Solid-State and Solution Structure of Lanthanide Complexes of a New Nonadentate Tripodal Ligand Containing Phenanthroline Binding Units

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The new nonadentate tripodal ligand trenphen {tris[(1,10-phenanthroline-2-carboxamido)-ethyl]amine} has been synthesized by condensation of tren [tris(2-aminoethyl)amine] with an excess of 1,10-phenanthroline-2-carboxylic acyl chloride. The ligand trenphen and its lanthanide complexes (Sm, Nd, Eu, Tb, and Lu) have been structurally characterized by single-crystal X-ray diffractometry. Crystals of trenphen$\cdot H_2O \cdot CH_3CN$, **1**, are monoclinic, space group $P2(1)/n$, $a = 14.9923(8)$ Å, $b = 17.4451(10)$ Å, $c = 17.1880(10)$ Å, $\beta = 114.8290(10)°$, $V = 4079.9(4)$ Å^3, $Z = 4$. The solid-state crystal structures of the isostructural [Ln(trenphen)](OTf)$_3 \cdot yH_2O \cdot xEt_2O \cdot zCH_3CN$ (OTf = CF_3SO_3) (Ln = Nd, $y = 0.5$, $x = 1$, $z = 3$ (**2**); Ln = Sm, $y = 0.5$, $x = 1$, $z = 3$ (**3**); Ln = Eu, $y = 0.5$, $z = 3$ (**4**); Ln = Tb, $y = 0.5$, $x = 1$, $z = 1.5$ (**5**); Ln = Lu, $y = 0.5$, $x = 1$, $z = 1.5$ (**6**)) (trigonal, P-3, $Z = 2$) show that the covalent tripod trenphen undergoes a rearrangement in the presence of lanthanide ions yielding three tridentate binding units which encapsulate the nine-coordinated lanthanide ion with a slightly distorted, tricapped, trigonal prismatic coordination geometry. The correlation observed between the decrease of Ln−N distances and the metal ionic radius indicates that trenphen, although containing rigid bidentate phenanthroline units, is sufficiently flexible to self-organize without steric constraints around lanthanide ions of different size. Solution-state NMR studies show that complexes **2**−**6** exist in acetonitrile solution as discrete rigid C_3-symmetric species retaining the triple-helical structure observed in the solid state. NMR and ES-MS titration show the formation of bimetallic and trimetallic species in the presence of an excess of metal, whereas mononuclear bistrenphen complexes are obtained in the presence of an excess of ligand.

Introduction

The application of lanthanide(III) complexes as contrast agents in magnetic resonance imaging, or as luminescent probes in biochemistry,[1] requires fine-tuning of the coordination sphere of the metal ion. Although flexible podate ligands[2−4] can yield an increased structural and electronic control of the lanthanide coordination site, relative to that of rigid receptors such as preorganized macrocycles or cryptands, the development of specific flexible receptors is very difficult because of the weak stereochemical preferences of lanthanide ions.[5] Tripodal ligands covalently assembled through an amide linkage of the binding units to [tris(2-aminoethyl)amine] (tren) as a common anchor have often been used in the preparation of complexes of the group d elements.[6−8] While there has recently been a growing interest in lanthanide complexes of tripodal ligands,[2,9−15] the tren anchor has been used only very rarely to organize bidentate or tridentate binding units through an amide linkage around lanthanide ions.[16−18]

The incorporation of 1,10-phenanthroline binding units in polydentate podands is of great interest in the design of new

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Table 1. Crystallographic Data for the Six Structures

	trenphen·H_2O·CH_3CN **1**	[Nd(trenphen)]$(OTf)_3$·Et_2O·$(MeCN)_3$·$(H_2O)_{0.5}$ **2**	[Sm(trenphen)]$(OTf)_3$·Et_2O·$(MeCN)_{1.5}$·$(H_2O)_{0.5}$ **3**	[Eu(trenphen)]$(OTf)_3$·$(MeCN)_3$·$(H_2O)_{0.5}$ **4**	[Tb(trenphen)]$(OTf)_3$·Et_2O·$(MeCN)_{1.5}$·$(H_2O)_{0.5}$ **5**	[Lu(trenphen)]$(OTf)_3$·Et_2O·$(MeCN)_{1.5}$·$(H_2O)_{0.5}$ **6**
formula	$C_{47}H_{41}N_{11}O_4$	$C_{58}H_{56}F_9N_{13}O_{13.5}S_3Nd$	$C_{55}H_{51.5}F_9N_{11.5}O_{13.5}S_3Sm$	$C_{54}H_{46}F_9N_{13}O_{12.5}S_3Eu$	$C_{55}H_{51.5}F_9N_{11.5}O_{13.5}S_3Tb$	$C_{55}H_{51.5}F_9N_{11.5}O_{13.5}S_3Lu$
fw	823.91	1562.58	1507.11	1496.18	1515.68	1531.73
cryst syst	monoclinic	trigonal	trigonal	trigonal	trigonal	trigonal
space group	*P*2(1)/*n*	*P*-3	*P*-3	*P*-3	*P*-3	*P*-3
a, Å	14.9923(8)	18.190(15)	18.309(5)	18.229(4)	18.136(3)	18.111(2)
b, Å	17.4451(10)	18.190(15)	18.309(5)	18.229(4)	18.136(3)	18.111(2)
c, Å	17.1880(10)	11.880(11)	11.789(4)	11.712(4)	11.678(3)	11.6382(19)
β, deg	114.8290(10)					
V, Å^3	4079.9(4)	3404(5)	3422.7(18)	3370.6(15)	3326.5(11)	3306.1
Z	4	2	2	2	2	2
D_{calc}, g cm^{-3}	1.341	1.524	1.462	1.474	1.513	1.539
μ(Mo Kα), mm^{-1}	0.089	0.949	1.039	1.114	1.250	1.681
temp, K	293(2)	143(2)	143(2)	143(2)	193(2)	193(2)
no. of params refined	723	306	303	301	307	305
R1, wR2[a]	0.0435, 0.1059	0.1069, 0.2840	0.1172, 0.2721	R1 = 0.1221, 0.2684	0.0982, 0.2693	0.1302, 0.2917

[a] Structure was refined on F_o^2 using all data: $wR2 = [\sum w(F_o^2 - F_c^2)^2]/\sum(F_o^2)^2]^{1/2}$, where $w^{-1} = [\sum F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2,0) + 2F_c^2]/3$.

tailored ligands in view of its ability to act as a powerful photosensitizer.[19,20] Lanthanide complexes of branched macrocyclic[21] or macrobicyclic[22] ligands containing 1,10-phenanthroline subunits have shown interesting photophysical properties. In addition to the potential application of lanthanide complexes of 1,10-phenanthroline-containing ligands as luminescent labels in fluoroimmunoassay,[1] 1,10-phenanthroline has also proven to be an efficient extractant for the selective separation of actinides(III) from lanthanides(III)[23,24] in nuclear waste retreatment. The assembly of binding units containing heterocyclic nitrogens through a tren-based trisamide moiety appears very desirable because of its ability to act as a protonation site[6,16] and because of the stability of the amide group in water or acidic conditions.

In this paper we report the new ligand trenphen {tris[(1,10-phenanthroline-2-carboxamido)ethyl]amine} and its coordination behavior with lanthanide(III) ions. Despite the tendency of lanthanide(III) to give polymeric species in the presence of flexible polydentate ligands, the ligand trenphen forms discrete nonadentate 1:1 complexes which display a rigid solution-state structure. Detailed descriptions of the solid- and solution-state structures of the 1:1 complexes [Ln(trenphen)]$^{3+}$ are presented. The various species formed at different metal-to-ligand ratios are also discussed.

Experimental Section

General Details. ^{1}H NMR spectra were recorded on Bruker AM-400, Bruker AC-200, and Varian U-400 spectrometers using deuterated MeOD, CD_3CN solutions with MeOH, CH_3CN as internal standards. Mass spectra were measured with a Finnigan LC-Q instrument. Elemental analyses were performed by SCA/CNRS, Vernaison, France.

Electronic spectra in the UV−visible range were recorded at 20 °C from 10^{-4} to 10^{-5} M acetonitrile solutions with a Hewlett-Packard 8453 spectrometer using quartz cells of 0.1-cm path length. Spectrophotometric titrations were performed with a Hewlett-Packard 8453 spectrometer connected to an external computer. In a typical experiment, 20 mL of a 10^{-4} M acetonitrile solution of trenphen was titrated at 20 °C with a solution of $Ln(CF_3SO_3)_3$ 10^{-3} M in acetonitrile. After each addition of 0.1 mL, the absorption spectra were recording using a quartz flow-cell of 0.1-cm path length. The absorbance values between 230 and 320 nm were transferred to the computer. A model for the distribution of species was fitted with a nonlinear least-squares algorithm to give the stability constants using the SPECFIT program.[25] Solvents and starting materials were purchased from Aldrich, Fluka, Acros, and Alfa and used without further purification unless otherwise stated. Dichloromethane was dried over P_2O_5 and then distilled under argon. Triethylamine and tris(2-aminoethyl)amine (tren) were dried over KOH and then distilled under argon.

X-ray Crystallography. All of the crystals were analyzed using a Bruker SMART CCD area detector three-circle diffractometer (Mo Kα radiation, graphite monochromator, $\lambda = 0.71073$ Å). To prevent loss of solvent, the crystals were quickly transferred from the mother liquor to a stream of cold nitrogen at −130 °C or at −80 °C on the diffractometer.

The cell parameters were obtained with intensities detected on three batches of 15 frames each, with an exposure time selected according to the crystal size (10 s for complexes **5** and **6**, 30 s for **4**, and 60 s for **2** and **3**). The crystal−detector distance was 5 cm. For three settings of Φ and 2Θ, 1200 (650 for **2**) narrow data frames were collected for 0.3° increments in ω. A full hemisphere of data was collected for complexes **2**, **4**, **5**, and **6** (a quadrant was collected for complex **3**). At the end of data collection, the first 50 frames were re-collected to establish that crystal decay had not taken place during the collection. Unique intensities with $I > 10\sigma(I)$ detected on all frames using the Bruker SMART program[26] were used to refine the values of the cell parameters. The substantial redundancy in data allows empirical absorption corrections to be applied using multiple measurements of equivalent reflection with the SADABS BRUKER program.[26] Space groups were determined from systematic absences, and they were confirmed by the successful solution of the structure (see Table 1). Complete information on crystal data and data collection parameters is given in the Supporting Information section below.

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The structures were solved by direct methods using the SHELXTL 5.03 package,[27] and all non-hydrogen atoms were found by difference Fourier syntheses. All non-hydrogen atoms (except C21 in complex **4**) were anisotropically refined on F^2. C21 in the europium complex was isotropically refined and hydrogen atoms were included in calculated positions. The complexes are located on a 3-fold axis with the metal and the apical nitrogen N1 in special position *2d*. The water molecule is disordered (1/2 occupancy) and the oxygen atom is located in special position *1b*. The Et_2O molecule in complexes **2**, **3**, **5**, and **6** is disordered around a 3-fold axis and refined with three atomic position (site occupancy 1/3 for the oxygen atom and 2/3 for the carbon atoms). In complexes **3**, **5**, and **6** the acetonitrile molecule is disordered with 1/2 occupancy. Complex **4** contains two disorded acetonitriles with 1/2 occupancy, with one of them disordered around a 3-fold axis.

Synthesis of Trenphen. 1,10-Phenanthroline-2-carboxylic acid was prepared according to the literature procedure[28] from 1,10-phenanthroline monohydrate (Acros).

^{1}H NMR (DMSO-d_6): δ ppm 9.13 (dd, H_9, $J_{8,9} = 4.3$ Hz, $J_{7,9} = 1.7$ Hz), 8.71 and 8.39 (AB, $H_{3,4}$, $J = 8.3$ Hz), 8.60 (dd, H_7, $J_{7,8} = 8.06$ Hz), 8.16 and 8.09 (AB, $H_{5,6}$, $J = 8.6$ Hz), 7.88 (dd, H_8).

MS/ES$^+$: *m/z* 225 $[M + H]^+$, 247 $[M + Na]^+$, 269 $[M - H + 2Na]^+$, 179 $[MH^+ - HCO_2H]^+$. MS/ES$^-$: *m/z* 223 $[M - H]^-$.

1,10-Phenanthroline-2-carboxylic acid (2.4 g, 10.7 mmol) was suspended in thionyl chloride (100 mL) and refluxed until complete dissolution (ca 2.5 h). After the resulting orange solution was cooled at room temperature, the excess thionyl chloride was evaporated. To remove any residual thionyl chloride, the yellow solid was suspended on toluene (50 mL) and then evaporated to dryness. This process was repeated twice. The resulting pale yellow solid was vacuum dried overnight and used without further purification.

Freshly distilled tren (320 μL, 2.6 mmol) was added under argon to a mixture of 1,10-phenanthroline-2-carboxylic acid chloride and freshly distilled triethylamine (3.5 mL, 30 mmol) in anhydrous dichloromethane (80 mL). The resulting brown solution was refluxed for 1 h and then cooled to room temperature. The solvent and the excess amine were evaporated. The resulting brown solid was recrystallized twice from a water/ethanol mixture (50/50) to give a yellow powder (1.68 g, 85% yield).

^{1}H NMR (DMSO-d_6): δ ppm 9.39 (t, $-NH-$, $^3J = 5.4$ Hz), 8.79 (dd, H_9, $^3J_{8,9} = 4.4$ Hz, $^3J_{7,9} = 1.8$ Hz), 8.21 (dd, H_7, $^3J_{7,8} = 8$ Hz), 7.99 (d, H_4, $^3J_{3,4} = 8.2$ Hz), 7.74 (d, H_3), 7.65 (d, H_6, $^3J_{5,6} = 8.8$ Hz), 7.58 (dd, H_8), 7.51 (d, H_5), 3.69 (broad q, $-NH-CH_2-CH_2-N-$, $^3J = 5.8$ Hz), 3.02 (broad t, $-NH-CH_2-CH_2-N-$).

^{13}C NMR (DMSO-d_6): δ ppm 168.1 ($>C{=}O$), 153.3, 153.2, 148.2, 146.5, 140.2, 139.4, 132.2, 131.9, 130.9, 129.3, 126.7, 123.1, 56.4, and 41.5 ($-CH_2-CH_2-$).

MS/ES$^+$: *m/z* 765 $[M + H]^+$, 787 $[M + Na]^+$, 516 $[M - Phen\text{-}CONHC_2H_3]^+$, 250 $[Phen - CONHC_2H_4]^+$.

Synthesis of [Ln(trenphen)](OTf)$_3$·yH$_2$O·xEt$_2$O·zCH$_3$CN (Ln = Nd, $y = 0.5$, $x = 1$, $z = 3$ (3); Ln = Eu, $y = 0.5$, $z = 3$ (4); Ln = Tb, $y = 0.5$, $x = 1$, $z = 1.5$ (5)). An equimolar quantity of the lanthanide salt $Ln(CF_3SO_3)_3$ was added to a suspension of trenphen (60 mg, 0.07 mmol) in acetonitrile (3 mL). The mixture, which became immediately clear, was stirred one night at room temperature. After diethyl ether was added, a yellow powder formed which was collected by filtration, washed several times with ether, and dried to give 70−75% of complexes **3**, **4**, and **5**. Satisfactory elemental analyses were obtained for the three complexes.

^{1}H NMR and ES-MS spectra were recorded for the complexes [Ln(trenphen)](OTf)$_3$. (Ln = Pr, Sm (**2**); Nd (**3**); Eu (**4**); Tb (**5**); and Lu (**6**)) prepared in situ.

ES-MS (10^{-2} M in methanol) $[Ln(trenphen)(CF_3SO_3)_2]^+$: Ln = Pr 1202.9 *m/z*, Ln = Nd 1205.8 *m/z*, Ln = Sm 1213.8 *m/z*, Ln = Eu 1214.7 *m/z*, Ln = Tb 1220.9 *m/z*, Ln = Lu 1236.8 *m/z*.

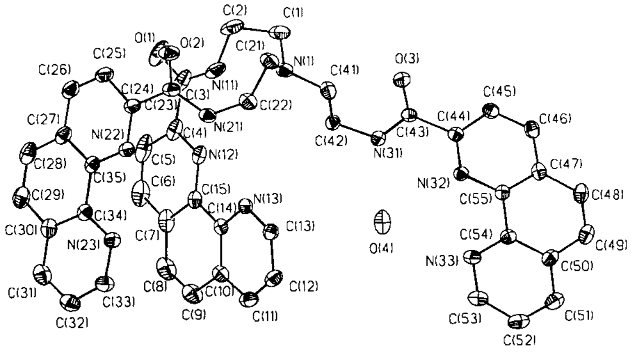
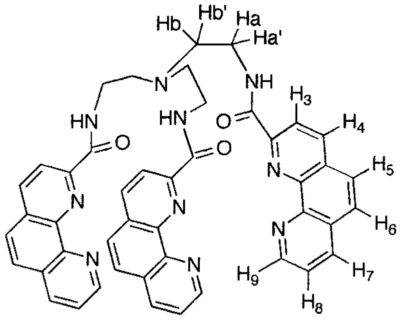


Figure 1. Side view of the crystal structure of trenphen with thermal ellipsoids at 30% probability.

Scheme 1



trenphen

Fragile crystals of complexes **2**, **3**, **4**, **5**, and **6** suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into a concentrated (10^{-2} M) acetonitrile solution.

Results and Discussion

Synthesis and Structure of the Ligand. 1,10-Phenanthroline-2-carboxylic acid was prepared as previously described[28,29] and then converted to the corresponding acyl chloride by addition of thionyl chloride. The ligand trenphen was obtained from the condensation of tren with an excess of 1,10-phenanthroline-2-carboxylic acyl chloride in dichloromethane in the presence of triethylamine with an overall yield of 85%. X-ray quality crystals of trenphen (**1**) were obtained from an acetonitrile solution. The crystal structure of trenphen, Figure 1, shows that in the three tridentate binding units the oxygens atoms of the carbonyl groups are oriented trans to the phenanthroline nitrogens. In one arm of the podand the pyramidal bridgehead nitrogen N(1) and the amide nitrogen N(31) adopt an antiperiplanar stereochemical conformation. In this arm, the amide proton is hydrogen-bound to the oxygen of a water molecule and to one phenanthroline nitrogen. The water molecule is also hydrogen-bound to the second phenanthroline nitrogen. In the two remaining arms, the amide nitrogens adopt a synclinal conformation relative to the bridgehead nitrogen N(1), as in the complexed form of the ligand. Hydrogen bonds are present between the bridgehead nitrogen and one amide proton (N(1)- - -H(11), 2.294(2) Å, N(1)- - -H(11)−N(11), 109.6°), which is also hydrogen-bound to one phenanthroline nitrogen (N(12)). Two phenanthroline units are nearly parallel (angle between the mean planes = 11.4°) with an interplanar distance of 3.4 Å, suggesting the presence of intramolecular stacking interactions.

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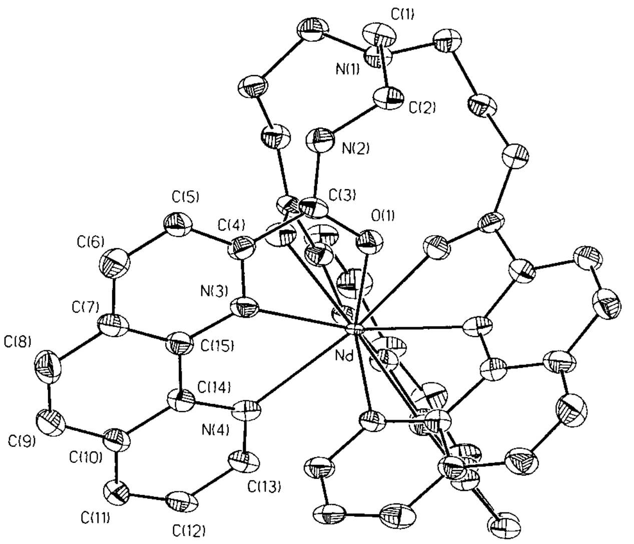

Figure 2. Side view of the crystal structure of the cation [Nd(trenphen)]$^{3+}$ with thermal ellipsoids at 30% probability.

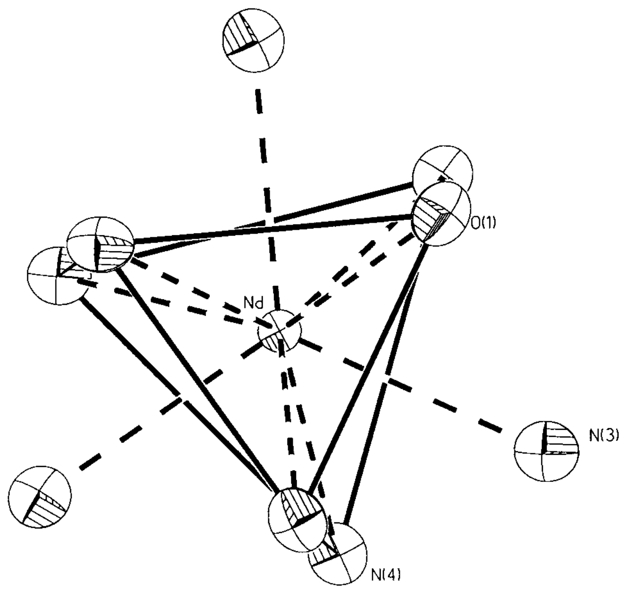

Figure 3. Coordination polyhedron of [[Nd(trenphen)]$^{3+}$.

The ^1H NMR spectra of trenphen in CD_3CN at 298 K (Figure 4 below) or DMSO-d_6 show the presence of only one set of signals with seven resonances for the phenanthroline protons and two resonances for the ethylene protons, in agreement with a dynamically averaged C_{3v}-symmetric solution structure as a result of the unhindered rotation about the C−N bonds of the amide group. The spectrum of a solution of trenphen in DMSO-d_6 is unchanged by the addition of an excess of triethylamine indicating that the deprotonation of the amide does not occur under these conditions. The addition of 1 equiv of triflic acid to a solution of trenphen in DMSO-d_6 leads to a downfield shift of the ethylene protons $H_{a/a'}$ ($\Delta\delta = 0.28$ ppm) and $H_{b/b'}$ ($\Delta\delta = 0.70$ ppm) and of the phenanthroline protons ($\Delta\delta = 0.29$ (H_9), 0.33 (H_8), 0.51 (H_7), 0.46 (H_6), 0.49 (H_5), 0.41 (H_4), and 0.38 (H_3) ppm). The addition of a second equivalent of triflic acid results in the further downfield shift of the ethylene protons $H_{a/a'}$ ($\Delta\delta = 0.07$ ppm) and $H_{b/b'}$ ($\Delta\delta = 0.15$ ppm) and of the phenanthroline protons ($\Delta\delta = 0.43$ (H_7), 0.31 (H_6), and 0.24 (H_9) ppm). The addition of a higher number of equivalents of triflic acid does not affect further the chemical shifts. These results suggest that protonation of the trenphen ligand occurs almost simultaneously at the apical nitrogen and at one phenanthroline nitrogen.

Crystal and Molecular Structure of Complexes of Trenphen. The structures of the complexes of trenphen [Ln(trenphen)](OTf)$_3y$H$_2$O·xEt$_2$O·zCH$_3$CN (Ln = Nd, $y = 0.5$, $x = 1$, $z = 3$ (**2**); Ln = Sm, $y = 0.5$, $x = 1$, $z = 3$ (**3**); Ln = Eu, $y = 0.5$, $z = 3$ (**4**); Ln = Tb, $y = 0.5$, $x = 1$, $z = 1.5$ (**5**); and Ln = Lu, $y = 0.5$, $x = 1$, $z = 1.5$ (**6**)) were determined by X-ray crystallography. Complexes **2**−**6** are isostructural, and accordingly only the neodymium complex is shown in Figure 2 and the coordination polyhedron is shown in Figure 3. Selected interatomic distances and angles are set out in Table 2. In the five complexes the metal ion is nine-coordinated by six nitrogens of the phenanthroline arms and the three amide oxygens. The coordination geometry can be described as a sligthly distorted, tricapped, trigonal prism with the capping positions occupied by three phenanthroline nitrogens (N(3)). Upon coordination, the three carbonyl groups which all point outside in the free ligand rotate inside to assume a cis position relative to the phenanthroline nitrogens, thereby yielding three tridentate arms which bind the metal ion in a nearly planar mode. In all complexes **2**−**6** the metal ion is located in the phenanthroline plane (average distance from the phenanthroline mean plane is 0.046 Å). The distance of the amide oxygen from the phenanthroline plane ranges from 0.36 Å for Nd to 0.18 Å for Lu. This shows that the carbonyl groups rotate increasingly toward the phenanthroline plane as the coordinated ions decrease in size. The metal ions sit on a crystallographic 3-fold symmetry axis relating the three chelating arms of the tripod. The M−N and M−O distances are in the range of those reported in the literature for Nd(III),[10,30] Sm(III),[14,30] nine-coordinated Eu(III),[17,31,32] Tb(III),[30] and Lu(III)[30,31] complexes. The ligand adopts a conical shape with an O(1)- - -O(1)#1 distance (3.03 Å for Nd, 2.99 Å for Sm, 2.99 Å for Eu, 2.96 Å for Tb, and 2.86 Å for Lu) shorter than the N(4)- - -N(4)#1 distance (3.52 Å for Nd, 3.46 Å for Sm, 3.45 Å for Eu, 3.40 Å for Tb, and 3.30 Å for Lu), as already observed for the protonated tripodal-ligand-containing tridentate pyridinedicarboxamide units recently reported by Piguet and coworkers.[17] In the complex of the protonated podate the metal is significantly closer to the lower (with respect to the capping nitrogen) triangular face of the trigonal prism, whereas in complexes **2**−**6** the metal ion is closer to the upper triangular face (distance from O(1)- - -O(1)#1- - -O(1)#2, 1.71 Å for Nd, 1.67 Å for Sm, 1.66 Å for Eu, 1.63 Å for Tb, and 1.60 Å for Lu; distance from N(4)- - -N(4)#1- - -N(4)#2, 1.77 Å for Nd, 1.72 Å for Sm, 1.70 Å for Eu, 1.69 Å for Tb, and 1.69 Å for Lu). This observation is consistent with an increased interaction of the metal with the carbonyl groups, due to the absence of the proton. The decrease observed for the M−N (0.151 Å for M−N(3) and 0.146 Å for M−N(4) from Nd to Lu) and M−O distances (a decrease of 0.146 Å for M−O from Nd to Lu) from Nd to Lu is clearly correlated to the decrease in ionic radius (from Nd to Lu a decrease of 0.13 Å is expected) in agreement with the presence of an essentially electrostatic metal−ligand interaction. The observed trend indicates the absence of inter-

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Table 2. Selected Bond Distances (Å) and Angles (deg) in Complexes **2**−**6**

	Nd(trenphen)	Sm(trenphen)	Eu(trenphen)	Tb(trenphen)	Lu(trenphen)
M−O(1)	2.445(6)	2.402(7)	2.394(5)	2.360(5)	2.299(4)
M−N(3)	2.604(8)	2.561(8)	2.573(6)	2.545(7)	2.453(6)
M−N(4)	2.697(8)	2.636(8)	2.620(5)	2.594(7)	2.551(6)
O(1)#1−M−O(1)	76.85(18)	77.0(3)	77.19(18)	77.7(2)	76.85(18)
O(1)−M−N(3)	65.0(2)	63.6(2)	64.31(17)	64.4(2)	65.0(2)
O(1)#1−M−N(3)	64.65(19)	65.1(2)	65.34(16)	130.6(2)	64.65(19)
O(1)#2−M−N(3)	130.24(19)	129.7(3)	130.55(17)	64.7(2)	130.24(19)
O(1)#2−M−N(3)#2	65.01(19)	63.6(2)	64.31(17)	64.4(2)	65.01(19)
N(3)−M−N(3)#2	119.06(5)	118.82(8)	119.08(4)	119.00(5)	119.06(5)
O(1)#1−M−N(4)	86.20(19)	85.7(2)	85.27(16)	145.2(2)	86.20(19)
O(1)−M−N(4)	130.46(18)	126.9(2)	127.71(19)	128.0(2)	130.46(18)
O(1)#2−M−N(4)	143.61(18)	146.6(2)	145.46(17)	85.2(2)	143.61(18)
N(3)−M−N(4)	65.64(19)	63.6(3)	63.58(19)	63.8(2)	65.64(19)
N(3)#2−M−N(4)	142.9(2)	143.6(3)	143.31(17)	80.6(2)	142.9(2)
N(3)#1−M−N(4)	79.03(18)	81.6(2)	80.28(18)	143.3(2)	79.03(18)
N(4)−M−N(4)#2	80.7(2)	82.1(3)	82.29(17)	81.9(2)	80.7(2)

Table 3. ^{1}H NMR Chemical Shifts for CD_3CN Solutions of Trenphen and [Ln(trenphen)]$(OTf)_3$ Complexes

	NH	$H_A/H_{A'}$	$H_A/H_{A'}$	$H_B/H_{B'}$	$H_B/H_{B'}$	H_3	H_4	H_5	H_6	H_7	H_8	H_9
trenphen	9.75	3.71	3.71	3.01	3.01	7.64	7.72	7.46	7.32	8.00	7.33	8.56
Pr	7.57	−4.51	−0.08	−3.06	−1.68	10.86	12.13	10.67	10.67	8.64	5.37	−5.11
Nd	9.99	2.15	0.93	1.23	0.62	10.03	10.58	9.65	9.14	8.98	7.61	4.97
Sm	8.67	2.82	2.62	2.25	1.90	8.57	9.21	8.45	8.45	8.58	7.07	6.03
Eu	7.40	8.80	4.82	5.79	5.36	5.23	6.35	5.83	5.83	8.30	6.92	11.41
Lu	9.11	3.62	2.95	2.51	2.76	8.41	8.97	8.33	8.33	8.66	7.40	7.57

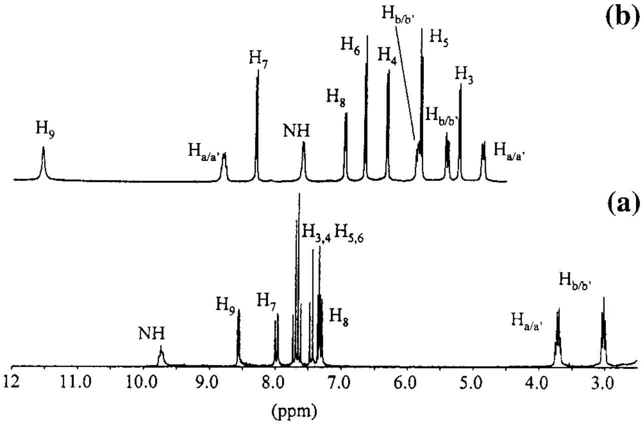

Figure 4. ^{1}H NMR spectra at 298 K of CD_3CN solutions of trenphen (a) and [Eu(trenphen)]$(OTf)_3$ (b).

strand interactions between the phenanthroline branches even in the presence of small lanthanide ions.

The trenphen ligand, although containing rigid bidentate phenanthroline units, is sufficiently flexible to self-organize without steric constraints around lanthanide ions of different size, leading to monomeric complexes in which the Ln(III) ion is nine-coordinated.

Solution Studies. Although the synthesis of the complexes [Ln(trenphen)]$(OTf)_3$ does not require the use of rigorously anhydrous conditions, these complexes dissociate completely in pure water, probably due to the high insolubility of trenphen in this solvent. NMR spectra in CD_3OD solution show that discrete 1:1 complexes form in this solvent which is less polar and less coordinating than water. Although the spectra of the La and Pr complexes are very broad at room temperature, the NMR spectra of the Eu and Lu complexes show the presence of a rigid C_3-symmetric species at 298 K with seven resonances for the phenanthroline protons and four resonances for the ethylene protons. At 303 K we observed for the europium ion the coalescence to a C_{3v}-symmetric species (only two resonances for the ethylene protons) exchanging rapidly between the two helical conformations of the tren moiety. The addition of 10% D_2O to a CD_3OD solution of the complex [Lu(trenphen)]$(OTf)_3$ does not result in a change of the NMR spectrum. The addition of 20% D_2O results in the appearance of additional broad signals in the spectrum which indicate the presence, in solution, of a fluxional species in addition to the rigid C_3-symmetric complex. We also recorded ^{1}H NMR spectra in acetonitrile (less polar and less coordinating than methanol) and we observed an increase of the kinetic inertness of these complexes with respect to that observed in methanol. The ^{1}H NMR spectra of a 1:1 solution of $Ln(OTf)_3$ (Ln = Pr, Nd, Sm, Eu (Figure 4), Tb, and Lu) and trenphen (10^{-2} M) in CD_3CN at 298 K show the presence of only one set of signals with seven resonances for the phenanthroline protons and four resonances for the diastereotopic ethylene protons. These features are consistent with the presence of a rigid species in solution retaining the C_3-symmetric helical structure observed in the solid state. The assignment of NMR chemical shifts reported in Table 3 was confirmed by two-dimensional COSY correlation spectra and NOESY spectra. The intramolecular NOE effects observed between the amide hydrogen and H_3 indicate that also in solution the oxygen atoms of the carbonyl groups adopt a cis position relative to that of the phenanthroline nitrogens. An analogous C_3-symmetric solution structure had been observed for the related tripodal-ligand-containing tridentate pyridine-dicarboxamide binding units which also adopt a cis−cis conformation.[17] The conformation of the Pr, Nd, and Lu complexes of trenphen remains blocked up to 343 K indicating a high kinetic inertness of the solution species. Nevertheless, for the La(III) ion a very broad NMR spectrum is observed in CD_3CN solution at a ratio M/L 1:1 which indicates the presence of a highly fluxional species. The NMR spectrum of the La complex remains very broad even at low temperatures (233 K).

The ^{1}H NMR spectra of solutions of $Ln(OTf)_3$ (Ln = Pr, Eu, and Lu) and trenphen in CD_3CN at 298 K at ratios $1 < M{:}L \leq 2$ show one set of very broad signals in addition to the set of signals of the 1:1 complex present in solution in the blocked C_3-symmetric conformation. At ratios $M{:}L > 2$ the NMR spectrum shows only one set of signals severely broadened by

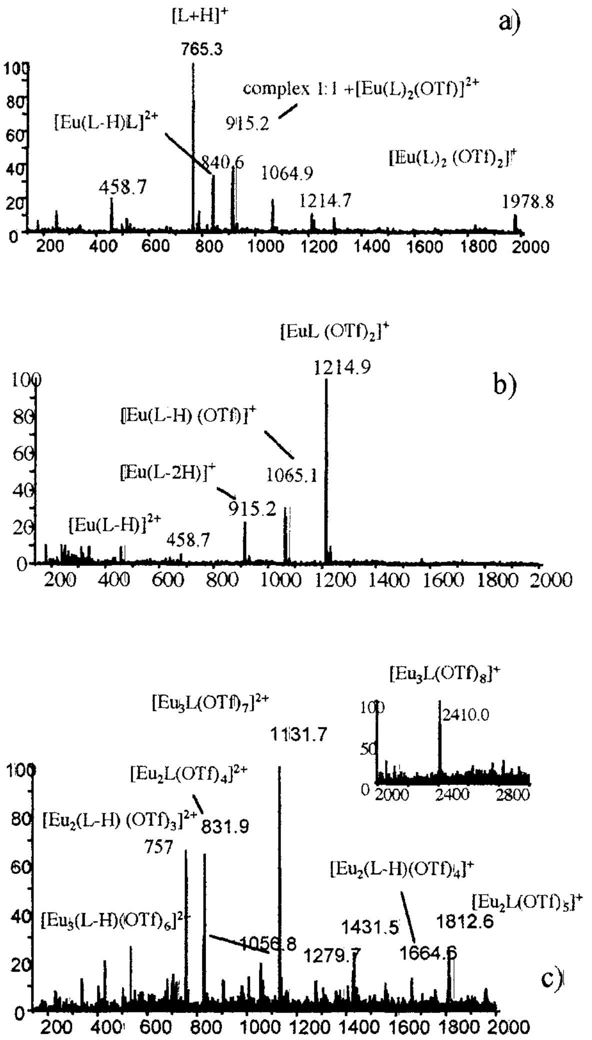

Figure 5. ES-MS spectra of 10^{-2} M acetonitrile solutions of trenphen after addition of 0.5 (a), 1 (b), and 3 (c) equiv of $\mathrm{Eu(OTf)_3}$.

intermolecular ligand exchanges. At ratios $1 < \mathrm{M{:}L} \leq 2$ the ES-MS spectra (at 10^{-2} M in acetonitrile) (Figure 5) show the peaks assigned to the 1:1 complex of trenphen and additional peaks assigned to $\{[\mathrm{Ln_2(trenphen)}](\mathrm{OTf})_4\}^{2+}$, $\{[\mathrm{Ln_2(trenphen)}](\mathrm{OTf})_5\}^{+}$, $\{[\mathrm{Ln_3(trenphen)}](\mathrm{OTf})_8\}^{+}$, and $\{[\mathrm{Ln_3(trenphen)}](\mathrm{OTf})_7\}^{2+}$, in agreement with the presence, in solution, of dimetallic and trimetallic complexes. At ratios $\mathrm{M{:}L} > 2$ the ES-MS spectra (at 10^{-2} M in acetonitrile) show only the presence of the dimetallic and trimetallic complexes.

The reaction of trenphen with an excess of lanthanide ions results in the formation of polymetallic species. The addition of an excess of trenphen to the complexes $[\mathrm{Ln(trenphen)}](\mathrm{OTf})_3$ leads to the formation of bisligand complexes. Indeed, ^{1}H NMR spectra of solutions of $\mathrm{Ln(OTf)_3}$ (Ln = Eu and Lu) and trenphen in $\mathrm{CD_3CN}$ (10^{-2} M) at 298 K at ratios $\mathrm{M{:}L} < 1$ show, in addition to the set of signals of the rigid C_3-symmetric 1:1 complex and to the signals of the free trenphen, the presence of another set of signals. The signals of the 1:1 complex disappear from the ^{1}H NMR spectrum at a ratio of M:L = 0.33. These features are explained by the formation of bisligand complexes of Eu and Lu in the presence of an excess of ligand. The complexity of the NMR spectrum at a ratio of M:L = 0.33 seems to indicate the presence, in solution, of species with low symmetry. The ES-MS spectra of 10^{-2} M acetonitrile solutions of trenphen after addition of 0.5 equiv of lanthanide ion (Pr, Eu, and Lu) show, in addition to the peaks attributed to the 1:1 complex, peaks corresponding to the free ligand and strong peaks assigned to $[\mathrm{Ln(trenphen\text{-}H)(trenphen)}]^{2+}$, $\{[\mathrm{Ln(trenphen)_2}](\mathrm{OTf})\}^{2+}$, and $\{[\mathrm{Ln(trenphen)_2}](\mathrm{OTf})_2\}^{+}$, in agreement with the presence, in solution, of bistrenphen complexes of the formula $[\mathrm{Ln(trenphen)_2}](\mathrm{OTf})_3$, (Figure 5). The ES-MS spectra recorded for a total ligand concentration of 10^{-4} M also show the presence of the peaks attributed to bistrenphen complexes, but the intensity of these peaks is very weak and much lower than those for a total ligand concentration of 10^{-2} M. The intensity of the peaks attributed to the bisligand complexes remains unchanged along the lanthanide series. These peaks are not observed for a total ligand concentration of 10^{-5} M.

Spectrophotometric titrations of solutions of trenphen in anhydrous acetonitrile (10^{-4} M) with $\mathrm{Ln(OTf)_3}$ (Ln = Pr, Nd, Eu, and Lu) (0−1 equiv) show a sharp end point at a ratio trenphen/Ln = 1, in agreement with the formation of the 1:1 complexes $[\mathrm{Ln(trenphen)}](\mathrm{OTf})_3$. Factor analysis suggests that two absorbing species are necessary to fit the experimental data, and the spectrophotometric data can be fitted by equilibrium (1) using nonlinear least-squares methods (root-mean-square difference between calculated and observed absorbances = 0.02) yielding $\log \beta 1 = 6.7(2)$ for Pr; $\log \beta 1 = 6.5(2)$ for Nd; $\log \beta 1 = 6.6(2)$ for Eu; and $\log \beta 1 = 6.6(2)$ for Lu. Addition of 5% water to the acetonitrile solution of trenphen does not result in a change of the stability constant value.

$$\mathrm{Ln}^{3+} + \text{trenphen} \leftrightarrow [\mathrm{Ln(trenphen)}]^{3+} \qquad (1)$$

Only a small decrease of the formation constants (ca. 1 log unit) is observed for trenphen with respect to the tripodal-ligand-containing pyridine-dicarboxamide binding units reported by Piguet,[17] which is in agreement with the similar affinity of lanthanides for amide oxygen donors and neutral aromatic nitrogen donors.[33] Attempts to introduce the absorbing species $\{[\mathrm{Ln(trenphen)_2}](\mathrm{OTf})_3\}$ in the fitting process failed. This is because only a minor amount of this species is expected in solution (for a total ligand concentration of 10^{-4} M) according to the electrospray data, or because the UV spectra of the monoligand and of the bisligand complexes are too similar. Although the spectrophotometric data do not allow the determination of a formation constant for the bistrenphen complexes, NMR and ES-MS data strongly support the formation of these species for all lanthanides. The crystal structure of Ln(III) complexes containing two hexadentate ligands has been reported,[14] but the solution structure of these complexes has not been described. The formation of a bisligand complex with a nonadentate ligand has been observed only once before for the larger lanthanide ions La and Pr.[17] The lack of formation of bisligand complexes with the smaller lanthanide ions for the nonadentate tripod described by Piguet could be explained by the increased sterical interactions of the pyridine-dicarboxamide arms with respect to those of the rigid phenanthroline binding units.

Concluding Remarks

The solid-state crystal structure and the solution structure of the isostructural $[\mathrm{Ln(trenphen)}](\mathrm{OTf})_3$ complexes have been determined. The covalent tripod trenphen easily undergoes rearrangement in the presence of lanthanide ions yielding three

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tridentate binding units which well-encapsulate the lanthanide ions. Trenphen acts as a nonadentate ligand for the lanthanide ions independently of the ion size and the resulting complexes display a rigid solution structure (with the exception of La). The exclusive formation of discrete 1:1 complexes at a 1:1 stoichiometric ratio and their high kinetic inertness in the presence of a potentially nonadentate flexible podand is remarkable. These results indicate that the tren-based trisamide moiety can provide a very efficient way of assembling bidentate chromophoric units around lanthanide ions for the development of luminescent lanthanide complexes. As expected, trenphen forms dimetallic and trimetallic species at high metal-to-ligand ratios. The formation, in the presence of an excess of ligand, of complexes containing two nonadentate podands for lanthanide ions of different sizes which seem to have a rigid solution structure is quite remarkable. We are currently investigating the solid-state and solution structures of these unusual species and researching the effect that using a different capping trisamine has on the coordination chemistry of the ligand. Studies of the luminescent properties of the complexes of trenphen are also in progress.

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Supporting Information Available: Complete tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, intramolecular and intermolecular hydrogen bonds distances and angles (in CIF format). A table of peaks observed by ES-MS for acetonitrile solutions of trenphen and Pr, Eu, Lu at metal/trenphen ratios = 1:1, 3:1, 1:2. ^{1}H NMR spectra of 10^{-2} solutions of trenphen after addition of 0.3, 0.5, and 1 equiv of Lu(OTf)$_3$ (**S1**); ^{1}H NMR spectra of 10^{-2} solutions of trenphen after addition of 0.3, 0.5, and 1 equiv of Eu(OTf)$_3$ (**S2**). This material is available free of charge via the Internet at http://pubs.acs.org.

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