SYNTHESIS, 1H, 13C NMR AND MAGNETIC STUDIES OF THE HOMODINUCLEAR LANTHANIDE(III) POLYMERIC COMPOUNDS FORMED WITH THE 1,5,9,13-TETRAAZACYCLOHEXADECANE LIGAND FLOR DE MARIA RAMIREZ[b]

Flor De Maria Ramirez[a]; Martha Elena Sosa-torres[b]; Miguel Castro[b]; Edlardo Baslurto-uribe[c]; Rafael Zamorano-ulloa[c]; Federioo Del Ríao-porttlla[d]

[a] Departamento de Quimica, Instituto National de Investigaciones Nucleares, Colonia, Escandón, México. D. F. [b] División de Estudios de Posgrado, Facultad de Quimica, UNAM, México, D. F. Mexico [c] Depto. de Fisica, Escuela Superior de Fisica v Matemáticas. IPS. Edif. 9 U. P. Zacatenco, Col. San Pedro Zacatenco, D. F México [d] Institute de Quimica, UNAM, México, Mexico, D.F.

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FLOR DE MARIA RAMIREZ[b], MARTHA ELENA SOSA-TORRES[a,*],
MIGUEL CASTRO[a], EDUARDO BASURTO-URIBE[c],
RAFAEL ZAMORANO-ULLOA[c] and FEDERICO DEL RÍO-PORTILLA[d]

[a] *División de Estudios de Posgrado, Facultad de Química, UNAM, 04510 México
D.F. México;* [b] *Instituto Nacional de Investigaciones Nucleares, Departamento de
Química, A.P. 18-1027, Colonia Escandón, México, D.F. 11801;* [c] *Depto. de Física,
Escuela Superior de Física y Matemáticas, IPN, Edif. 9 U.P. Zacatenco, Col.
San Pedro Zacatenco, CP 07738, D.F. México;* [d] *Instituto de Química, UNAM,
04510 México, D.F. México*

The synthesis of novel dinuclear lanthanide polymeric complexes from Nd(III), Eu(III), Gd(III), Tb(III), Er(III) and Lu(III) nitrates and the 1,5,9,13-tetraazacyclohexadecane macrocyclic ligand ([16]-ANE-N$_4$) is reported. These complexes were characterized by elemental and thermal analysis, IR, Raman, EPR, ^{1}H and ^{13}C NMR spectroscopies, and magnetic susceptibility. The polymeric weight of the compounds were determined by GPC, and these results are 6048, 5580 and 6175 g/mol, for the neodymium, europium and terbium compounds. An approximate structure is proposed for the gadolinium compound.

Keywords: tetraazacyclohexadecane; homodinuclear polymeric compound; lanthanides; synthesis; polymeric solution behaviour; ^{1}H and ^{13}C NMR

INTRODUCTION

Interest has been shown in dinuclear lanthanide(III) complexes because they are important as tunable photonic devices[1] with potential applications in biomedical

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* Author for correspondence.

diagnostics,[2] fluorescence imaging,[3] and paramagnetic contrast enhancing agents in magnetic resonance imaging.[4] The establishment of structural-magnetic correlations could be helpful not only for designing novel molecular magnetic materials but also for understanding the coordination chemistry of lanthanide complexes. The studies on magnetism of these types of complexes of the lanthanides will provide information on the involvement of the *f*-orbitals in magnetic interactions.

Homonuclear and heteropolynuclear complexes containing rare earth metals are of great interest because of their unique physicochemical properties.[5] In addition, homodinuclear or heterodinuclear complexes should be able to provide valuable information regarding Ln^{3+}-Ln^{3+} electronic and magnetic interactions, depending on the bridging ligands.[6] Some papers on dinuclear lanthanide(III) complexes with macrocyclic ligands have been reported recently.[7–11a,b] There are also several examples about polymeric lanthanide compounds.[12–15] Very interesting papers on metallic polymeric macrocyclic chains have also been reported.[16–18] However, to our knowledge, no reports have appeared on dinuclear lanthanide complexes with neutral saturated tetraaza-macrocyclic ligands.

In an attempt to better understand coordination chemistry of lanthanide(III) complexes, we now describe the synthesis and characterization of the new dinuclear polymeric compounds containing Nd(III), Eu(III), Gd(III), Tb(III), Er(III) and Lu(III) and the 1,5,9,13-tetraazacyclohexadecane macrocyclic ligand:
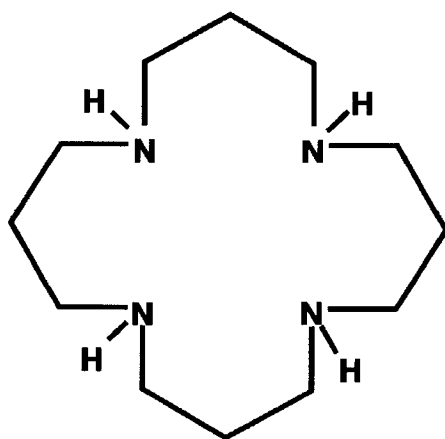
(16)-ANE-N$_4$ = L

FIGURE 1   [16]-ANE-N$_4$ = L

EXPERIMENTAL

Reagents

The hydrated lanthanide nitrates, $Nd(NO_3)_3 \cdot 5H_2O$, $Gd(NO_3)_3 \cdot 6H_2O$, $Tb(NO_3)_3 \cdot 5H_2O$, $Er(NO_3)_3 \cdot 5H_2O$ and $Lu(NO_3)_3 \cdot 5H_2O$, were purchased from Alfa Products (99.9%); the europium salt $Eu(NO_3)_3 \cdot 6H_2O$, was purchased from Johnson Mathey (99.9%) and from Aldrich (99.99%). These salts 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.

Preparations of Dinuclear Polymeric Complexes

The 1,5,9,13-tetraazacyclohexadecane macrocyclic ligand, ([16]-ANE-N_4), was synthesized according to the literature[19] and its full characterization was carried out.

The 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. 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-N$_4$ (1.235 mmol), was dissolved in 30 mL of hot anhydrous acetonitrile and added to the original reaction mixture. During the reaction time (5 h, for neodymium, europium and gadolinium and 10, 15 and 15 h for Tb, Er and Lu respectively) a solid formed. This solid was recovered by filtration under nitrogen and washed with anhydrous acetonitrile, to eliminate any unreacted $Ln(NO_3)_3$; then, it was washed with anhydrous ethyl ether, anhydrous n-hexane, and dried under vacuum; the compounds were further dried under P_2O_5 in a vacuum oven at 70° C and 21 mm Hg for several hours. The yields were about 60% for Nd(III), Eu(III), Gd(III), Tb(III), Er(III), and Lu(III). The reactions were carried out inside a glove box and kept under a 99.995% nitrogen atmosphere. These polymeric lanthanide compounds were also obtained by the same procedure by using the stoichiometric ratio 2:1 (ligand:metal).

Spectroscopic and Analytical Studies

IR spectra of nujol mulls and KBr pellets in the range 4000-450 cm^{-1} were recorded on a Perkin Elmer /1600 FT IR spectrometer.

Raman spectra were recorded on a SPEX 1403 spectrometer with an A Laser at 5145 Å and P = 200 mW.

^{1}H and ^{13}C NMR spectra were obtained in d^{6}-DMSO solutions by using a Bruker AM-360 MHz NMR spectrometer with TMS diluted in CDCl$_3$ as an internal standard. The complexes are very soluble in d^{6}-DMSO while the [16]-ANE-N$_4$ is not; for this reason, it was necessary to dissolve the macrocycle in CDCl$_3$ first and then mix the resulting solution with d^{6}-DMSO. The measurements were carried out at different temperatures, ranging from 294 to 343 K. A Varian NMR Unity Plus 500 spectrometer for Nd, Eu, Lu complexes was also used.

The magnetic susceptibility measurements were carried out on a Faraday balance (calibrated with Hg[Co(SCN)$_4$] as standard) and a Johnson Matthey balance (calibrated with a standard sealed solution of MnCl$_2$) at room temperature. Electron paramagnetic resonance spectra were recorded at X-band and at Q-band in a JEOL -RES3X spectrometer operating at 100 KHz modulation of the magnetic field and equipped with a liquid nitrogen temperature unit for low temperature measurements.

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

Elemental analyses (C, H, N) were performed at Christopher Ingold Laboratories at University College, London. Metal contents were determined by nuclear activation, and irradiations were carried out in the SIFCA facility of the Nuclear TRIGA Mark III Reactor of ININ Mexico.

Molecular weights were determined at 308.7 K by gel permeation chromatography (GPC) using a Millipore Waters Associates Apparatus with columns of Ultrastyragel 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 Differencial Refractometer and a Waters Data Module Recorder. The calibration curve was obtained with seven standards: 456, 500, 940, 1800, 2630, 4000, and 9000 D.

Molecular Calculations

Calculations for the gadolinium molecule were performed by use of the UNICHEM software, *via* the access of the CRAY YMP4/464 supercomputer facilities at the supercomputer center, UNAM.

RESULTS AND DISCUSSION

In our first attempts to investigate coordination of the tetraazamacrocyclic ligand with various metal ions, we discovered that the dryness of the solvent, the ligand, and in general of the reaction media are crucial to the preparation of these compounds. We also realized that the nitrate salts are very important to stabilize these compounds, since no stable compounds are formed when chloride salts are used. Synthesis of these complexes was finally achieved with great difficulty. From the elemental analyses (Table I), a minimum formula for these new compounds of the following type was worked out : $Ln_2(16\text{-}ANE\text{-}N_4)$ $(NO_3)_x(CHO_2)_y nCH_2O_2$. These compounds have been obtained at least four times, in each case, indicating reproducibility.

TABLE I   Elemental analyses of the dinuclear lanthanide polymeric compounds formed with the [16]-ANE-N$_4$ ligand and their minimum formula proposed

MINIMUM FORMULA	Calculated (%)				Found (%)			
	C	H	N	Ln	C	H	N	Ln
[16]-ANE-N$_4$	63.16	12.28	24.56		63.24	12.13	24.76	
			Nd				Nd	
1: $Nd_2(16\text{-}ANE\text{-}N_4)(NO_3)_3(CHO_2)_3CH_3CN$	23.23	3.90	12.75	32.82	23.12	4.00	11.67	32.16
				Eu				Eu
2: $Eu_2(16\text{-}ANE\text{-}N_4)(NO_3)_3(CHO_3)_3$	21.11	3.66	11.49	35.61	22.07	3.76	11.85	35.25
				Gd				Gd
3: $Gd_2(16\text{-}ANE\text{-}N_4)(NO_3)_4(CHO_2)_2CH_2O_2$	19.44	3.48	12.09	33.93	19.54	3.93	11.54	34.41
				Tb				Tb
4: $Tb_2(16\text{-}ANE\text{-}N_4)(NO_3)_4(CHO_2)_2CH_2O_2CH_3CN$	21.02	3.63	12.98	32.72	21.36	3.56	12.65	33.40
				Er				Er
5: $Er_2(16\text{-}ANE\text{-}N_4)(NO_3)_4(CHO_2)_2CH_2O_2$	19.06	3.41	11.83	35.32	19.26	3.11	10.26	36.35
				Lu				Lu
6: $Lu_2(16\text{-}ANE\text{-}N_4)(NO_3)_3(CHO_2)_3$	20.03	3.47	10.90	38.91	20.80	3.74	10.94	39.82

It was found that these species were formed independent of the stoichiometry (1.2:1 or 2:1) used. During the dehydration process formates and formic acids are formed due to reaction between the water of the lanthanide salts and the trimethylorthoformate.

The neodymium complex is light blue, the europium, gadolinium, terbium and lutetium complexes are light yellow, and that of erbium is light pink. They begin to decompose above 453 K. The six compounds were homogeneous powders in color and texture in each case. Powder X-ray diffraction of some of the complexes showed that they are amorphous; nevertheless, many attempts to get single crystals were done, unsuccessfully. Therefore, molecular weight determinations on the neodymium, europium, and terbium compounds were carried out, and these were found to be: 6048, 5580 and 6175 g/mol, respectively. From these results we can conclude that the new species are polymers and they are composed of seven elemental (minimum formula) units in each case.

When these polymeric compounds were dried at 343 K and 21 mm Hg for at least nine hours, no ligand was lost. This experiment was performed to confirm the absence of free ligand in our compounds, since the free ligand sublimes at 313 K under the same conditions. This also allowed us to confirm the thermal stability of the compounds.

The compounds were soluble in water, DMSO, DMF and N-methyl-pyrrolidone. The fact that all the compounds dissolved instantaneously in water, shows the absence of any lanthanide hydroxide or any hydroxo-lanthanide species.

These complexes do not demetallate in DMSO or DMF after months at 300 K, and under heating and vacuum (320 mm of Hg) at 313 K in DMSO. This indicates the stability of these complexes.

IR and Raman Spectroscopies

Table II shows the main IR bands of the lanthanide polymeric compounds and from this it can be observed that for all complexes the N—H stretching frequencies are broad and appear between 3448-3396 cm^{-1}. Their broadness is probably due to hydrogen bonding between NH— and the oxygens of the carboxylic or nitrate groups. Around 2954 and 2938 cm^{-1} are bands which are assigned to the methylenes of the macrocyclic ring shifted to higher energies compared with those of the free ligand. Around 1234, 1150 and 1090 cm^{-1} there are bands which correspond to C—N—C stretching vibrations,[20] the first of which appears about 30 cm^{-1} to lower frequency compared with that of the free ligand; the two latter appear about 20 cm^{-1} to higher frequencies, also compared with those of the free ligand. From the above evidence we propose that the macrocycle is coordinated to the lanthanide ions. There are also strong bands in the carbonyl region (1700-1580 cm^{-1}) characteristic of the v_{asym} (COO) and the v_{sym} (COO) (1420-1300cm^{-1}) stretching vibrations.[21] The separation (Δ) of the v_{asym} (COO) and the v_{sym}(COO) commonly used in diagnosing the nature of the bonded carboxylate group cannot be established unambigously, since in the same region other bands associated with coordinated nitrates appear. In the case of the neodymium compound a band at 1644 cm^{-1} is observed and for the europium compound a band is also present at 1644 cm^{-1}; such bands are assigned to the formate groups. In the case of the heavier lanthanide compounds two bands are observed between 1650–1580 cm^{-1}, which are assigned to COO^{-1} and COOH.[22] Two different bands in this region have appeared in lanthanide complexes, where the coordinated carboxylate and carboxylic acids are present in the molecule.[23] The bending vibration frequencies around 654–684 cm^{-1} correspond to the C-H of the formic and/or formate groups.

TABLE II Main IR bands in the normal region of the dinuclear lanthanide polymeric compounds (cm⁻¹)

	ν–NH-	ν–CH$_2$-	ν_s–C–N–C	ν_s–CN	$\nu(\nu_2+\nu_3)$ –NO$_3$	$\nu(\nu_2+\nu_5)$ –NO$_3$	ν_{as}COO	ν_{as}COOH	$\nu_1(A_1)$ NO$_3$
[16]-ANE-N$_4$	ν_s3490$_w$ 3280$_s$ ν_b1545$_w$ ν_r914$_m$ 854$_s$	ν_s2920$_s$ 2866$_s$ 2800$_s$ 2736$_s$ ν_b1478$_s$ 1464$_s$ 1426$_m$ 1336$_m$ ν_r779$_s$	ν_s1294$_s$ 1254$_m$ 1136$_s$ 1070$_s$ 1024$_m$						
1	3432$_{vs}$	2944$_m$		2396$_{vw,apr.}$	1634$_s$			1644$_{vs}$	1462$_s$
2	3396$_s$	2954$_{mw}$			1766$_w$ 1634$_s$	1698$_w$		1644$_s$	1434$_m$
3 1462$_s$	3448$_m$	2938$_m$			1770$_{vw}$	1700$_{vw}$		1650$_{vs}$	1586$_m$
4 1462$_m$	3402$_s$	2946$_m$		2362$_{vw,apr.}$	1644$_s$ 1750$_w$	1690$_m$		1644$_s$	1586$_{mw}$
5 1450$_m$	3412$_s$	2948$_m$			1766$_{mw}$	1705$_m$		1648$_s$	1586$_m$
6	3422$_s$	2950$_m$			1766$_{mw}$	1698$_m$ 1634$_s$		1644$_s$	1464$_{ms}$

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TABLE II *(Continued)*

	$\nu_4 (B_2)$ NO$_3$	ν_s—C—N—C	ν_s-C-N-C-	ν_s—C—N—C	$\nu_2 (A_1)$ NO$_3$	$\nu_3 (A_1)$ NO$_3$	$\nu_6 (B_1)$ NO$_3$	ν_b—C—H
1	1306ms	1234doublett	1150vw 1190w	1082mw	1034m	818w	738mw 722vs	668w 654
2	1304s	1238w	1150w 1190w	1112mw 1064mw 1090mw	1032ms	818w	742mw 722s	668mw 654w
3	1308vs	1238w	1150w 1190vvw	1113w 1088w	1036ms	815w	738m 722w	656w
4	1316m	1234m	1140w	1110mw	1036m	818w	744mw	656w 668w
5	1310m	1234mw	1140w 1150vw 1190(indef.)	1088mw	1040mw		744mw	660mw
6	1306s	1234w		1088mw	1034mw	816w	742m	668mw 684w

Our compounds present five different zones associated with coordinated nitrates,[24-25] with bands in the region of 1464-1434 cm^{-1}, 1304-1316 cm^{-1} and finally those that appear about 1034–1040 cm^{-1}, 815-818 cm^{-1} and 722–744 cm^{-1}. In the cases of the four heavier lanthanide ions, Gd, Tb, Er and Lu, a set of bands, at 1700$_{vw}$ and 1770$_{vw}$ for gadolinium appear; at 1690$_m$ and at 1750$_w$ for the terbium complex; at 1705$_s$ and at 1766$_w$ for the erbium complex; and at 1698$_m$ cm^{-1} and at 1766$_{mw}$ cm^{-1}, for the lutetium complex. The differences between these two frequencies are between 60–80 cm^{-1}; we can tentatively assign this value to coordinated nitrate groups, forming bridges between the two metal ions.[24] This does not exclude the possibility of forming bridges through formate groups.

The Raman spectrum of the neodymium complex shows a band at 1037 cm^{-1}, which is characteristic of coordinated nitrate.[25]

Finally, the neodymium and terbium complexes show very weak bands at 2396 and 2362 cm^{-1}, respectively, which are assigned to coordinated acetonitrile.

It must be mentioned that when the compound is mulled in KBr, a NO$_3$- band appears around 1384 cm^{-1}, which is absent in nujol mulls. This is indicative of an anionic exchange.[26]

Thermal Analysis

The polymeric compounds showed similar thermal (TGA/DTA) behavior, Figure 2. The TGA/DTA of the dinuclear terbium complex, used as an example, shows a loss of weight that corresponds to an acetonitrile just before 458 K; then, between 458 and 558 K, there is loss of the macrocyclic ligand and two formates. The loss between 558 and 873 K corresponds to two nitrates and one formic acid. The weight of the residue corresponds to Tb$_2$(NO$_3$)$_2$.
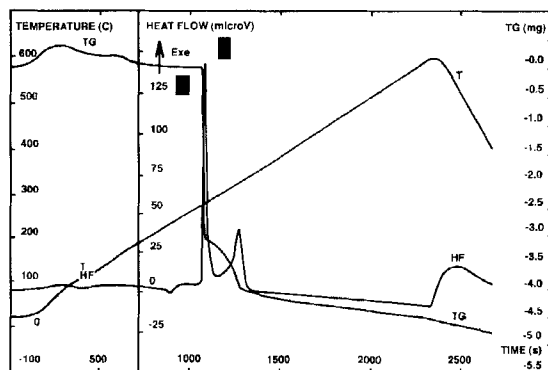

FIGURE 2 TGA/DTA of the Tb$_2$(16-ANE-N$_4$)(NO$_1$)$_4$(CHO$_2$)$_2$CH$_2$O$_2$CH$_3$CN under argon atmosphere.

An independent experiment was recorded to examine the thermal behavior of the free ligand, which decomposed between 423 and 593 K.

In general all our dinuclear polymeric compounds lose the macrocyclic ligand around 523 and 623 K. However, the formates and nitrates are not lost with a pattern. This is shown in Table III.

The simple and similar pattern of the thermal diagrams (as an example, see Figure 2) of our six complexes is consistent with pure compounds, since mixtures would show a more complex pattern.

It can be observed from Table III, that the formed residues depend on the original composition of the compounds. For instance, in the case of the analogous gadolinium and erbium complexes, which contain formic acids, the residues only contain carbonates. On the other hand, the recorded infrared spectrum of the formed residue of the europium compound shows five bands: at 1650, 1615, 1502, 1400 and at 588 cm^{-1}. The band at 1650 cm^{-1} can be assigned to a C-O stretching vibration of the carbonate, the band at 1615 cm^{-1} and at 1502 cm^{-1} could be due to coordinated nitrate. The band at 1400 cm^{-1} could be assigned to nitro groups, and finally the very intense and sharp band at 588 cm^{-1} corresponds to europium-oxygen vibrations. The residues were not soluble in any organic solvents, water nor in diluted or concentrated nitric acid.

Conductivity Measurements

Conductivity measurements were carried out for the Nd, Eu and Tb complexes at different concentrations. Molar conductances of the terbium complex were plotted *vs.* the concentrations of the polymer (Figure 3). From this graph, it can
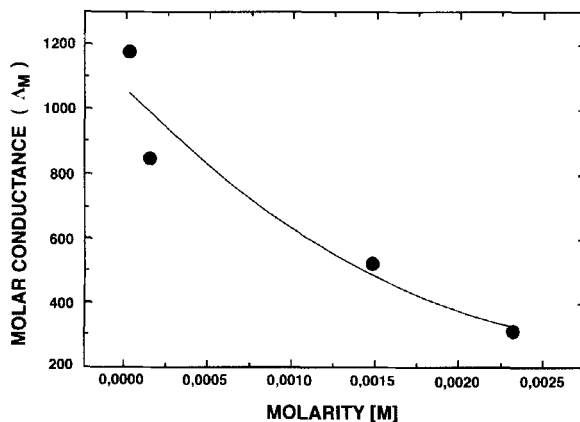

FIGURE 3   Conductivity behaviour of the Tb$_2$(16-ANE-N$_4$) (NO$_3$)$_4$(CHO$_2$)$_2$CH$_2$O$_2$CH$_3$CN polymer in DMSO at different molarities, at 297 K.

TABLE III Thermal decomposition of the dinuclear lanthanide polymeric complexes

$Nd_2(16\text{-}ANE\text{-}N_4)(NO_3)_3(CHO_2)_3CH_3CN$	$Eu_4(16\text{-}ANE\text{-}N_4)(NO_3)_3(CHO_2)_3$	$Gd_2(16\text{-}ANE\text{-}N_4(NO_3)_4(CHO_2)_2CH_2O_2$	$Tb_2(16\text{-}ANE\text{-}N_4)(NO_3)_4(CHO_2)_2CH_2O_2CH_3CN$	$Er_2(16\text{-}ANE\text{-}N_4)(NO_3)_4(CHO_2)_2CH_2O_2$	$Lu_2(16\text{-}ANE\text{-}N_4)(NO_3)_3(CHO_2)_3$	$[16]\text{-}ANE\text{-}N_4$
Lost components:	Lost components:	Lost components:	Lost components:	Lost components:	Lost components:	Lost components:
427–578 K (16-ANE-N₄)+ CH₃CN+ 2[CHO₂]	525–678 K (16-ANE-N₄) +CHO₂	353–520 K CH₂O₂	353–546 K CH₃CN	423–629 K (16-ANE-N₄) +2[NO₃]	430–565 K (16-ANE-N₄) [CHO₂]	423–593 K (16)-ANE-N₄
578–899 K NO₃+CHO₂	678–870 K 1CHO₂+1NO₃	520–673 K (16-ANE-N₄) +4[NO₃]	546–558 K (16-ANE-N₄) +2[NO₂]	629–961 K 2[NO₃]	565–1093 K 2[NO₃]	
899–1273 K Changes without appreciable loss	870–1273 K Changes without appreciable loss	673–1273 K It was not studied	546–869 K 1[NO₃]+ CH₂O₂			
Found residue: 45.83%	56.00	49.07	48.15	50.28	55.04	1.88
Calculated Residue: 46.66%	55.43	48.51	45.52	49.68	55.84	
Residue: Nd₂(NO₃)₂	Eu₂(NO₃)(NO₂)(CO₃)	Gd₂(CO₃)₂	Tb₂(NO₃)₂	Er₂(CO₃)₂	Lu₂(CO₃)₂NO₂	

be observed that the behavior in solution of this compound does not follow a simple linear dependence; instead it is quite clear that, as the concentration of the polymer decreases, the molar conductance increases markedly.

Therefore, in order to interpret our molar conductance results, we divided the conductance values by 7 (in order to have the conductance contribution per elemental unit); these are listed in Table IV. The plot of the new molar conductance values follow the same pattern found for the conductances of the polymers.

TABLE IV   Molar conductances of the dinuclear lanthanide polymeric compounds in DMSO at different concentrations*

COMPOUNDS	MOLARITY (M)	Λ_M, ohm $^{-1}cm^2mol^{-1}$
$Nd_2(16\text{-}ANE\text{-}N_4)(NO_3)_3(CHO_2)_3CH_3CN$	1.49×10^{-5}	190
	1.61×10^{-4}	121
	1.46×10^{-3}	78
$Eu_2(16\text{-}ANE\text{-}N_4)(NO_3)_3(CHO_2)_3$	1.83×10^{-5}	119
	1.64×10^{-4}	97
	1.70×10^{-3}	62
	1.91×10^{-5}	168
	1.48×10^{-4}	121
$Tb_2(16\text{-}ANE\text{-}N_4)$	1.48×10^{-3}	75
$(NO_3)_2(CHO_2)_2CH_2O_2CH_3CN$		
	2.32×10^{-3}	45

It has been fully documented by Bünzli *et al.*[28] that the number and type of species in solution, *i.e.*, $[Ln\text{-}(NO_3)(DMSO)]_y^{2+}$, $[Ln(NO_3)_2(DMSO)_x]^+$, and $[Ln(NO_3)_3(DMSO)_3]$, depend on the ratio, R = DMSO/$[Ln^{3+}]$. This ratio reflects the replacement of inner-sphere coordinated nitrates by DMSO molecules. In general, for the different compounds, when R is small the compounds tend to be neutral species, while when R is large they tend to be more ionized. This was confirmed by conductivity and spectroscopic measurements. When the concentration of the anhydrous lanthanide nitrate salt is 0.0001 M, the solution shows a higher conductivity value as compared to the 0.05 M solution, which exhibits the smallest value. Additionally, Bünzli and Vuckovic[28d] found for a 0.01 M solution of neodymium nitrate in DMSO molar conductances of 208 and 242 ohm^{-1}cm^{2}mol^{-1} for R = 0 and R = 4.5, respectively, and they assigned these values to a 2:1 electrolyte.

Molar conductance values for our complexes in DMSO at different concentrations show the same behavior as Bünzli previously found.[28] For example, in the case of the terbium complex at 0.0000191 M concentration, the solution presents the highest conductivity value, in contrast, the most concentrated solution studied, 0.00232 M shows the lowest conductivity value. This indicates that the more diluted species are more ionized, while at 0.00148 M the species are

partially solvolyzed, and for this reason, the solutions behave as 1:1 – 2:1 electrolytes.[27] From these results, an equilibrium between the $\{[Tb_2(16\text{-}ANE\text{-}N_4)(NO_3)_2(CHO_2)_3]^+\}$ and $\{[Tb_2(16\text{-}ANE\text{-}N_4)(NO_3)(CHO_2)_3]^{2+}\}$ species is indicated. Since ionization of formic acid in DMSO showed a very low molar electrical conductance (0.96 ohm^{-1}cm^{2}mol^{-1}), there was no need to correct these results in the cases where formic acid is present in the compounds.

The terbium solution at 0.00232 M behaves as a 1:1 electrolyte. Thus, at higher concentration, *i.e.*, that used for the ^1H and ^{13}C NMR (about 0.01 M), the species in DMSO solution must be neutral. This type of behavior is consistent with the molar conductance results of the other compounds. Therefore, we can conclude from the previous results that the species in very concentrated solutions as well as in solid state is neutral.

NMR Spectroscopy

A) ^1H NMR

Since the [16]-ANE-N_4 ligand is not soluble in d^6-DMSO, it was necessary to dissolve it in $CDCl_3$, and this solution was then mixed with d^6-DMSO to record its spectrum; The complexes are very soluble in d^6-DMSO.

Figures 4a and 4b show the ^1H NMR spectra at 297 and 353 K of a concentrated solution of the terbium compound. The spectrum at 297 K shows a peak at 1.04 ppm, which is assigned to the CH_3 of the acetonitrile. In the region of 1.20 ppm to 2.35 ppm, a multiplet is observed; the integration corresponds to 8H assigned to beta-CH and 2 NH. At 2.49 ppm the DMSO signal is observed. A broad signal between 2.85 and 4.00 ppm is found that is consistent with 2H of 2NH and 16H of the alfa-CH-; two signals found from 7.65 to 9 ppm correspond to the CH of O=CHOH and to the two CH of the two O=CHO^{-1}. A variable temperature study was performed from 297 to 353 K. As the temperature increased, slight changes in the spectra can be interpreted as changes in the conformation of the complex.

Similar studies for the other lanthanide complexes, are consistent with the proposed elemental Formula. There are clear differences among them. The gadolinium complex shows very broad signals, and the terbium and neodymium complexes show broad signals; in contrast, the europium complex (Figure 5a) shows narrow signals and the lutetium complex (Figure 5c) shows very sharp peaks. After heating the solution up to 363 K, the samples were left until they reached room temperature and the spectra were recorded again. These spectra were the same as those recorded before heating. This indicates that in very concentrated DMSO solutions, the compounds are kinetically and thermodynamically stable at least up to 363 K.
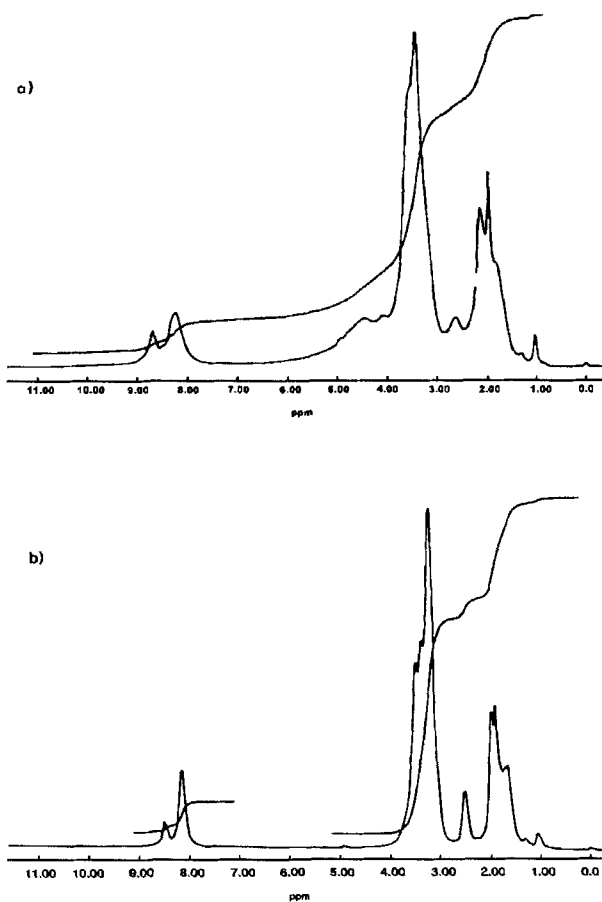
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FIGURE 4 ^{1}H NMR of the Tb$_2$ (16-ANE-N$_4$)(NO$_3$)$_4$(CHO$_2$)$_2$CH$_2$O$_2$CH$_3$CN in d^6-DMSO a) at 297 K and b) at 353 K.

B) ^{13}C NMR

The ^{13}C NMR spectrum of the terbium complex at 300 K shows complex signals between 15 and 30 ppm, which can be assigned to the non-equivalent β-carbons, and between 42 and 55 ppm to non equivalent α-carbons. The carbons of the formic acid (163 ppm)[29] and the formate groups (153 ppm)[29] can be clearly distinguished. The ^{13}C NMR spectra at 300 K of the other complexes are consistent with their ^{1}H NMR spectra.
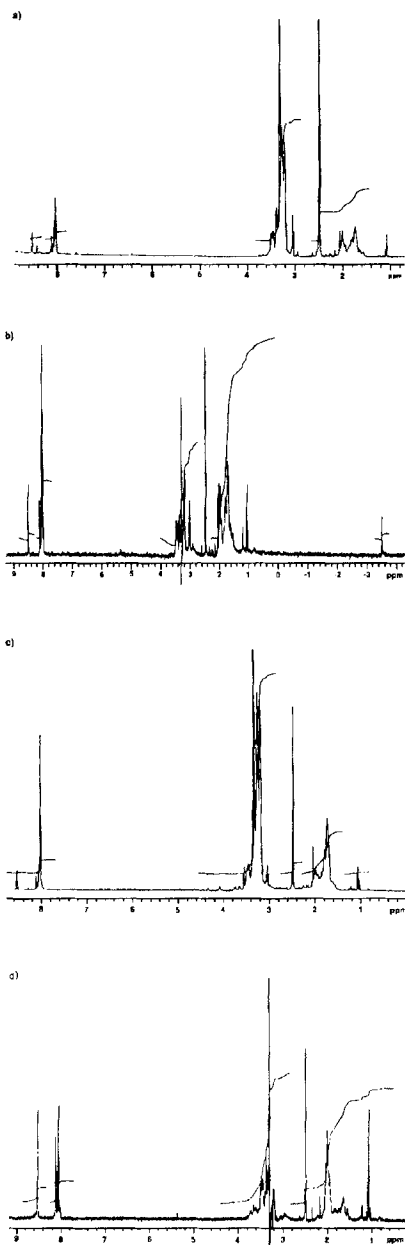
FIGURE 5 ^{1}H NMR in d^6-DMSO of Eu$_2$(16-ANE-N$_4$) (NO$_3$)$_3$ (CHO$_2$)$_3$ a) 0.01 M and b) 0.0002 M; of Lu$_2$(16-ANE-N$_4$) (NO$_3$)$_3$ (CHO$_2$)$_3$, c) 0.01 M, d) 0.0002 M. In the diluted samples the signal around 3.3 ppm (absorbed water in d^6-DMSO) was suppressed.

In order to know if we could establish any difference between the species at 0.01 M and those at 0.0001 M of the neodymium complex by ^{1}H NMR in the d^6-DMSO, we obtained their ^{1}H NMR spectra (Figure 6a and 6b) showing significant differences. First, the spectrum of the more diluted compound (0.0001 M) (Figure 6b) shows defined peaks between 0.80–2.20 ppm, which correspond to the methylene protons. At 2.49 ppm, the signal of DMSO is observed. A multiplet appears from 3 to 3.8 ppm. A singlet that can be assigned to the three protons of the free acetonitrile appears at 6.64 ppm. Another signal is observed at 8.01 ppm, which integrates for 7 protons and can be associated to 3 formates and 4 NH that fortuitously appear at the same chemical shift. Since at this concentration the compound is solvolyzed, consequently leaving ionic nitrates as well as formates in the solution, ion-pairs or ion-triplets can be formed; the N-H shifting in our case is probably due to this effect, since there are several examples in the literature where the protons of the coordinated amines are shifted as a result of this interaction.[30] However, as this neodymium complex is paramagnetic, the possibility of a paramagnetic effect cannot be ruled out; this shall be discussed below.

In contrast, the ^{1}H NMR spectrum of the more concentrated complex (0.01 M) (Figure 6a) shows very broad bands between 1.4 and 4.8 ppm and another between 7.9 and 9 ppm, which can be assigned to the protons of the macrocyclic ligand and the protons of the formates, respectively. The fact that the spectrum is very broad is consistent with an interaction between the paramagnetic metal ions through the bridging ligands, which can be the nitrates, formates and/or the macrocyclic ligand. The previous results give evidence that, at this concentration, the complex in solution is the dinuclear polymeric compound that we proposed in the solid state.

In order to see if the effect observed in the ^{1}H NMR spectrum of diluted solutions of the neodymium complex was unique, we decided to record the ^{1}H NMR spectra of dilute solutions of the paramagnetic europium and the diamagnetic lutetium complexes; these are shown in Figure 5b and 5d. The spectra of the three dilute species show well-defined peaks whose integration is different from that shown in the spectra of their corresponding concentrated samples. The integration in the dilute samples increased markedly in the 1 to 2 ppm region; this can be interpreted as coordination of DMSO molecules, which is consistent with the interpretation of the conductivity results.

The spectrum of the dilute europium complex (Figure 5b) shows a peak shifted upfield (–3.5 ppm), which was observed neither in the concentrated sample nor in the other dilute samples. Therefore, this effect can be assigned to the paramagnetism of the europium species. On the other hand, the spectrum of the dilute lutetium complex (Figure 5d) shows changes that cannot be assigned to any paramagnetic effect; thus, these changes must be due to formation of ion-pairs or ion-triplets mentioned above.[30]
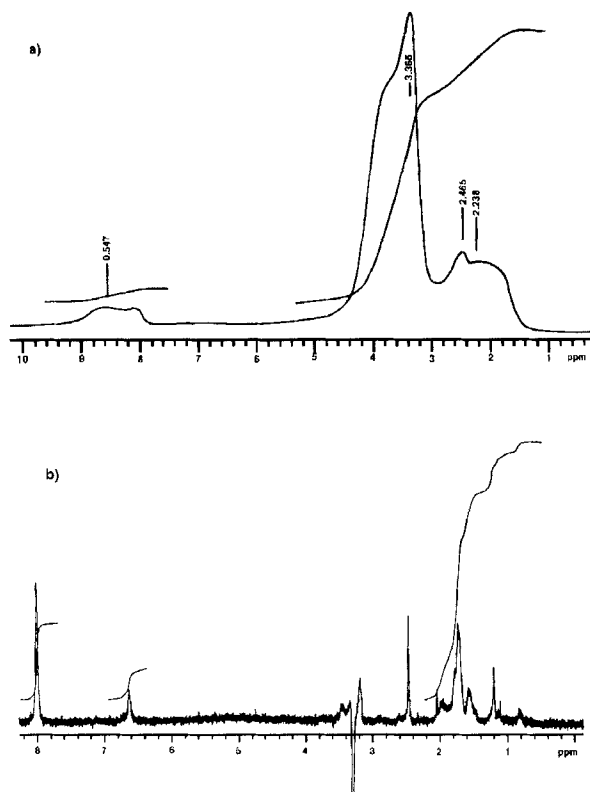
FIGURE 6 ^{1}H NMR of the $Nd_2(16$-ANE-$N_4)(NO_3)_3(CHO_2)_3CH_3CN$ in $^2H_6$-DMSO a) at 0.01 M b) at 0.0001 M (the signal around 3.3 ppm (absorbed water in d^6-DMSO) was suppressed).

The additional downfield proton shifts observed in the neodymium and europium complexes must be due to the paramagnetism of these complexes, consistent with the very well known paramagnetic effect of lanthanide compounds.[31] In order to assign unambiguosly the exact kind of effect, further studies need to be carried out.

Based on all the previous results, we propose that these new dinuclear lanthanide polymeric complexes in the solid state and in concentrated DMSO solution are neutral. We also propose that each metal ion in the elemental unit of these polymers have at least a coordination number of eight; the two lanthanide atoms sharing the macrocyclic ligand and some bridging nitrates. The remaining nitrates are also coordinated. This does not exclude the possibility of also having formates and

formic acid (when present) coordinated as bridges. Acetonitrile (when present) is also coordinated.

Using Stereo Drieding Models we can see that the dinuclear unit of our compound is quite distorted. Because of the lack of X-ray structural information, due to the amorphous nature of these polymers, we used a visualization computational tool, the Unichem, (see below) to construct a reliable structure of the elemental unit of the gadolinium compound. Although this structure is approximate, it is consistent with the experimental findings mentioned above.

A Computational Visualization

With the help of computational tools, as the Unichem software,[32] for visualization of molecular structures, a construction was done for the structure of the basic unit. Unichem takes into account the average bonding capabilities of the chosen atoms. For instance, the atoms present hybridizations according to the number (and kind) of atoms to which they are bonded directly. This simple criteria allowed us to obtain the structure of the elemental unit of the dinuclear gadolinium compound, $Gd_2(16$-ANE-$N_4)$ $(NO_3)_4(CHO_2)_2CH_2O_2$; this geometry is displayed in Figure 7. From this proposed structure, an estimation of bond lenghts (Å) and bond angles (°) of the coordination sphere are obtained, and some selected values are listed in Table V. Despite the approximate nature of the structural parameters, their values are similar to those reported in the literature for structures determined by X-ray diffraction for similar molecules.[13,33–34]

TABLE V   Selected bond distances and bond angles of the elemental unit of the dinuclear gadolinium polymeric compounds obtained by theoretical calculations

BOND DISTANCES (Å)		INTERBOND ANGLES (°)	
Gd1—O2 bridging nitrate	2.248	O2—Gd1—O20	53.17
Gd1—Gd6	3.05	O2—Gd1—O14	124.136
Gd1—07 bridging nitrate	2.252	O5—Gd6—N22	67.8
Gd1—O15 bridging formate	2.699	O20—Gd1—O7	123.15
Gd1—O20 bridging formate	2.096	O5—Gd6—N21	111.60
Gd1—041 chelated formate	2.540	O20—Gd1—N27	66.83
		O2—Gd1—N26	119.99
Gd1—N26	2.600	N27—Gd1—N26	116.43
Gd1—N27	2.897	N21—Gd6—N22	94.00

TABLE V *(Continued)*

BOND DISTANCES (Å)		INTERBOND ANGLES (°)	
Gd6—O10 bridging nitrate	2.215	O10—N8—O7	120.00
Gd6—O11 nitrate	2.444	Gd6—O10—N8	120.246
Gd6—O5 nitrate	2.197	O10—Gd6—O18	124.157
Gd6—O37 chelate nitrate	2.540	O11—Gd6—O17	167.24
Gd6—O17 bridging formate	2.457	O14—Gd1—N27	81.249
Gd6—O18 bridging formate	2.500	O14—Gd1—N26	111.53
Gd6—N21	3.041	O2—Gd1—N27	93.662
		O2—Gd1—N26	119.998
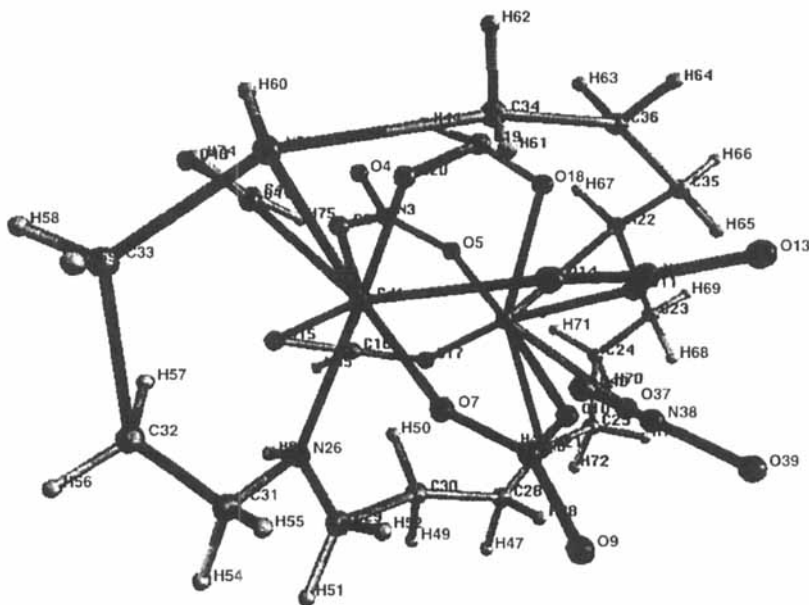
FIGURE 7   Perspective view of the molecular structure of the elemental unit $Gd_2(16\text{-ANE-}N_4)$ $(NO_3)_4(CHO_2)_2CH_2O_2$, as visualized by Unichem.

It is clear from Figure 7, that the two gadolinium atoms form a dinuclear center through three bridging nitrates, two bridging formates and one bridging macrocyclic ligand. There are also unidentate nitrate and formic acid ligands which complete the coordination sphere (CN = 8) for each gadolinium. From the arrangement of the molecule it can be seen that the nitrates or the formic acid can participate with extra bonds thus explaining the formation of the polymer. The coordination of the nitrates is very versatile;[13,35] as an example, in the dimeric $[Pb_2([16]-ANE-N_4)_2(NO_3)_2]^{2+}$ species, where two elemental units are bridged through two nitrates, one tetracoordinated and another tricoordinated. This explains why, when the reaction is carried out using chloride salts, no stable complexes are obtained. It is important to mention, that the elemental unit repeated seven times is not a fortuitous fact, since for the only three molecular weight determinations performed, number seven was obtained. An arrangement of seven elemental units stabilizes a defined structure under the reaction conditions.

Preliminary luminiscence results on the europium (III) and terbium (III) complexes at 300 and 20 K indicate that the central ions are equivalent and the environment around them shows low symmetry.[41] This provides evidence that these complexes are pure, since the luminiscence response is very sensitive to the local symmetry of the compounds.

EPR Spectroscopy

Powder X- and Q-band EPR spectra at 77 K of the polymeric gadolinium compound are shown in Figure 8. Each singlet is centered at g = 1.967 and have rather narrow widths of 440 and 600 Gauss, respectively. The spectra at room temperature are identical to those shown at 77 K with the same g position and surprisingly with the same widths. Our 440 Gauss and 600 Gauss width structureless X- and Q- band EPR singlets are consistent with a magnetically concentrated system showing exchange narrowing.

The Q-band spectrum has increased width (a factor 1.36) from the width at X-band, showing the existence of hyperfine structure still unresolved at Q-band. On the other hand, the lack of dependence of the line-width with temperature for each spectrum (Figure 8) may indicate that the spin-lattice relaxation processes and the spin-spin relaxation processes contribute similarly to the linewidth.

Effective Magnetic Moments

Magnetic susceptibilities for each compound were measured, and the molar magnetic susceptibility corrected for diamagnetic contribution (X_{mcd}) was used to determine the experimental effective magnetic moments μ_{eff} of the compounds
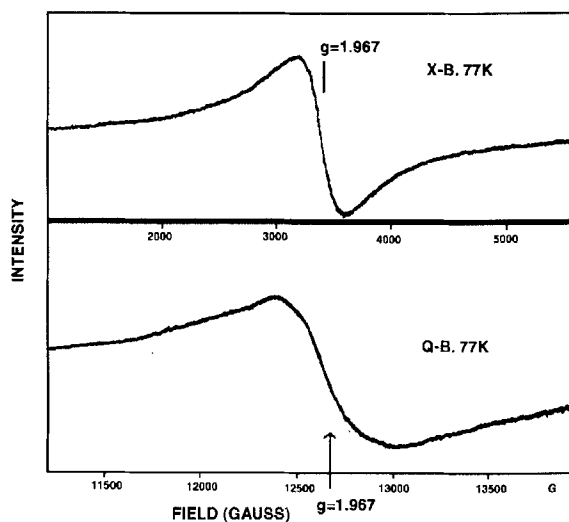
FIGURE 8   Powder EPR spectra of the $Gd_2(16\text{-ANE-}N_4)$ $(NO_3)_4(CHO_2)_2CH_2O_2$ at 77 K. a) X band spectrum, ν = 9.455 GHz, g = 1.967; Γ = 440 gauss, b) Q band spectrum ν = 35.1 GHz, g = 1.967; Γ = 600 Gauss.

by equation $\mu_{eff} = 2.828\ (X_{med} \times T)^{1/2}$. The results are shown in Table VI. Except for the erbium compound, these values are lower than the values calculated with the equation $\mu_{eff} = \{g_1^{2}[J_1(J_1 + 1)] + g_2^{2}\ [J^{2}(J_2 + 1)]\}^{1/2}$ valid for two independent magnetic moments J_1 and J_2.[36-38] This equation considers two independent lanthanide ions in the same structural unit, i.e., with no exchange interaction. These results are also shown in Table VI. The magnetic moment is reported for the minimum formula in each case, although, we cannot exclude interactions caused by the formation of the polymer.

TABLE VI   Effective magnetic moments(μ_{eff}) of the dinuclear lanthanide polymeric compounds

LANTHANIDE COMPOUNDS	$\mu_{eff}(BM)$	$\mu_{eff}(BM)$
Minimum formula	experimental	calculated
$Nd_2(16\text{-ANE-}N_4)$ $(NO_3)_3(CHO_2)_3CH_3CN$	4.71	5.20
$Eu_2(16\text{-ANE-}N_4)$ $(NO_3)_3(CHO_2)_3$	4.61	5.10
$Gd_2(16\text{-ANE-}N_4)$ $(NO_3)_4(CHO_2)_2CH_2O_2$	10.87	11.23
$Tb_2(16\text{-ANE-}N_4)$ $(NO_3)_4(CHO_2)_2CH_2O_2CH_3CN$	13.25	13.72
$Er_2(16\text{-ANE-}N_4)$ $(NO_3)_4(CHO_2)_2CH_2O_2$	13.57	13.57
$Lu_2(16\text{-ANE-}N_4)$ $(NO_3)_3(CHO_2)_3$	0.00	0.00

The magnetic susceptibility calculation for the Eu(III) compound had to consider up to the 3rd excited state due to thermal population of the excited states of the Eu(III) ion.[38-39] For convergence of the magnetic susceptibility value, in addition to considering the excited states, more accurate eigenergies E_n values than the ones obtained from first order perturbation theory had to be considered, as was pointed out many years ago by Van Vleck.[39]

The experimental magnetic results for the Nd(III), Eu(III), Gd(III), and Tb(III) compounds are lower than those calculated, suggesting an antiferromagnetic interaction between the two metals in the elemental units of the polymer. This can be explained as two metals in the dinuclear elemental unit linked together by several bridging ligands, as shown in Figure 7. Another possible reason for the decreased magnetic moments, might be antiferromagnetic coupling by formation of the polymer.[40] In order to confirm that these smaller values are due to antiferromagnetism, magnetic susceptibility measurements have to be performed as a function of temperature.

Overall, these results suggest that in our bridged Gd-Gd compound, the *4f*-electrons, though highly localized on each ion site, do interact with each other, probably through somewhat delocalized molecular orbitals. A theoretical study of this compound is in progress. These novel compounds may give insight into the nature of bonding between the gadolinium centers, the type of the magnetic coupling, *etc.*

The results reported in this paper show the first preparation of dinuclear lanthanide polymeric complexes formed with the [16]-ANE-N_4 macrocycle and, the first example of lanthanide polymeric complexes formed with a neutral saturated tetraazamacrocyclic ligand. The stability of the lanthanide-nitrogen bond is such that in the presence of nitrates and formic/formate ligands, bridges are formed satisfying the coordination sphere and promoting polymerization. The formation of these polymers allows us to propose the interactions of the *4f*-electrons through delocalized molecular orbitals.

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