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Heterodinuclear Macrocyclic Complexes Containing Both Nickel(II) and Lanthanide(III) Ions

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Introduction

Heterodinuclear complexes often exhibit unique properties that distinguish them from the analogous homodinuclear or mononuclear complexes. In particular, when two different metal ions are bound by the ligand(s) in the close proximity, the two metal centers may cooperate in catalytic processes. Such a cooperativity is in fact observed for some metalloenzymes or low-valent metal clusters.

Another interesting catalytic systems are formed when the reactivity of the metal ion is tuned by the macrocyclic ligand. To mention just two examples, transition metal complexes of porphyrins are involved in numerous catalytic oxidations,[1] while lanthanide complexes of macrocyclic Schiff bases or Schiff base-derived ligands are excellent catalysts for RNA hydrolysis.[2]

The heterodinuclear and heteropolynuclear complexes containing both transition metal and lanthanide ions are rare,[3] and study of these complexes has concentrated on the interesting magnetic properties of $Gd^{III}-Cu^{II}$ couple. Since the lanthanide and transition metal ions differ remarkably in their chemistry, the combination of the different reactivities of these ions may lead, in our opinion, to unique catalytic systems. In the search of such systems we have undertaken the synthesis of complexes that incorporate both type of ions within the well-defined macrocyclic environment.

We have chosen for this purpose the macrocyclic Schiff base $\mathbf{L}^{-2}$ ($\mathbf{H_2L}$ = 11,22-dimethyl-3,7,15,18-tetraazatricyclo[18,3,1,$1^{9,13}$]pentacosa-1(24),2,7,9(25),10,12,14,18,20,22-decaene-5,24,25-triol) (Figure 1) because of the documented ability of $\mathbf{L}^{-2}$ to form heterodinuclear complexes containing relatively large Pb(II) ion.[4] In general, macrocyclic Schiff bases are synthetically flexible ligands and tuning of their core diameter allows selective coordination of metal ions of different size. For example, the products of 2+2 condensation of 2,6-diformylphenols with diamines are suitable for coordination of two transition metal ions,[5] while analogous macrocycles obtained from 2,6-diformylpyridine are fit for coordination of large lanthanide ions.[6]

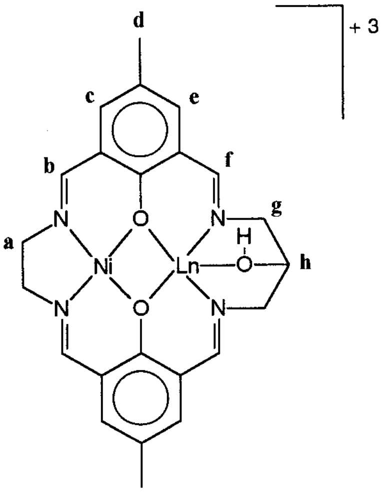

Figure 1. General structure and NMR labeling scheme of **[LnNiL]-Cl$_3$** (chloride anions omitted) complexes.

In this report we present the synthesis of **[LnNiL]Cl$_3$** complexes of the ligand $\mathbf{L}^{-2}$, where Ln = La(III), Ce(III), Pr(III), Nd(III), Sm(III), or Eu(III). To the best of our knowledge, this is the first example of complexes containing transition metal and lanthanide ions, both coordinated within the macrocyclic core. The compounds have been characterized by spectroscopic methods, including detailed ^{1}H and ^{13}C NMR analysis of paramagnetic species. In the case of the **[LaNiL]-Cl$_3$** complex the X-ray crystal structure has also been determined.

Experimental Section

Synthesis. 2,6-Diformyl-4-methylphenol[8] and [*N,N′*-bis(3-formyl-5-methylsalicylidene)ethylenediaminato]nickel(II)[5b,8] were prepared by literature methods. Lanthanide salts (99.9%) and deuterated solvents were obtained from Aldrich. Other reagents and solvents were of analytical grade and used without further purification.

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[LaNiL]Cl$_3$: 204.5 mg of [*N*,*N*′-bis(3-formyl-5-methylsalicylidene)-ethylenediaminato]nickel(II) (0.5 mmol) and 185.7 mg of $LaCl_3 \cdot 7H_2O$ (0.5 mmol) in 30 mL of methanol were stirred at reflux for 30 min. A 45 mg amount of 2-hydroxypropylene-1,3-diamine (0.5 mmol) was then added, and the mixture was refluxed for 15 h to give orange-red solution. It was filtered and evaporated to dryness. The residue was recrystallized twice from methanol/acetonitrile and dried in a vacuum to give 285 mg of crystalline orange complex. Yield 80.5%. Anal. Calcd for $C_{23}H_{24}O_3N_4Cl_3NiLa$: C, 39.00; H, 3.41; N, 7.91. Found: C, 38.64; H, 3.62; N, 7.88. ^1H NMR (CD_3OD, see Figure 1 for labeling scheme): δ 9.74 (2H, s, H_b), 8.35 (2H, s, H_f), 7.55 (2H, d, H_e), 7.42 (2H, s, H_c), 4.60 (1H, t, H_h), 4.09 (2H, q, H_g), 4.07 (4H, m, H_a and $H_{a'}$), 3.86 (2H, d, $H_{g'}$), 2.35 (6H, s, H_d). ^{13}C NMR (CD_3OD): δ 169.94 (C_f), 165.01 (C_b), 155.34 (phenolic), 142.88 (C_e), 139.56 (C_c), 129.31 (aromatic), 128.28 (aromatic), 125.08 (aromatic), 70.70 (C_h), 63.62 (C_g), 58.16 (C_a),19.84 (C_d).

The remaining lanthanide complexes were obtained in the same way as **[LaNiL]Cl$_3$**.

[CeNiL]Cl$_3$: Anal. Calcd for $C_{23}H_{24}O_3N_4Cl_3NiCe$: C, 38.93; H, 3.41; N, 7.90. Found: C, 38.70; H, 3.63; N, 8.02. ^1H NMR (CD_3OD): δ 13.07 (2H, s, H_f), 9.40 (2H, s, H_b), 7.48 (2H, s, H_e), 6.78 (2H, s, H_c), 5.98 (2H, d, H_g), 3.05 (2H, s, H_a), 2.08 (6H, s, H_d), 1.28 (2H, s, $H_{a'}$), −1.12 (1H, s, H_h), −1.51 (2H, d, $H_{g'}$). ^{13}C NMR (CD_3OD) δ 168.65 (C_f), 162.10 (C_b), 152.16 (aromatic), 141.68 (C_e), 138.12 (C_c), 134.87 (aromatic), 129.43 (aromatic), 126.60 (aromatic), 59.36 (C_g), 55.88 (C_a), 52.97 (C_h), 19.47 (C_d).

[PrNiL]Cl$_3$: Anal. Calcd for $C_{23}H_{24}O_3N_4Cl_3NiPr$: C, 38.89; H, 3.41; N, 7.89. Found: C, 38.55; H, 3.73; N, 7.58. ^1H NMR (CD_3OD): δ 3.38 (2H, s, H_a), 0.07 (2H, s, $H_{a'}$), 8.85 (2H, s, H_b), 7.24 (2H, s, H_c), 2.44 (6H, s, H_d), 8.02 (2H, s, H_e), 20.00 (2H, s, H_f), 5.35 (2H, s, H_g), −4.01 (2H, s, $H_{g'}$), −4.01 (1H, s, H_h). ^{13}C NMR (CD_3OD): δ 168.15 (C_f), 160.84 (C_b), 152.46 (aromatic), 145.77 (aromatic), 141.13 (C_e), 138.44 (C_c), 132.78 (aromatic), 131.11 (aromatic), 54.21 (C_a), 51.83 (C_g), 31.56 (C_h), 19.44 (C_d).

[NdNiL]Cl$_3$: Anal. Calcd for $C_{23}H_{24}O_3N_4Cl_3NiNd$: C, 38.70; H, 3.39; N, 7.85. Found: C, 38.24; H, 3.65; N, 7.96. ^1H NMR (CD_3OD): δ 4.26 (2H, s, H_a), 3.71 (2H, s, $H_{a'}$), 10.87 (2H, s, H_b), 8.18 (2H, s, H_c), 2.45 (6H, s, H_d), 7.62 (2H, s, H_e), 23.27 (2H, s, H_f), 8.28 (2H, s, H_g), 5.39 (2H, s, $H_{g'}$), 8.18 (1H, s, H_h) ^{13}C NMR (CD_3OD): δ 168.40 (C_f), 162.98 (C_b), 150.51 (aromatic), 145.86 (aromatic), 139.48 (C_e), 139.00 (C_c), 136.58 (aromatic), 131.24 (aromatic), 62.09 (C_g), 56.64 (C_a), 51.93 (C_h),19.15 (C_d).

[SmNiL]Cl$_3$: Anal. Calcd for $C_{23}H_{24}O_3N_4Cl_3NiSm$: C, 38.37; H, 3.36; N, 7.78. Found: C, 38.17; H, 3.61; N, 7.89. ^1H NMR (CD_3OD) δ 4.25 (2H, s, H_a), 4.18 (2H, s, $H_{a'}$), 12.16 (2H, s, H_b), 7.34 (2H, s, H_c), 2.34 (6H, s, H_d), 7.65 (2H, s, H_e), 7.92 (2H, s, H_f), 4.02 (2H, d, H_g), 3.36 (2H, d, $H_{g'}$), 3.71 (1H, s, H_h). ^{13}C NMR (CD_3OD) δ 171.99 (C_f), 164.83 (C_b), 155.07 (aromatic), 143.30 (C_e), 139.39 (C_c), 131.54 (aromatic), 129.36 (aromatic), 125.69 (aromatic), 69.80 (C_h), 63.87 (C_g), 55.92 (C_a),19.85 (C_d).

[EuNiL]Cl$_3$: Anal. Calcd for $C_{23}H_{24}O_3N_4Cl_3NiEu$: C, 38.29; H, 3.35; N, 7.77. Found: C, 37.93; H, 3.76; N, 7.39. ^1H NMR (CD_3OD): δ 6.67 (4H, s, H_a and $H_{a'}$), 19.21 (2H, s, H_b), 6.54 (2H, s, H_c), 2.10 (6H, s, H_d), 7.49 (2H, s, H_e), −18.96 (2H, s, H_f), −0.22 (2H, s, H_g), −5.02 (2H, s, $H_{g'}$), −2.84 (1H, s, H_h), ^{13}C NMR (CD_3OD): δ 172.40 (C_f), 169.38, 159.33, 149.76 (C_e), 138.67 (C_c), 109.68, 104.9, 96.3, 61.50 (C_g), 54.97 (C_a), 20.71 (C_d).

Methods. The NMR spectra were taken on Bruker AMX 300 spectrometer. The chemical shifts were referenced to the residual solvent signal or TMS. The **[LaNiL]Cl$_3$** complex was taken as a diamagnetic reference compound for the calculations of isotropic shifts. The resulting isotropic shifts were fit to eq 2 as described elsewhere.[7] The magnitude COSY spectrum was acquired using 512 data points in both dimensions. The data were processed by using a square sine bell window in both dimensions and zero filled to 1K × 1K matrix. The phase-sensitive (TPPI) NOESY spectra were recorded using mixing times varying from 15 to 400 ms. HMQC spectra were recorded using BIRD preparation period and 512 × 512 data points. A square sine function was used for apodization in both dimensions. Electronic spectra were measured on Cary 5 UV−vis−NIR spectrophotometer. IR spectra were recorded on Bruker IFS 113V instrument using KBr pellets and Nujol mulls. Elemental analyses were obtained from elemental analyses facility in this department.

Table 1. Crystallographic Data

empirical formula	$C_{23}H_{24}Cl_3LaN_4NiO_3$
formula weight	708.4
temperature	298(2) K
wavelength	0.710 73 Å
space group (no.)	$P2_1/c$ (14)
unit cell dimensions	$a = 9.435(7)$ Å
	$b = 17.917(11)$ Å
	$c = 15.449(10)$ Å
	$\beta = 106.77(6)^o$
volume	2501(3) Å^3
Z	4
density measured	1.91 Mg/m^3, by flotation in CH_3Cl/CH_3Br
density calculated	1.882 Mg/m^3
absorption coefficient μ_{calc}	2.79 mm^{-1}
final R^a indices [$I \geq 2\sigma(I)$]	$R(F) = 0.0299$, $R_w(F^2) = 0.0627$
final R indices [all reflections]	$R(F) = 0.0422$, $R_w(F^2) = 0.0669$

^{a} $R(F) = \sum|F_o - F_c|/\sum|F_c|$; $R_w(F^2) = \sqrt{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2}$.

X-ray Analysis. Single crystals of **[LaNiL]Cl$_3$** were obtained by slow diffusion of acetonitrile into methanol solution of the complex. A suitable crystal was cut from a larger one, and mounted on a Kuma KM4 diffractometer with κ geometry and a graphite monochromator. The unit cell parameters were determined from angular settings of 25 reflections with 2θ between 18 and 24°. The stability of data collection was monitored with 3 control reflections remeasured every 100 intensities. The data were corrected for Lorentz and polarization factors, but not extinction. Absorption corrections were calculated using the ABSORB program.[9] The position of the lanthanum ion was found from a Patterson map, other atoms were found from subsequent difference Fourier syntheses. The C-bonded hydrogen atoms were placed from geometry, and the O-bonded ones were found in a difference Fourier map. The structure was refined with full-matrix least-squares with all non-hydrogen atoms anisotropic, and the hydrogen atoms isotropic with their temperature factors linked with those of the respective C or O atoms. During the refinement it was necessary to assume disorder of a fragment composed of two carbon atoms (C9 and C10) and their hydrogen atoms because of anomalous temperature factors of the respective C atoms. The occupancy factors for both positions of the fragment refined to 0.46(3) (C9−C10) and 0.54(3) (C91−C101). The calculations were performed with SHELXS[10a] and SHELXL-93[10b] programs with commonly used atom scattering factors and anomalous dispersion corrections.[11] The basic crystallographic data are presented in Table 1 and other details of data collection and the structure refinement are given in Supporting Information.

Results and Discussion

The mixed lanthanide(III)−nickel((II) complexes, **[LnNiL]-Cl$_3$** , where Ln = La(III), Ce(III), Pr(III), Nd(III), Sm(III), or Eu(III), have been synthesized in a stepwise synthetic strategy developed by Okawa and others for macrocyclic heterodinuclear systems.[4,8,12] The IR spectra of the obtained series of compounds are almost identical that suggests the similar structure of the **[LnNiL]Cl$_3$** complexes. The observation of the C═N bands at 1606 and 1632−1635 cm^{-1} confirms the formation of the Schiff

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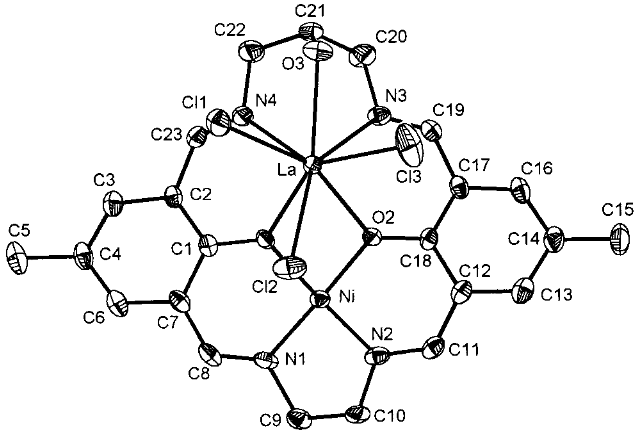

Figure 2. ORTEP drawing of the **[LaNiL]Cl$_3$** molecule together with the atom labeling scheme. Hydrogen atoms are omitted for clarity.

base ligand and the 3340 cm^{-1} band indicates the presence of protonated alcoholic group. The UV−vis spectra of **[LnNiL]Cl$_3$** complexes (CH$_3$OH solutions) are also very similar to each other and are dominated by intense ligand bands at 223, 253, 319, and 382 nm (the latter is the $\pi-\pi^*$ transition of the azomethine group), while the d−d transition of the square-planar Ni(II) appear as shoulder at ca. 540 nm. The f−f transitions of Ln(III) ions are visible only above 550 nm, in the region not obscured by the ligand and d−d absorptions.

The chemical shifts of **[LnNiL]Cl$_3$** complexes exhibit strong temperature dependence, typical for paramagnetic complexes. The shifts are also somewhat concentration dependent, which may point to some degree of solvent coordination, association of the complexes in solution, or partial deprotonation of the alcoholic group.

The ^{1}H NMR spectra of freshly prepared CD$_3$OD solutions of **[EuL]Cl$_3$** complex show only one pure complex present. On standing, however, a growing amount of new paramagnetic species is formed. Similar decomposition process is observed for the other **[LnNiL]Cl$_3$** complexes (see e.g. signals indicated by asterisk in Figure 3). The rate of this decomposition process is increasing along the lanthanide ion series. Likely this fact reflects the poor match of the smaller Ln^{3+} ions with the coordinating compartment of the ligand **L**$^{-2}$. This effect causes the decrease of stability of the **[LnNiL]Cl$_3$** complexes with the decreasing radius of the Ln(III) ion. Such behavior explains why the synthesis of late **[LnNiL]Cl$_3$** complexes is not straightforward. In fact, the smaller lanthanide ions form complexes under the same reaction conditions as applied for early lanthanide ions. In this case, however, the reaction yields mixtures of different complexes. The separation and characterization of these complexes are now in progress.

Crystal Structure. The X-ray crystal structure of the **[LaNiL]Cl$_3$** complex (Figure 2) reveals essentially planar ligand backbone (with the exception of the bent fragment N3, N4, O3, C20, C21, and C22), similar to that observed in the related complex[4] [PbCuL](ClO$_4$)$_2$·DMF. The eight-coordinate La(III) ion is displaced 1.71 Å above the mean plane defined by the two phenolic oxygen atoms O1 and O2 and the two imino nitrogen atoms N3 and N4. Its coordination sphere is completed by three chloride anions, which form a plane almost parallel (the inclination angle is 9.4°) to the previous plane, and by the protonated alcoholic oxygen atom O3 (which belongs to neither plane) and is highly irregular. The coordination geometry imposed by the macrocyclic ligand brings about a kind of clustering of the Cl$^-$ anions, what in turn, together with differences among the lengths of La(III)−ligand bonds, is one of the reasons of large asymmetry of the coordination environment of La(III). The Ni(II) ion is placed in the center of the slightly distorted square defined by the two remaining imino nitrogen atoms and the bridging phenolic oxygen atoms. The metal−ligand bond lengths, presented in Table 2, are typical for La(III) (the Cambridge Structural Database query gave the following results: La−Cl 2.722−3.019 Å, mean 2.865 Å; La−N$_{\text{Schiff}}$ 2.484−2.818 Å, mean 2.656 Å; La−OH 2.483−2.659 Å, mean 2.559 Å), whereas they may be regarded as rather short ones in the case of Ni(II) (the CSD data: Ni−N$_{\text{Schiff}}$ 1.823−1.914 Å, mean 1.860 Å; Ni−OH 1.901−2.292 Å, mean 2.099 Å), in accord with the low-spin nature of this ion.

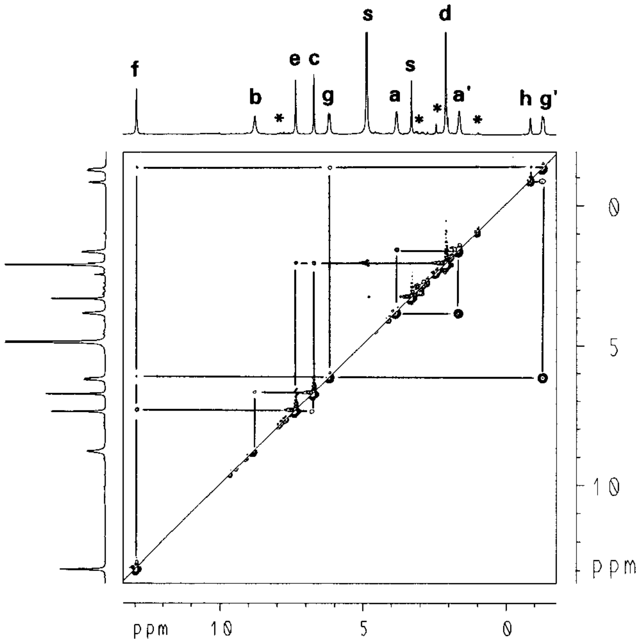

Figure 3. NOESY (upper left) and COSY (lower right) spectra of **[CeNiL]Cl$_3$** (CD$_3$OD solution, 294 K); s, solvent and HDO signals; *, impurities (see text for details).

Table 2. Distances (Å) and Angles (deg) for the Coordination Environments of Lanthanum and Nickel

Distances			
La−O(2)	2.541(4)	La−Ni	3.370(2)
La−O(3)	2.565(4)		
La−O(1)	2.573(3)	Ni−N(2)	1.831(4)
La−N(4)	2.642(5)	Ni−N(1)	1.834(4)
La−N(3)	2.691(4)	Ni−O(2)	1.846(3)
La−Cl(3)	2.754(2)	Ni−O(1)	1.856(4)
La−Cl(2)	2.810(2)		
La−Cl(1)	2.838(2)		
Angles			
O(2)−La−O(3)	124.58(13)	N(4)−La−Cl(2)	126.85(10)
O(2)−La−O(1)	57.00(11)	N(3)−La−Cl(2)	145.31(10)
O(3)−La−O(1)	128.26(12)	Cl(3)−La−Cl(2)	88.42(7)
O(2)−La−N(4)	102.10(14)	O(2)−La−Cl(1)	158.43(8)
O(3)−La−N(4)	63.62(14)	O(3)−La−Cl(1)	75.26(12)
O(1)−La−N(4)	65.98(13)	O(1)−La−Cl(1)	105.27(9)
O(2)−La−N(3)	64.38(11)	N(4)−La−Cl(1)	78.20(12)
O(3)−La−N(3)	60.35(13)	N(3)−La−Cl(1)	133.63(10)
O(1)−La−N(3)	92.95(12)	Cl(3)−La−Cl(1)	103.08(7)
N(4)−La−N(3)	70.96(13)	Cl(2)−La−Cl(1)	81.06(8)
O(2)−La−Cl(3)	89.39(11)		
O(3)−La−Cl(3)	81.54(13)	N(2)−Ni−N(1)	86.7(2)
O(1)−La−Cl(3)	143.18(10)	N(2)−Ni−O(2)	94.9(2)
N(4)−La−Cl(3)	143.84(11)	N(1)−Ni−O(2)	177.2(2)
N(3)−La−Cl(3)	84.02(11)	N(2)−Ni−O(1)	177.1(2)
O(2)−La−Cl(2)	81.79(9)	N(1)−Ni−O(1)	96.0(2)
O(3)−La−Cl(2)	151.33(10)	O(2)−Ni−O(1)	82.49(14)
O(1)−La−Cl(2)	73.44(9)		

NMR Spectral Assignment of the [LnNiL]Cl$_3$ Complexes. The ^{1}H NMR spectrum of **[LaNiL]Cl$_3$** solution in CD$_3$OD shows two imino and two benzo protons in accord with the asymmetrical nature of the complex. The identity of the macrocylic ligand was confirmed by the full assignment of the spectrum based on the NOESY measurement. Similarly, the ^{13}C NMR spectrum (CD$_3$OD solution) of the complex confirms that the structure of the complex observed for the solid is preserved in the solution. All twelve expected signals are observed in the spectrum; the carbons connected to hydrogens have been assigned on the basis of HMQC experiment. The chemical shifts of the ^{1}H and ^{13}C signals, as well as line splitting pattern, agree well with the structure of the macrocyclic Schiff base $\mathbf{L}^{-2}$ and the diamagnetic character of the **[LaNiL]Cl$_3$** complex.

In the case of paramagnetic Ce(III), Pr(III), Nd(III), and Eu(III) (and to a smaller extent Sm(III)) derivatives the chemical shifts of protons and carbons are difficult to predict *a priori*. Particularly the shifts of signals due to positions **f**, **g**, and **h** (see labeling scheme, Figure 1), close to Ln(III) ion, exhibit large influence of the paramagnetic metal ion. Moreover, the ^{1}H NMR lines are in most cases too broad for the *J* splitting to be detected. For those reasons, the assignment of the spectra has to be based on 2D techniques.

In the case of **[CeNiL]Cl$_3$** complex the signals of protons **d** at 2.08 ppm and **h** at −1.12 ppm can be easily found on the basis of integration (intensity 6H and 1H, respectively). Analysis of the NOE connectivities along the ligand framework, starting from the known position **h**, enables the firm assignment of the spectra. Thus, the signal **h** shows both COSY and NOESY correlation (Figure 3) to the signal **g′**, which, in turn, shows both COSY and NOESY correlation to the geminal proton **g** (in this case line broadening is not severe and actual splitting of signals **g** and **g′** is observed). Both signals **g** and **g′** give a NOESY cross-peak to the signal **f**. The observation of the COSY (large *J* splitting) between the signals **h** and **g′** and not between **h** and **g**, together with the known Karplus relation indicates that the position **g′** corresponds to the equatorial methylene proton and position **g** to the axial one. In the similar fashion, the sequence of signals **f**, **e**, **d**, **c**, and **b** can be assigned on the basis of the other observed NOESY cross-peaks. Additionally COSY correlation between the aromatic protons **c** and **e** is observed. The remaining pair of signals, correlated both in NOESY and COSY spectra, must correspond to geminal protons **a** and **a′** (the NOESY cross-correlation between the hydrogen **b** and the pair of geminal hydrogen atoms **a**, **a′** is not observed due to the fast relaxation).

Similar analysis of COSY and NOESY spectra of Pr(III), Nd(III), Sm(III), and Eu(III) complexes confirms the same type of ligand coordination in these complexes. In the case of Pr(III), Nd(III), and Eu(III) derivatives some of the cross-peaks observed for **[LaNiL]Cl$_3$**, **[CeNiL]Cl$_3$**, and **[SmNiL]Cl$_3$** are missing due to relatively short relaxation times. Nevertheless, with the additional assumption that, in general, the isotropic shifts of the proton set H_f, H_g, H_g, and H_h, are larger than those of H_a, $H_{a'}$, and H_b, the full spectral assignments of these complexes were possible.

The HMQC spectra of the **[LnNiL]Cl$_3$** complexes allowed us to correlate the ^{13}C signals with the assigned signals of connected protons, with the exception of some **[EuNiL]Cl$_3$** signals (Table 3). The spectra provided also additional confirmation of the assignment of the pairs of geminal protons **a**, **a′** and **g**, **g′**.

Table 3. Isotropic Shifts (ppm) of **[LnNiL]Cl$_3$** Complexes (294 K, CD$_3$OD Solutions)

	Ce(III)	Pr(III)	Nd(III)	Sm(III)	Eu(III)
H^a	−1.02	−0.69	0.19	0.18	2.60
$H^{a'}$	−2.79	−4.00	−0.36	0.11	2.60
H^b	−0.34	−0.89	1.13	2.42	9.47
H^c	−0.64	−0.18	0.76	−0.08	−0.88
H^d	−0.27	0.09	0.10	−0.01	−0.25
H^e	−0.07	0.47	0.07	0.10	−0.06
H^f	4.72	11.65	14.92	−0.43	−27.31
H^g	1.86	1.26	1.53	−0.07	−4.31
$H^{g'}$	−5.37	−7.87	4.19	−0.50	−8.88
H^h	−5.72	−8.61	3.58	−0.89	−7.44
C^a	−2.28	−3.95	−1.52	−2.24	−3.19
C^b	−2.91	−4.17	−2.03	−0.18	−
C^c	−1.44	−1.12	−0.56	−0.17	−0.89
C^d	−0.37	−0.40	−0.69	0.01	0.87
C^e	−1.20	−1.75	−3.40	0.42	6.88
C^f	−1.39	−1.79	−1.54	2.05	2.47
C^g	−4.25	−11.79	−1.53	0.25	−2.12
C^h	−17.73	−39.14	−18.77	0.90	−

Analysis of the Isotropic Shifts of the Paramagnetic [LnNiL]Cl$_3$ Complexes. In the paramagnetic complex the observed nucleus experiences additional shift, called the isotropic shift, δ_{iso}, that arises from the interaction of the nuclear and electronic spins.[13] The isotropic shift can be separated into through-space (dipolar contribution δ_{dip}) and through-bonds (contact contribution δ_{con}):

$$\delta_{\mathrm{iso}} = \delta_{\mathrm{dip}} + \delta_{\mathrm{con}} \tag{1}$$

The dipolar shift is given by eq 2:[14]

$$\delta_{\mathrm{dip}} = D_1G_1 + D_2G_2 = \frac{\bar{\chi} - \chi_{zz}}{2N}\left\langle\frac{1 - 3\cos^2\theta}{r^3}\right\rangle + \frac{\chi_{xx} - \chi_{zz}}{2N}\left\langle\frac{\sin^2\theta\cos 2\varphi}{r^3}\right\rangle \tag{2}$$

where χ_{xx}, χ_{yy}, and χ_{zz} are the principal components of magnetic susceptibility tensor and r, θ, and φ are polar coordinates of the given nucleus. In the case of lanthanide complexes of axial symmetry the eq 2 can be written in simplified form:[15]

$$\delta_{\mathrm{dip}} = C_jG \tag{3}$$

where C_j depends on the Ln(III) ion and G contains the information about crystal field parameters and position in space of given nucleus.

The contact shift is given by the formula[16]

$$\delta_{\mathrm{con}} = A\langle S_z\rangle/\gamma\hbar B_0 = A'\langle S_z\rangle \tag{4}$$

where A is the hyperfine coupling constant, and $\langle S_z\rangle$ is the spin expectation value.

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Table 4. Values of Parameters *G*, *A*′, Agreement Factors AF, and Calculated Contact, δ_{con}, and Dipolar, δ_{dip}, Contributions to the Isotropic Shifts of the Selected Protons (Positions **f**, **g**, **g**′, and **h** Indicated by the Superscript)

	Ce(III)	Pr(III)	Nd(III)	Sm(III)	Eu(III)	*G* (error)	*A*′ (error)	AF[a]
$\delta^{\mathbf{f}}_{con}$	2.53	7.67	11.60	−0.15	−27.59	−0.21 (0.30)	−2.58 (0.23)	0.099
$\delta^{\mathbf{f}}_{cdip}$	1.31	2.29	0.87	0.14	−0.83			
$\delta^{\mathbf{g}}_{con}$	0.37	1.12	1.71	−0.02	−4.06	−0.04 (0.08)	−0.38 (0.06)	0.260
$\delta^{\mathbf{g}}_{dip}$	0.25	0.43	0.17	0.03	−0.16			
$\delta^{\mathbf{g}'}_{con}$	1.15	3.50	5.30	−0.07	−12.60	0.78 (0.22)	−1.18 (0.17)	0.297
$\delta^{\mathbf{g}'}_{dip}$	−5.00	−8.55	−3.26	−0.54	3.11			
$\delta^{\mathbf{h}}_{con}$	1.13	3.41	5.16	−0.07	−12.28	0.99 (0.22)	−1.15 (0.17)	0.227
$\delta^{\mathbf{h}}_{dip}$	−6.25	−10.92	−4.17	−0.69	3.97			

[a] Defined as in ref 18b.

As can be seen from Table 3, the isotropic shifts of the series of **[LnNiL]Cl$_3$** complexes vary considerably and depend both on the position of given nucleus and on the type of paramagnetic Ln(III) ion. That observation, however, does not point to any major structural differences of **[LnNiL]Cl$_3$** complexes, but reflects the different magnetic properties of Ln(III) ions and different relative contributions of contact vs dipolar shifts in each case.

The trial of the evaluation of the latter contribution was based on the computer simulation[3a,7,17] of eq 2. First the data were fit assuming dominant dipolar contribution for all protons in the complex. For instance the dipolar shifts calculated in this way for [**CeNiL]Cl$_3$** are equal to −0.38, −0.91, −0.92, −0.78, −0.49, −0.70, −0.02, 0.68, −2.83, and −6.97 ppm for the positions **a** to **h**, respectively. Such calculations including all positions in the fitting procedure gave, however, very large (in the order of 50%) values of agreement factor *R*. The poor agreement of the fit arises inevitably from the presence of sizable contact contributions. On the other hand, inclusion of contact shifts as fitting parameters gave better *R* values (5.5% to 20.5%, see Supporting Information for results). This improvement is, however, deceptive, since inclusion of the contact shift at given position as fitting parameter is equivalent to omitting this position from the fitting procedure.[7a] In the case of [**LnNiL]Cl$_3$** complexes, the signals **f**, **g**, **g**′, and **h**, which are strongly influenced by the contact contributions, bear also most information about the parameters of eq 2. For this reason the calculations based on the shifts of the remaining signals cannot be regarded as accurate.

Better estimation of contact and dipolar contributions to the paramagnetic shift was made on the basis of the Reilley method,[18] which combines eqs 1, 3, and 4 into:

$$\delta_{iso}/C_j = G + A'\langle S_z\rangle/C_j \qquad (5)$$

In the idealized situation of the exactly isostructural series of Ln(III) complexes, the crystal field parameters, geometrical factors and hyperfine coupling constants are equal in each complex and hence are the constants G and A′. Since the values of $\langle S_z\rangle$ and C_j are known,[15,16] the linear fit of the eq 5, written for a set of Ln(III) complexes, gives the constants *G* and *A*′ for each position. Thus the dipolar and contact shifts can be calculated using eqs 3 and 4, respectively. Despite the fact that the coordination sphere of the Ln(III) ions in the **[LnNiL]Cl$_3$** complexes is not of axial symmetry, the above method gives the crude estimation of the contact and dipolar shifts and shows that both are important in the case of **[LnNiL]Cl$_3$** complexes (Table 4). The contact contributions strongly dominate the shifts of [**EuNiL]Cl$_3$**, while the dipolar shifts are relatively important in the case of **[CeNiL]Cl$_3$**. It should be mentioned that the calculated contact contributions to the isotropic shifts of the imino proton **f** are similar to those of imino protons of other Ln(III) macrocyclic complexes.[7]

The line widths of the paramagnetic **[LnNiL]Cl$_3$** complexes follow neither the $1/r^6$ dependence (where *r* is the proton−paramagnetic metal ion distance), expected for dominant dipolar or Curie relaxation mechanism, nor the square dependence on the chemical shifts, expected for contact relaxation.[13] In particular the signals **a**, **a**′, and **b** are broader than expected. This latter observation may reflect the dynamic process arising from the flexibility of the lateral ethylene chain, and is in accord with the disorder of that chain observed in the crystal structure.[19]

Conclusions

The macrocyclic ligand derived from 2,6-diformyl-4-methylphenol, 2-hydroxypropylene-1,3-diamine, and ethylenediamine is able to coordinate simultaneously nickel(II) and Ln(III) ions, where Ln = La, Ce, Pr, Nd, Sm, and Eu. Characterization of solutions of the obtained heterodinuclear complexes by 2D NMR techniques is consistent with the solid-state X-ray crystal structure of the Ni^{II}−La^{III} complex. The synthesis and characterization of **[LnNiL]Cl$_3$** complexes with heavier lanthanide(III) ions are currently in progress. Preliminary study indicates that the described synthetic approach can be used to obtain analogous heterodinuclear complexes with transition ions other than nickel(II).

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Supporting Information Available: Details of computer simulation of eq 2, fitting results of isotropic shifts of **[LnNiL]Cl$_3$** complexes, δ^{iso}_{ij}/C_j vs $\langle S_z\rangle_j/C_j$ plots, $\delta^{iso}_{ij}/\langle S_z\rangle_j$ vs $C_j/\langle S_z\rangle_j$ plots, and a stereoview of the **[LaNiL]Cl$_3$** complex and an X-ray crystallographic file, in CIF format, for the structure of **[LaNiL]Cl$_3$** complex are available free of charge via the Internet at http://pubs.acs.org.

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(19) An alternative explanation can be based on the possibility that a small fraction of the **[LnNiL]Cl$_3$** complex is in a 5- or 6-coordinate, high-spin Ni(II) state, that is, in the fast equilibrium with the dominant low-spin Ni(II) form.