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Synthesis and Characterization of the Complexes of Lanthanide(III) Chlorides and Nitrates with the Tetradentate Schiff Base Diethyl(ethylenebis-β-aminocrotonate)

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Summary. The Schiff base ligand diethyl(ethylenebis-β-aminocrotonate) (LH_2) reacts with lanthanide(III) chlorides and nitrates in various solvents to give solid complexes of the stoichiometries $Ln(LH_2)Cl_3$ (Ln = La – Yb), $Ln(LH_2)_2Cl_3$ (Ln = La – Sm), $Ln_2(LH_2)_3Cl_6$(Ln = Eu – Yb) and $Ln(LH_2)(NO_3)_3$ (Ln = La – Yb). Properties, conductivity measurements, X-ray powder patterns, thermal data, magnetic moments and spectroscopic (IR, ^{1}H-NMR, electronic diffuse reflectance and solid state emission f – f spectra) are discussed in terms of the nature of the bonding and the possible structural types.

Keywords. Lanthanide(III) complexes; Schiff bases; Diethyl(ethylenebis-β-aminocrotonate); Magnetic moments; f – f spectra of lanthanide(III) complexes; Coordination of ester groups.

Synthese und Charakterisierung der Komplexe von Lanthanid(III)chloriden und -nitraten mit der vierzähnigen Schiff-Base Diethyl(ethylenbis-β-aminocrotonat)

Zusammenfassung. Der Schiffbasen-Ligand Diethyl(ethylenbis-β-aminocrotonat) reagiert mit Lanthanid(III)chloriden und -nitraten in verschiedenen Lösungsmitteln unter der Bildung von festen Komplexen der Stöchiometrien $Ln(LH_2)Cl_3$ (Ln = La – Yb), $Ln(LH_2)_2Cl_3$ (Ln = La – Sm), $Ln(LH_2)_3Cl_6$ (Ln = Eu – Yb) und $Ln(LH_2)(NO_3)_3$ (Ln = La – Yb). Die allgemeinen Eigenschaften, Leitfähigkeitsmessungen, Röntgen-Pulverdiagramme, thermische Daten, magnetische Momente und spektroskopische Daten (IR, ^{1}H-NMR, Elektronenreflexionsspektren und Festkörperemissions-f – f-Spektren) werden im Hinblick auf die Bildungsverhältnisse im Komplex und strukturelle Möglichkeiten diskutiert.

Introduction

Transition metal complexes of Schiff base ligands are of interest [1, 2] since they exhibit a marked tendency to oligomerize, thus leading to novel structural types, they display a wide variety of magnetic properties, may serve as models for biologically important species and they are also relevant to the macrocyclic effect.

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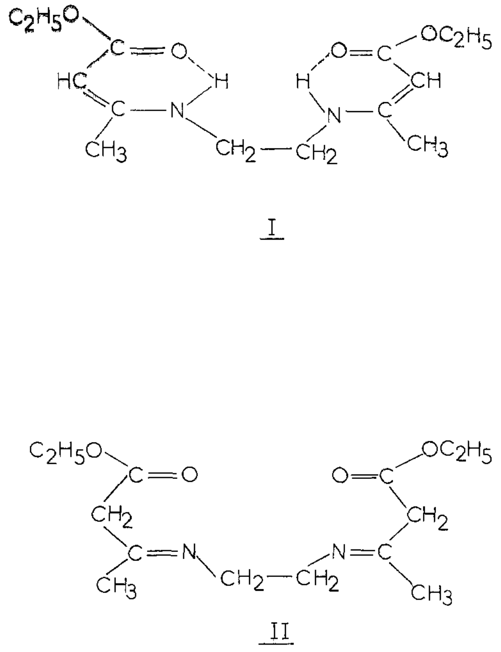

I

II

Fig. 1. The hydrogen-bonded ketamine(I) and ketimine(II) tautomeric forms of the ligand LH_2; the free molecule and the coordinated ligand are both present in the ketamine form (see text)

Schiff base ligands have played a key role in our understanding of the coordination chemistry of lanthanides [3–5]. Paramagnetic Eu(III) and Gd(III) complexes with Schiff bases are presently undergoing extensive study as contrast agents in magnetic resonance imaging [6].

Although lanthanide(III) complexes of the "classical" tetradentate Schiff base ligand bis(acetylacetone)ethylenediamine have been prepared and studied [7–9], no complexes of Schiff base ligands derived from β-ketoesters have been known. As a continuation of our interest on the coordination chemistry of lanthanides(III) [10–14], this work describes the preparation and study of complexes of lanthanide(III) chlorides and nitrates with diethyl(ethylenebis-β-aminocrotonate), abbreviated as LH_2 (Fig. 1).

Experimental Part

The salts $LnCl_3 \cdot nH_2O$ and $Ln(NO_3)_3 \cdot nH_2O$ ($n = 6, 7$) were obtained from Aldrich, Fluka and Ventron. LH_2 was synthesized as described earlier [15]. Metal, chloride, carbon, hydrogen and nitrogen analyses were performed by conventional gravimetric, potentiometric and microanalytical methods. Physicochemical measurements and spectroscopic techniques were carried out by published methods [16, 17].

The complexes $Ln(LH_2)Cl_3$ were prepared by adding a vigorously stirred warm solution of LH_2 (5.8 mmol) in methanol (35 ml) to a hot solution of the required lanthanide(III) chloride (6.2 mmol) in methanol (35–40 ml) in the presence of excess of triethylorthoformate (*TEOF*) as dehydrating agent (method A). The complexes $Ln(LH_2)_2Cl_3$ (Ln = La – Sm) and $Ln_2(LH_2)_3Cl_6$ (Ln = Eu – Yb) were prepared by adding a warm solution of the appropriate metal chloride (3.0 mmol) in acetonitrile (20 ml) in the presence of excess *TEOF* to a solution of LH_2 (6.5 mmol) in 30–35 ml of acetonitrile (method B). For the preparation of the nitrate compounds $Ln(LH_2)(NO_3)_3$ to 2.0 mmol of the required hydrated lanthanide(III) nitrate in 30 ml of warm absolute ethanol was added 15 ml of *TEOF* as dehydrating agent and the solution was refluxed for 30 min; to this solution 2.0 mmol of LH_2 in 20–25 ml of hot anhydrous ethanol was added dropwise under vigorous stirring (method C).

Solid product formation was usually very rapid (5–10 min), but completely stoichiometric products were obtained only after the reaction mixtures were heated under reflux for 1–3 h. This procedure was particularly necessary working with method B, due to the reduced solubilities of the anhydrous metal chlorides in acetonitrile. Some of the 1 : 1 chloride and nitrate complexes were slowly deposited during reflux and crystallization was completed by cooling the mixtures in the refrigerator overnight. All precipitates were collected by filtration, washed with hot solvent (the same used for their preparation) and ether and dried in vacuum over silica gel. The solid products isolated by method B were stirred again in warm acetonitrile to remove unreacted starting materials, then filtered off, washed an dried as above.

A final point of synthetic interest is the use of *TEOF*. In general, it is not possible to prepare pure complexes working with method B without the use of *TEOF*. In methods A and C the nature of the lanthanide(III) ion was indicated to be a controlling factor in the reactions attempted without *TEOF*. Working with La(III), Ce(III), Pr(III), Nd(III), Sm(III) and Eu(III) using method A and with La(III), Ce(III), Pr(III), Nd(III) and Sm(III) following method C, hydroxo-derivatives of uncertain nature and poor analytical results were isolated. Working with the hydrated salts of the heavier lanthanides pure complexes of the general formulae $Ln(LH_2)Cl_3 \cdot nH_2O$ and $Ln(LH_2)(NO_3)_3 \cdot nH_2O$ (n = 1–3) were obtained; these products were hydroscopic microcrystals and underwent slow hydrolytic decomposition in contact with atmospheric moisture.

Results and Discussion

The first preparation of the Schiff base diethyl(ethylene-β-aminocrotonate)(LH_2) was reported a century ago [18]. Martell and his co-workers [15] synthesized the same compound from the reaction of ethylacetoacetate and ethylenediamine in a 2 : 1 molar ratio using aqueous ethanol as a solvent. The IR spectrum [15] exhibited $\nu(N-H)$, $\nu(C=O)_{free}$ and $\nu(C=O)_{hydrogen\text{-}bonded}$ at 3 260 (s), 1 730 (w) and 1 645 (s) cm^{-1}, respectively, in agreement with formula **I**. Holm und Dudek [19] studied the tautomeric equilibrium of LH_2 by ^{1}H-NMR spectroscopy; the spectra of LH_2 indicated [19] that in common solvents this compound exists almost entirely in the hydrogen-bonded tautomeric ketamine form **I** and not in the ketimine form **II**. Both the IR (KBr) and ^{1}H-NMR ($CDCl_3$) spectra of the quantity of LH_2 prepared by us are identical with those reported [15, 19], thus confirming that the free ligand is present in the Ketamine form **I**.

Preparative data, colours, molar conductivity values and effective magnetic moments of the prepared complexes are given in Table 1. The complexes are microcrystalline or powder-like, relatively stable in atmospheric conditions, insoluble in benzene, ether, chloroform, alcohols and acetone, slightly soluble in nitromethane and soluble in *DMF* and *DMSO*; however, the 2 : 3 chloride complexes **19**–**26** are insoluble in *DMF* and *DMSO*. Most of the complexes are decomposed by water and mineral acids. Because of the insolubility of the prepared complexes in suitable solvents we could not grow crystals for single-crystal X-ray structural studies. The molar conductivity values of the compounds **1**–**13** and **27**–**39** are in accord with them being formulated as non-electrolytes [20]. The Λ_M values of **14**–**18**, which are formulated as cationic $[Ln(LH_2)_2]^{3+}$ complexes (see concluding remarks), indicate 1 : 3 electrolytes [20].

The X-ray powder diffraction patterns indicate the formation of five groups of isostructural compounds. The first group includes the complexes **1**–**12**, the second the complexes **14**–**18**, the third the complexes **19**–**26**, the fourth the complexes **27**–**32** and the fifth the complexes **33**–**37**. The pattern of **13** resembles those of the first

Table 1. Preparative data, colours, molar conducitivity values and effective magnetic moments of the prepared complexes

Compound number	Complex	Method of preparation[a]	Yield (%)	Colour	Λ_M^d ($S\,cm^2\,mol^{-1}$)	μ_{eff}^g (BM)
1	$La(LH_2)Cl_3$	A	62^b	white	8^e	^{h}
2	$Ce(LH_2)Cl_3$	A	63^b	white	6^f	2.45
3	$Pr(LH_2)Cl_3$	A	59^b	pale green	9^f	3.43
4	$Nd(LH_2)Cl_3$	A	57^b	pale lilac	4^f	3.56
5	$Sm(LH_2)Cl_3$	A	61^b	cream	11^f	1.54
6	$Eu(LH_2)Cl_3$	A	64^b	white	8^f	3.41
7	$Gd(LH_2)Cl_3$	A	60^b	white	7^f	7.93
8	$Tb(LH_2)Cl_3$	A	55^b	white	6^f	9.52
9	$Dy(LH_2)Cl_3$	A	63^b	cream	9^f	10.56
10	$Ho(LH_2)Cl_3$	A	67^b	pale yellow	9^f	10.44
11	$Er(LH_2)Cl_3$	A	72^b	pink	8^f	9.40
12	$Tm(LH_2)Cl_3$	A	66^b	pale green	6^f	7.36
13	$Yb(LH_2)Cl_3$	A	49^b	white	5^f	4.41
14	$La(LH_2)_2Cl_3$	B	78^c	white	97^e	^{h}
15	$Ce(LH_2)_2Cl_3$	B	82^c	off-white	121^e	2.57
16	$Pr(LH_2)_2Cl_3$	B	84^c	pale green	109^e	3.50
17	$Nd(LH_2)_2Cl_3$	B	79^c	pale violet	104^e	3.61
18	$Sm(LH_2)_2Cl_3$	B	84^c	pale yellow	111^e	1.60
19	$Eu_2(LH_2)_3Cl_6$	B	80^c	white	^{i}	3.52
20	$Gd_2(LH_2)_3Cl_6$	B	79^c	white	^{i}	7.99
21	$Tb_2(LH_2)_3Cl_6$	B	81^c	white	^{i}	9.61
22	$Dy_2(LH_2)_3Cl_6$	B	84^c	white	^{i}	10.67
23	$Ho_2(LH_2)_3Cl_6$	B	78^c	pale yellow	^{i}	10.58
24	$Er_2(LH_2)_3Cl_6$	B	82^c	pink	^{i}	9.62
25	$Tm_2(LH_2)_3Cl_6$	B	82^c	pale green	^{i}	7.52
26	$Yb_2(LH_2)_3Cl_6$	B	77^c	white	^{i}	4.64
27	$La(LH_2)(NO_3)_3$	C	87^c	white	4^e	^{h}
28	$Ce(LH_2)(NO_3)_3$	C	86^c	off-white	8^f	2.59
29	$Pr(LH_2)(NO_3)_3$	C	88^c	pale green	10^f	3.54
30	$Nd(LH_2)(NO_3)_3$	C	91^c	pale lilac	13^f	3.64
31	$Sm(LH_2)(NO_3)_3$	C	93^c	cream	8^f	1.66
32	$Eu(LH_2)(NO_3)_3$	C	84^c	white	7^f	3.57
33	$Gd(LH_2)(NO_3)_3$	C	88^c	white	6^f	8.01
34	$Tb(LH_2)(NO_3)_3$	C	87^c	cream	14^f	9.59
35	$Dy(LH_2)(NO_3)_3$	C	90^c	white	11^f	10.64
36	$Ho(LH_2)(NO_3)_3$	C	91^c	yellowish	9^f	10.59
37	$Er(LH_2)(NO_3)_3$	C	83^c	pinkish	8^f	9.55
38	$Tm(LH_2)(NO_3)_3$	C	84^c	pale green	7^f	7.48
39	$Yb(LH_2)(NO_3)_3$	C	89^c	off-white	9^f	4.53

[a] See also text

[b] Based on the ligand

[c] Based on the metal

[d] Values of molar conductivity for $10^{-3}\,M$ solutions at 25°C; conductivities were measured immediately after dissolution; the conductivities of most solutions increase with time

[e] In *DMSO*

[f] In *DMF*

[g] Per lanthanide(III) at room temperature

[h] Diamagnetic

[i] Insoluble

group, but this compound is not exactly isostructural with **1–12**. The same is true for the patterns of **38** and **39** which resemble those of the fifth group. Some minor variations in line spacings, which are observed within a given group, are consistent with a decrease in unit cell volume attributable to the lanthanide contraction [21].

The thermal decomposition of the prepared complexes was studied using TG (30–650°C) and DTG techniques. The data for **1–13** and **19–39** present no special interest as their decomposition is characterized by rather complex degradation mechanisms; these complexes decompose without the formation of stoichiometric intermediates – no stoichiometric compounds can be assigned to the curves' inflections. The 1 : 2 chloride complexes **14–18** decompose via stable intermediates. Their TG and DTG curves show a first mass loss between 200 and 245°C, which corresponds exactly to the release of one ligand molecule; a plateau is reached at about 250 up to 270°C:

$$[Ln(LH_2)_2]Cl_3 \xrightarrow[N_2]{200\text{–}245^\circ C} [Ln(LH_2)Cl_3] + \uparrow LH_2 \; ; Ln = \mathrm{La, Ce, Pr, Nd, Sm.}$$

14–18 **14a–18a**

The IR and solid state f – f spectra, the μ_{eff} values and the X-ray powder patterns of the products isolated after TG experiments up to 255°C (**14a–18a**) are exactly the same like the corresponding data for the complexes **1–5** isolated by synthetic procedures. So, the 1 : 1 chloride complexes can also be prepared from the 1 : 2 ones by thermal decomposition. Mass loss calculations show that the final decomposition residues in most complexes are lanthanide(III) oxides.

The room temperature magnetic moments of the prepared complexes show little deviation from Van Vleck values, indicating thereby that the 4f electrons do not participate much in bonding [22]; these electrons are well shielded by the $(5s^2)$ $(5p^6)$ octet.

The diffuse reflectance spectra of the prepared complexes involve mainly intraligand and f – f transitions. The values of the bonding parameters $\bar{\beta}$ (nephelauxetic ratio), δ (Sinha's parameter) and $b^{1/2}$(covalent factor) (Table 2) of the Pr(III), Nd(III), Sm(III), Ho(III) and Er(III) complexes, calculated from the f – f spectra by standard equations [23–25], indicate that the interaction between the trivalent lanthanides and LH_2, Cl^- and NO_3^- is essentially electrostatic and that there is a small participation of 4f orbitals in bonding [23–25].

The shape and fine structure of some "hypersensitive" f – f bands for Nd(III), Ho(III) and Er(III) have been related to the coordination number [26, 27]. For Nd(III) four transitions are sensitive to coordination environment but one, the $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ at about 590 nm, is particularly so. By comparing the spectra of standard Nd(III) complexes with those of our complexes in the region of the above mentioned transition, it is concluded that **4** is 7-coordinated, **17** is 8-coordinated, while **30** has a coordination number of ten or more [3, 26, 27]. Analogous studies [26–28] for the Ho(III) (in the region of the hypersensitive $^5I_8 \rightarrow {}^5G_6, {}^5F_4$ transition at about 450 nm) and Er(III) (in the region of the hypersensitive $^4I_{15/2} \rightarrow {}^2H_{11/2}$ transition at about 530 nm) complexes demonstrate that **10** and **11** are 7-coordinated, **36** and **37** are 9-coordinated, while **23** and **24** are either 7- or 8-coordinated.

It is known that useful information concerning the nature of the chromophore

Table 2. Bond parameters of the Pr(III), Nd(III), Sm(III), Ho(III), and Er(III) complexes of LH_2 calculated from the f−f diffuse reflectance spectra

Complex	$\bar{\beta}$	δ(%)	$b^{1/2}$
3	0.994[a]	+0.60	0.055
4	0.992[b]	+0.81	0.063
5	0.993[c]	+0.70	0.059
10	0.994[d]	+0.60	0.055
11	0.995[e]	+0.50	0.050
16	0.997[a]	+0.30	0.039
17	0.996[b]	+0.40	0.045
18	0.996[c]	+0.40	0.045
23	0.997[d]	+0.30	0.039
24	0.996[e]	+0.40	0.045
29	0.999[a]	+0.10	0.022
30	0.999[b]	+0.10	0.022
31	0.998[c]	+0.20	0.032
36	0.997[d]	+0.30	0.039
37	0.996[e]	+0.40	0.045

[a] Calculated from the $^3H_4 \rightarrow {}^1D_2$, $^3P_0$, $^3P_1$, and $^3P_2$ transitions

[b] From the $^4I_{9/2} \rightarrow {}^4F_{5/2}$, $^2H_{9/2}$, ($^4F_{7/2}$, $^4S_{3/2}$), $^2H_{11/2}$, ($^4G_{5/2}$, $^2G_{7/2}$), ($^2K_{13/2}$, $^4G_{7/2}$, $^4G_{9/2}$), $^2K_{15/2}$, ($^2G_{9/2}$, $^2D_{3/2}$, $^2P_{3/2}$), $^4G_{11/2}$, and ($^2P_{1/2}$, $^2D_{5/2}$) transitions

[c] From the $^6H_{5/2} \rightarrow {}^4M_{15/2}$, $^4I_{13/2}$, (^6P, ^4P)$_{5/2}$, $^6P_{3/2}$, and $^6P_{7/2}$ transitions

[d] From the $^5I_8 \rightarrow {}^5F_5$, ($^5S_2$, $^5F_4$), $^5F_3$, $^5F_2$, ($^5G_6$, $^5F_1$), (^5G, $^3G_5$)$_5$, $^3H_6$, and (^5G, ^3H)$_5$ transitions

[e] From the $^4I_{15/2} \rightarrow {}^4F_{9/2}$, $^4S_{3/2}$, $^2H_{11/2}$, $^4F_{7/2}$, ($^4F_{5/2}$, $^4F_{3/2}$), (^2G, ^4F, ^2H)$_{9/2}$, and $^4G_{11/2}$ transitions

and geometry of the complexes can be obtained by the study of the emission f−f spectra. Among the lanthanide(III) complexes in which strong emission has been observed, the Eu(III) complexes have been the subject of very extensive studies since the low *J*-values give rise to a smaller number of closely spaced energy levels. Details of the solid state emission spectra of the Eu(III) complexes are given in Table 3.

In **32** the $^5D_0 \rightarrow {}^7F_0$ transition can be taken as forbidden, the spectrum showing in the relevant region a line of an intensity less than 0.3% of the most intense $^5D_0 \rightarrow {}^7F_2$ transition. Synthetic and spectroscopic data suggest that the complex $Eu(LH_2)(NO_3)_3$ (**32**) consists of the ten-coordinated EuN_2O_8 entity acquired by the tetradentate LH_2 ligand and three bidentate nitrato ligands (see also concluding remarks). The almost exclusive geometries for ten-coordination are the bicapped square antiprism (D_{4d}) and the bicapped dodecahedron (D_2 or C_{2v}) [29]. The appearance of three lines in the region of the $^5D_0 \rightarrow {}^7F_1$ transition and three ones in the region of the $^5D_0 \rightarrow {}^7F_2$ transition and the non-activation of the $^5D_0 \rightarrow {}^7F_0$ transition agrees with a bicapped dodecahedral geometry for **32** and a D_2 site symmetry for the Eu(III) ion [30, 31].

The fluorescence spectra of **6** and **19** are similar. The spectra show a single symmetric broad band at 578.5 and 579.5 nm, respectively, associated with the $^5D_0 \rightarrow {}^7F_0$ transition [31]. The exhibition of this line is consistent with the following

Table 3. Solid state fluorescence spectra[a] (nm) of the Eu(III) complexes of LH_2 (s strong; m medium; w weak; sh shoulder; b broad; v very)

Assignment	**6**[b]	**19**[b]	**32**[c]
$^5D_0 \rightarrow {}^7F_0$	578.5 w	579.5 w	580.0 w
$^5D_0 \rightarrow {}^7F_1$	589.5 m, 593.0 m	591.0 m, 594.0 m	591.0 m, 592.5 m, 595.0 w
$^5D_0 \rightarrow {}^7F_2$	612.5 s, 616.5 vs, 621.0 sh	613.0 vs, 617.5 s, 622.0 sh	612.0 sh, 614.0 vs, 620.5 w
$^5D_0 \rightarrow {}^7F_3$	647.0 w, 650.5 sh, 652.5 w	649.0 w, 651.0 sh, 654.0 w	650.0 sh, 654.0 wb
$^5D_0 \rightarrow {}^7F_4$	683.0 sh, 689.0 sh, 691.5 m, 696.0 sh, 699.0 vs	683.5 sh, 688.5 sh, 692.0 m, 694.0 sh, 696.0 w, 699.5 vs	682.5 w, 688.0 w, 693.5 w, 701.0 w

[a] Obtained at liquid nitrogen temperature by exciting with near UV radiations

[b] Emission originates almost totally from the $^5D_0$ excited state; bands associated with $^5D_{1,2} \rightarrow {}^7F_{0,1,2}$ transitions are very weak

[c] Emission arises also from the $^5D_1$ level; two weak and rather broad components of the $^5D_1 \rightarrow {}^7F_1$ transition and two weak components and one shoulder of the $^5D_1 \rightarrow {}^7F_2$ transition appear in the 533–545 and 550–564 nm regions, respectively

site symmetries [31]: C_n, C_s and $C_{n'v}$ (n = 2, 3, 4, 6; n' = 1, 2, 3, 4, 6). The magnetic-dipole allowed $^5D_0 \rightarrow {}^7F_1$ transition consists of two medium components between 589.5 and 594.0 nm. One very intense line, one intense line and one shoulder between 612.5 and 622.0 nm arise from the electric-dipole allowed $^5D_0 \rightarrow {}^7F_2$ transition. The absence of an inversion centre is confirmed by the larger intensities of the transitions to the $J = 2$ and $J = 4$ sublevels, with respect to the intensity of the magnetic-dipole allowed transition to the $J = 1$ sublevel [32]. The number of transitions observed to $J = 0$, 1, 2 and 4 is 1, 2, 3 and 5 for **6** and 1, 2, 3 and 6 for **19**; in C_{3v} symmetry 1, 2, 3 and 5 transitions to these sublevels are active, respectively, and in C_{2v} symmetry 1, 3, 4 and 7 transitions are allowed, respectively [30, 32]. Therefore, we believe that the C_{3v} site symmetry is the most consistent for the Eu(III) ion in **6** and **19**. This site symmetry, together with the physical and other spectral data obtained for these complexes (see concluding remarks), let us assign 7-coordinate structures for **6** and **19**, corresponding to distorted capped octahedra [29, 30]. However, it must be noted that the energy difference between this model and the capped trigonal prism (C_{2v}) is small [31].

The IR spectrum of LH_2 exhibits the $\nu(N-H)$, $\nu(C=O)_{free}$, $\nu(C=O)_{hydrogen\text{-}bonded}$ and $\nu(C-O)$ modes at 3260 (s), 1730 (w), 1645 (s) and 1270 (s) cm^{-1}, respectively [15].

In the spectra of all the complexes prepared, a single (or double in a few cases) strong band for the N−H stretching mode appears at 3200–3170 cm^{-1}, in the region characteristic of secondary amines. This is a very strong evidence that LH_2 is present in the Ketamine form in all the complexes. The large systematic shift of the $\nu(N-H)$ band to lower frequencies in the spectra of **1**–**39**, in comparison with the frequency of this mode in the spectrum of LH_2, confirms the coordination of both nitrogens [33, 34]. The splitting of the $\nu(N-H)$ band for the complexes of heavier lanthanides may be a consequence of decrease in crystal radius and greater crowding and enhanced steric interactions that result for the heavier lanthanide(III) ions [34].

The significant changes in the characteristic ester ligand bands upon complexing are the decrease in ν(C=O) by 35–45 cm^{-1} and the increase in ν(C−O) by 25–35 cm^{-1}. These shifts indicate coordination through the carbonyl oxygens of the ester groups [35].

In compounds containing ionic nitrates, the ν_3(E′) mode of the ion occurs as a single strong band at 1 350–1 400 cm^{-1} [35]; the absence of such a band in the spectra of the nitrate complexes **27**–**39** confirms that ionic nitrates are absent. If coordination occurs through one or two O-atoms, the symmetry is lowered from D_{3h} to C_{2v} in both instances and all six normal modes of vibration become IR active. In the spectra of **27**–**32**, vibrations of nitrates appear at about 1 520 (ν_1A_1, vs), 1 280 (ν_4B_2, s), 740 (ν_3A_1, m) and 705 (ν_5B_2, w) cm^{-1}; the ν_2A_1 and ν_6B_1 modes of the C_{2v} nitrato groups were not assigned because the 1 050–1 000 and 800–830 cm^{-1} regions are obscured by strong bands of the coordinated organic ligand. The observed vibrational fundamentals of the nitrato groups are strongly indicative of the presence of bidentate nitrates, because the separation of the two highest frequency nitrato modes is larger than 180 cm^{-1} [35]. The IR spectra of **33**–**39** are very complex in the regions of the nitrato vibrations. They exhibit the above mentioned modes of the bidentate nitrates and also bands at 1 420 (ν_4B_2, s) 1 295 (ν_1A_1, m) and 750 (ν_3A_1, w) cm^{-1} typical of monodentate nitrato ligands [35]; this fact supports a structure with bidentate and monodentate nitrato groups being simultaneously involved. The possibility of bidentate bridging nitrates in **27**–**39** can be ruled out, because the highest frequency nitrato mode appears below 1 550 cm^{-1} [36].

The far-IR region (450–150 cm^{-1}) of the free ligand spectrum has several medium to weak bands. This would indicate that some of the other bands observed in this region would be assignable to ν(*Ln*−N), ν(*Ln*−$O_{\text{carbonyl ester}}$), ν(*Ln*−$ONO_2$) and ν(*Ln*−Cl). A comparison, however, of the far-IR spectra between *L*H_2 and its lanthanide(III) complexes fails to give clearcut assignments. Few reliable studies of the far-IR spectra of the lanthanide(III) complexes have been made. A medium band at 335–317 cm^{-1} in the spectra of all the complexes prepared probably arises from the ν(*Ln*-N) vibration [8, 33]. In the spectra of the chloride complexes **1**–**13** and **19**–**26** two and one, respectively, strong bands, which must be due to ν$(Ln-Cl)_t$, appear between 247 and 229 cm^{-1} [37].

The ^{1}H-NMR study of the diamagnetic complexes **1**, **14**, and **27** in *DMSO-d*$_6$ was based on comparisons with related compounds [19, 38, 39] and on deuterium exchange experiments. The ^{1}H-NMR spectrum of *L*H_2 in *DMSO-d*$_6$ solution gave the following chemical shifts: δ (relative to *TMS*) 1.23 (triplet, 6 H, CH_3 of the ester group), 1.93 (singlet, 6 H, CH_3), 3.37 (triplet, 4 H, CH_2CH_2), 3.97 (quartet, 4 H, CH_2 of the ester group), 4.40 (singlet, 2 H, C=CH) and 8.79 ppm (singlet broad, 2 H, NH). The ^{1}H-NMR spectra of **1**, **14**, and **27** in *DMSO-d*$_6$ are similar, suggesting the same mode of coordination of *L*H_2 in the three La(III) complexes. The spectra exhibit a triplet at δ 1.28 ppm downfield from *TMS* assigned to the methyl protons of the ester group, one peak at δ 1.90 ppm due to the remaining methyl hydrogens, a doublet at δ 3.68 ppm assigned to the ethylene bridge protons, a sharp singlet at δ 4.47 ppm due to the vinylic hydrogen and a broad singlet at δ 10.73 ppm assigned to the secondary amine proton; the broad character of this peak is due primarily to N^{14} quadrupole relaxation [19]. The occurrence of the last signal indicates that *L*H_2 is present in the ketamine form in the La(III) complexes. The spectra of the complexes remained unchanged only for 8–10 minutes. The spectra of **1**, **14**, and **27** show a characteristic downfield shift of the NH resonance relative to LH_2, clearly indicating the coordination of the secondary amino nitrogen to La(III) [40].

Concluding Remarks

From the overall study presented it is concluded that in all the complexes prepared the molecule LH_2 is present in the ketamine tautomeric form and behaves as a tetradentate ligand bonding through both nitrogens and ester oxygens. From available data a coordination number of seven is assigned to the 1 : 1 chloride complexes **1**–**13** with the participation of the three terminal chloro ligands in the coordination sphere of the lanthanide(III) ion. Distorted capped octahedral structures are proposed for **1**–**12** taking into account that **1**–**5** and **7**–**12** are isostructural with $Eu(LH_2)Cl_3$ (**6**), which has a solid state emission f–f spectrum indicative of this structure. Physical and spectroscopic data suggest that the complexes **14**–**18** consist of the coordination entity $[Ln(N)_4\ (O_{\text{carbonyl ester}})_4]^{3+}$ formed by two tetradentate chelated LH_2 ligands. Our data do not permit differentiation between square antiprismatic, dodecahedral, bicapped trigonal prismatic or cubic structures. The 2 : 3 chloride complexes **19**–**26** most probably exist in a dimeric $[(LH_2)ClLn(LH_2)LnCl(LH_2)]^{4+}\ 4\,Cl^-$ form with the simultaneous presence of two tetradentate chelated and one bis-bidentate bridging LH_2 ligands per dimer and with each lanthanide(III) ion exhibiting N_3O_3Cl coordination; a complex hydrogen bonding scheme involving the amino hydrogens, $-OC_2H_5$ oxygens and not-coordinated chloride ions could bind these dimeric units strongly in the crystal lattice. Distorted capped octahedral coordination environments around each metal ion are proposed bearing in mind that the complexes **20**–**26** are isostructural with $Eu_2(LH_2)_3Cl_6$ (**19**), which has an emission f–f spectrum indicative of this geometry. Molecular models show that the proposed dimeric structure is quite feasible. There is little doubt, both from synthetic and spectroscopic data, that the compounds **27**–**32** consist of the monomeric 10-coordinated $[Ln(N)_2\ (O_{\text{carbonyl}})_2\ (O_{\text{nitrato}})_6]$ coordination sphere formed by three bidentate chelated nitrato groups and one tetradentate chelated LH_2 ligand. Ten-coordination attained by three bidentate chelated nitrato groups and chelated organic ligands has been established by single-crystal X-ray structural studies [29]. Bicapped dodecahedral geometries with a D_2 site symmetry for the Ln(III) ion are assigned for **27**–**32** taking into account that **27**–**31** are isostructural with $Eu(LH_2)(NO_3)_3$ (**32**), which has a solid state emission f–f spectrum characteristic of this geometry. Finally, a tentative coordination number of nine is assigned to the complexes **33**–**39**, both from physical and spectroscopic data, with bidentate chelated and monodentate nitrato groups being simultaneously involved. Our data do not permit differentiation between monocapped square antiprismatic and tricapped trigonal prismatic geometries.

The proposed decrease in coordination number from Eu(III) in the series of complexes prepared by method B and from Gd(III) in the nitrato complexes series is obviously a consequence of a decrease in ionic radii due to the "lanthanide contraction".

Although it is difficult to decide on monomeric or polymeric structures, the solubilities, the other physical properties, and the data from the spectral studies suggest rather a monomeric nature for **1**–**18** and **27**–**39**.

It is worth noting that on complexing with lanthanide(III) chlorides and nitrates in alcohols and acetonitrile the carbonyl ester oxygens of LH_2 are coordinated although we expected that this interaction would not be stabilized because of the poor donor strength of the ester group [2]. The ester group coordination in the studied complexes is partly attributed to the fact that this interaction is stabilized by the additional closure of two stable 6-membered chelate rings (chelate effect) and partly to the absence of water (use of *TEOF*) during the preparation of the complexes; the water molecule is a particularly strong ligand toward the lanthanide ions and thus competes effectively for coordination sites [41], while alcohols and acetonitrile are weaker donors to lanthanides(III) compared with water [42].

The stoichiometric and structural versatility observed in the lanthanide(III) complexes of LH_2 arises from the lack of strong crystal field effects for the 4f electronic configurations as well as from the large ionic radii of these metal ions, which change markedly with atomic number. The predominant ionic character in the bonding in the prepared complexes has in consequence a variety of coordination numbers and inorganic ligand arrangements as steric and electrostatic factors become dominant.

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