

NEW MONONUCLEAR LANTHANIDE(III) MACROCYCLIC POLYMERIC COMPLEXES WITH THE 1,5,9,13- TETRAAZACYCLOHEXADECANE LIGAND: THEIR MAGNETIC STUDIES AND SEMIEMPIRICAL CALCULATIONS

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Novel mononuclear lanthanide polymeric complexes are formed with Nd(III), Eu(III), Gd(III), Tb(III), Er(III) and Lu(III) nitrates and the 1,5,9,13-tetraazacyclohexadecane ligand. These compounds were characterized by elemental and thermal analysis, IR, EPR, ¹H and ¹³C NMR spectroscopies and magnetic susceptibility at variable temperature. The molecular weight of the compounds was determined by gel permeation chromatography, the results of which are 6272, 6120 and 4121 g/mol for Nd(III), Gd(III) and Er(III) compounds, respectively. The structures for the monomeric unit and the polymers were calculated by the force-field method. Each lanthanide compound showed specific and unusual magnetic properties which were associated with the particular arrangement of the elemental units in each polymer.

Keywords: Tetraazacyclohexadecane; mononuclear lanthanide(III) polymeric complexes; magnetic susceptibility; ¹H, ¹³C NMR and EPR; force-field method (FFM)

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INTRODUCTION

There has been a growing interest in understanding the coordination chemistry of lanthanide complexes through the magnetic properties of macrocyclic complexes.¹⁻³ For instance, the large chemical shift in proton nuclear magnetic resonance spectroscopy shown by lanthanide cryptates or coronates from their paramagnetism has been taken as a measure of their covalent character.⁴⁻⁶ On the other hand, the high stability of the [Gd(DOTA)] complexes, (DOTA = 1,4,7,10-tetraazacyclododecane 1,4,7,10-N,N',N'',N''' tetraacetate), in aqueous medium, makes them useful contrast-enhancing agents in magnetic resonance imaging for diagnosis in medicine.² Many studies have been devoted to synthesis of binucleating macrocyclic and macroacyclic compounds because the organization provided by an appropriately designed binucleating ligand may confer unusual structural features and magnetic optical catalytic properties.⁷ The design and synthesis of polynuclear systems have allowed the preparation of sophisticated molecular optical and magnetic devices.⁸ The study of bridged lanthanide complexes is very important since structural-magnetic correlations can be established in these compounds.^{9,10} Indeed, the magnetic properties of the lanthanide(III) compounds, and even of the mononuclear species, are still not well understood.⁹

This research studies new mononuclear lanthanide(III) macrocyclic polymeric complexes formed with the 1,5,9,13-tetraazacyclohexadecane ligand, $[\text{Ln}(16\text{-ANE-N}_4)(\text{NO}_3)_x(\text{CHO}_2)_y(\text{CH}_2\text{O}_2)_z]_n$, in order to understand the nature of their chemical bonding through their magnetic properties.

EXPERIMENTAL

Reagents

The hydrated lanthanide nitrates $\text{Nd}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and $\text{Lu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ were purchased from Alfa Products (99.9%) and europium salt $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ from Johnson Mathey (99.9%) and Aldrich (99.99%) and were used without further purification. Anhydrous trimethyl orthoformate, calcium hydride 4-40 mesh and anhydrous acetonitrile (<0.005% water) were purchased from Aldrich, n-hexane, anhydrous ethyl ether from Merck and Baker and 99% purity acetonitrile (0.2% water) from Merck.

Preparation of Mononuclear Polymeric Complexes

Stoichiometry 1.2 : 1 (Ligand : Metal)

The 1,5,9,13-tetraazacyclohexadecane macrocyclic ligand ([16]-ANE-N₄) was synthesized according to the literature¹¹ and its full characterization was performed.

Preparations of the neodymium **1**, europium **2**, gadolinium **3**, terbium **4**, erbium **5**, and lutetium **6** complexes were carried out as follows: the hydrated lanthanide nitrates (1.029 mmol) in each case were dissolved in 120 mL of acetonitrile (< 0.005% water), and in order to dehydrate the lanthanide salt, 30 mL of trimethyl orthoformate (TMOF) was added to this solution. This solution was then refluxed for 5 h in the case of neodymium, terbium, erbium and lutetium and 6 h for europium and gadolinium. After that, the dried ligand, [16]-ANE-N₄ (1.235 mmol), was dissolved in 30 mL of hot anhydrous acetonitrile (previously dehydrated with calcium hydride and filtered immediately with Whatman paper #3) and added to the original reaction mixture. When the reaction was over, (5 h for neodymium, europium and gadolinium and 10, 15 and 15 h for Tb, Er and Lu, respectively) the precipitate^{12a,b} was filtered with a glass frit funnel (4–8 μ) and recovered. The filtrate was concentrated to one half of its original volume at 60°C on a rotary evaporator. To the final solution was added dropwise anhydrous ether until a turbid solution was observed. The solution was kept in the refrigerator for three days. The solid formed was then recovered (Whatman paper #42) washed with anhydrous ethyl ether and anhydrous hexane exhaustively and finally dried under vacuum. The compounds were further dried under P₂O₅ into a vacuum oven at 70°C and 21 mm of Hg for several hours.

The yields were approximately 20% for Nd(III), Eu(III) and Gd(III) compounds and 15% for Tb(III), Er(III) and Lu(III) compounds. The reaction was carried out inside a glove box and kept at all times under 99.995% nitrogen atmosphere.

Stoichiometry 2 : 1 (Ligand : Metal)

The neodymium **7**, europium **8**, and gadolinium **9**, complexes were prepared as follows: in each case, the hydrated lanthanide nitrates (0.686 mmol) were dissolved in 80 mL of acetonitrile (< 0.005% water) and, in order to dehydrate the lanthanide salt, to this solution was added 20 mL of TMOF. This solution was then refluxed for 5 h in the case of neodymium, and 6 h for europium and gadolinium. After that, the dried ligand [16]-ANE-N₄

(1.372 mmol) was dissolved in 20 mL of hot anhydrous acetonitrile (previously dehydrated with calcium hydride and filtered immediately with Whatman paper #3) and added to the original reaction mixture. After 5 h the precipitates^{12a,b} were filtered separately with a glass frit funnel (4–8 μ). The solids formed were recovered and isolated, as previously described.^{12a,b} The yields were about 70% for Nd(III), 20% for Eu(III) and 55% for Gd(III) compounds, respectively. The reaction was carried out inside a glove box and kept under 99.995% nitrogen.

Elemental analysis for **1** was found to be: C, 27.03; H, 3.97; N, 13.76; Nd, 21.59. Nd[16]-ANE-N₄(NO₃)₃ · 3CH₂O₂, requires: C, 25.85; H, 4.88; N, 14.08; Nd, 20.72%. **2**, found: C, 25.96; H, 3.97; N, 12.95; Eu, 22.01. Eu[16]-ANE-N₄(NO₃)₃ · 3CH₂O₂ requires: C, 25.57; H, 4.83; N, 13.92; Eu, 21.59%. **3**, found: C, 25.44; H, 3.70; N, 12.72; Gd, 22.23.

Gd[16]-ANE-N₄(NO₃)₃ · 4CH₂O₂ requires: C, 25.42; H, 4.77; N, 12.97; Gd, 20.82%. **4**, found: C, 26.30; H, 4.17; N, 15.63. Tb[16]-ANE-N₄(NO₃)₃ · 3CH₂O₂ · CH₃CN requires: C, 27.14; H, 4.96; N, 14.89%. **5**, found: C, 27.00; H, 4.70; N, 15.37; Er, 29.68. Er[6]-ANE-N₄(NO₃)₂ · CHO₂ requires: C, 27.65; H, 5.18; N, 14.88; Er, 29.62%. **6**, found: C, 29.41; H, 4.41; N, 18.47. Lu[16]-ANE-N₄(NO₃)₃ · CH₂O₂ · 3CH₃CN requires: C, 30.09; H, 5.18; N, 18.47%.

Spectroscopic and Analytical Studies

IR spectra of the KBr pellets in the range 4000–450 cm⁻¹ were recorded on a Perkin Elmer/1600 FTIR spectrometer.

¹H and ¹³C NMR spectra were obtained in *d*₆-DMSO solutions by using a Bruker AM-360 MHz NMR spectrometer with TMS diluted in CDCl₃ as an internal standard. While the complexes are very soluble in *d*₆-DMSO, the [16]-ANE-N₄ is not; for this reason, it was necessary first to dissolve it in CDCl₃ and then mix the resulting solution with *d*₆-DMSO. The measurements were carried out at different temperatures, ranging from 294 to 343 K.

The magnetic susceptibility measurements were carried out on a Faraday balance and a Johnson Matthey balance at room temperature. In the case of the first equipment, the setup was calibrated with Hg[Co(SCN)₄] as standard, and the second one was calibrated with a standard sealed solution of MnCl₂.

The magnetic susceptibilities at variable temperature were measured using a SQUID-based magnetometer.

Electron paramagnetic resonance spectra were recorded at X-band (0 to 10,000 G) at 300 and 4.2 K in a Varian E-109 spectrometer.

The TGA/DTA analyses were carried out by using a Setaram TGDTA.92 instrument at 283 K min^{-1} (from 293 to 1273 K) under argon flow.

Elemental analyses (C, H, N) were performed at Christopher Ingold Laboratories at University College, London. The metal content was determined by the nuclear activation technique with the irradiation performed in the SIFCA facility of the Nuclear TRIGA Mark III Reactor of ININ Mexico.

The molecular weights were determined at 308.7 K by gel permeation chromatography (GPC) using a Millipore Waters Associates Apparatus with columns of Ultrastayragel of 500 Å and the linear column of 10^3 – 10^6 Å using N, N-dimethylformamide as eluent and polystyrene as standard; the apparatus was coupled to a Millipore Waters 410 Differential Refractometer and a Waters Data Module Recorder. The calibration curve was obtained with seven standards: 456, 500, 940, 1800, 2630, 4000 and 9000 D.

Because of the hygroscopic nature of the europium(III) compound, the powder sample was sealed into a small quartz tube for luminescence studies. An emission spectrum at room temperature was recorded with a Perkin Elmer Model MPF-44B fluorescence spectrophotometer and corrected by the lamp intensity and the photomultiplier response. The excitation source was 150-W Xenon lamp.

The luminescence spectrum of the hydrated europium(III) salt was obtained. The [16]-ANE- N_4 ligand showed no luminescence spectrum.

Molecular Calculations

In order to identify the most probable configuration for the elemental structure, analytical data were used and a primary structure was generated; the geometry optimization was done using a force-field method^{13a} with an error factor of 1×10^{-4} kcal/mol. This method calculates the energy of a specific structure as a function of the atom characteristic parameters (distances, angles, torsion angles, van der Waals interactions, *etc.*) by the classical principles of molecular dynamics.

Once the elemental structure had been built up, a geometry calculation was applied to generate a random order for the polymer compounds, optimized as a function of the energy. The energy minimization made one of the optimal configurations. In this way, it is possible to consider this calculated structure as an excellent approach.

We used the Cerius² software^{13b} (Polymer Builder, OFF and Blends modules) of Molecular Simulation Inc. and a Silicon Graphics Inc. Solid Impact workstation with a R10000 processor and 256 Mb in RAM.

RESULTS AND DISCUSSION

Our research on the coordination chemistry of the tetraazamacrocyclic ligands with lanthanide ions shows that in addition to dinuclear lanthanide polymeric compounds,^{12,14} mononuclear lanthanide polymeric compounds are also formed, depending upon the reaction conditions.^{12b} From the elemental analyses, a minimum formula for these new complexes of the following type was deduced: $\text{Ln}(\text{16-ANE-N}_4)(\text{NO}_3)_x(\text{CHO}_2)_y(\text{CH}_2\text{O}_2)_z$ for the Nd(III), Eu(III), Gd(III), Tb(III), Er(III) and Lu(III) ions. For isolation of these mononuclear compounds the solvent used to dissolve the ligand was further dehydrated with calcium hydride. These complexes have been obtained at least three times in each case, indicative of their reproducibility. The compounds are very sensitive to air humidity.

The neodymium(III) complex is a light blue-violet compound, europium(III), terbium(III) and lutetium(III) complexes are white and erbium(III) is a light pink complex. All start to decompose above 453 K except the lutetium(III) complex, which melts at 491 K. These complexes are amorphous homogeneous powders. Therefore, molecular weight determinations on the Nd(III), Gd(III) and Er(III) compounds were carried out and found to be: 6272, 6120 and 4121 g/mol, respectively. These results indicate that the new species are polymeric and are composed of nine, eight and seven units in each case. As for the dinuclear lanthanide polymeric compounds,¹² these mononuclear polymeric compounds are thermally stable.

The Nd(III), Eu(III) and Gd(III) complexes were soluble in DMSO, DMF, N-methyl-pyrrolidone and H₂O. The Tb(III), Er(III) and Lu(III) complexes were also slightly soluble in MeOH, and the Er(III) compound is also slightly soluble in acetone.

IR Spectroscopy

The IR spectra of **1**, **2**, **3**, **4**, **5** and **6** were similar to each other in the medium infrared region. Figure 1 shows the spectrum of compound **5**, which is representative of these compounds. The N–H, C–N–C and H–C–H–C–H– vibration bands of the free macrocyclic ligand^{11,12a,b} shifted upon coordination to the metal ion. Thus, the main N–H stretching frequencies appear between 3416–3422 and 740–750 cm⁻¹; the C–N–C symmetric vibration frequencies appear at 1240, 1228–1200 and 1086–1014 cm⁻¹. The bands corresponding to (–CH₂–)₃ groups were observed around 2946 cm⁻¹. When three or four formic acids were present, strong bands appeared in the range of 1630–1650 and 1585–1580 cm⁻¹ (weak bands) due to the

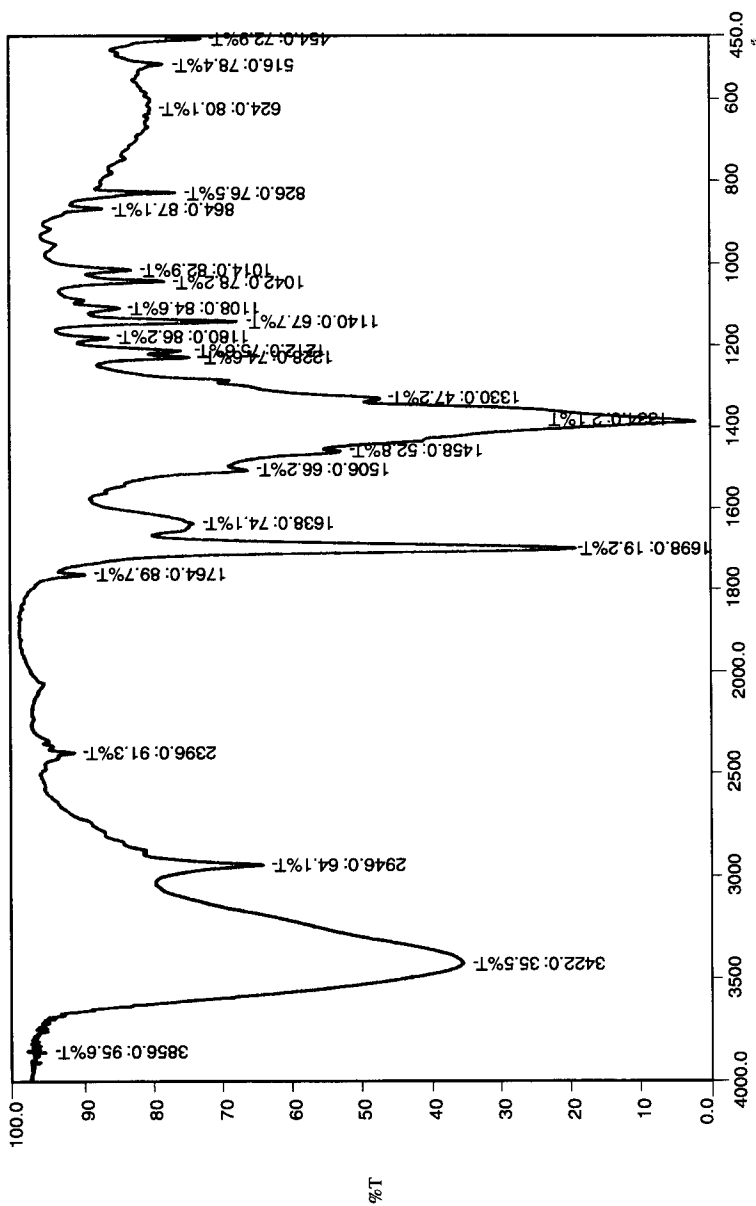


FIGURE 1 IR spectrum of the mononuclear erbium(III) macrocyclic polymer in KBr.

asymmetric vibrations of the COO groups. However, the compounds which contained less than three formic acids presented only one intense band between 1630 and 1642 cm^{-1} . The C–H vibration frequency of the formic acids was observed to be between 654 and 624 cm^{-1} . The coordinated nitrates showed very weak bands between 1700 and 1780 and medium bands at 1450–1460, 1322–1300, 1042–1034 and 816–820 cm^{-1} . It is important to mention that a strong band centered at 1384 cm^{-1} was also observed which is normally assigned to ionic nitrates. In the case of the erbium compound, the appearance of such a band is not consistent with the electrolytic behavior of the compound^{12b} which is a neutral complex in water and DMSO,^{12b} but is due to anionic exchange when these compounds are milled in KBr, as previously reported.^{12,15}

Thermal Analysis

These compounds follow a similar thermal (TGA/DTA) decomposition pattern. In compound **2**, for example, a loss between 468 and 623 K is observed, corresponding to formic acid and the macrocyclic ligand. Between 623 and 1087 K a second loss that corresponds to the remaining formic acids and one nitrate and the partial decomposition of other nitrate is also seen. The weight of the residue corresponds to EuONO_3 . The composition of this residue is consistent with that observed for other macrocyclic lanthanide complexes.^{16,17} The simple and similar pattern of the thermal diagrams of our six complexes is consistent with pure compounds.

NMR Spectroscopy

(A) ^1H NMR

The [16]-ANE- N_4 ligand was dissolved in CDCl_3 and then mixed with d_6 -DMSO in order to record its spectrum. **1**, **2**, **3**, **4** and **5** were dissolved in d_6 -DMSO.

Figure 2(a) and (b) show the ^1H NMR spectra at 300 and 343 K, respectively, of a concentrated (0.05 M) solution of the erbium(III) compound. At 300 K, the integration between 1.35 and 2.35 ppm corresponds to 8H assigned to beta-CH. At 2.49 ppm the DMSO signal is observed. The peak centered at 2.55 integrated for 2 protons, which were assigned to 2NH of the macrocyclic ligand. Between 2.75–3.40 and 3.57–4.40 ppm the signals correspond to 10H and 6H assigned to alfa-CH. A doublet which corresponds to 1H (CH) of the formate ligand is observed

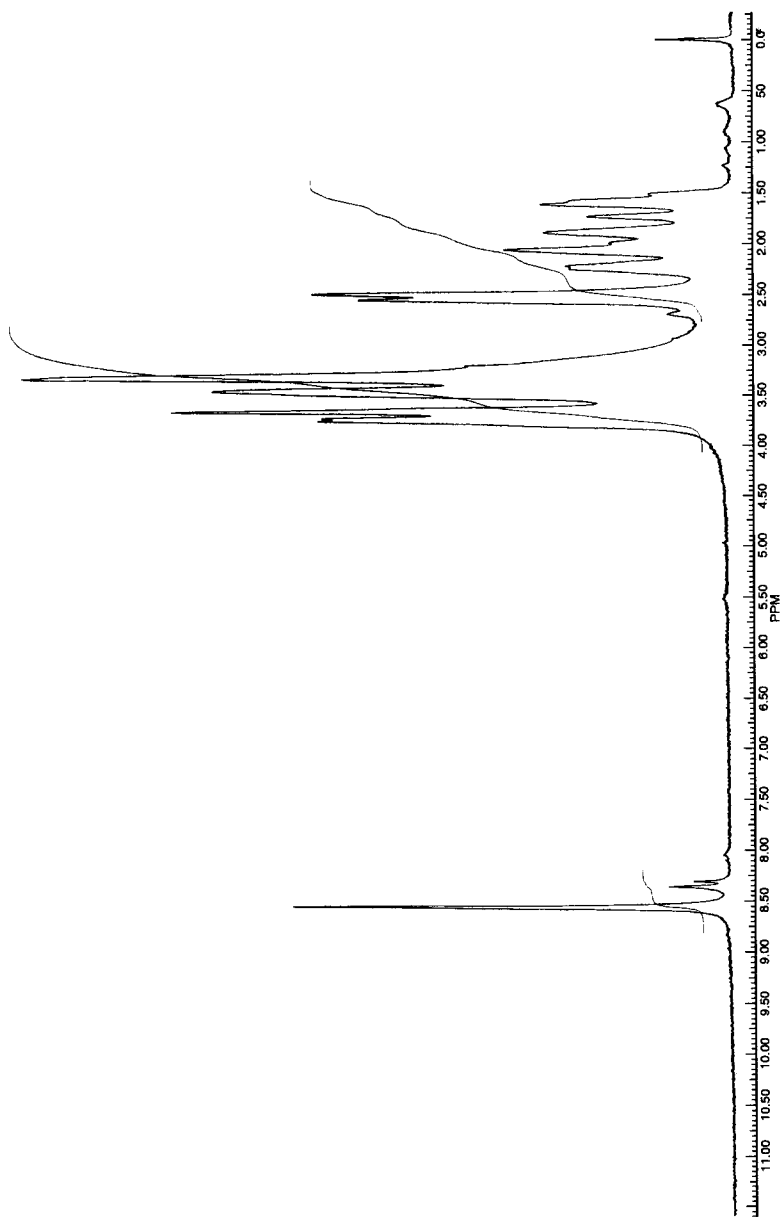


FIGURE 2(a)

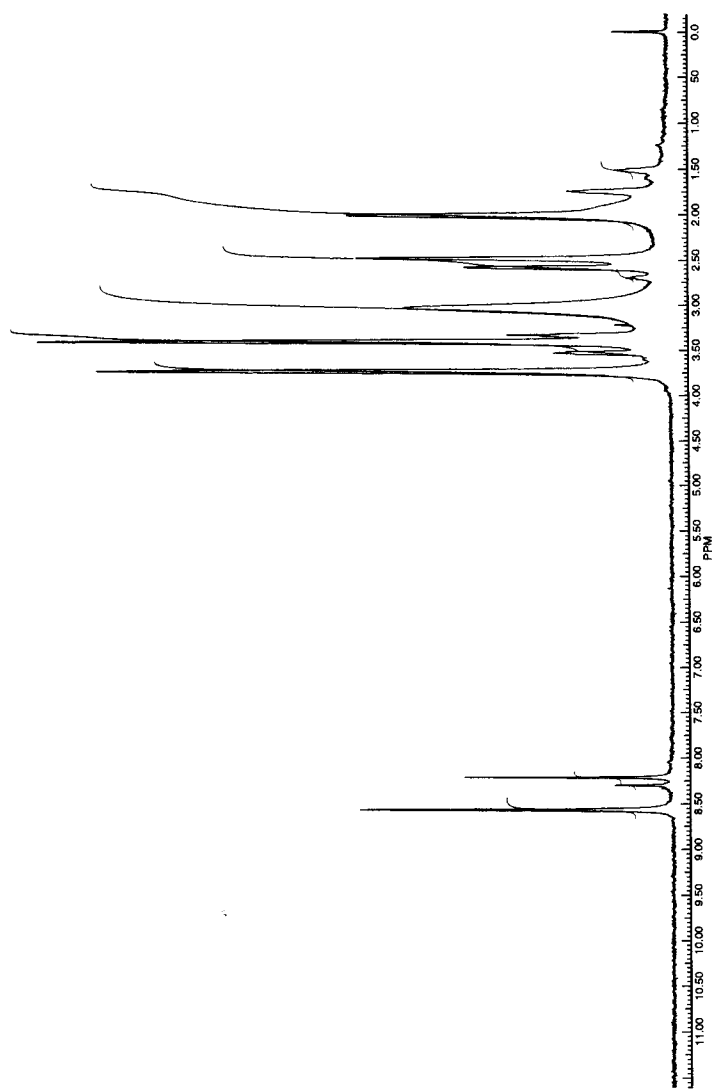


FIGURE 2(b)

FIGURE 2 ^1H NMR spectrum of the mononuclear erbium(III) macrocyclic polymer in d_6 DMSO (a) at 300 K and (b) 343 K.

between 8.25 and 8.45 ppm. There is a broad singlet between 8.45 and 8.75 ppm, which is consistent with 2H (NH) of the macrocyclic ligand. We suggest that the shifting of these protons might be due to the paramagnetism of the metal ion. A variable temperature study was performed from 300 to 343 K. The spectrum at 343 K looks quite different from that at 300 K, the beta-CH are observed at 1.52, 1.76 and 2.03 ppm, the alfa-CH at 3.04, 3.34, 3.55 and 3.75 ppm. The NH at 2.54 and 8.57 ppm and the formate appears as a doublet at 8.20 and 8.30 ppm. The shifting of the signals can be ascribed to a change in the conformation of the macrocyclic ligand in the compound. After heating the solution to 343 K, the samples were left until they reached room temperature again and the spectra were recorded. This spectrum was the same as that recorded before heating, thus showing a kinetically and thermodynamically stable compound.

Studies of the same type were performed for the other lanthanide complexes, which showed similar behavior. Therefore we can suggest that 1, 2 and 4 are kinetically and thermodynamically stable in DMSO solution.

The ¹H spectra of 1, 2, 4 and 5 show a similar pattern. The main peaks are collected in Table I.

(B) ¹³C NMR

The ¹³C NMR spectra of the Nd(III), Eu(III) and Er(III) complexes at 300 K (90.6 MHz) showed several peaks. The main peaks are collected in Table II. The previous assignation was confirmed by a DEPT (Distortionless Enhanced by Polarization Transfer) study.^{12b} The erbium complex

TABLE I ¹H NMR (ppm) in *d*₆-DMSO at 300 K of the mononuclear lanthanide(III) macrocyclic polymeric complexes: [Ln(16-ANE-N₄)(NO₃)_x(CHO₂)_y(CH₂O₂)_z]_n

Compound	beta-CH ₂	alfa-CH ₂	-NH	-NH (D ₂ O exchange)	HCOOH	HCOOH
(1)	1.61, 1.75	3.23 3.30 3.40-3.70	2.07 2.45 8.04*	2.07 2.45 8.04	1.95	8.04**
(2)	1.60, 1.77	3.0-3.35 3.45-3.80	2.05 2.07 2.9-3.35** 8.04*	2.05 2.07 2.9-3.35** 8.04*	1.95	8.04**
(4)	1.71, 2.08	3.28 3.33 3.60-3.90	2.01 3.46 8.62	3.45 8.59	4.08	8.19 8.29
(5)	1.60, 1.72, 1.90, 2.05 2.20	3.30, 3.63, 3.70, 3.75	2.55 8.56			8.30 8.30

*NH in the methine region; **NH in the alfa-methylene region.

TABLE II ^{13}C NMR (ppm) in d_6 -DMSO at 300 K of the mononuclear lanthanide(III) macrocyclic polymeric complexes: $[\text{Ln}(16\text{-ANE-N}_4)(\text{NO}_3)_x(\text{CHO}_2)_y(\text{CH}_2\text{O}_2)_z]_n$

Compound	$\beta\text{-CH}_2$	$\alpha\text{-CH}_2$	HCOOH	HCOO
(1)	30.05, 29.08, 28.56, 28.49, 28.40, 27.89, 27.65, 26.55	45.26, 45.82 45.91, 46.04, 46.21, 46.48, 46.59	163, 162.87	
(2)	30.20, 29.20, 28.71, 28.63, 28.55, 27.96, 27.81, 26.69	45.94, 46.16, 46.33, 46.71	162.82	
(5)	25.46, 20.60, 18.46	47.73, 50.39 55.68		153.40

showed a singlet at 153.40 ppm which was assigned to HCOO whereas those of Nd(III) and Er(III) compounds around 163 ppm corresponded to HCOOH ligand.

Computer Simulation of the Molecules

The simulations of the monomer and the polymer molecules of Nd(III), Gd(III) and Er(III) were made with a force-field method,¹³ based on the classical principles of considering atoms as points joined by springs with characteristic parameters defined by empirical analysis.

According to the results obtained by the above mentioned method, the minimum energy configurations support coordination numbers of eleven, twelve and eight for Nd(III), Gd(III) and Er(III), respectively. These coordination numbers have also been observed for other macrocyclic lanthanide compounds.^{5,16,18f,g} Selected values of distances, angles and torsion angles for these compounds are given in Tables III–V. The calculated bond lengths, angles and torsion angles show significant differences among the Nd(III), Gd(III) and Er(III) compounds.

For the three compounds, the obtained metal–nitrogen bond lengths are within the reported values for other lanthanide complexes.¹⁸ In the complexes reported in this paper, the Ln–N bond lengths are longer than the Ln–O distances calculated for the molecular unit, as observed for other complexes.¹⁸ However, in our complexes the Ln–N distances show important variations, indicating distortion of the macrocycle which imposes peculiar configurations to the molecules in each case, (see Figure 3(a)–(c) and Tables III–V).

These results explain why these compounds are stabilized as polymers. From other experimental Ln–N distances reported in the literature, specifically for Ln–cyclen,^{18g} and Ln–hexacyclen^{18e} complexes, it has been observed that distances in Er–cyclen complex are between 2.46 and

TABLE III Selected bond lengths, bond angles, torsion angles of the monomeric unit of Nd(III) compound

<i>Bond lengths (Å)</i>		<i>Bond angles (°)</i>		<i>Torsion angles (°)</i>	
		N2-Nd1-N3	94.2		
		N2-Nd1-N4	169.6		
		N2-Nd1-N5	93.6		
		N3-Nd1-N4	89.7		
		N4-Nd1-N5	82.5		
Nd1-N2	2.39	Nd1-N2-C9	111.1	C14-N4-Nd1-O29	62.1
Nd1-N3	2.41	Nd1-N3-C12	111.1	C14-N4-Nd1-O24	90.8
Nd1-N4	2.65	Nd1-N4-C12	68.1	C14-N4-Nd1-N2	95.2
Nd1-N5	2.41	Nd1-N5-C17	110.8	C14-N4-Nd1-O35	-121.9
Nd1-O33	2.27	N4-Nd1-O26	70.7	C14-N4-Nd1-O37	-89.5
Nd1-O32	2.33	N4-Nd1-O32	83.2	C14-N4-Nd1-O26	67.0
Nd1-O37	2.47	N4-Nd1-O24	85.7	Nd1-N2-C20-C19	-61.9
Nd1-O24	2.52	N4-O38-O29	41.4	Nd1-O26-N6-O28	-136.2
Nd1-O35	2.55	O32-O33-Nd1	65.0	Nd1-O26-N6-O27	110.9
Nd1-O29	2.40	Nd1-O24-O25	141.0	C20-C19-C18-N5	-57.0
Nd1-O26	2.54	N5-Nd1-O24	72.4	N3-C12-C13-C14	85.5
		N3-Nd1-O33	80.0	C12-C13-C14-N4	-57.6
		O29-Nd1-O26	24.4	C14-N4-C5-C16-	-158.3
		O32-Nd1-O37	29.1	O30-N7-O29-Nd1	125.9
		N3-Nd1-O32	88.7		
		N5-Nd1-O35	77.1		

TABLE IV Selected bond lengths, bond angles, torsion angles of the monomeric unit of Gd(III) compound

<i>Bond lengths (Å)</i>		<i>Bond angles (°)</i>		<i>Torsion angles (°)</i>	
		N2-Gd1-N3	87.6		
		N2-Gd1-N4	168.0		
		N2-Gd1-5	87.2		
		N3-Gd1-N4	93.7		
		N4-Gd1-N5	92.9		
Gd1-N2	2.54	Gd1-N4-C15	115.5	C15-Gd1-O33-N6	159.4
Gd1-N3	2.37	Gd1-N2-C20	124.9	C15-Gd1-N5-C12	20.7
Gd1-N4	2.38	C17-N5-Gd1	120.8	C15-Gd1-N2-C20	-2.8
Gd1-N5	2.50	C9-N2-Gd1	114.7	C15-Gd1-N3-C17	-8.2
Gd1-O33	2.4	Gd1-O37-C24	144.2	C12-C13-C14-N4	52.5
Gd1-O34	2.36	N2-Gd1-O34	35.5	Gd1-C9-N7-O29	167.9
Gd1-O37	2.54	O37-Gd1-O33	27.8	Gd1-O25-N8-O27	-1.7
Gd1-O30	2.39	O34-Gd1-N3	92.7	Gd1-O27-N8-O25	1.7
Gd1-O27	2.28	O33-Gd1-N2	91.6	Gd1-C13-C14-N4	12.6
Gd1-O25	2.31	O33-Gd1-O39	154.8	Gd1-C19-C20-N2	-12.6
Gd1-O39	2.61	O33-Gd1-O27	126.7	Gd1-C16-C17-N5	1.4
		O33-Gd1-N5	95.1	N2-C9-C10-C11	-80.2
		N3-Gd1-O30	83.6	N3-C12-C13-C14	-69.1
		O27-Gd1-O25	52.8	N4-C15-C16-C17	68.2
		O25-Gd1-O28	27.4	N5-C18-C19-C20	64.4
		Gd1-O37-O30	69.2	C17-N5-C18-C19	139.9

TABLE V Selected bond lengths, bond angles, torsion angles of the monomeric unit of Er(III) compound

Bond lengths (Å)		Bond angles (°)		Torsion angles (°)	
		N2-Er1-N3	86.4	N4-Er1-N3-C11	-8.4
		N2-Er1-N4	176.5		
		N2-Er1-N5	90.7		
Er1-N2	2.30	N3-Er1-N4	94.2		
Er1-N3	2.32	N4-Er1-N5	87.7	N4-Er1-N5-C17	-176.0
Er1-N4	2.33	O27-Er1-O22	169.1	N4-Er1-N2-C8	-149.7
Er1-N5	2.49	O27-Er1-N2	82.3	N4-Er1-N3-C10	-135.6
Er1-O27	2.25	N2-Er1-O22	98.2	N4-Er1-N5-C16	7.9
Er1-O22	2.34	N4-Er1-O27	94.2	N5-Er1-N14-C14	19.7
Er1-O24	2.24	O27-Er1-N3	87.7	N5-Er1-N2-C19	19.8
Er1-O26	2.21	N4-Er1-O21	85.3	N4-Er1-N2-C19	83.5
N2-C8	1.47	Er1-O22-C21	121.0	N5-Er1-N2-O22	180.0
N3-C10	1.48	Er1-N3-C11	115.7	N6-O27-Er1-O22	50.9
N4-C14	1.48	Er1-O26-N7	102.5	O28-O27-Er1-N4	-76.1
Er1-N7	2.82	Er1-C12-C11	68.9	Er1-N2-C19-C18	-62.9
Er1-O23	3.32	C19-N2-Er1	112.1	Er1-N5-C16-C15	7.2
Er1-C18	3.51	Er1-C9-C10	63.5	Er1-N3-C10-C9	-63.4
Er1-C19	3.17	Er1-N4-C14	110.6	Er1-O24-N7-O26	9.9
Er1-C9	3.55	C16-N5-Er1	125.6	N5-Er1-N4-C13	150.5
N5-C11	1.51	C16-N5-Er1	125.6		

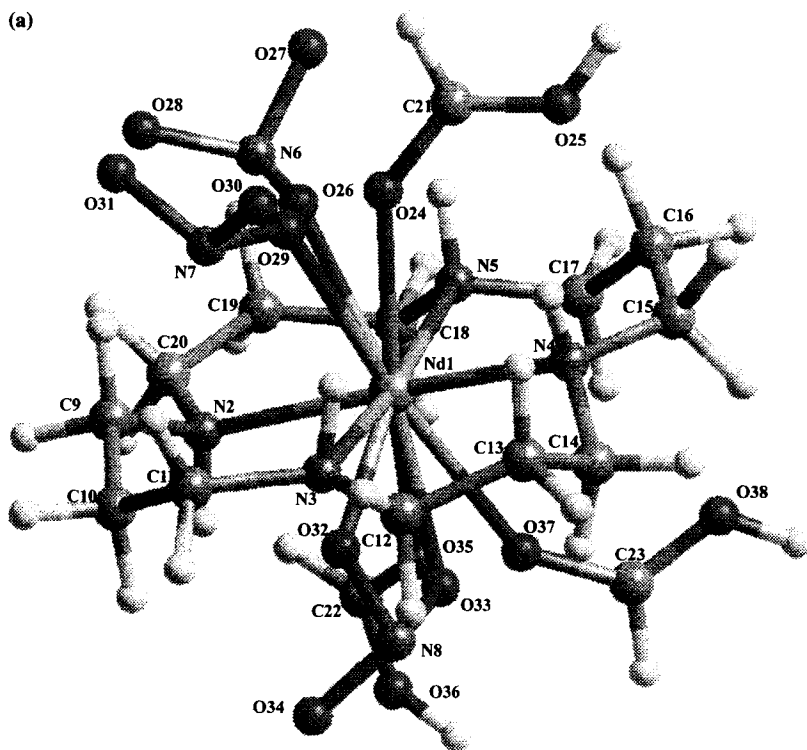


FIGURE 3(a)

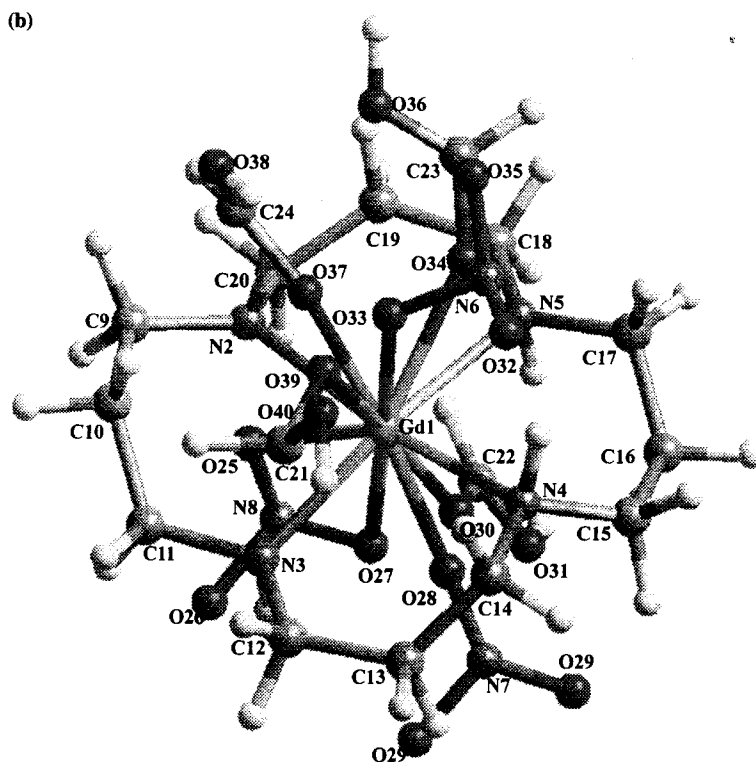


FIGURE 3(b)

2.51 Å, in the case of Er-hexacyclen complex they are between 2.51 and 2.61 Å, and in the case of the Nd-hexacyclen complex they are between 2.65 and 2.75 Å. It is interesting to note that in Ln-(DOTA) derivatives^{18h-k} and related compounds,¹⁸ⁱ the experimental Ln-N bond lengths are within the same range.

If we compare these distances with our calculated results, in the case of the Er(III)-tetraazacyclohexadecane they are found to be 2.30 and 2.49 Å and in the case of the Nd(III)-tetraazacyclohexadecane they are between 2.40 and 2.65 Å. In our case these distances are shorter and the range among the distances is larger. This could be the result of the extra methylene groups between the nitrogen donors in the macrocycle. Therefore, this ligand acquires different conformations¹¹ from those of cyclen and cyclen-derivative ligands. The distorted arrangement prevents stabilization of the monomers; in addition the versatile mode of coordination of nitrate^{12,15b,18d} and formate^{12,15a} ligands contribute to stabilize these compounds as polymers.

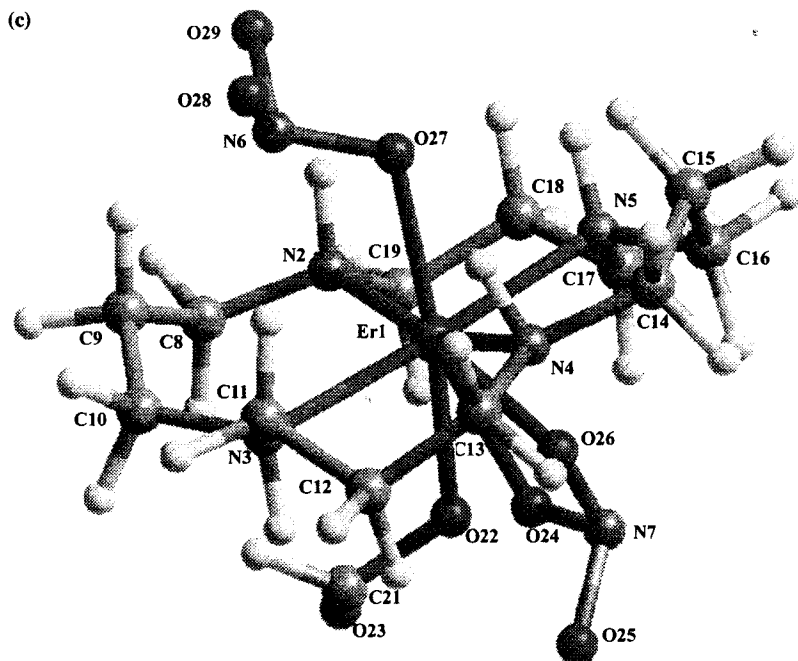


FIGURE 3(c)

FIGURE 3 (See Colour Plate at back of issue.) Perspective view of the molecular structure of the elemental unit of (a) $\text{Nd}([16]\text{-ANE-N}_4)(\text{NO}_3)_3\text{CH}_2\text{O}_2$, (b) $\text{Gd}([16]\text{-ANE-N}_4)(\text{NO}_3)_3\text{4-CH}_2\text{O}_2$ and (c) $\text{Er}([16]\text{-ANE-N}_4)(\text{NO}_3)_2(\text{CHO}_2)$, as visualized by Cerius.

The molecular mechanics calculations for our complexes are similar to those reported by *ab initio* calculations for $\text{Gd}(\text{DOTA})$ derivatives.^{18j}

As mentioned in the experimental section, the molecular weight determinations indicate that these compounds are polymers; therefore, the minimum energy configurations were also performed for the polymeric compounds and the structures of the polymers built. Figure 4 is an example. From these results the intermolecular metal–metal distances are found to be 6.98, 7.35, 7.56 and 7.89 in the case of the neodymium compound. For the gadolinium compound the distances are 4.64, 7.94, 10.63 and 12.31. In the case of the erbium complex the distances are 5.97, 7.11, 7.72 and 13.81 Å. As can be seen, the metal–metal distances vary significantly within the same polymeric compound and also among the different polymers. This supports the fact that the polymers are not linear and that each one keeps its own properties.



FIGURE 4 (See Colour Plate at back of issue.) Perspective view of the molecular structure of the polymeric compound (a) $[\text{Nd}(\text{[16]-ANE-N}_4)(\text{NO}_3)_3\text{3CH}_2\text{O}_2]_n$ as visualized by Cerius.

This could be an explanation of the unusual magnetic properties found for these lanthanide complexes, which will be discussed below.

EPR Spectroscopy

The powder X-band EPR spectra at 4.2 K were recorded for Nd(III), Gd(III), Tb(III) and Er(III) complexes. From all these spectra, it is important to note that the spectrum of the neodymium compound covers the whole field studied, namely from 0 to 10,000 G, while for the rest of the

lanthanide complexes the features appear in the range 0 to about 5,000 G. The spectrum of the neodymium compound (Figure 5) is the only one that shows hyperfine splitting, even though all the other nuclei have a nuclear spin abundance higher than that for neodymium.^{1,19} From these considerations, we may suggest that the observed splitting must be due to a superhyperfine interaction between the paramagnetic neodymium and the nitrogen ligands.

The spectrum may be described as axial with $g_{\perp} = 2.7$ (linewidth = 200 G), and $g_{\parallel} = 0.9$ (linewidth = 600 G). Only the parallel component shows superhyperfine splitting. Thus, the Hamiltonian that describes the spectrum is:

$$H = \beta S_z g_{\parallel} H_z + \beta g_{\perp} (S_x H_x + S_y H_y) + A_{\parallel} S_z I_z,$$

where the first and second terms correspond to the axial electronic Zeeman interaction and the third term corresponds to the superhyperfine interaction, where A_{\parallel} stands for the superhyperfine coupling constant. The simulated spectrum yields $A_{\parallel} = 0.0567 \text{ cm}^{-1}$ and may be indicative of an interaction between the nitrogen orbitals and those of the neodymium ion. The sequential broadening of the superhyperfine features with increasing

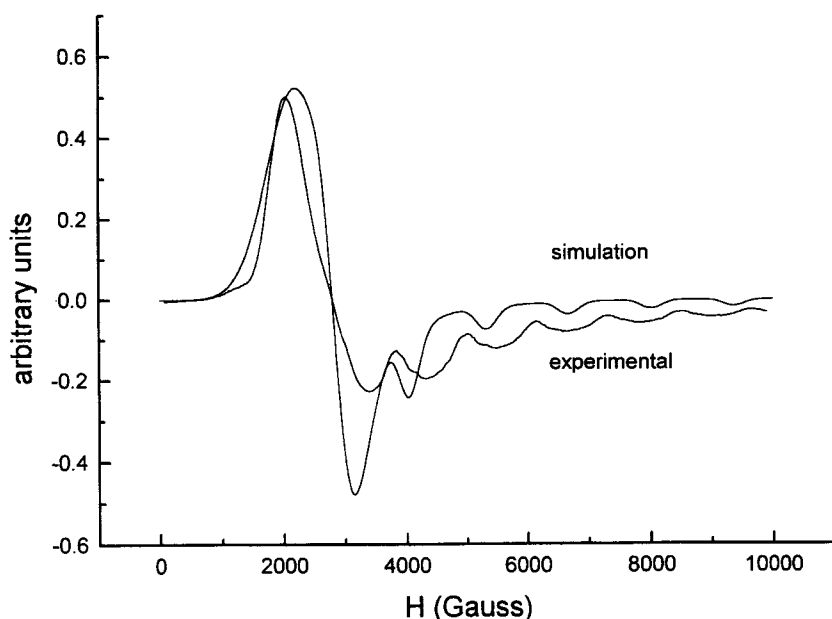


FIGURE 5 Powder EPR spectrum at 4.2 K of the mononuclear neodymium(III) macrocyclic polymer.

applied magnetic field is indicative of g -strain broadening.²⁰ The Nd(III) is a Kramer ion in which $g_{\perp} > g_{\parallel}$ has been observed in compounds in which the $J=9/2$ manifold lies lowest for the doublet ground state,²¹ which is confirmed in our case.

The terbium and erbium complexes at 4.2 K have a highly asymmetric feature without hyperfine splitting, which is indicative of a highly anisotropic crystal field, as expected.^{22,12b}

The gadolinium complex at 4.2 K shows a typical axial spectrum with $g_{\parallel} = 6.1$ (linewidth = 200 G), and $g_{\perp} = 1.9$ (linewidth = 500 G) (Figure 6). The spectrum was simulated with the following Hamiltonian:

$$H = \beta S_z g_{\parallel} H_z + \beta g_{\perp} (S_x H_x + S_y H_y)$$

The simulation considering a Lorentzian line shape fits well with the experimental spectrum. In this complex the anisotropy in g ($\Delta g = 4.2$) is substantially larger than that found in the neodymium species ($\Delta g = 1.8$), which may be due to a larger zero-field splitting in gadolinium.

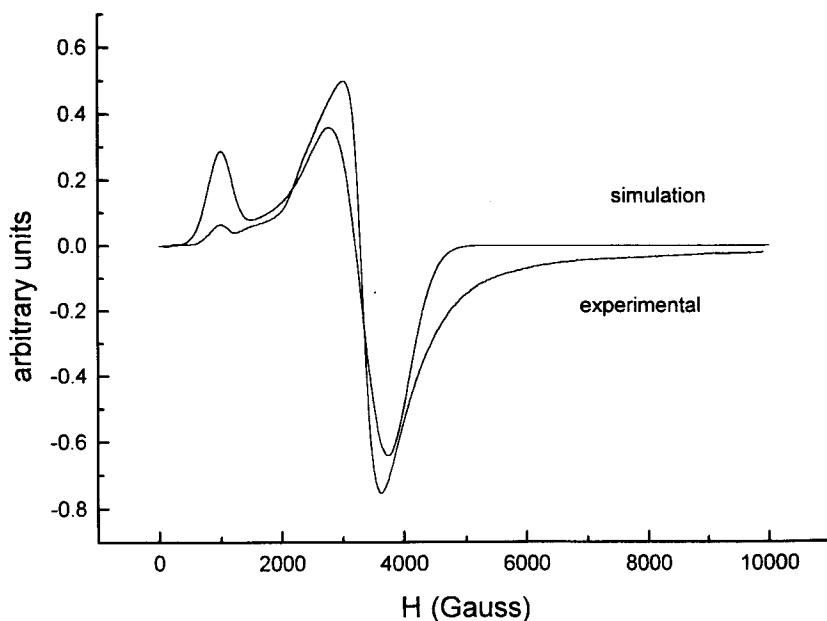


FIGURE 6 Powder EPR spectrum at 4.2 K of the mononuclear gadolinium(III) macrocyclic polymer.

Magnetic Susceptibility

The magnetic properties also provide insight on the chemical bonding of these new mononuclear lanthanide(III) macrocyclic polymers. Magnetic susceptibilities for each compound were measured, and the molar magnetic susceptibility corrected from diamagnetic contribution (χ_{Mdc}) was used to determine the experimental effective magnetic moments (μ_{eff}) of the compounds by $\mu_{\text{eff}} = 2.828(\chi_{\text{Mdc}} \cdot T)^{1/2}$. The results are shown in Table VI. The calculated values were obtained according to the equation, $\mu_{\text{eff}} = g[J(J+1)]^{1/2}$. These polymeric compounds show some important differences to the calculated magnetic moments, normally expected for Ln(III) compounds.²³⁻²⁵ In order to understand this unusual magnetic behavior, we studied the magnetic susceptibility as a function of temperature and magnetic field for the gadolinium and europium complexes to give insights into their magnetic properties and the nature of their chemical bond.

For most of the trivalent lanthanide ions the $^{2S+1}L_J$ free ion ground state is so well separated in energy from the first excited state that only this ground state is thermally populated at room temperature and below.

Gadolinium The ground state arising from the $4f^7$ configuration is $^8S_{7/2}$. Since $L=0$, there is no spin-orbit coupling. Furthermore, the first excited state is located at some $3 \times 10^4 \text{ cm}^{-1}$ above the ground state. The zero-field splitting within this ground state is very weak (of the order of 10^{-2} cm^{-1}) and not detectable with magnetic measurements except at very low temperatures. Thus the magnetic susceptibility for gadolinium is almost isotropic and follows the Curie-Law $\chi T = Ng^2\beta^2 S(S+1)/3k$, in this case $\chi T = 21N\beta^2/k = 7.88 \text{ cm}^3 \text{ K mol}^{-1}$.²⁶ However, we obtained $\chi T = 8.91 \text{ cm}^3 \text{ K mol}^{-1}$ at room temperature in a Faraday balance (and $9.5 \text{ cm}^3 \text{ K mol}^{-1}$ with a SQUID magnetometer). Because of this unexpectedly large magnetic value, the gadolinium(III) compound was synthesized and characterized

TABLE VI Effective magnetic moments, μ_{eff} (BM) of the mononuclear lanthanide macrocyclic polymeric compound

Compounds	μ_{eff}	
	Experimental	Calculated
Nd([16]-ANE-N ₄)(NO ₃) ₃ 3CH ₂ O ₂	3.88	3.62
Eu([16]-ANE-N ₄)(NO ₃) ₃ 4CH ₂ O ₂	3.40	3.61*
Gd([16]-ANE-N ₄)(NO ₃) ₃ 4CH ₂ O ₂	8.91	7.94
Tb([16]-ANE-N ₄)(NO ₃) ₃ 2CH ₂ O ₂ CH ₃ CN		9.72
Er([16]-ANE-N ₄)(NO ₃) ₂ (CHO ₂)	8.54	9.57
Lu([16]-ANE-N ₄)(NO ₃) ₃ CH ₂ O ₂ 3CH ₃ CN	0.0	0

*The μ_{eff} was calculated by mixing of the ground and the highest levels.

again and the magnetic moment was reproduced. The measurement was repeated with a SQUID magnetometer as a double check. From Figure 7 there can be observed an example of *Curie-Weiss* behavior which was fitted by using $\Theta_w = -1.44$ K. This is indicative of a very low antiferromagnetic behavior. The plot of χT vs. T (Figure 8) shows this behavior. The high observed value for the product χT could be interpreted in terms of a spin-spin exchange coupling mechanism due to the branched polymeric nature of the compound.

Europium The free-ion excited states are thermally populated for europium(III). The 7F ground term is split by the spin-orbit coupling into seven states 7F_j , with J taking the integers values from 0 to 6.^{9b,27} In this case, the spin-orbit coupling parameter is of the order of 300 cm^{-1} , quite small indeed. The effective magnetic moment of 3.40 BM found for compound **2** is very close to that reported for Eu(III) ions by Van Vleck,²⁷ who considered the mixing of ground and higher energy terms as well as the independent

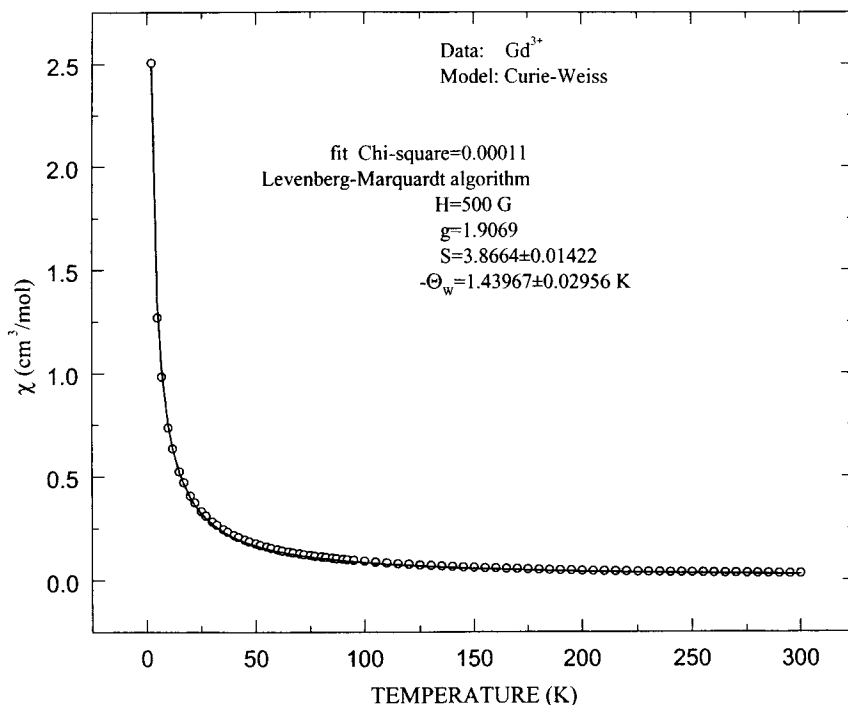


FIGURE 7 Molar magnetic susceptibility vs. temperature of the mononuclear gadolinium (III) macrocyclic polymer.

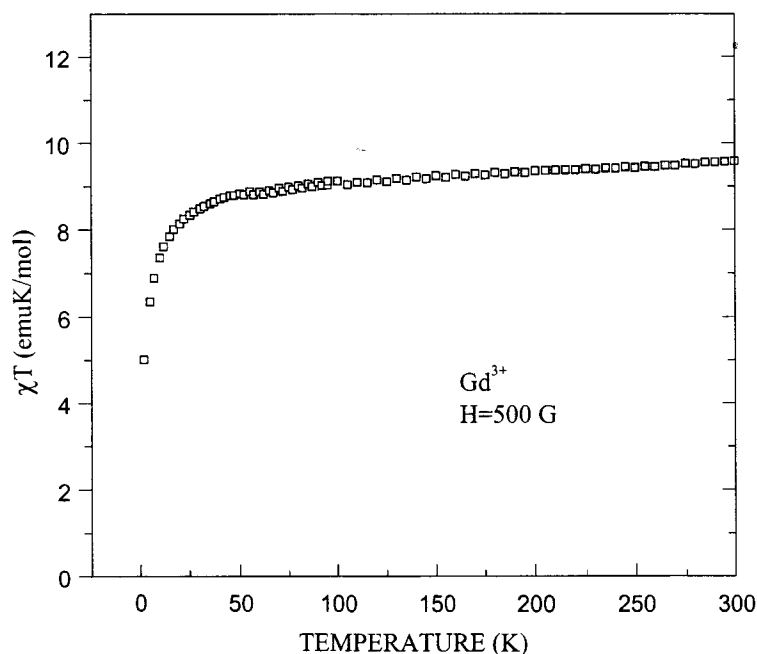


FIGURE 8 χT product vs. temperature of the mononuclear gadolinium(III) macrocyclic polymer.

term of temperature. As for other Eu(III) compounds, our europium(III) complex does not show *Curie-Weiss* behavior.^{9,26,27} In Figure 9 we show χ^{-1} vs. T , where the linear part of the curve extrapolates to negative Weiss Θ_w , from room temperature to about 150 K. Nevertheless, the plot of M vs. H , Figure 10, shows a superparamagnetic behavior which increases at low temperature, thus indicating a ferromagnetic nature of the powder compound.

Luminescence

Emission Spectrum

The emission spectrum of the mononuclear europium(III) compound **2** (Figure 11) was obtained by irradiating the sample at a constant excitation wavelength of 393 nm, that is, exciting to the 5L_6 (395 nm) level and emission lines $^5D_0 \rightarrow ^7F_0$, $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_4$ were observed. These four transitions are normally observed in europium(III) compounds, and

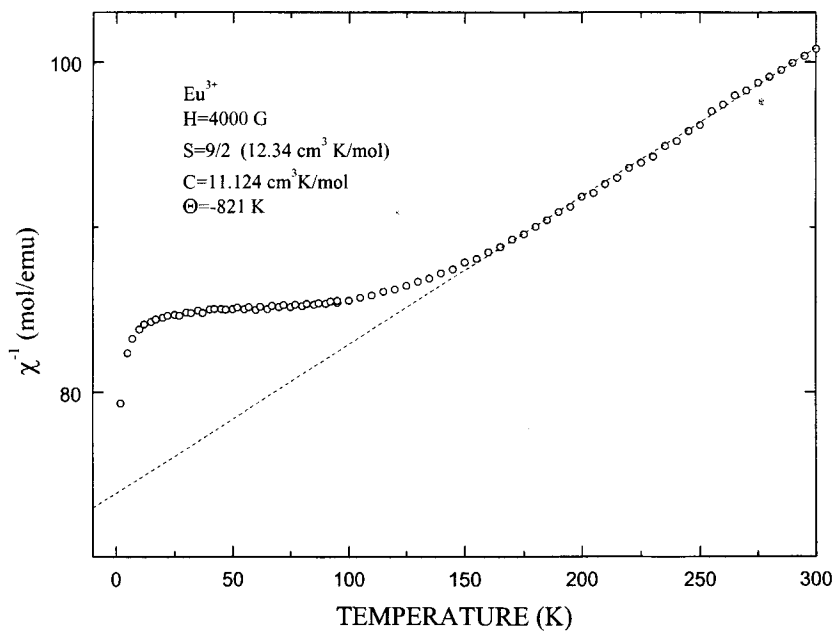


FIGURE 9 Inverse of the molar magnetic susceptibility vs. temperature of the mononuclear europium(III) macrocyclic polymer.

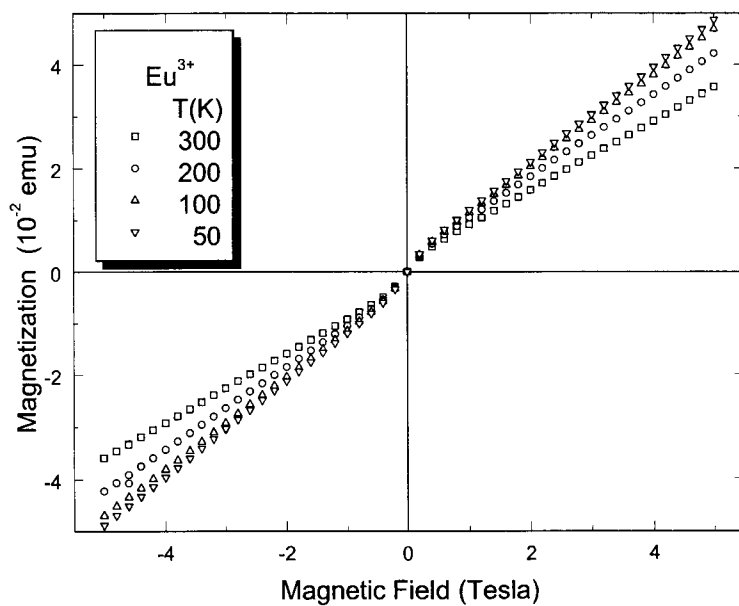


FIGURE 10 Magnetization vs. magnetic field of the mononuclear europium(III) macrocyclic polymer.

the intensity and multiplicity have served to elucidate the environment of the europium site.

The transition ${}^5D_0 \rightarrow {}^7F_0$ (577–581 nm) is a nondegenerate forbidden transition which gains intensity through *J*-mixing in C_s , C_n and C_{nv} symmetries.¹ The multiplicity of this signal can be used to diagnose the site symmetry around the metal ion.²⁸ The signal cannot be split by any crystal field; therefore, the number of peaks in this region of the spectrum is indicative of the number of non-octahedral emitting species in the sample, which is the number of different species in the compound. In our Eu(III) complex, a medium broad band is present around 580 nm. The considerable width of this band which is common in polymeric compounds, suggests that more than one peak comprises the signal which indicates more than one coordination environment around the metal centers in the polymer. The latter can be inferred from Figure 4 and the related discussion which indicates that the arrangement of the elemental units in the polymer is not linear and that the metal centers do not have exactly the same symmetry sites. Although, it is not possible to assign a specific symmetry site for the europium complex, our evidence suggests the existence of a single polymeric compound.

The transitions: ${}^5D_0 \rightarrow {}^7F_1$ (585–600 nm) and the ${}^5D_0 \rightarrow {}^7F_2$ (610–625 nm) observed in **2** can be taken as evidence that the metal ion is not on an inversion center in this complex. The origin of these bands has been already discussed.^{1,14}

The transition ${}^5D_0 \rightarrow {}^7F_4$ (680–710 nm) is sensitive to the environment of the europium(III) ion. Compound **2** shows a broad and slight structured band at 300 K and for this reason it was studied at 20 K. It did not change at low temperature, suggesting that the broadness of this signal is due to the polymeric nature of the sample and not to vibronic transitions or impurities.¹

Intrinsic Emission Spectrum

It has been established that intrinsic emission is an important aspect in lanthanide coordination compounds because it reflects the metal–ligand interactions.²⁹ In the europium(III) compound, **2**, discussed in this paper, we observe a significant intrinsic emission. When the Eu(III) compound is excited at 393 nm, a very broad band at 436 nm is observed, which was assigned to an intrinsic emission (Figure 11), since the free macrocyclic ligand exhibits no emission spectrum nor do the other ligands. This emission is a particular feature of compound **2** where, energy transfer between the metal ion and the ligands occurs. The elemental units are joined through the

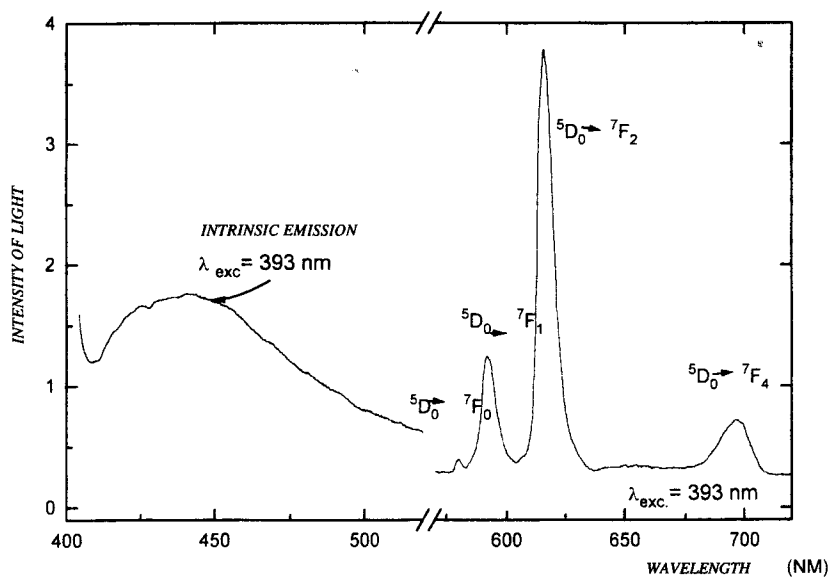


FIGURE 11 Emission spectrum of the mononuclear europium(III) macrocyclic polymer at 300 K.

formates, nitrates and the macrocyclic ligand forming a nonlinear mononuclear polymer, one metal ion per one macrocyclic ligand in each elemental unit (see Figure 4). Intrinsic emission was also observed in the previously studied dinuclear polymeric compounds of Eu(III) and Tb(III),¹⁴ two metal ions per one macrocyclic ligand in each elemental unit, with intramolecular bonds between the metallic centers in the elemental unit and the intermolecular bonds among the metallic centers in the polymer responsible for the observed intrinsic emission.¹⁴ Hence, the intermolecular interactions among the metallic centers of the elemental units in the mononuclear macrocyclic complex give rise to the intrinsic emission, supporting the proposed nature of the polymer. From analysis of the whole emission spectrum, we conclude that the metal centers in our europium(III) polymeric compound are not in equivalent sites.

CONCLUSIONS

The results reported in this paper show the first preparation of mononuclear lanthanide(III) polymeric compounds formed with the [16]-ANE-N₄ macrocyclic ligand. Each lanthanide compound showed specific and unusual

magnetic properties which were assigned to the particular arrangement of the elemental units in each polymer. The magnetic behavior of the obtained complexes and the emission spectra of compound **2**, give evidence of the branched nature of these polymers. Due to the characteristic emission spectrum of **2** we conclude that the europium centers are not in equivalent sites. The EPR spectrum of Nd(III) and NMR spectra of Er(III) compounds are indicative of the covalent character in the chemical bonding.

The results of the calculated molecules for the elemental units and for the polymers, by means of the force-field method support the magnetic and spectroscopic findings of the prepared complexes and our proposals.

From all the previous results, then, we propose that the 4*f*-electrons participate with a substantial covalent character in the chemical bonding of these novel complexes.

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References

- [1] J.-C.G. Bünzli and G.R. Choppin, *Lanthanide Probes in Life, Chemical and Earth Sciences* (Elsevier Science Publishers, B.V. Amsterdam, 1989), p. 127.
- [2] (a) K. Micskei, L. Helm, E. Brücher and A.E. Merbach, *Inorg. Chem.*, **32**, 3844 (1993); (b) J.F. Desreux, *Inorg. Chem.*, **19**, 1319 (1980); (c) K. Kumar and M.F. Tweedle, *Pure and Appl. Chem.*, **65**, 515 (1993); (d) S. Aime, M. Botta, G. Ermondi, E. Terreno, P.L. Anelli, F. Fedeli and F. Uggeri, *Inorg. Chem.*, **35**, 2726 (1996); (e) S. Bénazeth, J. Purans, M.-C. Chalbot, M.K. Nguyen-van-Duong, L. Nicolas, F. Keller and A. Gaudemer, *Inorg. Chem.*, **37**, 3667 (1998).
- [3] (a) P.-A. Pittet, D. Früh, V. Tissières and J.-C.G. Bünzli, *J. Chem. Soc. Dalton Trans.*, 895 (1997); (b) V. Martínez, F. de M. Ramírez and J. Padilla, *Polyhedron*, **13**, 965 (1994); (c) W. De W. Horrocks Jr. and C.-P. Wong, *J. Am. Chem. Soc.*, **98**, 7157 (1976).
- [4] P. Guerreiro, P.A. Vigato, J.-C.G. Bünzli and E. Moret, *J. Chem. Soc. Dalton Trans.*, 647 (1990).
- [5] V. Alexander, *Chem. Rev.*, **95**, 273 (1995).
- [6] (a) S. Aime, L. Barbero, M. Botta and G. Ermondi, *J. Chem. Soc. Dalton Trans.*, 225 (1992); (b) S. Aime, A.S. Batsanov, M. Botta, J.A.K. Howard, D. Parker, K. Senanayake and G. Williams, *Inorg. Chem.*, **33**, 4696 (1994).

- [7] C. Benelli, P. Guerriero, S. Tamburini and P.A. Vigato, *Mat. Chem. and Phys.*, **31**, 137 (1992).
- [8] (a) J.-C.G. Bünzli, E. Moret, V. Casellato, P. Guerriero and P.A. Vigato, *Inorg. Chim. Acta*, **150**, 133 (1988); (b) I.A. Kahwa, S. Folkes, D.J. Williams, S.V. Ley, C.A. O'Mahoney and G.L. McPherson, *J. Chem. Soc., Chem. Commun.*, 1531 (1989).
- [9] (a) A. Panagiotopoulos, T.F. Zafirooulos, S.P. Perlepes, E. Bakalbassis, I. Masson-Ramade, O. Kahn, A. Terzis and C.P. Raptopoulou, *Inorg. Chem.*, **34**, 4918 (1995); (b) M. Andruh, E. Bakalbassis, O. Kahn, J.C. Trombe and P. Porcher, *Inorg. Chem.*, **32**, 1616 (1993).
- [10] C.-I. Deng, Z.-H. Jiang, D.-Z. Liao, S.-P. Yan and G.-L. Wang, *Synth. React. Inorg. Met.-Org. Chem.*, **23**, 247 (1993).
- [11] W.L. Smith, J.D. Ekstrand and K.N. Raymond, *J. Am. Chem. Soc.*, **100**, 3539 (1978).
- [12] (a) F. de M. Ramirez, M.E. Sosa-Torres, M. Castro, E. Basurto-Urbe, R. Zamorano-Ulloa and F. Del Río-Portilla, *J. Coord. Chem.*, **41**, 303 (1997); (b) F. de M. Ramirez, Ph.D. Thesis Novel Lanthanide Complexes Formed with Tetraazamacrocyclic Ligands, F.Q. UNAM, Mexico, 1996.
- [13] (a) U. Dinur and A.T. Hagler, "Approaches to Empirical Force Fields" in Reviews of Comp. Chemistry, Vol. 2 (Lipkowitz, K.B. and Boyd, D.B. Eds.; VCH, New York Chapter 4, 1991); (b) Cerius² Force Field Based Simulations April 1997 (San Diego; Molecular Simulation Inc. 1997).
- [14] F. de M. Ramirez, M.E. Sosa-Torres, E. Camarillo, H. Murrieta and J.M. Hernández, *J. Coord. Chem.*, **46**, 335 (1999).
- [15] (a) G.D. Deacon and R.J. Phillips, *Coord. Chem. Rev.*, **33**, 227 (1980); (b) N.W. Alcock, E.H. Curzon and P. Moore, *J. Chem. Soc. Dalton Trans.*, 2813 (1944).
- [16] J.-C.G. Bünzli and D. Wessner, *Coord. Chem. Rev.*, **60**, 191 (1984).
- [17] F. de M. Ramirez, M. Solache-Rios and A. Campero, *Inorg. Chem.*, **30**, 321 (1991).
- [18] (a) I.A. Kahwa, S. Folkes, D.J. Williams, S.V. Leigh, C.A. O'Mahoney and G.L. McPherson, *J. Chem. Soc. Chem. Commun.*, 1531 (1989); (b) S. Liu, L. Gelminy, S.J. Rettig, R.C. Thompson and C. Orvig, *J. Am. Chem. Soc.*, **114**, 6081 (1992); (c) S. Wang, Y. Zhu, Y. Cui, L. Wang and Q. Luo, *J. Chem. Soc. Dalton Trans.*, 2523 (1994); (d) L.-W. Yang, S. Liu, S.J. Rettig and C. Orvig, *Inorg. Chem.*, **34**, 4921 (1995); (e) X.-H. Bu, S.-L. Lu, R.-H. Zhang, H.-G. Wang and X.-K. Yao, *Polyhedron*, **16**, 3247 (1997); (f) D. Li, X. Gan, M. Tan and X. Wang, *Polyhedron*, **16**, 3991 (1997); (g) R.-Y. Wang, J.-J. Zhao, T.-Z. Jin, G.-X. Xu, Z.-Y. Zhou and X.-Ge. Zhou, *Polyhedron*, **17**, 43 (1998); (h) S. Aime, A. Barge, M. Botta, M. Fasano, J.D. Ayala and G. Bombieri, *Inorg. Chim. Acta*, **246**, 423 (1996); (i) S. Aime, A. Barge, F. Benetollo, G. Bombieri, M. Botta and F. Uggeri, *Inorg. Chem.*, **36**, 4287 (1997); (j) U. Cosentino, G. Moro, D. Pitea, A. Villa, P.C. Fantucci, A. Maiocchi and F. Uggeri, *J. Phys. Chem. A*, **102**, 4606 (1998); (k) M.R. Spirllet, J. Rebizant, X. Wang, T. Jin, D. Gilsoul, V. Comblin, F. Maton, R.N. Muller and J.F. Desreux, *J. Chem. Soc. Dalton Trans.*, 497 (1997); (l) F. Benetollo, G. Bombieri, G. Depaoli and M.R. Truter, *Inorg. Chim. Acta*, **245**, 223 (1996).
- [19] John A. Weil, James R. Bolton and John E. Wertz, *Electron Paramagnetic Resonance* (Wiley-Interscience, New York, 1994), p. 535].
- [20] F.E. Mabbs and D. Collison, *Electron Paramagnetic Resonance of d Transition Metal Compounds* (Elsevier: Amsterdam, 1992), p. 274.
- [21] J.W. Orton, *Electron Paramagnetic Resonance* (Gordon and Breach Science Publishers: New York, 1968), p. 213.
- [22] E.A. Boudreaux and L.N. Mulay, *Theory and Applications of Molecular Paramagnetism* (Wiley-Interscience: New York, 1976).
- [23] E. Basurto-Urbe, M.Sc. Thesis "Simulation of EPR Spectra for Lanthanide Compounds" ESFN, IPN, Mexico. 1996.
- [24] S. Cotton, *Lanthanides and Actinides* (MacMillan Education LTD England, first edition, 1991), p. 27.
- [25] J.E. Huheey, E.A. Keiter and R.L. Keiter, *Inorganic Chemistry "Principles, Structure and the Reactivity"* (Harper Collins College Publishers, fourth edition, 1993) p. 464.
- [26] O. Kahn, *Molecular Magnetism*, (VCH Publishers, Inc. 1993), p. 47.

- [27] (a) J.H. Van Vleck, *J. Appl. Physics*, **39**, 365 (1968); (b) J.H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London, fourth edition, 1952), p. 245.
- [28] J.H. Forsberg, *Coord. Chem. Rev.*, **10**, 195 (1973).
- [29] F.S. Richardson, *Chem. Rev.*, **82**, 541 (1982).