Inorg. Chem. **1995,** *34,* 3520−3527

X-ray and Multinuclear Magnetic Resonance Study of the Complexes of Lanthanum(III) with 2,2′:6′,2″-Terpyridine

Monique Fréchette* and Corinne Bensimon

Ottawa-Carleton Chemistry Institute, University of Ottawa Campus, Ottawa, Ontario K1N 6N5, Canada

Received March 6, 1995[⊗]

The reaction between $La(NO_3)_3\cdot 6H_2O$ and 2,2′:6′,2″-terpyridine (terpy) in acetonitrile solution was investigated by ^1H, ^{17}O, and ^{139}La NMR spectroscopy. The crystal structure of $[La(NO_3)_2(terpy)_2]$ $[La(NO_3)_4(terpy)]\cdot CH_3CN\cdot {}^1/_2H_2O$ was determined by X-ray diffraction: triclinic; space group $P\bar{1}$; $a = 14.979(4)$ Å, $b = 17.501(10)$ Å, $c = 11.603(5)$ Å; $Z = 2$; $\alpha = 106.34(4)°$, $\beta = 94.22(3)°$, $\gamma = 83.30(3)°$. At convergence, $R_F = 0.053$ and $R_w = 0.032$ for 4012 reflections. In solution, the ^{139}La NMR data indicate the formation of three different complex species with one or two terpy in the La(III) coordination shell. ^{17}O NMR spectroscopy indicates that during the complexation by terpy, coordinated water is totally displaced from the coordination sphere whereas the nitrate groups remain partially bound. Proton NMR data confirm the total displacement of water and show that two terpy molecules are in close proximity when they are coordinated to the same La(III) ion. From the NMR results, it is shown that during the complexation process seven different La(III) species can be observed: $[La(NO_3)_3(CH_3CN)_4]$, $[La(NO_3)_3(CH_3CN)_3(H_2O)]$, $[La(NO_3)_3(terpy)(CH_3CN)]$, $[La(NO_3)_3(terpy)(H_2O)]$, $[La(NO_3)_4(terpy)(CH_3CN)]^-$, $[La(NO_3)_4(terpy)(H_2O)]^-$, and $[La(NO_3)_2(terpy)_2]^+$. The structure of the cationic complex in solution shows similarities with the solid state compound, but the anionic complex is affected by solvation. Comparisons are made with the La(III) complexes previously obtained with 1,10-phenanthroline and 2,2′-bipyridine as well as with data reported in the literature.

Introduction

The interest in lanthanides (Ln) is chiefly ruled by their promising utilization due to their low toxicity, their cheapness, and their powerful paramagnetic, luminescent, and radioactive properties.[1−4] Even though the lanthanides and their complexes are associated with important industrial and biological uses, little is known about their reactivity and behavior, particularly in solution. Therefore, the characterization of the complexes of Ln(III) in solution with respect to the coordination number, bonding, molecular geometry, and thermodynamic and kinetic stability appears essential not only in chemistry but also in several other connected disciplines.[5−9]

Although most of the known complexes have been synthesized by using chelating anionic ligands with oxygen donors[10] or ionophores,[11] more and more Ln(III) complexes derived from nitrogen donors are being isolated and studied.[12−19] These complexes are demonstrating that the Ln(III)−N interaction is stronger than previously believed. Therefore, the N-donor chelators might be playing an unexpected role on the Ln(III) behavior and consequently may be fair competitors with respect to O-donors for the Ln(III) coordination sites.

In recent works,[20,21] carried out to collect information on the complexes of La(III) with N-donor ligands, ^{139}La NMR used in conjunction with ^{17}O, ^{13}C, and ^1H NMR, has successfully led to the structural and thermodynamic characterization of the 1,10-phenanthroline (phen) and 2,2′-bipyridine (bipy) complexes of La(III) in CH_3CN. These studies were of great interest because they unequivocally allowed the characterization of the solvated La(III) species which up to now were principally deduced from the isolated solid complexes.

In this work, a multi-NMR study of the La(III) complexes is done following the mixing of $La(NO_3)_3\cdot 6H_2O$ and 2,2′:6′,2″-terpyridine (terpy) in acetonitrile. Because of the presence of three coordinating N-atoms on the terpy molecule, the complexation process with terpy can be different in comparison with bipy and phen and lead to the formation of new species and to the expulsion of nitrate. Some results are available from the research on the Ln−terpy systems.[22−31] However, most of the

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⊗ Abstract published in *Advance ACS Abstracts,* June 1, 1995.

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data characterized the terpy complexes in the solid state and only a few have been reported with La(III).

From the present multi-NMR results, it is shown how the coordination number and the molecular structures of the solvated La(III) complexes with terpy can be determined. The equilibrium scheme of the La(III) complexation with terpy is given. Finally, X-ray data are reported and prove useful in identifying the La(III) species present in solution.

Experimental Section

Materials and Samples. $La(NO_3)_3{\cdot}6H_2O$ (Aldrich, 99.99%) was kept in a desiccator over drierite and used as received. 2,2′:6′,2″-Terpyridine (terpy) (Aldrich, 98%) and acetonitrile-d_3 (Aldrich, 99% D) were used as received. Acetonitrile (BDH) was dried as previously described.[20] All solutions and NMR samples were prepared and kept under argon and then sealed with Parafilm.

NMR Measurements. ^{139}La, ^{17}O, and ^{1}H NMR spectra were recorded at 25.0 ± 0.5 °C on a Varian XL-300 spectrometer using resonance frequencies of 42.37, 40.66, and 299.94 MHz respectively. No lock was used (except for ^{1}H NMR), the field drift being negligible. Additional technical information and NMR standards were previously described.[20]

For the recording of the ^{139}La NMR spectra, a delay of 30 μs between the end of the pulse and the start of the acquisition was chosen to minimize baseline distortion. For $0 < \varrho = [terpy]_0/[La(III)]_0 < 1.070$, because of slow exchange between different ^{139}La sites, a curve-fitting analysis was used to obtain the intensities (I), line widths ($\upsilon_{1/2}$), and chemical shifts (δ) of the decomposed signals.

The ^{17}O NMR water signal is easily detectable but the nitrate signal was only observed at high concentrations after overnight accumulations and in absence of terpy. When terpy is added to the $La(NO_3)_3{\cdot}6H_2O$ solutions, precipitation occurs rapidly, and no NMR nitrate signal was detected.

Crystallographic Analysis. Crystalline $[La(NO_3)_2(terpy)_2][La(NO_3)_4(terpy)]{\cdot}CH_3CN{\cdot}0.5H_2O$ was precipitated from the NMR sample when $\varrho = [terpy]_0/[La(III)]_0 = 8$ with $[La(III)]_0 = 5.32 \times 10^{-3}$ M. The compound was kept at 5 °C for, at least, a month to observe the crystallization. The crystals were isolated by decantation.

Data Collection. A crystal of $La_2N_{16}O_{18}C_{47}H_{33}{\cdot}0.5H_2O$ having dimensions of 0.2 × 0.1 × 0.3 mm was mounted on a glass capillary. All the measurements were made on a Rigaku diffractometer with Mo Kα radiation.

The cell constants and the orientation matrix for data collection were obtained from least-squares refinement using the setting angles of 25 reflections in the range $30 < 2\theta < 40$, and they corresponded to a triclinic cell with dimensions: $a = 14.979(4)$ Å, $b = 17.501(10)$ Å, $c = 11.603(5)$ Å, $\alpha = 106.34(4)$, $\beta = 94.22(3)$, $\gamma = 83.30(3)$. For $Z = 2$ and fw = 1395.67, the calculated density is 1.600 g/cm³. On the basis of the systematic absence, the space group was determined to be $P\bar{1}$.

The data were collected at a temperature of 22 °C using the $\omega-2\theta$ scan technic to a maximum 2θ value of 40°. It was impossible to go higher in 2θ, because the crystal decomposed.

Data Reduction. A total of 5338 reflections were collected. The unique set contains only 5063 reflections. The standards were measured after every 150 reflections. A crystal decay was noticed. The three standards dropped by 25.6% in average during the data collection. The data were collected for Lorentz and polarization effects.[32] No absorption correction was made because the crystal died during the data collection. Efforts to obtain new crystals were made, but were unsuccessful.

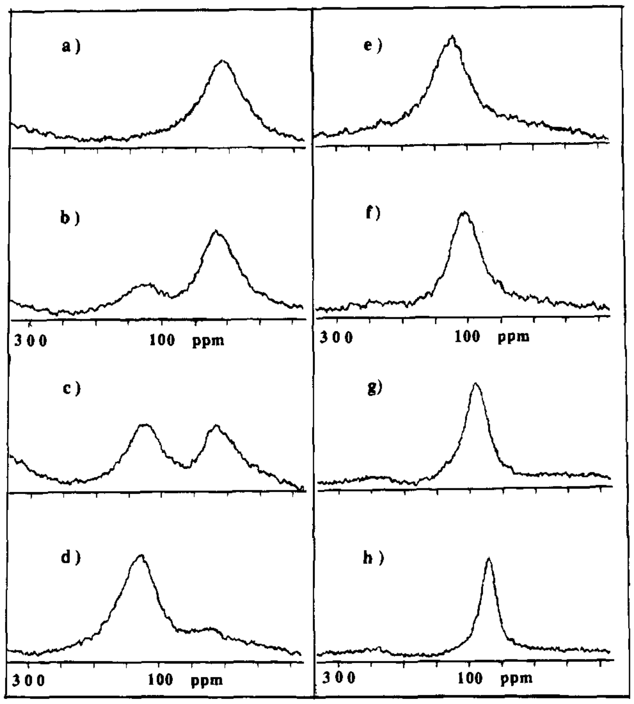

Figure 1. ^{139}La NMR spectra at 42,37 MHz of $La(NO_3)_3{\cdot}6H_2O$ in CH_3CN in the presence of increasing concentration of terpy. $\varrho = [terpy]_0/[La(III)]_0 = 5.32 \times 10^{-3}$ M. Key: (a) $\varrho = 0$; (b) $\varrho = 0.31$; (c) $\varrho = 0.62$; (d) $\varrho = 0.92$; (e) $\varrho = 1.07$; (f) $\varrho = 1.38$; (g) $\varrho = 2.04$; (h) $\varrho = 7.98$.

Solution and Refinement. The structure was solved by direct methods. All the atoms were refined anisotropically except the hydrogens. The hydrogen atoms were calculated. The final cycle of full matrix least-squares refinement was based on 4012 observed reflections ($I > 2.5\sigma(I)$) and 738 variable parameters. Weights based on counting statistics were used. The maximum and minimum peaks on the final differences Fourier map corresponded to 1.200 and −1.200 e/Å³, respectively.

All the calculations were performed using the NRCVAX crystallographic software package.[33]

Results

^{139}La NMR Data. Some of the ^{139}La NMR spectra obtained when terpy was increasingly added to a 5.32×10^{-3} M $La(NO_3)_3{\cdot}6H_2O$ in CH_3CN are shown in Figure 1. In absence of terpy ($\varrho = [terpy]_0/[La(III)]_0 = 0$), the ^{139}La spectrum of $La^{3+}(s)$ is characterized by a single Lorentzian line with a chemical shift, $\delta = 11 \pm 4$ ppm, and a line width value, $\upsilon_{1/2} = 2.98 \pm 0.10$ kHz, in agreement with previous data.[20,21]

With the addition of terpy, at least two other ^{139}La sites can be identified. A first complex species appears at $\varrho < 1.1$. The corresponding NMR spectra show two sites in slow exchange. As observed, the signal intensities are dependent on $[terpy]_0$ but the δ and $\upsilon_{1/2}$ values remain unchanged. These two signals have been identified as the solvated species $La^{3+}(s)$ and $La(terpy)^{3+}(s)$, the latter species appearing downfield around $\delta = 125$ ppm.

For $\varrho > 1.1$, spectra clearly indicate the presence of at least one other ^{139}La site in fast exchange with $La(terpy)^{3+}(s)$ (see Figure 1). Indeed, the ^{139}La NMR spectra consist of a single

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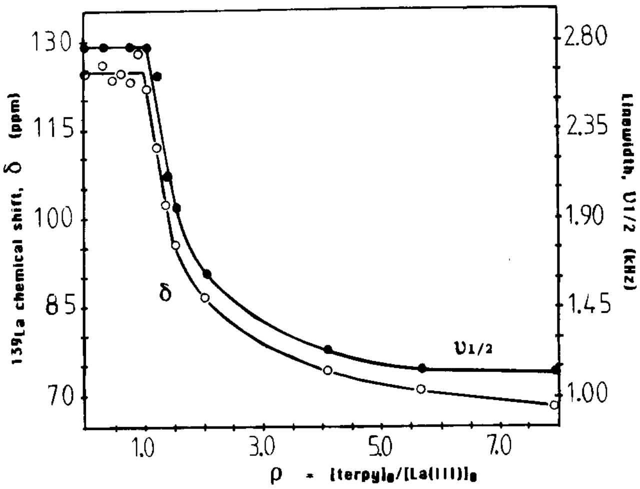

Figure 2. Variation of the chemical shift, δ, and line width, $v_{1/2}$, of the ^{139}La resonances when terpy is increasingly added in a solution of $La(NO_3)_3{\cdot}6H_2O$ in CH_3CN. $[La(III)]_0 = 5.32 \times 10^{-3}$ M.

Table 1. Chemical Shift, δ, and Line Width, $v_{1/2}$, of the ^{139}La Resonances

species	δ, ppm	$v_{1/2}$, kHz
$La(NO_3)_3(s)$	11 ± 4	2.98 ± 0.10
$La(NO_3)_3(terpy)(s)$	125 ± 3	2.78 ± 0.10
$La(NO_3)_4(terpy)^-(s)$	125 ± 3	2.78 ± 0.10
$La(NO_3)_2(terpy)_2{}^+(s)$	68 ± 1	1.12 ± 0.01
$La(NO_3)_3(s)^a$	10 ± 5	2.9 ± 0.3
$La(NO_3)_3(bipy)(s)^a$	82 ± 6	>3.0
$La(NO_3)_3(bipy)_2(s)^a$	150	
$La(NO_3)_3(s)^b$	10 ± 4	2.9 ± 0.2
$La(NO_3)_3(phen)(s)^b$	80 ± 5	2.35 ± 0.15
$La(NO_3)_3(phen)_2(s)^b$	150 ± 6	2.06 ± 0.09

[a] From ref 21. [b] From ref 20.

Lorentzian line appearing increasingly upfield as ϱ rises. This behavior reflects the formation of $La(terpy)_2{}^{3+}(s)$ which is completed when δ = 68.4 ppm.

Additional information about species in solution can be obtained from Figure 2 showing how the δ and $v_{1/2}$ of the ^{139}La signal vary for $1 < \varrho < 8$. For ϱ = 1.0 up to 1.5, the δ and $v_{1/2}$ values vary linearly with ϱ whereas for $\varrho > 1.5$ the δ and $v_{1/2}$ variations are much slower. According to equilibrium laws, these sudden changes in the trend of the δ and $v_{1/2}$ variations around ϱ = 1.5 can only be explained if in addition to the formation of the $La(terpy)_2{}^{3+}(s)$ species, another La(III) species is also formed in solution. The presence of this additional species is confirmed with the help of the crystallographic data and may be described as another 1:1 La(III)−terpy complex containing an additional nitrate group in its inner sphere (see discussion). The ^{139}La NMR spectra data are summarized in Table 1.

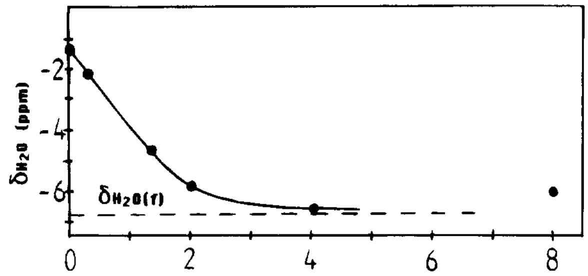

Figure 3. ^{17}O NMR chemical shift of H_2O as a function of $\varrho = [terpy]_0/[La(III)]_0$ with $[La(III)]_0 = 5.32 \times 10^{-3}$ M.

Table 2. Chemical Shift, δ, and Line Width, $v_{1/2}$, of the H_2O and NO_3^- ^{17}O Resonances

		NO_3^-	
	H_2O δ, ppm	δ, ppm	$v_{1/2}$, kHz
$La(NO_3)_3{\cdot}6H_2O$ + terpy in CH_3CN			
(a) $[La(III)]_0 = 5.32 \times 10^{-3}$ M			
ϱ = 0	−1.28	*d*	*d*
ϱ = 0.31	−2.16	*d*	*d*
ϱ = 1.38	−4.74	*d*	*d*
ϱ = 2.04	−5.89	*d*	*d*
ϱ = 4.08	−6.63	*d*	*d*
ϱ = 7.98	−6.10	*d*	*d*
(b) $[La(III)]_0 = 2.70 \times 10^{-2}$ M			
ϱ = 0	3.31	425 ± 1	1.15 ± 0.10
$\varrho > 1.5^a$	−6.73 ± 0.02	*d*	*d*
$H_2O(f)^b$	−6.88		
$KNO_3(satd)^c$	−6.16	427	0.15
$NH_4NO_3(satd)^c$	−6.01	423	0.15
$NO_3^-(c)^c$		425 ± 3	1.3 ± 0.2

[a] From precipitated solutions with $[La(III)] > 1.6 \times 10^{-2}$ M. [b] From ref 20. [c] From ref 21. [d] Not observed.

^{17}O NMR Data. ^{17}O NMR spectra were recorded on solutions of $La(NO_3)_3{\cdot}6H_2O$ (5.32×10^{-3} M) in CH_3CN with increasing terpy concentrations. The titration curve showing the chemical shift of H_2O, $\delta(H_2O)$, against ϱ is illustrated in Figure 3. The steady upfield shift variations of H_2O with the addition of terpy indicate that the H_2O molecules, initially coordinated to the La(III) ions, are expelled from the coordination sphere during the complexation reaction. Indeed, the water triplet resonance[34] drawns near to the chemical shift of free water in CH_3CN which is −6.88 ppm. After reaching a value as low as −6.63 ppm, $\delta(H_2O)$ moves slightly downfield, possibly due to specific interactions between H_2O and the uncomplexed terpy or the free NO_3^- ions which are expelled from the La(III) coordination sphere. Curiously, the $\delta(H_2O)$ value of −6.10 ppm now obtained when ϱ = 7.98, agrees with the chemical shift of the residual water in CH_3CN saturated with KNO_3 or NH_4NO_3 ($\delta(H_2O) = -6.08 \pm 0.08$ ppm) (Table 2).

Contrary to the H_2O signal, the NO_3^- resonance could not be detected from the $La(NO_3)_3{\cdot}6H_2O$ solutions having concentrations lower than 1.0×10^{-2} M because of the large line width value of coordinated NO_3^- (1.3 ± 0.2 kHz).[21] No signal for nitrate was observed although it is partially displaced. This is the likely result of a fast exchange between the free NO_3^- (=0.15 kHz) and the remaining coordinated NO_3^- (=1.15 kHz) which gives populated-averaged line widths still too large to be detected. The NO_3^- signal was only observed when $[La(III)]_0 = 2.70 \times 10^{-2}$ M for ϱ = 0; $\delta(NO_3^-) = 425 \pm 1$ ppm, and $v_{1/2}(NO_3^-) = 1.15 \pm 0.10$ kHz. However, when terpy was added to the La(III) solution, an insoluble La(III) complex was rapidly precipitated and no NO_3^- signal was observed. Only the H_2O resonance at −6.73 ± 0.02 ppm could be detected. Finally, a terpy−La(III) solution was prepared with $[La(III)]_0 = 1.62 \times 10^{-2}$ M, but precipitation also occurred while recording the spectrum.

^1H NMR Data. The ^1H NMR data were recorded on solutions of terpy (3.75×10^{-3} M) in CH_3CN with increasing amounts of $La(NO_3)_3{\cdot}6H_2O$ so that $0 < R = [La(III)]_0/[terpy]_0 < 1.7$. Both the water and terpy resonances were observed.

The water titration curve illustrating $\delta(H_2O)$ against *R* is shown in Figure 4. Results first indicate the absence of water

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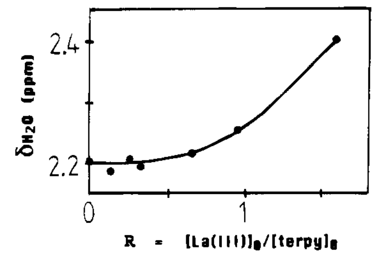

Figure 4. 4. ^{1}H NMR chemical shift of H_2O as a function of R = $[La(III)]_0/[terpy]_0$ with $[terpy]_0 = 3.75 \times 10^{-3}$ M.

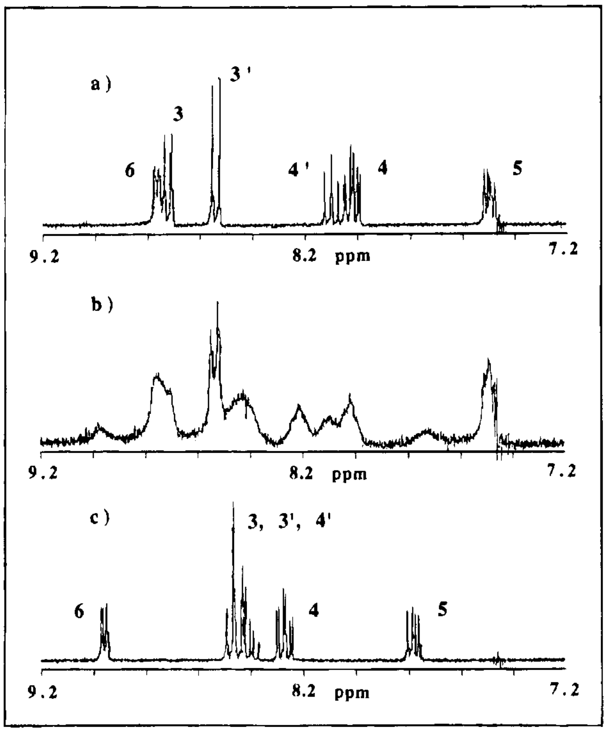

Figure 5. ^{1}H NMR spectra of terpy in CH_3CN for different values of R. $R = [La(III)]_0/[terpy]_0$ with $[terpy]_0 = 3.75 \times 10^{-3}$ M. Key: (a) R = 0; (b) R = 0.31; (c) R = 1.60.

in the coordination sphere of the $La(terpy)_2^{3+}(s)$ species because for $R < 0.3$, the water chemical shifts ($\delta(H_2O) = 2.20 \pm 0.01$ ppm) are identical to the chemical shift of the residual free water in the terpy solution. For $R > 0.3$, the water peak appears increasingly downfield in agreement with the presence of coordinated water in the inner sphere of the other La(III) species.

The proton chemical shifts of the dissolved terpy in CH_3CN is shown in Figure 5a, the proton assignment agreeing with the study of Lytle et al.[35] With the addition of $La(NO_3)_3{\cdot}6H_2O$, another series of terpy sites are observed. These sites characterize the complexed terpy. Because of a moderately slow exchange between the free and complexed terpy (up to R = 1.0), the two series of ^{1}H signals appear as large peaks instead of multiplets and show variable intensities related to the populations of the free and complexed terpy in solution (see Figure 5b). Finally, for $R > 1.0$, the well resolved multiplets only indicate the presence of complexed terpy (see Figure 5c) with $\delta(H_i)$ values characterizing the terpy in the $La(terpy)^{3+}(s)$ complex.

It can also be observed that the H-4 and H-5 chemical shifts of complexed terpy (terpy (c)) appear slightly more downfield as the R value increases, the total shift variations being 0.07 and 0.08 ppm respectively. These small variations are the result of the presence of two sets of resonances for H-4 and H-5, one for terpy in $La(terpy)^{3+}(s)$ and one for terpy in $La(terpy)_2^{3+}(s)$. The chemical shifts of H-4 and H-5 of terpy in $La(terpy)_2^{3+}(s)$ appears respectively 0.07 and 0.08 ppm more upfield than terpy in $La(terpy)^{3+}(s)$. According to similar studies,[20,21] the distinction between the two types of complexed terpy should be attributed to the presence of an anisotropic contribution in the $La(terpy)_2^{3+}(s)$ species due to the proximity of two terpy moieties. The ^{1}H NMR data are given in Table 3.

Table 3. ^{1}H NMR Spectral Data

	δ (±0.01 ppm)					
species	H-3	H-3′	H-4	H-4′	H-5	H-6
terpy(f)	8.72	8.54	8.02	8.10	7.49	8.76
terpy(1:1)	8.45[a]	8.47[a]	8.27	8.39[a]	7.78	8.96
terpy(1:2)	8.42[b]	8.42[b]	8.20	8.42[b]	7.70	8.96
bipy(f)	8.47		7.95		7.44	8.71
bipy(1:1)	8.38		8.20		7.70	8.87
bipy(1:2)	8.41		8.08		7.56	8.74

[a] Hard to identify; averaged value 8.43 ± 0.04 ppm. [b] Averaged value: large signal.

Table 4. Crystallographic Data for $[La(NO_3)_2(terpy)_2][La(NO_3)_4(terpy)]{\cdot}CH_3CN{\cdot}{}^1/_2H_2O$

chem	$La_2N_{15}O_{18}C_{45}H_{33}$ +	V	2896.3 Å^3
formula	$^1/_2$ H_2O + CH_3CN	Z	2
fw	1395.67	space group	$P\bar{1}$
a, Å	14.979(4)	T, °C	22
b, Å	17.501(10)	λ, Å	0.709 30 (Mo Kα)
c, Å	11.603(5)	ϱ_{obsd}, g cm^{-3}	1600
α, deg	106.34(4)	μ, mm^{-1}	0.77
β, deg	94.22(3)	R^a	0.053
γ, deg	83.30(3)	$R_w{}^b$	0.063

[a] $R = \sum(F_o - F_c)/\sum F_o$. [b] $R_w = (\sum w(F_o - F_c)^2/\sum w(F_o)^2)^{1/2}$.

Crystallographic Data. Figure 6 shows the ORTEP drawings of $[La(NO_3)_2(terpy)_2]^+$ and $[La(NO_3)_4(terpy)]^-$. Each complex ion is shown in an orientation which emphasizes its structure. Important bond lengths and angles are given in Table 5; atomic parameters x, y, z, and B_{iso} are reported in Table 6.

The lanthanum ion in $[La(NO_3)_2(terpy)_2]^+$ is 10-coordinate with six nitrogens and four oxygens from two chelating terpy and two bidentate NO_3^- respectively. In $[La(NO_3)_4(terpy)]^-$, the lanthanum ion is 11-coordinate with four NO_3^- and one terpy acting as chelating ligands. The averaged La–N and La–O bond distances, in both the cationic and anionic La(III) complex species, are 2.68(3) and 2.63(5) Å and are typical of the corresponding La–N and La–O bond distances (2.67(3) and 2.60(2) Å, respectively) previously found in the $La(bipy)_2(NO_3)_3$[36] and $La(NO_3)_3(phen)_2$[20] complexes. However in each complex, one La–N bond distance is longer than expected (La(1)–N(4) = 2.74 Å and La(2)–N(9) = 2.77 Å) but is still in agreement with the La–N distances of 2.755 Å previously found in $[La(EDTA)(H_2O)_3]^-$.[37]

According to a study of Durham and colleagues,[22] the terpy molecule planarly bound to La should lead to La–N bond distances of 2.5 Å. It is clear from our data that distortions of the terpyridine system occurred. The dihedral angles between two planes belonging to the same terpy molecule show deviations as large as 4.8–28.6° with an average value around 16°. However, it is not necessarily the nitrogens belonging to the most distorted planes which form the longest La–N bonds.

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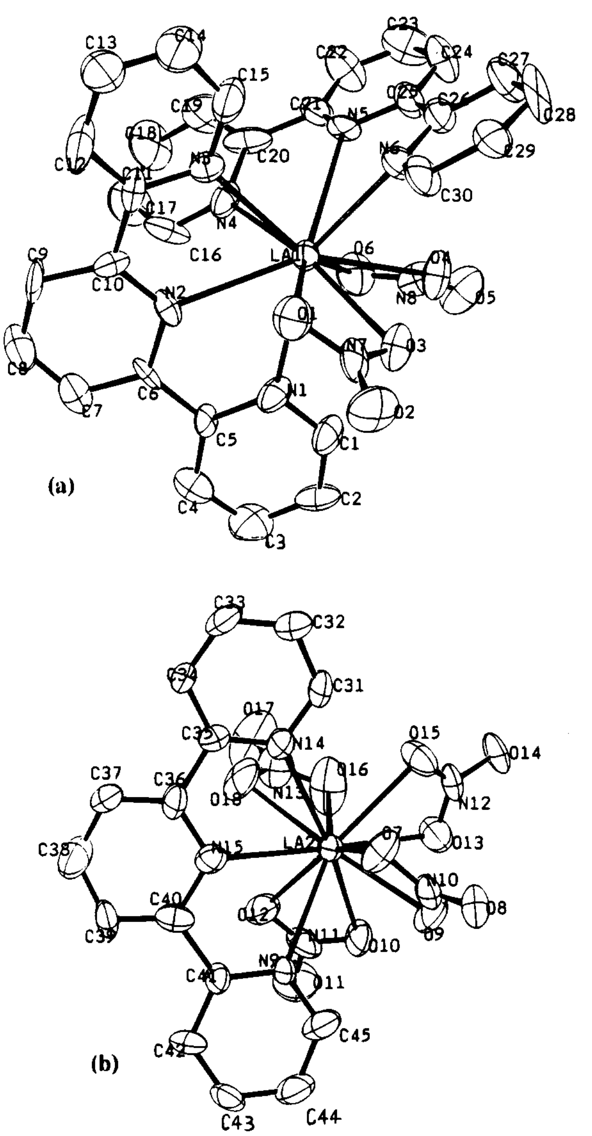

Figure 6. ORTEP drawing and numbering scheme of (a) [La(NO$_3$)$_2$(terpy)$_2$]$^+$ (b) [La(NO$_3$)$_4$(terpy)]$^-$.

Table 5. Selected Bond Lengths and Bond Angles

[La(NO$_3$)$_2$(terpy)$_2$]$^+$ molecule 1		[La(NO$_3$)$_4$(terpy)]$^-$ molecule 2	
	Bond Lengths (Å)		
La(1)−N(1)	2.673(13)	La(2)−N(9)	2.769(12)
La(1)−N(2)	2.681(11)	La(2)−N(14)	2.705(13)
La(1)−N(3)	2.649(12)	La(2)−N(15)	2.709(13)
La(1)−N(4)	2.736(13)	La(2)−O(7)	2.608(13)
La(1)−N(5)	2.685(10)	La(2)−O(9)	2.644(12)
La(1)−N(6)	2.674(12)	La(2)−O(10)	2.602(11)
La(1)−O(1)	2.627(11)	La(2)−O(12)	2.616(12)
La(1)−O(3)	2.646(11)	La(2)−O(13)	2.656(12)
La(1)−O(4)	2.633(10)	La(2)−O(15)	2.605(11)
La(1)−O(6)	2.636(11)	La(2)−O(16)	2.602(13)
		La(2)−O(18)	2.684(13)
	Bond Angles (deg)		
N(1)−La(1)−N(2)	60.5(4)	N(9)−La(2)−N(15)	59.0(4)
N(2)−La(1)−N(3)	61.4(4)	N(14)−La(2)−N(15)	59.1(4)
N(4)−La(1)−N(5)	61.9(4)		
N(5)−La(1)−N(6)	60.1(4)		
N(1)−La(1)−N(3)	121.5(4)	N(9)−La(2)−N(14)	111.9(4)
N(4)−La(1)−N(6)	119.0(4)		

Distortion from planarity is common to the geometry of complexed terpy[24,38] and could be attributed to steric and ligand−ligand interactions.[24] The increase of the La−N bond and rotation of the rings could also represent the best compromise for bringing the coordinated atoms as close as possible to the La(III) ion and minimizing the van der Waals repulsions between the terpy hydrogen atoms.[38]

Discussion

According to previous papers,[20,21] it was concluded that when La(NO$_3$)$_3$·6H$_2$O is dissolved in CH$_3$CN, the three NO$_3^-$ ions belong to the La(III) coordination sphere of the solvated La(III) species, La^{3+}(s). The presence of the three nitrate groups in the inner sphere of La(III)(s) agrees with the low molar conductivity values obtained for La(NO$_3$)$_3$ in CH$_3$CN by Forsberg and Wathen[39] and with the constant ^{139}La NMR chemical shift variations observed for the progressive addition of NBu$_4$NO$_3$ to La(ClO$_4$)$_3$ in acetonitrile reported by Evans and Missen.[40] Therefore, La^{3+}(s) is better defined as La(NO$_3$)$_3$(s).

As recently shown by using a multi-NMR analysis,[20,21] the La(NO$_3$)$_3$(s) corresponds to the La(NO$_3$)$_3$(CH$_3$CN)$_4$ species in equilibrium with La(NO$_3$)$_3$(CH$_3$CN)$_3$(H$_2$O).[21] The presence of four additional "solvent" molecules (CH$_3$CN, H$_2$O) in the inner sphere complexes is in good agreement with the spectroscopic conclusions of investigations concerning the lanthanide(III) nitrate solvation in aqueous and organic solvents, previously reported by Bunzli et al.[41−43] Also, as shown by the ^{17}O NMR data, some water is initially coordinated to La(III). As expected by the Le Chatelier principle, the amount of coordinated water increases when dissolving La(NO$_3$)$_3$·6H$_2$O in increasing concentrations. Furthermore, according to the thermodynamics of equilibrium, the amount of coordinated water is very low because by quintupling [La(III)]$_0$ (see Table 2), the ^{17}O chemical shift of water is dramatically changed. That amount of coordinated water was estimated to be less than one molecule, as discussed in a previous paper,[21] leading to an equilibrium between an aquo and anhydrous complex species, each having a coordination number of 10. However because the coordinated and free water are in fast exchange on the ^{139}La NMR time scale, only a single ^{139}La resonance is observed. This resonance line is characterized by weight averaged δ and $v_{1/2}$ values which are 11 ± 4 ppm and 2.98 ± 0.10 kHz respectively (see Table 1).

The first La(III) complex of terpy appears 114 ppm downfield on the ^{139}La NMR scale and shows spectroscopic similarities with the phen and bipy complexes of La(III) previously described.[20,21] For each bidentate phen or bipy molecule added in the coordination sphere of La(NO$_3$)$_3$(s), an averaged constant chemical shift variation ($\Delta\delta$) of 70 ppm was observed. According to the monotonic relationships usually obtained between δ and the number of coordinated atoms,[40,43] a value of 105 ppm was expected for the addition of the first terpy molecule. The experimental value of 114 ppm is within the experimental error and confirms the presence of terpy as a tridentate ligand.

The constant high ^{139}La frequency shift of *ca.* 38 ppm found here for the bonding of each N-atom of terpy also suggests that H$_2$O and CH$_3$CN are simultaneously expelled from the coordination sphere with the addition of terpy, just as in the case of phen and bipy.[20,21] Furthermore, we do believe that the

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Table 6. Atomic Parameters x, y, z, and B_{iso} Where Esds Refer to the Last Digit Printed

	x	y	z	B_{iso},[a] Å^2		x	y	z	B_{iso},[a] Å^2
La(1)	0.61330(6)	0.74660(5)	0.09267(8)	2.31(4)	C(6)	0.4508(10)	0.6028(8)	0.0131(14)	2.6(7)
La(2)	0.16966(6)	0.67155(6)	−0.37352(8)	2.88(5)	C(7)	0.3735(11)	0.5692(10)	0.01174(16)	3.7(9)
N(1)	0.5667(9)	0.6297(8)	−0.0985(11)	3.4(7)	C(8)	0.3333(12)	0.5845(11)	0.1239(17)	4.5(10)
N(2)	0.4900(8)	0.6524(7)	0.1133(11)	2.7(6)	C(9)	0.3710(11)	0.6317(10)	0.2274(16)	3.7(9)
N(3)	0.5572(9)	0.7598(8)	0.3093(10)	3.2(7)	C(10)	0.4515(11)	0.6625(9)	0.2180(13)	2.8(7)
N(4)	0.4520(9)	0.8388(8)	0.1006(12)	3.4(7)	C(11)	0.4966(11)	0.7127(10)	0.3279(15)	3.5(9)
N(5)	0.6127(9)	0.9056(6)	0.1840(11)	2.7(6)	C(12)	0.4781(13)	0.7122(14)	0.4436(17)	5.4(12)
N(6)	0.7519(8)	0.8072(7)	0.2338(11)	2.9(6)	C(13)	0.5205(14)	0.7582(12)	0.5426(16)	5.2(11)
N(7)	0.7499(8)	0.5988(8)	0.0770(11)	3.3(7)	C(14)	0.5804(14)	0.8044(14)	0.5238(16)	6.0(13)
N(8)	0.6668(10)	0.8183(8)	−0.1024(12)	3.8(7)	C(15)	0.5969(12)	0.8038(13)	0.4042(16)	4.9(11)
N(9)	0.0926(8)	0.5743(8)	−0.5784(11)	3.2(7)	C(16)	0.3732(12)	0.8056(9)	0.0689(17)	4.4(9)
N(10)	0.2739(9)	0.5056(9)	−0.4097(12)	3.8(8)	C(17)	0.2918(14)	0.8506(13)	0.0790(22)	6.4(13)
N(11)	0.1460(10)	0.7376(10)	−0.5900(12)	4.7(9)	C(18)	0.2903(14)	0.9311(15)	0.1226(23)	7.3(14)
N(12)	0.3535(8)	0.7114(7)	−0.2580(12)	3.3(7)	C(19)	0.3694(15)	0.9662(11)	0.1542(21)	6.4(12)
N(13)	0.1148(11)	0.8484(9)	−0.2522(16)	5.8(10)	C(20)	0.4525(13)	0.9199(9)	0.1408(15)	4.2(10)
N(14)	0.0963(9)	0.6636(10)	−0.1715(12)	4.3(8)	C(21)	0.5419(11)	0.9540(9)	0.1634(15)	3.5(8)
N(15)	−0.0017(9)	0.6351(7)	−0.3782(11)	3.0(6)	C(22)	0.5425(14)	1.0323(11)	0.1671(20)	5.6(11)
N(16)	1.0607(21)	0.8992(19)	0.086(3)	13.6(9)	C(23)	0.6242(16)	1.0597(10)	0.1855(20)	6.1(12)
O(1)	0.6885(8)	0.6189(7)	0.1522(10)	4.1(6)	C(24)	0.7014(13)	1.0118(11)	0.2057(19)	5.2(11)
O(2)	0.8007(8)	0.5374(7)	0.0682(11)	5.0(6)	C(25)	0.6937(12)	0.9359(10)	0.2065(15)	3.7(9)
O(3)	0.7578(7)	0.6478(7)	0.0165(10)	3.8(6)	C(26)	0.7696(11)	0.8811(10)	0.2402(14)	3.3(8)
O(4)	0.7249(8)	0.7884(7)	−0.0384(10)	4.3(6)	C(27)	0.8519(12)	0.9089(11)	0.2796(18)	4.7(10)
O(5)	0.6912(9)	0.8430(8)	−0.1820(11)	5.8(7)	C(28)	0.9201(12)	0.8558(13)	0.3153(19)	5.6(12)
O(6)	0.5854(8)	0.8156(8)	−0.0834(10)	4.7(6)	C(29)	0.9005(12)	0.7831(10)	0.3187(15)	3.9(9)
O(7)	0.2116(8)	0.5303(7)	−0.3399(11)	5.1(7)	C(30)	0.8176(11)	0.7576(10)	0.2751(15)	3.5(9)
O(8)	0.3218(8)	0.4427(8)	−0.4173(11)	5.2(7)	C(31)	0.1482(12)	0.6620(13)	−0.0712(16)	4.9(11)
O(9)	0.2916(8)	0.5530(8)	−0.4691(10)	4.8(6)	C(32)	0.1125(13)	0.6729(14)	0.0388(15)	5.6(12)
O(10)	0.2203(8)	0.6977(8)	−0.5676(10)	4.6(7)	C(33)	0.0216(13)	0.6858(13)	0.0466(15)	5.1(10)
O(11)	0.1378(11)	0.7595(11)	−0.6808(13)	8.2(11)	C(34)	−0.0322(11)	0.6848(11)	−0.0553(14)	4.1(10)
O(12)	0.0843(8)	0.7482(7)	−0.5192(10)	4.9(6)	C(35)	0.0069(11)	0.6743(10)	−0.1622(13)	3.4(9)
O(13)	0.3344(8)	0.7158(9)	−0.3633(11)	5.4(7)	C(36)	−0.0472(11)	0.6686(10)	−0.2772(15)	3.2(9)
O(14)	0.4232(8)	0.7339(8)	−0.2058(11)	5.2(7)	C(37)	−0.1378(12)	0.6934(11)	−0.2755(14)	4.0(9)
O(15)	0.2970(8)	0.6881(8)	−0.2055(10)	4.7(7)	C(38)	−0.1829(13)	0.6818(12)	−0.3836(18)	5.4(11)
O(16)	0.1906(10)	0.8229(8)	−0.2888(17)	7.9(10)	C(39)	−0.1438(11)	0.6428(10)	−0.4917(16)	3.7(9)
O(17)	0.0897(12)	0.9202(9)	−0.2147(19)	9.8(12)	C(40)	−0.0523(12)	0.06227(9)	−0.4870(14)	3.3(9)
O(18)	0.0579(9)	0.7992(8)	−0.2669(12)	6.0(8)	C(41)	0.0022(10)	0.5838(9)	−0.5930(13)	2.8(8)
O(19)	0.304(3)	0.892(3)	0.456(4)	12.6(13)	C(42)	−0.0408(12)	0.5548(10)	−0.7047(13)	3.5(9)
C(1)	0.6095(11)	0.6180(11)	−0.2012(15)	3.8(10)	C(43)	0.0090(12)	0.5187(10)	−0.8018(14)	3.7(8)
C(2)	0.5832(13)	0.5706(10)	−0.3092(14)	4.1(9)	C(44)	0.1014(13)	0.5097(11)	−0.7873(15)	4.7(10)
C(3)	0.5118(13)	0.5284(12)	−0.3126(16)	5.1(10)	C(45)	0.1405(13)	0.5372(11)	−0.6737(15)	4.6(9)
C(4)	0.04661(12)	0.5380(10)	−0.2077(16)	4.2(9)	C(46)	0.9967(21)	0.9007(19)	0.025(3)	10.2(8)
C(5)	0.4953(9)	0.5888(9)	−0.1014(13)	2.3(8)	C(47)	0.9122(20)	0.9061(17)	−0.036(3)	9.2(7)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

coordination number of the 1:1 La(III)−terpy complex is 10 as are the ones found for the corresponding bipy and phen complexes as well as for La^{3+}(s). These expectations are deduced from similarities in the bipy, phen, and terpy behaviors. Moreover, dramatic changes in the magnitude and/or direction of the $\Delta\delta$ values were previously obtained following a variation in the coordination number,[40] with the addition of different ligands in the La(III) coordination sphere,[40,44] or the expulsion of various species from the inner sphere complexes.[40,44]

The water expulsion is confirmed by the constant upfield shift of the water ^{17}O NMR signal with the addition of terpy, indicating an increasing amount of noncoordinated water. However, at $\varrho = 1.00$, the chemical shift of water dissolved in CH_3CN has not been reached, meaning that water is only partially expelled from the inner sphere with the addition of the first terpy molecule. Moreover, we must assume that because the coordination number is 10 and less than one water molecule is still coordinated, CH_3CN is also present in the La(III) coordination sphere. Indeed, even if H_2O is a very good competitor with respect to CH_3CN, the huge difference in H_2O and CH_3CN concentrations indicates that both species are simultaneously coordinated and share the last coordination site.

Finally, the three coordinated nitrate ions are not released when $La(terpy)^{3+}$(s) is formed. Indeed, even if the ^{17}O NMR experiments did not permit the detection of the NO_3^- signal, many works prove that they are strongly bonded and not easily expelled. In a calorimetric and conductimetric study, Forsberg shows that the more basic ligand diethylenediamine (dien), used instead of terpy in the complexation reaction, does not displace NO_3^- when the first ligand molecule is added.[16] Also the reported studies with phen and bipy clearly indicate that two molecules of bases (four N-atoms) can be added without expelling the NO_3^-.[20,21]

According to the present results the 1:1 La(III)−terpy complex is best described by an equilibrium between $La(NO_3)_3(terpy)(CH_3CN)$ and $La(NO_3)_3(terpy)(H_2O)$. The coordination number of La(III) is 10 with three bidentate NO_3^-, one tridentate terpy, and one CH_3CN or water molecule completing the inner sphere complexes. The above description of the 1:1 complex is in agreement with a previous work of Melby et al.[29] reporting the formation of $[Tb(NO_3)_3(terpy)(H_2O)]$. It was also shown by Durham et al.[45] that the tridentate ligand, 2,4,6-tri-α-pyridyl-1,3,5-triazine (TPT) reacts with the lanthanide nitrate to give $[Ln(TPT)(NO_3)_3(H_2O)]$. Futhermore, in a recent paper, Piguet et al.[19] showed that the ligand 2,6-bis(1-methylbenzimidazol-2-yl)pyridine (mbzimpy), analogous to terpy, reacts with Eu(III) in methanol to give $[Eu(mbzimpy)(NO_3)_3(CH_3OH)]$. Studies with other analogues of terpy, but

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more substituted, led to complexes having no coordinated solvent molecule, a probable consequence of the greater steric requirements of the ligands.[15,19]

The ^{139}La NMR data are also indicative of the formation of the $La(terpy)_2^{3+}(s)$ species for $\varrho > 1.0$. For this particular complexation step, the dramatic changes in the magnitude and direction of the chemical shift variations suggest either a change in the coordination number of the La(III) ions, or the addition/expulsion of new ligands in/from the inner sphere, or both.

The most revealing structural conclusions are obtained from the crystallographic analysis. The ORTEP representation (Figure 6) shows the formation of a cationic 1:2 complex arising from the expulsion of both one coordinated nitrate ion and the remaining solvating CH_3CN/H_2O molecules from the inner sphere of the 1:1 complex. That result is particularly interesting because previous conclusions led us to believe that weakly basic N-donors (such as terpy, phen, and bipy) could not displace the NO_3^- anions from the coordination sphere.[16] Surprisingly, terpy competes effectively with the nitrate ligand, and the apparent ease with which the first NO_3^- is replaced looks really promising for further works.

The stoichiometry of the cationic 1:2 complex isolated in the solid state persists in acetonitrile solution as exemplified by ^{1}H and ^{17}O NMR measurements. Indeed, both methods indicate that solutions containing large excesses of terpy i.e. for which the presence of the 1:2 complex is exclusive or highly preponderant, are characterized by a water chemical shift very similar to the chemical shift of free water in CH_3CN. Therefore, water is not present in the coordination sphere of the 1:2 complex in solution. Consequently, CH_3CN must also be absent because H_2O always competes with CH_3CN for the available coordination sites.

No direct NMR information was obtained to confirm the expulsion of NO_3^-, but the value of −6.10 ppm found here for the ^{17}O NMR resonance of water when $\varrho = 7.98$ led us to believe that it is a likely result of specific interactions between H_2O and the free NO_3^-. Moreover, the residual water in saturated solution of KNO_3 or NH_4NO_3 also resonates at the same frequency (6.08 ± 0.08 ppm). The release of one NO_3^- anion is in good agreement with the conductimetric study of Forsberg and Wathen.[39] Indeed, the conductance titration curve of $Nd(NO_3)_3$ with diethylenetriamine (dien) is characterized by a sharp increase in conductivity between the 1:1 and 2:1 ligand to metal mole ratios, corresponding to an uniunivalent (1:1) electrolyte behavior. Futhermore, infrared spectra on acetonitrile solutions of lanthanides complexes having two coordinated dien or three coordinated en molecules also suggest the presence of ionic NO_3^-.[16,39,46]

Finally, the analysis of the ^{1}H NMR spectra shows the presence of an anisotropic contribution associated with the formation of the cationic 1:2 complex. Even though the contribution is small and reduced by a probable intramolecular configurational equilibrium in solution,[21,47] this is indicative of the proximity of the two terpy molecules in the inner sphere of the 1:2 complex. This new experimental evidence associated with the previous conclusions tells us that the three-dimensional structures of $[La(NO_3)_2(terpy)_2]^+$ in solution and in the solid state are very similar.

According to the ^{139}La NMR titration curve shown in Figure 2, at least one other La(III) complex must be formed when $\varrho > 1.0$ in addition to $[La(NO_3)_2(terpy)_2]^+$. Indeed, calculations of the stability constant done on the basis of the exclusive formation of the 1:2 complex, were not conclusive and indicated a decreasing value as ϱ increases. Moreover, the titration curve being obviously linear for $1.0 < \varrho < 1.5$ clearly indicates a chemical process thermodynamically more stable than for $\varrho > 1.5$.

Since another species is formed and since coordinated nitrate ions are expelled when a second terpy molecule is bound in the 1:1 inner sphere complex, it is strongly suggested that the released nitrate also competes for the same coordination sites available on the 1:1 complex, leading to the simultaneous formation of the anionic species, $La(NO_3)_4(terpy)^-(s)$. The formation of the anionic complex explains the linear section ($1.0 > \varrho > 1.5$) of the ^{139}La NMR titration curve (Figure 2). The crystal structure of the compound illustrated by the ORTEP drawing on Figure 6, also supports the formation of the complex anion. According to literature, the simultaneous formation of complex cations and anions is well known when polycyclic ligands are used (such as crown ether and cryptands) in Ln(III) complex syntheses.[11,48] However, no such ions were previously reported when complexes were synthesized from acyclic N-donors.

The crystal structure of the complex anion $[La(NO_3)_4(terpy)]^-$ indicates a coordination number of 11 without solvent molecules belonging to the coordination sphere. However in solution, the ^{17}O NMR data for $\varrho > 1.5$ clearly shows the presence of coordinated water which must essentially belong to the inner sphere of the anionic complex. Consequently, CH_3CN must also be bound, and the anionic complex in solution is best described by an equilibrium between $[La(NO_3)_4(terpy)(CH_3CN)]^-$ and $[La(NO_3)_4(terpy)(H_2O)]^-$. Therefore, if NO_3^- and terpy respectively maintained their bidentate and tridentate coordination, the coordination of the solvated anionic complex would be 12. It was previously reported that solvation upon dissolution may change the coordination number because the energy of reorganization in going from one coordination number value to the following one is usually small.[10]

No other experimental evidences emphasize the formation of the anionic complex in solution and oddly enough, both the ^{139}La NMR chemical shift and the line width of the anionic complex are found identical to the values obtained for the 1:1 complex. However, this spectral behavior does not deny the formation of the anionic complex. Indeed, a previous work of Evans and Missen[40] showed that different species, successively formed during the course of a titration, can have very similar spectral characteristics. This behavior could also be a likely consequence of the presence of two unidentate nitrate groups in the inner sphere of the anionic complex. Therefore, the revised coordination number of the anionic complex would be 10 with six O-atoms, three N-atoms, and one solvent molecule (CH_3CN/H_2O) coordinated to La(III), just as found for the neutral 1:1 complex.

Some data found in the literature supports the idea of having a complex anion and cation simultaneously in solution. Hirashima and Shiokawa reported that the stoichiometry of the crystalline lanthanide complexes with the poly(oxyethylene) $HO(CH_2CH_2O)_2H$ (EO_2) was not determined because the mixed product (the 1:1 and 1:2 complexes) was deposited.[49] Finally, the calorimetric titration curve of $Nd(NO_3)_3$ with dien[39] shows two enthalpy changes between the 1:1 and 2:1 ligand to metal ion mole ratios even though only one was reported by the authors. Therefore, $[Nd(NO_3)_2(dien)_2]NO_3$ is formed following

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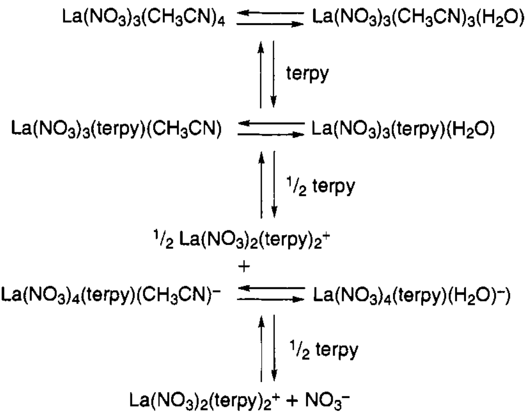
two distinctive steps as suggested here for the formation of [La$(NO_3)_2$(terpy)$_2$]NO_3 (see the equilibrium scheme).

For $\varrho > 1.5$, [La$(NO_3)_2$(terpy)$_2$]$^+$ is still formed but not as easily because terpy must replace the ligands present in the inner sphere of the complex anion. The process included the expulsion of two nitrate ions and one solvent molecule (CH_3CN/H_2O) to satisfy the formation of the anhydrous 1:2 complex previously described. There was no indication of the addition of a third terpy molecule. The complete equilibrium scheme of the La(III) complexation with terpy is illustrated as follows:



According to the literature, terpy was expected to form complexes as weak as those formed with bipy because of strain experienced by the third pyridyl ring which counterbalances the increase of stability due to the availability of the additional pyridyl nitrogen.[50] The general trend of the results indicates that the 1:1 complex species are not only more stable than the corresponding La–bipy complex but also more stable than the La–phen complex with a stability constant higher than 4.0. The simultaneous formation of the complex anion and cation is also thermodynamically favoured according to the ^{139}La NMR titration curves. However, from proton NMR data, it is found that terpy is partially free when the complex ions are formed, therefore suggesting that the corresponding stability constant is probably smaller than it was originally believed. Moreover, results indicate that the displacement of the first nitrate ion is done very easily, which is an unexpected conclusion considering the weak basicity of the pyridyl nitrogens.

Acknowledgment. "Le Conseil de l'Education Franco-Ontarienne" (CEFO) and the Development Fund of the Faculty of Science of the University of Ottawa are gratefully acknowledged for operating grants.

Supplementary Material Available: Table S-I, listing of crystallographic experimental details; Table S-II, calculated atomic parameters *x*, *y*, *z*, and B_{iso} including values for hydrogens; Table S-III, anisotropic temperature factors; Table S-IV, bond distances; Table S-V, bond angles; Table S-VI, distances to the least-squares planes and dihedral angles; Figure S-1, stereoview of packing diagram (15 pages). Ordering information is given on any current masthead page.

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