Preparation of $Na_2HL_C$:** Methanolic solutions of NaOH ($0.90 \times 10^{-3}$ mol) and $Na_2L'$ ($0.30 \times 10^{-3}$ mol) were added in succession to a methanolic solution of Moden·3 HCl ($0.30 \times 10^{-3}$ mol). The resulting yellow solution was refluxed for 3 h, then reduced in volume. The subsequent addition of 3 mL of ethanol formed a precipitate that was filtered off. The solution was evaporated to dryness and the residue treated with 1-propanol. The solution, clarified by filtration, was evaporated to dryness; the yellow solid obtained was filtered, washed twice with 1-propanol and dried in vacuo. IR $\tilde{\nu}$ = 1624 (C=N) $cm^{-1}$. $C_{37.5}H_{55}N_3O_{9.5}Na_{2.5}Cl_{0.5}$: calcd. C 58.12, H 7.15, N 5.42; found C 58.05, H 7.14, N 6.60. $^1H$ NMR ($CD_3OD$): δ = 8.26 (s, 2 H, 4-H), 7.19 (d, 1 H, 10-H), 7.01 (d, 2 H, 3-H), 6.90 (m, 1 H, 12-H), 6.86 (d, 2 H, 2-H), 6.66 (t, 1 H, 1-H), 6.65 (t, 1 H, 11-H), 6.34 (d, 1 H, 13-H), 4.24 (m, 4 H, 8-H), 4.03 (m, 4 H, 9-H), 3.90 (m, 4 H, 5-H), 3.81 (s, 2 H, 7-H), 2.97 (m, 4 H, 6-H) ppm.

**Preparation of $NaH_2L_C$:** Methanolic solutions of Moden·3 HCl ($0.30 \times 10^{-3}$ mol) neutralized with NaOH ($0.90 \times 10^{-3}$ mol) and $H_2L'$ ($0.30 \times 10^{-3}$ mol) were added dropwise to a flask containing $Et_2O$. The suspension was stirred for 2 h at room temp. The white precipitate was filtered, dried in vacuo and then dissolved in $CHCl_3$. The resulting solution was clarified by filtration and re-

duced in volume, then petroleum ether was added and the yellow solid obtained was filtered and dried in vacuo. IR $\tilde{\nu}$ = 1639 (C=N) $cm^{-1}$. $C_{29}H_{32}N_3O_6Na_{12.5}Cl_{11.5}$: calcd. C 28.70, H 2.66, N 3.46; found 28.91, H 2.63, N 3.04. MS: *m*/*z* (%) = 542 (55) $[Na(H_3L_C)]^+$. $^1H$ NMR ($CD_3OD$): δ = 8.27 (s, 2 H, 4-H), 7.15 (d, 1 H, 10-H), 7.03 (d, 2 H, 3-H), 6.93 (m, 1 H, 12-H), 6.87 (d, 2 H, 2-H), 6.72 (t, 1 H, 1-H), 6.68 (t, 1 H, 11-H), 6.30 (d, 1 H, 13-H), 4.24 (m, 4 H, 8-H), 3.99 (m, 4 H, 9-H), 3.88 (m, 4 H, 5-H), 3.81 (s, 2 H, 7-H), 2.98 (m, 4 H, 6-H) ppm. $^{13}C$ NMR ($CD_3OD$): δ = 166.85 (C-4), 128.62 (C-10), 128.10 (C-12), 124.16 (C-2), 119.42 (C-11), 115.85 (C-1), 115.29 (C-13), 113.83 (C-3), 68.31 (C-9), 66.58 (C-8), 55.94 (C-6), 55.15 (C-7), 52.11 (C-5) ppm.

**Complexes**

**Preparation of $[LnNa(Na_xL_A)(Cl)_{1+x}]\cdot nH_2O$ ($x$ = 0, 1):** $LnCl_3\cdot 6H_2O$ ($0.20\times10^{-3}$ mol) (where Ln = Y, Lu, Yb, Tm, Tb, Eu) in methanol (20 mL) was added to a methanolic solution (20 mL) of $Na_3L_A$ ($0.20\times10^{-3}$ mol). The solution obtained was refluxed for 2 h, then evaporated to dryness and the resulting residue was treated twice with 1-propanol. The yellow precipitate was filtered, washed with diethyl ether and dried in vacuo. The reported stoichiometry and the Na/Ln/Cl ratio were ascertained by SEM-EDS together with elemental analysis.

**$[YNa(NaLA)(Cl)_2]\cdot 3NaCl\cdot 2H_2O$:** IR $\tilde{\nu}$ = 1636 (C=N) $cm^{-1}$. $C_{24}H_{30}N_3O_9Na_5Cl_5Y$: calcd. C 32.55, H 3.41, N 4.74; found C 32.00, H 3.34, N 4.63. $^1H$ NMR ($CD_3OD$): δ = 8.34 (s, 2 H, 4), 7.13 (d, 2 H, 2), 7.00 (d, 2 H, 3), 6.67 (t, 2 H, 1), 4.27 (m, 4 H, 8), 4.04 (m, 4 H, 9), 3.96 (m, 4 H, 5), 3.79 (s, 2 H, 7), 2.75 (m, 4 H, 6) ppm.

**$[LuNa(NaL_A)(Cl)_2]\cdot 4.5NaCl\cdot PrOH$:** IR $\tilde{\nu}$ = 1625 (C=N) $cm^{-1}$. $C_{27}H_{34}N_3O_8Na_{6.5}Cl_{6.5}Lu$: calcd. C 29.93, H 3.16, N 3.88; found C 29.41, H 2.76, N 3.60.

**$[YbNa(NaL_A)(Cl)_2]\cdot 1.3NaCl\cdot 3.2H_2O$:** IR $\tilde{\nu}$ = 1637 (C=N) $cm^{-1}$. $C_{24}H_{32.4}N_3O_{10.2}Na_{3.3}Cl_{3.3}Yb$: calcd. C 34.34, H 3.89, N 5.01; found: C 34.60, H 3.68, N 4.95.

**$[TmNa(L_A)(Cl)]\cdot 5.5NaCl\cdot 2.5H_2O$:** IR $\tilde{\nu}$ = 1625 (C=N) $cm^{-1}$. $C_{24}H_{31}N_3O_{9.5}Na_{6.5}Cl_{6.5}Tm$: calcd. C 27.14, H 2.94, N 3.96; found C 27.10, H 2.95, N 3.05.

**$[TbNa(L_A)(Cl)]\cdot 0.6NaCl\cdot 0.3H_2O$:** IR $\tilde{\nu}$ = 1625 (C=N) $cm^{-1}$. $C_{24}H_{26.6}N_3O_{7.3}Na_{1.6}Cl_{1.6}Tb$: calcd. C 39.69, H 3.69, N 5.79; found: C 39.54, H 3.68, N 4.21.

**$[EuNa(L_A)(Cl)]$:** IR $\tilde{\nu}$ = 1619 (C=N) $cm^{-1}$. $C_{24}H_{26}N_3O_7NaClEu$: calcd. C 42.46, H 3.86, N 6.19; found: C 43.10, H 3.66, N 4.50. $^1H$ NMR ($CD_3OD$): δ = 28.99 (s, 2 H, 7-H), 3.46 (t, 2 H, 1-H), 2.33 (t, 2 H, 8-H), 1.23 (d, 2 H, 9-H), 1.09 (d, 2 H, 9-H), 0.97 (d, 2 H, 3-H), 0.25 (t, 2 H, 2-H), –0.36 (t, 2 H, 8-H), –6.96 (s, 2 H, 6-H), –8.68 (s, 2 H, 5-H), –19.93 (s, 2 H, 6-H), –20.12 (s, 2 H, 5-H), –28.28 (s, 2 H, 4-H) ppm.

**Preparation of $[Ln_2(L_A)(Cl)_3]\cdot nH_2O\cdot m$PrOH:** The same synthetic procedure used for $[LnNa(NaL_A)(Cl)]\cdot nH_2O$, but a 12 h reflux (when Ln = Y, Lu, Yb, Nd) leads to the homodinuclear complexes $[Y_2(L_A)(Cl)_3]\cdot 1NaCl\cdot 7.7H_2O$; $[Lu_2(L_A)(Cl)_3]\cdot 4.8NaCl\cdot 0.3$PrOH; $[Yb_2(L_A)(Cl)_3]\cdot 4NaCl\cdot 1.3H_2O$; $[Nd_2(L_A)(Cl)_3]\cdot 1.2NaCl\cdot 1.2$PrOH.

**$[Y_2(L_A)(Cl)_3]\cdot NaCl\cdot 7.7H_2O$:** IR $\tilde{\nu}$ = 1655 $cm^{-1}$ (C=N) $cm^{-1}$. $C_{24}H_{41.4}N_3O_{14.7}NaCl_4Y_2$: calcd. calcd.C 30.35, H 4.39, N 4.42; found C 30.26, H 4.39, N 5.08.

**$[Lu_2(L_A)(Cl)_3]\cdot 4.8NaCl\cdot 0.3$PrOH:** IR $\tilde{\nu}$ = 1639 (C=N) $cm^{-1}$. $C_{24.9}H_{28.4}N_3O_{7.3}Na_{4.8}Cl_{7.8}Lu_2$: calcd. C 24.45, H 2.34, N 3.43; found C 24.37, H 2.27, N 2.92.

**$[Yb_2(L_A)(Cl)_3]\cdot 4NaCl\cdot 1.3H_2O$:** IR $\tilde{\nu}$ = 1624 $cm^{-1}$ (C=N) $cm^{-1}$. $C_{24}H_{28.6}N_3O_{8.3}Na_4Cl_7Yb_2$: calcd. C 24.47, H 2.45, N 3.57; found C 24.58, H 2.45, N 2.98.

**$[Nd_2(L_A)(Cl)_3]\cdot 1.2NaCl\cdot 1.2$PrOH:** IR $\tilde{\nu}$ = 1654 (C=N) $cm^{-1}$. $C_{27.6}H_{35.6}N_3O_{8.2}Na_{1.2}Cl_{4.2}Nd_2$: calcd. C 32.97, H 3.57, N 4.18; found C 32.88, H 3.59, N 4.05.

**Preparation of $[Ln(HL_B)(Cl)_2]\cdot xNaCl\cdot yH_2O$:** NaOH in methanol (20 mL) was added to a methanolic solution (20 mL) of DETPY·3 HCl ($0.10\times10^{-2}$ mol) until pH = 7–8. The appropriate lanthanide chloride hydrate $LnCl_3\cdot nH_2O$ ($0.10\times10^{-2}$ mol) (where Ln = Y, Yb, Lu, Tm, Tb with $n$ = 6 and Ln = La, Ce with $n$ = 7), and the diformyl derivative $H_2L'$ ($0.10\times10^{-2}$ mol) were added in succession and the resulting solution refluxed for 2 h. The solution was clarified by filtration, then evaporated to dryness. The solid obtained was washed twice with ethanol. The yellow precipitate was filtered, washed with diethyl ether and dried in vacuo. The reported stoichiometry and the Ln/Cl ratio were ascertained by SEM-EDS together with elemental analysis.

**$[Y(HL_B)(Cl)_2]\cdot 2.9NaCl\cdot 0.6H_2O$:** IR $\tilde{\nu}$ = 1647 (C=N) $cm^{-1}$. $C_{27}H_{32.2}N_4O_{5.6}Na_{2.9}Cl_{4.9}Y$: calcd. C 39.00, H 3.90, N 6.74; found C 39.86, H 3.80, N 4.76. $^1H$ NMR ($CD_3OD$): δ = 8.66 (s, 2 H, 4-H), 8.45 (d, 1 H, 13-H), 7.93 (t, 1 H, 11-H), 7.58 (d, 1 H, 10-H), 7.37 (m, 1 H, 12-H), 7.33 (d, 2 H, 3-H) 7.15 (2-H), 6.78 (t, 2 H, 1-H), 4.55 (m, 8 H, 8-H + 9-H), 4.08 (s, 2 H, 7-H), 4.00 (m, 4 H, 5-H), 3.04 (m, 4 H, 6-H) ppm. $^{13}C$ NMR ($CD_3OD$): δ = 171.97 (4), 151.79 (16), 135.31 (14), 128.80 (13), 127.45 (15), 130.29 (3), 120.08 (2), 118.41 (1), 73.78 (8), 68.75 (9), 57.03 (6), 52.29 (5), 61.86 (7) ppm. Similar results were obtained for the diamagnetic complexes $[La(HL_B)(Cl)_2]\cdot 10NaCl\cdot 2.5H_2O$, and for the paramagnetic $[Ce(HL_B)(Cl)_2]\cdot 6.4NaCl\cdot 7H_2O$, $[Yb(HL_B)(Cl)_2]\cdot 7NaCl\cdot 0.1H_2O\cdot 1.6$EtOH, $[Tb(HL_B)(Cl)_2]\cdot 7.7NaCl\cdot 5.3H_2O$, $[Tm(HL_B)(Cl)_2]\cdot 7.6NaCl\cdot$EtOH. IR $\tilde{\nu}$ = 1617 (C=N, Tm complex)–1652 (C=N, Tb complex) $cm^{-1}$.

**$[La(HL_B)(Cl)_2]\cdot 10NaCl\cdot 2.5H_2O$:** IR $\tilde{\nu}$ = 1625 (C=N) $cm^{-1}$. $C_{27}H_{36}N_4O_{7.5}Na_{10}Cl_{12}La$: calcd. C 24.37, H 2.73, N 4.21; found C 25.02, H 2.72, N 3.84.

**$[Ce(HL_B)(Cl)_2]\cdot 6.4NaCl\cdot 7H_2O$:** IR $\tilde{\nu}$ = 1638 (C=N) $cm^{-1}$. $C_{27}H_{45}N_4O_{12}Na_{6.4}Cl_{8.4}Ce$: calcd. C 29.96, H 3.77, N 4.66; found C 27.71, H 3.73, N 6.39. $^1H$ NMR ($CD_3OD$): δ = 21.30 (s, 2 H, 4-H), 11.50 (d, 1 H, 13-H), 11.36 (d, 2 H, 2-H), 9.27 (t, 1 H, 11-H), 9.10 (d, 1 H, 10-H), 9.04 (d, 2 H, 3-H), 8.62 (m, 3 H, 12-H + 1-H), 4.77 (m, 4 H, 9-H), 5.01 (s, 2 H, 7-H), 3.66 (m, 4 H, 8-H), 8.01 (broad, 4 H, aliph.), –11.46 (broad, 4 H, aliph.) ppm.

**$[Yb(HL_B)(Cl)_2]\cdot 7NaCl\cdot 0.1H_2O\cdot 1.6$EtOH:** IR $\tilde{\nu}$ = 1624 (C=N) $cm^{-1}$. $C_{31.8}H_{40.8}N_4O_{6.7}Na_7Cl_9Yb$: calcd. C 29.79, H 3.37, N 4.59; found C 29.73, H 3.37, N 3.63.

**$[Tb(HL_B)(Cl)_2]\cdot 7.7NaCl\cdot 5.3H_2O$:** IR $\tilde{\nu}$ = 1652 (C=N) $cm^{-1}$. $C_{27}H_{41.6}N_4O_{10.3}Na_{7.7}Cl_{9.7}Tb$: calcd. C 25.60, H 3.31, N 4.42; found C 25.63, H 3.32, N 4.72.

**$[Tm(HL_B)(Cl)_2]\cdot 7.6NaCl\cdot$EtOH:** IR $\tilde{\nu}$ = 1617 (C=N) $cm^{-1}$. $C_{29}H_{37.4}N_4O_{6.2}Na_{10.5}Cl_{10.5}Tm$: calcd. C 28.51, H 3.05, N 4.59; found C 28.58, H 2.95, N 3.23.

**Preparation of $[Ln_2(L_B)(Cl)_4]\cdot xNaCl\cdot yH_2O$:** The same procedure was used as for $[Ln(HL_B)(Cl)_2]$, but a 12 h reflux of the appropriate solution (when Ln = Y, Lu, Dy with $n$ = 6 and Ln = La with $n$ = 7) leads to the homodinuclear complexes $[La_2(L_B)(Cl)_4]\cdot 8NaCl\cdot 3.9H_2O$, $[Y_2(L_B)(Cl)_4]\cdot 0.6NaCl\cdot 7.5H_2O\cdot 3$MeOH, $[Lu_2(L_B)(Cl)_4]\cdot 2.7NaCl\cdot 6.6H_2O$, $[Dy_2(L_B)(Cl)_4]\cdot 4.5\ NaCl\cdot 9H_2O\cdot$MeOH.

**$[La_2(L_B)(Cl)_4]\cdot 8NaCl\cdot 3.9H_2O$:** IR $\tilde{\nu}$ = 1647 (C=N) $cm^{-1}$. $C_{27}H_{37.8}N_4O_{8.9}Na_8Cl_{12}La_2$: calcd. C 22.40, H 2.63, N 3.87; found

C 22.71, H 2.63, N 3.78. $^1$H NMR ($CD_3OD$): δ = 8.53 (s, 2 H, 4-H), 8.46 (d, 1 H, 13-H), 7.91 (d, 1 H, 11-H), 7.61 (d, 1 H, 10-H), 7.39 (t, 1 H, 12-H), 7.27 (d, 2 H, 3-H), 7.09 (d, 2 H, 2-H), 6.71 (t, 2 H, 1-H), 4.51 (m, 8 H, 8-H + 9-H), 4.09 (s, 2 H, 7-H), 4.02 (m, 4 H, 5-H), 3.09 (m, 4 H, 6-H) ppm.

**$[Y_2(L_B)(Cl)_4]\cdot 0.6\,NaCl\cdot 7.5\,H_2O\cdot 3\,MeOH$:** IR ṽ = 1654 (C=N) cm$^{-1}$. $C_{30}H_{57}N_4O_{15.5}Na_{0.6}Cl_{4.6}Y_2$: calcd. C 33.48, H 5.34, N 5.20; found C 33.65, H 5.34, N 5.12.

**$[Lu_2(L_B)(Cl)_4]\cdot 2.7\,NaCl\cdot 6.6\,H_2O$:** IR ṽ = 1658 (C=N) cm$^{-1}$. $C_{27}H_{43.2}N_4O_{11.6}Na_{2.7}Cl_{6.7}Lu_2$: calcd. C 25.76, H 3.46, N 4.45; found C 25.65, H 3.45, N 4.65.

**$[Dy_2(L_B)(Cl)_4]\cdot 4.5\,NaCl\cdot 9\,H_2O\cdot MeOH$:** IR ṽ = 1655 (C=N) cm$^{-1}$. $C_{28}H_{52}N_4O_{15}Na_{4.5}Cl_{8.5}Dy_2$: calcd. C 23.78, H 3.71, N 3.96; found C 23.69, H 3.67, N 4.34.

**Preparation of $[LnNa(L_C)(Cl)]\cdot x\,NaCl\cdot y\,H_2O$:** $LnCl_3\cdot nH_2O$ ($5\times10^{-2}$ mol) (where Ln = Y, Yb, Lu, Tm, Tb, Dy, Eu, Er with $n$ = 6 and Ln = La, Ce with $n$ = 7) dissolved in methanol was added to a methanolic solution of $Na_2HL_C$ ($5\times10^{-2}$ mol). The solution was refluxed for 3 h, then evaporated to dryness. The crude product was treated with 1-propanol and the yellow solid obtained was filtered, washed with 2-propanol and dried in vacuo. The reported stoichiometry and the Na/Ln/Cl ratio were ascertained by SEM-EDS together with elemental analysis.

**$[LuNa(L_C)(Cl)]\cdot 4.2\,NaCl\cdot 1.7\,H_2O$:** IR ṽ = 1626 (C=N) cm$^{-1}$. $C_{29}H_{33.4}N_3O_{7.7}Na_{5.2}Cl_{5.2}Lu$: calcd. C 33.95, H 3.28, N 4.10; found C 33.91, H 3.28, N 3.68. $^1$H NMR ($CD_3OD$): δ = 8.35 (s, 2 H, 4-H), 7.13 (d, 2 H, 3-H), 7.02 (d, 1 H, 10-H), 6.96 (d, 2 H, 2-H), 6.93 (m, 1 H, 12-H), 6.62 (t, 2 H, 1-H), 6.51 (t, 1 H, 11-H), 6.34 (d, 1 H, 13-H), 4.30 (m, 4 H, 8-H), 4.13 (m, 2 H, 5-H), 4.08 (m, 4 H, 9-H), 3.85 (m, 2 H, 5-H), 3.76 (s, 2 H, 7-H), 3.23 (m, 2 H, 6-H), 2.84 (m, 2 H, 6-H) ppm. $^{13}$C NMR ($CD_3OD$): δ = 171.71 (4), 132.05 (10), 130.89 (12), 128.80 (2), 119.37 (13), 117.34 (11), 116.45 (3), 115.52 (1), 70.21 (9), 67.07 (8), 57.97 (7), 57.05 (5), 55.04 (6) ppm. ESI-MS: $m/z$ (%) = 715 (100) $[LuNa(L_C)]^+$.

**$[YNa(L_C)(Cl)]\cdot 2.2\,NaCl\cdot 0.7\,MeOH$:** IR ṽ = 1625 (C=N) cm$^{-1}$. $C_{29.7}H_{32.8}N_3O_{6.7}Na_{3.2}Cl_{3.2}Y$: calcd. C 43.78, H 4.06, N 5.16; found C 43.81, H 4.04, N 4.72. Similar results were obtained for the paramagnetic complexes $[YbNa(L_C)(Cl)]\cdot 4.1\,NaCl$, $[TbNa(L_C)(Cl)]\cdot 1.5\,NaCl$, $[TmNa(L_C)]Cl\cdot 4.3\,NaCl$, $[DyNa(L_C)(Cl)]\cdot 2.3\,NaCl$, $[EuNa(L_C)(Cl)]\cdot 6.5\,NaCl$. IR $\upsilon_{C=N}$ varies within the range 1620–1629 cm$^{-1}$.

**$[EuNa(L_C)(Cl)]\cdot 6.5\,NaCl$:** IR ṽ = 1623 (C=N) cm$^{-1}$. $C_{29}H_{30}N_3O_6Na_{7.5}Cl_{7.5}Eu$: calcd. C 31.47, H 2.73, N 3.80; found C 31.60, H 2.73, N 3.56. $^1$H NMR ($CD_3OD$), paramagnetic: δ = 19.46 (s, 2 H, 6-H), 11.37 (d, 1 H, 13-H), 5.67 (m, 2+ 1 H, 9-H + 11-H), 5.31 (t, 1 H, 12-H), 4.42 (m, 2 H, 8-H), 4.22 (m, 2 H, 5-H), 4.21 (t, 2 H, 1-H), 4.19 (t, 1 H, 10-H), 3.95 (m, 2 H, 9-H), 2.63 (t, 2 H, 8-H), 1.98 (d, 2 H, 3-H), 0.52 (d, 2 H, 2-H), –1.00 (s, 2 H, 6-H), –9.57 (s, 2 H, 5-H), –12.87 (s, 2 H, 7-H), –29.90 (s, 2 H, 4-H) ppm. $^{13}$C NMR ($CD_3OD$): δ = 152.38 (4), 134.24 (10), 131.98 (2), 124.39 (12), 119.55 (6), 113.57 (11), 110.98 (3), 106.16 (1), 92.04 (5), 77.10 (13), 76.90 (7), 70.99 (9), 66.90 (8) ppm.

**$[YbNa(L_C)(Cl)]\cdot 4.1\,NaCl$:** IR ṽ = 1626 (C=N) cm$^{-1}$. $C_{29}H_{30}N_3O_6Na_{5.1}Cl_{5.1}Yb$: calcd. C 35.27, H 3.06, N 4.25; found C 35.29, H 2.76, N 3.86. ESI-MS: $m/z$ (%) = 713 (100) $[YbNa(L_C)]^+$.

**$[TbNa(L_C)(Cl)]\cdot 1.5\,NaCl$:** IR ṽ = 1623 (C=N) cm$^{-1}$. $C_{29}H_{30}N_3O_6Na_{2.5}Cl_{2.5}Tb$: calcd. C 42.40, H 3.68, N 5.11; found C 42.72, H 3.64, N 4.74. ESI-MS: $m/z$ (%) = 699 (100) $[TbNa(L_C)]^+$.

**$[TmNa(L_C)(Cl)]\cdot 4.3\,NaCl$:** IR ṽ = 1625 (C=N) cm$^{-1}$. $C_{29}H_{30}N_3O_6Na_{5.3}Cl_{5.3}Tm$: calcd. C 35.00, H 3.04, N 4.22; found C 35.03, H 2.53, N 3.69. ESI-MS: $m/z$ (%) = 708 (100) $[TmNa(L_C)]^+$.

**$[DyNa(L_C)(Cl)]\cdot 2.3\,NaCl$:** IR ṽ = 1623 (C=N) cm$^{-1}$. $C_{29}H_{30}N_3O_6Na_{3.3}Cl_{3.3}Dy$: calcd. C 39.95, H 3.47, N 4.82, found C 40.07, H 3.22, N 4.23. ESI-MS: $m/z$ (%) = 704 (100) $[DyNa(L_C)]^+$.

**Preparation of $[Ln(H_3L_C)(Cl)_3]\cdot x\,LiCl\cdot y\,EtOH$:** LiOH ($0.9\times10^{-3}$ mol) dissolved in ethanol was added to an ethanolic suspension of Moden·3 HCl ($0.3\times10^{-3}$ mol) up to pH ≈ 8. $LnCl_3\cdot n\,H_2O$ ($0.3\times10^{-3}$ mol) (where Ln = Lu, Eu, Tb, Y with $n$ = 6, Ln = La with $n$ = 7) was added to an ethanolic solution of $H_2L'$ ($0.3\times10^{-3}$ mol) and the two solutions were mixed and refluxed for 5 h. The yellow solution, reduced in volume under reduced pressure, separated a yellow precipitate which was filtered, washed with ethanol and dried in vacuo. The reported stoichiometry and the Ln/Cl ratio were ascertained by SEM-EDS together with elemental analysis.

**$[Eu(H_3L_C)(Cl)_3]\cdot 0.6\,LiCl$:** IR ṽ = 1647 (C=N) cm$^{-1}$. $C_{29}H_{33}N_3O_6Li_{0.6}Cl_{3.6}Eu$: calcd. C 43.36, H 4.14, N 5.23; found C 43.40, H 4.03, N 4.91. $^1$H NMR ($CD_3OD$), paramagnetic: δ = 11.83 (s, broad, 8 H, aliph.), 7.42 (d, 1 H, 13-H), 7.06 (t, 1 H, 12-H), 6.67 (m, 2 H, 10-H + 11-H), 6.53 (m, 2 H, 7-H), 5.96 (d, 2 H, 2-H), 5.93 (s, 2 H, 4-H), 5.33 (s, broad, 8 H, aliph.), 4.00 (t, 2 H, 1-H), 2.22 (d, 2 H, 3-H) ppm.

**$[Lu(H_3L_C)(Cl)_3]\cdot 1\,LiCl\cdot 1.4\,H_2O$:** IR ṽ = 1651 (C=N) cm$^{-1}$. $C_{29}H_{35.8}N_3O_{7.4}LiCl_4Lu$: C 40.11, H 4.15, N 4.84; found C 40.36, H 4.15, N 4.39. $^1$H NMR ($CD_3OD$): δ = 8.63 (s, 2 H, 4-H), 7.39 (d, 2 H, 3-H), 7.17 (d, 2 H, 2-H), 7.16 (d, 1 H, 10-H), 6.89 (t, 1 H, 12-H), 6.81 (t, 2 H, 1-H), 6.75 (d, 1 H, 13-H), 6.66 (t, 1 H, 11-H), 4.67 (m, 4 H, 8-H), 4.56 (m, 4 H, 9-H), 4.13 (m, 4 H, 5-H), 3.85 (s, 2 H, 7-H), 3.04 (m, 4 H, 6-H) ppm.

**$[La(H_3L_C)(Cl)_3]\cdot 1.8\,LiCl\cdot 2.9\,H_2O$:** IR ṽ = 1645 (C=N) cm$^{-1}$. $C_{29}H_{38.8}N_3O_{8.9}Li_{1.8}Cl_{4.8}La$: calcd. C 41.20, H 4.63, N 4.97; found C 41.15, H 4.61, N 5.24.

**$[Tb(H_3L_C)(Cl)_3]\cdot 0.2\,LiCl\cdot EtOH$:** IR ṽ = 1653 (C=N) cm$^{-1}$. $C_{31}H_{39}N_3O_7Li_{0.2}Cl_{3.2}Tb$: calcd. C 44.36, H 4.68, N 5.01; found C 44.48, H 4.67, N 5.00.

**$[Er(H_3L_C)(Cl)_3]\cdot 2\,LiCl\cdot H_2O\cdot EtOH$:** IR 1652 (C=N) cm$^{-1}$. $C_{31}H_{41}N_3O_8Li_2Cl_5Er$: calcd. C 39.52, H 4.39, N 4.46; found C 40.00, H 4.39, N 4.42.

**X-ray Crystallographic Study:** Diffraction data were collected at room temperature on a Philips PW1100 automatic four-circle diffractometer (FEBO System) using the graphite-monochromated Mo-Kα radiation and ω-2θ scan method. Lattice parameters were obtained from least-squares refinement of the setting angles of 30 reflections with $10 \le 2\theta \le 24°$. Table 1 lists a summary of the crystallographic data and structure refinement. No sign of crystal deterioration was revealed by monitoring three standard reflections after every 200 measurements but the quality of the crystals was very poor, even after several attempts with different crystals. The structure was solved by standard Patterson methods and subsequently completed by a combination of least-squares techniques and Fourier syntheses with SHELX program.[33,34] All the benzene rings were refined as rigid bodies, the hydrogen atoms were included in the idealized positions with fixed C–H distances (C–H = 0.93 Å) and isotropic temperature factors fixed to $1.2\times U$(eq) of the preceding carbon atom.

The poor quality of the crystals did not give very good data. In particular, serious disorder in the C3–C5, O5 atoms and the coordinated propanol molecule was found and high values of thermal parameters were maintained to absorb the disorder.

Listing of selected bond lengths and angles pertinent to the coordination sphere are summarized in Table 2. Additional crystallographic data, atomic coordinates, anisotropic thermal parameters, and full listings of bond lengths and angles are provided as supplementary material to CCDC. Final geometrical calculations and drawings were carried out with the PARST program[35] and the XP utility of the Siemens package[36] respectively, running on a DIGITAL ALPHA-AXP 300 computer.

CCDC-251962 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystal and intensity data for the DyNa complex.

| | |
|---|---|
| Empirical formula | $C_{32}H_{30}ClDyN_3NaO_7$ |
| Formula mass | 789.53 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ (no. 14) |
| $a$ [Å] | 9.601(2) |
| $b$ [Å] | 12.927(2) |
| $c$ [Å] | 26.638(4) |
| β [°] | 99.55(3) |
| $V$ [Å$^3$] | 3260(1) |
| $Z$ | 4 |
| Calcd. density [g cm$^{-3}$] | 1.609 |
| μ [mm$^{-1}$] (Mo-$K\alpha$) | 2.437 |
| Range of rel. transm. factors[a] [%] | 88–100 |
| θ limits [°] | 6.3–52 |
| Data collected/unique | 6749/6606 |
| Data observed | 6443 [$F \geq 3\sigma(F)$] |
| No. of parameters (obsd. per parameter) | 351 (9.8) |
| $R(\Sigma(\|F_o\| - \|F_c\|) / \Sigma\|F_o\|)$ | 0.059 |
| $R_w[\Sigma w(\|\|F_o\| - \|F_c\|)^2 / \Sigma w(F_o)^2]^{1/2}$ | 0.130 |
| Highest map residual [e Å$^{-3}$] | 1.12 |

[a] Corrections: Lorentz-polarization and absorption (empirical, ψ scan).

Table 2. Selected bond lengths [Å] and angles [°] of the DyNa complex .

| Bond lengths [Å] | | | |
|---|---|---|---|
| Dy–O(1) | 2.236(5) | Na–O(1) | 2.354(6) |
| Dy–O(2) | 2.226(4) | Na–O(2) | 2.323(5) |
| Dy–O(3) | 2.185(6) | Na–O(4) | 2.410(7) |
| Dy–N(1) | 2.474(8) | Na–O(5) | 2.40(1) |
| Dy–N(2) | 2.556(7) | Na–O(6) | 2.376(8) |
| Dy–N(3) | 2.494(7) | Na–O(7) | 2.33(1) |
| Dy–Cl | 2.719(2) | | |
| | | N(1)–C(7) | 1.24(2) |
| Dy···Na | 3.496(3) | N(3)–C(19) | 1.26(1) |
| **Angles [°]** | | | |
| O(1)–Dy–O(2) | 79.2(2) | O(1)–Na–O(2) | 74.9(1) |
| O(1)–Dy–N(1) | 74.3(3) | O(2)–Na–O(4) | 66.2(2) |
| N(1)–Dy–N(2) | 70.5(3) | O(4)–Na–O(5) | 63.6(4) |
| N(2)–Dy–N(3) | 68.3(2) | O(5)–Na–O(6) | 68.4(4) |
| N(3)–Dy–O(2) | 73.7(2) | O(1)–Na–O(6) | 66.2(3) |
| O(1)–Dy–O(3) | 88.7(2) | O(1)–Na–O(7) | 115.2(4) |
| N(1)–Dy–O(3) | 98.5(2) | O(2)–Na–O(7) | 113.9(4) |
| N(2)–Dy–O(3) | 75.0(3) | O(4)–Na–O(7) | 113.8(3) |
| N(3)–Dy–O(3) | 94.8(2) | O(5)–Na–O(7) | 96.8(6) |
| O(2)–Dy–O(3) | 92.3(2) | O(6)–Na–O(7) | 102.5(4) |
| Cl–Dy–O(1) | 98.5(1) | | |
| Cl–Dy–O(2) | 93.5(1) | | |
| Cl–Dy–N(1) | 79.2(2) | Line Cl–Dy / Dy–O(3) 171 | |
| Cl–Dy–N(2) | 96.4(2) | | |
| Cl–Dy–N(3) | 80.9(2) | | |

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