

**SPECTROSCOPIC STUDIES OF SOME LANTHANIDE(III) NITRATE COMPLEXES
SYNTHESIZED FROM A NEW LIGAND 2,6-BIS-(SALICYLALDEHYDE
HYDRAZONE)-4-CHLOROPHENOL**

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(Received July 17, 2002; revised November 1, 2002)

ABSTRACT. The ligand 2,6-bis-(salicylaldehydehydrazone)-4-chlorophenol (H_5L) and its binuclear lanthanide(III) nitrate complexes $\{[Ln_2(H_4L)_3(NO_3)](NO_3)_2 \cdot mH_2O\}$ where $Ln = La, Ce, Pr, Nd, Sm, Gd, Dy, Er, Yb$ and Y , have been synthesized. The complexes were characterized by chemical analysis, conductance, magnetic moment measurements and infrared spectra. Infrared study indicates that the ligand behaves both as neutral and ionic O donors and as neutral N donors.

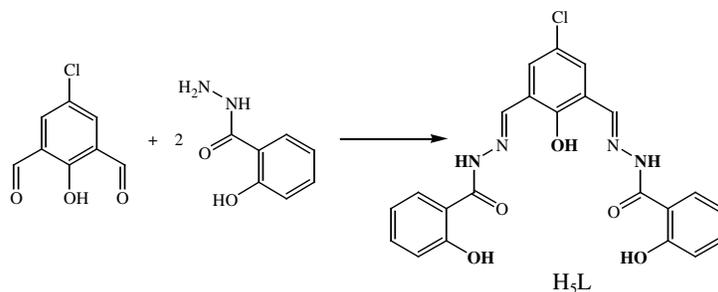
KEY WORDS: Lanthanide(III) complexes, Schiff base, 2,6-bis-(Salicylaldehydehydrazone)-4-chlorophenol, Infrared spectra, Molar conductivities, Magnetic moment

INTRODUCTION

The use of trivalent lanthanide ions and those metal and related (*e.g.* Y(III)) to control reactions involving the formation of imines groups is well known. The reaction is widely used to synthesize lanthanide complexes from macrocyclic [1-3] and macroacyclic [4-6] ligands. These complexes have been extensively studied in the past decade. They are used as catalysts [7] in transesterification, as radiopharmaceuticals [8] and as fluoroimmuno assay reagents [9, 10]. Certain Eu(III) and Nd(III) complexes have been reported to set as lasers [3]. In this work we describe the preparation of the ligand 2,6-bis-(salicylaldehydehydrazone)-4-chlorophenol (H_5L). This phenol-based macroacyclic ligand have two similar metal-binding sites sharing the phenolic oxygen atom. Due to the flexibility of the arms it was able to adjust its cavity to match the sized metal ions.

Two methods for the preparation of complexes containing macrocyclic ligands have been reported in the literature. The first method involves condensation of keto precursors with polyamines by the template method [11, 12] and in the second method, the ligand is first synthesized and isolated and the metal ion added to prepare the complexes [13, 14]. In our previous research on transition metal complexes we have used both routes [15-18]. Herein we report the reaction of H_5L with a range of Ln ($Ln = La, Ce, Pr, Nd, Sm, Gd, Dy, Er, Yb$ and Y) to give $\{[Ln_2(H_4L)_3(NO_3)](NO_3)_2 \cdot mH_2O\}$. It's to be noted that H_5L terminology is used to indicate that the ligand has five potentially replaceable protons. In the reaction only one H atom is replaced (the o-chlorophenol proton) to give an H_4L ligand. The characterization of these new lanthanides complexes is also described.

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Scheme 1

EXPERIMENTAL

Reagents

The $\text{Ln}(\text{NO}_3)_3 \cdot m\text{H}_2\text{O}$ complexes were obtained from Aldrich and were used without purification. The salicylaldehydehydrazide, ethanol and methanol were obtained from Jansen and were used without further purification. The 2,6-diformyl-4-chlorophenol was synthesized using an improvement on the method described in the literature by recrystallizing the compound in *n*-hexane/chloroform [16].

Magnetic measurement was carried out at room temperature with a Gouy balance and CuSO_4 was used as a calibrant. Infrared spectra of the compounds were recorded on a Perkin Elmer 580 B FTIR spectrophotometer as Nujol mulls using CsF windows or KBr pellets in the range $4000\text{--}400\text{ cm}^{-1}$. Electronic spectra were recorded on a Jasco spectrophotometer. Elemental analyses were obtained from the Microanalytical Service of the University of Padova (Italy).

Synthesis of 2,6-bis(salicylaldehydehydrazone)-4-chlorophenol (H₅L). 2,6-diformyl-4-chlorophenol (2 g, 10.8 mmol) and salicylaldehydehydrazide (3.3 g, 21.7 mmol) were dissolved in 30 mL of ethanol and two drops of glacial acetic acid were added. The mixture was then refluxed for two hours. Upon cooling, a yellowish precipitate was obtained. The product was isolated by filtration, washed with $2 \times 10\text{ mL}$ of ether and dried at room temperature over P_4O_{10} . The yield was 83% and the melting point is $>230\text{ }^\circ\text{C}$.

Synthesis of complexes

{[La₂(H₅L)₃(NO₃)](NO₃)₂·6H₂O}. The ligand H₅L (0.2 g, 0.409 mmol) was suspended in 20 mL of methanol. Lanthanum(III) nitrate hexahydrate (0.15 g, 0.416 mmol) was dissolved in 10 mL of methanol and the solution obtained was added to the previous suspension. The mixture was stirred and refluxed for one hour. Upon cooling the yellow precipitate obtained was filtered off and washed with $2 \times 20\text{ mL}$ of Et_2O . The compound was dried at room temperature over P_4O_{10} . Yield 65%.

{[Ce₂(H₅L)₃(NO₃)](NO₃)₂·7H₂O}. The procedure for $\{[\text{La}_2(\text{H}_5\text{L})_3(\text{NO}_3)](\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}\}$ was repeated and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.1917 g, 0.416 mmol) was used instead of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. A yellow precipitate was obtained washed with Et_2O and dried over P_4O_{10} . Yield 60%.

{[Gd₂(H₅L)₃(NO₃)](NO₃)₂·6H₂O}. The ligand H₅L (0.1 g, 0.2045 mmol) was suspended in 10 mL of methanol and $\text{LiOH} \cdot \text{H}_2\text{O}$ (0.019 g, 0.452 mmol) was added. An orange precipitate was

formed. A solution of gadolinium(III) nitrate hexahydrate (0.1028 g, 0.2228 mmol) in 15 mL of methanol was added. The mixture was then refluxed for one hour. After cooling the precipitate was isolated by filtration. The yellow solid was washed with 2 x 20 mL of ether and dried over P₄O₁₀. Yield 70%.

$\{[Nd_2(H_4L)_3(NO_3)](NO_3)_2 \cdot 5H_2O\}$. The procedure for $\{[Gd_2(H_4L)_3(NO_3)](NO_3)_2 \cdot 6H_2O\}$ was repeated and Nd(NO₃)₃·6H₂O (0.0977 g, 0.2228 mmol) was used instead of Gd(NO₃)₃·6H₂O. A yellow precipitate was obtained washed with Et₂O and dried over P₄O₁₀. Yield 63%.

$\{[Sm_2(H_4L)_3(NO_3)](NO_3)_2 \cdot 4H_2O\}$. The procedure for $\{[Gd_2(H_4L)_3(NO_3)](NO_3)_2 \cdot 6H_2O\}$ was repeated and Sm(NO₃)₃·6H₂O (0.0991 g, 0.2228 mmol) was used instead of Gd(NO₃)₃·6H₂O. A yellow precipitate was obtained washed with Et₂O and dried over P₄O₁₀. Yield 55%.

$\{[Y_2(H_4L)_3(NO_3)](NO_3)_2 \cdot 2H_2O\}$. To H₅L (0.1 g, 0.2045 mmol) in 20 mL of methanol, was added LiOH·H₂O (0.019 g, 0.452 mmol). To the orange solution obtained was added Y(NO₃)₃·6H₂O (0.0783 g; 0.2045 mmol). A yellow precipitate was formed immediately. The mixture was refluxed for one hour. Upon cooling the product was filtered off and washed with 2 x 15 mL of MeOH and 2 x 15 mL of Et₂O before being dried over P₄O₁₀. Yield 75%.

$\{[Dy_2(H_4L)_3(NO_3)](NO_3)_2 \cdot 5H_2O\}$. The procedure for $\{[Gd_2(H_4L)_3(NO_3)](NO_3)_2 \cdot 6H_2O\}$ was repeated and Dy(NO₃)₃·6H₂O (0.1017 g, 0.2228 mmol) was used instead of Gd(NO₃)₃·6H₂O. A yellow precipitate was obtained washed with Et₂O and dried over P₄O₁₀. Yield 49%.

$\{[Er_2(H_4L)_3(NO_3)](NO_3)_2 \cdot 4H_2O\}$. The procedure for $\{[Gd_2(H_4L)_3(NO_3)](NO_3)_2 \cdot 6H_2O\}$ was repeated and Er(NO₃)₃·6H₂O (0.1028 g, 0.2228 mmol) was used instead of Gd(NO₃)₃·6H₂O. A yellow precipitate was obtained washed with Et₂O and dried over P₄O₁₀. Yield 53%.

$\{[Pr_2(H_4L)_3(NO_3)](NO_3)_2 \cdot 5H_2O\}$. The procedure for $\{[Gd_2(H_4L)_3(NO_3)](NO_3)_2 \cdot 6H_2O\}$ was repeated and Pr(NO₃)₃·6H₂O (0.0969 g, 0.2228 mmol) was used instead of Gd(NO₃)₃·6H₂O. A yellow precipitate was obtained washed with Et₂O and dried over P₄O₁₀. Yield 55%.

$\{[Yb_2(H_4L)_3(NO_3)](NO_3)_2 \cdot 4H_2O\}$. The procedure for $\{[Gd_2(H_4L)_3(NO_3)](NO_3)_2 \cdot 6H_2O\}$ was repeated and Yb(NO₃)₃·6H₂O (0.1041 g, 0.2228 mmol) was used instead of Gd(NO₃)₃·6H₂O. A yellow precipitate was obtained washed with Et₂O and dried over P₄O₁₀. Yield 69%.

RESULTS AND DISCUSSIONS

We have found that the reaction between 2,6-diformyl-4-chlorophenol and salicylaldehyde hydrazide in ethanol gives a yellow identifiable solid. From this ligand (H₅L) we have prepared complexes using hydrated lanthanide nitrates. The presence of the -Cl group in the *para* position of phenol moiety promote the reaction of the Schiff base as monoanionic ligand and the formation of the binuclear complexes containing three monoanionic Schiff base and three nitrate groups. The general composition of all the complexes correspond to $\{[Ln_2(H_4L)_3(NO_3)](NO_3)_2 \cdot nH_2O\}$ where Ln = La, Ce, Pr, Nd, Sm, Gd, Dy, Er, Yb and Y. The compounds were purified in suitable solvents and analytically pure material was obtained. The analytical data of the ligand and the complexes are summarized in Table 1. The complexes are air-stable and non-hygroscopic and could be stored at room temperature without alteration. The products have poor solubility in common organic solvents.

Table 1. Analytical data for the ligand and the complexes of the ligand.

Compounds	Found (calc.) %			Colour
	C	H	N	
C ₂₂ H ₁₇ N ₄ O ₅ Cl.2H ₂ O	54.36 (54.05)	4.58 (4.33)	11.25 (11.46)	Yellowish
{[La ₂ (H ₄ L) ₃ (NO ₃)](NO ₃) ₂ .6H ₂ O}	41.11 (41.12)	2.96 (3.13)	11.13 (10.90)	Yellow
{[Ce ₂ (H ₄ L) ₃ (NO ₃)](NO ₃) ₂ .7H ₂ O}	40.54 (40.69)	2.87 (3.21)	10.91 (10.78)	Yellow
{[Pr ₂ (H ₄ L) ₃ (NO ₃)](NO ₃) ₂ .5H ₂ O}	41.33 (41.43)	3.18 (3.06)	10.67 (10.98)	Yellow
{[Nd ₂ (H ₄ L) ₃ (NO ₃)](NO ₃) ₂ .5H ₂ O}	41.16 (41.28)	2.99 (3.04)	10.69(10.94)	Yellow
{[Sm ₂ (H ₄ L) ₃ (NO ₃)](NO ₃) ₂ .4H ₂ O}	41.22 (41.67)	3.01 (2.97)	10.86 (11.05)	Yellow
{[Gd ₂ (H ₄ L) ₃ (NO ₃)](NO ₃) ₂ .6H ₂ O}	39.98 (40.36)	3.09 (3.15)	10.56 (10.70)	Yellow
{[Dy ₂ (H ₄ L) ₃ (NO ₃)](NO ₃) ₂ .5H ₂ O}	40.16 (40.51)	3.09 (2.99)	10.50 (10.74)	Yellow
{[Er ₂ (H ₄ L) ₃ (NO ₃)](NO ₃) ₂ .4H ₂ O}	39.99 (40.69)	3.09 (2.90)	10.45 (10.78)	Yellow
{[Yb ₂ (H ₄ L) ₃ (NO ₃)](NO ₃) ₂ .4H ₂ O}	39.93 (40.45)	2.80 (2.88)	10.53 (10.72)	Yellow
{[Y ₂ (H ₄ L) ₃ (NO ₃)](NO ₃) ₂ .2H ₂ O}	45.02 (45.06)	2.88 (2.99)	11.33 (11.97)	Yellow

Infrared spectra. The ligand is expected to be heptadentate, the possible coordination sites being phenol-oxygen (three), azomethine nitrogen (two) and the amide groups (two). Comparison of the infrared spectra of the ligand and the complexes suggests that the ligand is pentadentate with ligand coordinating to the metal through the two carbonyl-oxygen, the one 4-chlorophenol oxygen and two azomethine sites.

The infrared spectrum of the ligand was devoid of absorptions characteristic of an NH₂ function. A strong band at *ca.* 1635 cm⁻¹ is assigned to the ν(C=O) vibration. The band due to the ν(C=N) vibration is observed at 1614 cm⁻¹ as a strong band. The N-H stretching vibrations occur at 3290 and 3220 cm⁻¹. The broad band of medium intensity occurring in the range 3500-3400 cm⁻¹ is due to the O-H stretching vibration of the phenolic OH groups.

Upon coordination, the band due to the N-H stretching vibrations in the free ligand remains unaffected precluding the possibility of coordination through the amide oxygen in his amide form.

A considerable lowering of the ν(C=O) frequency is observed in the spectra of all the complexes, indicating a decrease in the stretching force constant of the C=O bond as a consequence of the coordination of the oxygen atom to the metal ion. This band appears at *ca.* 1615 cm⁻¹.

The important band at 1614 cm⁻¹ in the free ligand attributed to ν(C=N), is shifted to lower frequencies and appears in the region 1595-1520 cm⁻¹ in the spectra of all the complexes. This fact suggests the involvement of the nitrogen atom of the azomethine moiety in the coordination of the ligand to the metal ion.

The bands at 3500-3400 cm⁻¹ are affected by metal coordination. The interpretation of these bands due to the ν(OH) of the phenolic groups is frustrated by the presence of three phenolic groups in the ligand. The broad band of medium intensity occurring in 3300-3400 cm⁻¹ region is due to the symmetric and the antisymmetric O-H stretching vibrations of the lattice water [19]. No characteristic band of coordinated water molecules was observed. In the region 410-480 cm⁻¹ a medium-intensity band characteristic of a ν(Ln-O) vibration of the phenolic oxygen was observed [20]. Bands in the far infrared spectra, in the region 280-240 cm⁻¹ can be assigned to ν(Ln-N) vibration in the new complexes [20].

From the infrared spectra of the nitrate complexes, information regarding the possible bonding modes of the nitrate group was obtained. The bands at *ca.* 1468-1440 cm⁻¹ and 1320-1300 cm⁻¹ are due respectively to ν(N=O) (ν1) and ν_{as}(NO₂) (ν5) of the coordinated nitrate. The ν_s(NO₂) (ν2) is detected at *ca.* 1040-1030 cm⁻¹. These facts are characteristic of bidentate

chelating nitrate [19,21]. The separation $\Delta\nu = \nu_1 - \nu_5$ has been used as criterion of differentiation between mono and bidentate chelating nitrates, with $\Delta\nu$ increasing as the coordination changes from mono to bidentate and/or bridging modes. The magnitude of this separation for these complexes (Table 2) is indicative of a bidentate nitrate [22]. The strong and sharp band at 1380 cm^{-1} is characteristic of ionic nitrate. In summary, these nitrate complexes contains both coordinated and ionic nitrates.

Table 2. Infrared data of the ligand and the lanthanides complexes of the ligand.

Compounds	Macroacyclic ligand			Exocyclic ligand bidentate nitrate			Ionic nitrate	Lattice water	
	$\nu(\text{C-H})$	$\nu(\text{C=O})$	$\nu(\text{C=N})$	ν (N=O) (ν_1)	ν_{asym} (NO ₂) (ν_5)	ν_{sym} (NO ₂) (ν_2)	$\Delta\nu^*$	ν (N=O) (ν_3)	$\nu(\text{O-H})$
$\text{C}_{22}\text{H}_{16}\text{N}_4\text{O}_5\text{Cl}\cdot 2\text{H}_2\text{O}$	3000	1635	1614						
$\{[\text{La}_2(\text{H}_4\text{L})_3(\text{NO}_3)](\text{NO}_3)_2\cdot 6\text{H}_2\text{O}\}$	2920	1615	1595	1440	1320	1040	120	1380	3220
$\{[\text{Ce}_2(\text{H}_4\text{L})_3(\text{NO}_3)](\text{NO}_3)_2\cdot 7\text{H}_2\text{O}\}$	2922	1615	1592	1440	1320	1037	120	1381	3220
$\{[\text{Pr}_2(\text{H}_4\text{L})_3(\text{NO}_3)](\text{NO}_3)_2\cdot 5\text{H}_2\text{O}\}$	2930	1614	1558	1464	1315	1037	149	1377	3220
$\{[\text{Nd}_2(\text{H}_4\text{L})_3(\text{NO}_3)](\text{NO}_3)_2\cdot 5\text{H}_2\text{O}\}$	2940	1614	1560	1435	1315	1037	120	1379	3200
$\{[\text{Sm}_2(\text{H}_4\text{L})_3(\text{NO}_3)](\text{NO}_3)_2\cdot 4\text{H}_2\text{O}\}$	2919	1612	1560	1466	1315	1035	151	1380	3220
$\{[\text{Gd}_2(\text{H}_4\text{L})_3(\text{NO}_3)](\text{NO}_3)_2\cdot 6\text{H}_2\text{O}\}$	2945	1614	1558	1431	1315	1035	116	1378	3220
$\{[\text{Dy}_2(\text{H}_4\text{L})_3(\text{NO}_3)](\text{NO}_3)_2\cdot 5\text{H}_2\text{O}\}$	2918	1616	1558	1433	1315	1035	118	1375	3200
$\{[\text{Er}_2(\text{H}_4\text{L})_3(\text{NO}_3)](\text{NO}_3)_2\cdot 4\text{H}_2\text{O}\}$	2940	1616	1523	1469	1310	1043	159	1375	3200
$\{[\text{Yb}_2(\text{H}_4\text{L})_3(\text{NO}_3)](\text{NO}_3)_2\cdot 4\text{H}_2\text{O}\}$	2935	1616	1558	1469	1315	1035	154	1377	3200
$\{[\text{Y}_2(\text{H}_4\text{L})_3(\text{NO}_3)](\text{NO}_3)_2\cdot 2\text{H}_2\text{O}\}$	2945	1616	1560	1435	1315	1040	120	1375	3210

* $\Delta\nu = \nu_1 - \nu_5$.

Electronic spectra. The electronic spectra of the complexes were recorded in freshly prepared dmf solutions. The spectra are virtually identical for all the complexes. A fairly symmetrical new band is observed for each complex at *ca.* 407 nm. This band disappears when the complex is treated with NaBH_4 in order to reduce the C=N group in saturated moiety. Therefore the absorption at *ca.* 407 nm must be associated with the C=N chromophore coordinated to the metal ion through the nitrogen atom. The UV spectra of the complexes provided also further information. An intense band was also observed at *ca.* 335 nm, in some of the complexes. It was absent both for the free ligand and the nitrate salts. This band is assigned to charge transfer between the coordinated ligand and the metal ion. The electronic spectral data are summarized in Table 3.

Magnetic moments. The magnetic moment of the lanthanide(III) complexes are summarized in Table 3. The values show little deviation from the theoretical values predicted for the trivalent lanthanide ions. This fact suggests that the 4f electrons do not participate in the bond formation of the metal to the ligand [23].

Molar conductivities. The molar conductivities of the complexes were measured in dimethyl formamide (dmf) for freshly prepared solutions and after standing for two weeks. The conductivities increased very slightly with time in dmf for all the complexes except for Sm. This is probably due to the very slow replacement of the coordinated nitrate by the solvent molecules. The values of these conductance are in the range $27\text{--}70\text{ Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ in dmf and are less than those reported for 1:1 electrolytes in this solvent [24]. This is indicative that these complexes dissociate very slightly in this solvent. In contrast to the infrared spectra where the compounds were formulated as 1:2 electrolytes with two nitrates as counter ions, the molar conductivities show that all the nitrates ions are present in the coordination sphere in solution. This suggests

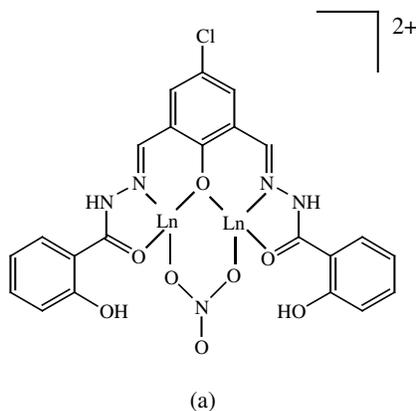
that the behaviors of the complexes in solid state are different from the behaviors when the compounds are in dmf the solution.

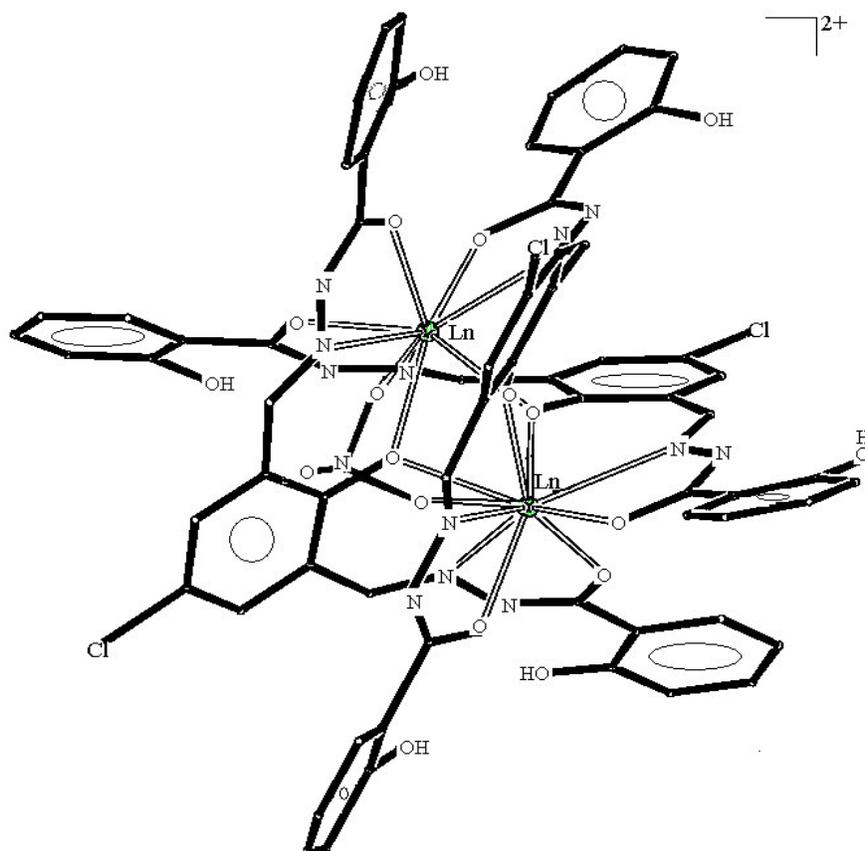
Table 3. Electronic data, magnetic moments and conductance data of the complexes.

Complexes	UV bands	$\Lambda/\Omega^{-1}\text{cm}^2\text{mol}^{-1}$		μ/μ_B
		fresh	2 weeks after	
$\text{C}_{22}\text{H}_{16}\text{N}_4\text{O}_5\text{Cl}\cdot 2\text{H}_2\text{O}$	270, 320, 345, 365, 420, 440, 475	-	-	-
$\{[\text{La}_2(\text{H}_4\text{L})_3(\text{NO}_3)](\text{NO}_3)_2\cdot 6\text{H}_2\text{O}\}$	270, 320, 350 sh, 360, 375 sh	54	56	Diam.
$\{[\text{Ce}_2(\text{H}_4\text{L})_3(\text{NO}_3)](\text{NO}_3)_2\cdot 7\text{H}_2\text{O}\}$	267, 305 sh, 320, 405	64	70	3.41
$\{[\text{Pr}_2(\text{H}_4\text{L})_3(\text{NO}_3)](\text{NO}_3)_2\cdot 5\text{H}_2\text{O}\}$	265, 305 sh, 335, 353, 405, 425 sh	57	62	5.41
$\{[\text{Nd}_2(\text{H}_4\text{L})_3(\text{NO}_3)](\text{NO}_3)_2\cdot 5\text{H}_2\text{O}\}$	265, 335, 407, 417 sh	55	60	5.38
$\{[\text{Sm}_2(\text{H}_4\text{L})_3(\text{NO}_3)](\text{NO}_3)_2\cdot 4\text{H}_2\text{O}\}$	265, 323 sh, 335, 407, 418 sh	52	52	2.22
$\{[\text{Gd}_2(\text{H}_4\text{L})_3(\text{NO}_3)](\text{NO}_3)_2\cdot 6\text{H}_2\text{O}\}$	265, 333, 345 sh, 410, 430 sh	57	62	13.13
$\{[\text{Dy}_2(\text{H}_4\text{L})_3(\text{NO}_3)](\text{NO}_3)_2\cdot 5\text{H}_2\text{O}\}$	265, 330, 340, 353, 405, 418 sh	49	58	18.08
$\{[\text{Er}_2(\text{H}_4\text{L})_3(\text{NO}_3)](\text{NO}_3)_2\cdot 4\text{H}_2\text{O}\}$	265, 323 sh, 340, 352, 407, 425 sh	27	29	16.38
$\{[\text{Yb}_2(\text{H}_4\text{L})_3(\text{NO}_3)](\text{NO}_3)_2\cdot 4\text{H}_2\text{O}\}$	263, 310 sh, 335, 350, 405, 420 sh	53	61	7.44
$\{[\text{Y}_2(\text{H}_4\text{L})_3(\text{NO}_3)](\text{NO}_3)_2\cdot 2\text{H}_2\text{O}\}$	340, 353 sh, 405, 418 sh	45	54	Diam.

CONCLUSION

The electrolytic conductivity data indicate that the lanthanide nitrates complexes do not behave as electrolytes in dimethylformamide. The infrared spectra indicate that not all the nitrate groups are involved in the coordination. IR data reveal the presence of bidentate and ionic nitrate in these complexes. The organic ligand acts as a pentadentate ligand via the anionic oxygen of the one 4-chlorophenol group, the oxygen of the two amide functions and the nitrogen of the two azomethine groups. Three molecules of the macro acyclic ligand with two similar metal-binding sites sharing the phenolic oxygen atom act with two lanthanides ions. This suggests that, in these complexes each Ln(III) ion is surrounded by seven oxygen atoms and three nitrogen atoms producing a ten coordination number complex (Figure 1).





(b)

Figure 1. Schematic proposed structure: (a) two monodeprotonated ligand (H_4L) were omitted for clarity, and (b) structure with all the three monoanionic Schiff base ligand.

ACKNOWLEDGMENT

The authors thank the Third World Academy of Science (TWAS) for financial support under the research grant N° 97-034 RG/CHE/AF/AC.

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