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## Structures in Solution and in the Solid State of the Complexes of Lanthanum(III) with 1,10-Phenanthroline. X-ray Crystallographic and $^1\text{H}$ , $^{13}\text{C}$ , $^{17}\text{O}$ , and $^{139}\text{La}$ Solution NMR Studies

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The reaction between hexahydrated lanthanum(III) nitrate and 1,10-phenanthroline (phen) in acetonitrile solution was investigated by  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{17}\text{O}$ , and  $^{139}\text{La}$  NMR spectroscopy. The crystal structure of trinitratobis(1,10-phenanthroline)lanthanum(III) ( $\text{La}(\text{NO}_3)_3(\text{C}_{12}\text{H}_8\text{N}_2)_2$ ) was determined by X-ray diffraction: monoclinic; space group  $C2/c$ ;  $a = 11.2252(8) \text{ \AA}$ ,  $b = 18.1844(14) \text{ \AA}$ ,  $c = 13.1278(8) \text{ \AA}$ ;  $Z = 4$ ;  $\beta = 100.416(5)^\circ$ . At convergence,  $R_f = 0.031$  and  $R_w = 0.032$  for 2059 reflections. In solution,  $^{139}\text{La}$  NMR spectra have shown up to three sites in slow exchange with variable intensities. They were attributed to solvated La(III) ions and to two complex species with one or two phen ligands in the La(III) coordination shell. A more complete structural analysis by  $^{17}\text{O}$  NMR spectroscopy indicated that during the course of the complexation by phen, coordinated water was totally expelled from the La(III) coordination sphere, whereas all three nitrate groups remained coordinated. Proton NMR data have confirmed the total displacement of water. In addition, the proton chemical shifts of phen, in comparison with the  $^{13}\text{C}$  NMR data, clearly showed an anisotropic shielding contribution when two phen ligands were coordinated to La(III). This indicates that the two phen molecules are in a close vicinity in the coordination sphere. From the NMR results, one can conclude that the structure in solution of the 2:1 complex,  $\text{La}(\text{NO}_3)_3(\text{phen})_2$ , is very similar to the solid-state one. From  $^{139}\text{La}$  NMR spectroscopy, the populations of the various La(III) species were obtained and the apparent formation constants were calculated.

### Introduction

Rare earth metal cations (noted below as "Ln(III)") are of growing importance for their industrial,<sup>1,2</sup> chemical,<sup>3,4</sup> biochemical, and medicinal applications.<sup>5-9</sup> They are major constituents of several ceramic superconductors.<sup>10</sup>

Although rare earth metal cations are widely used, little is known about the stability and the structure of their complexes in solution. Because of their hard character, their complexes with anionic ligands containing oxygen as donor atoms have been the most studied,<sup>11,12</sup> as were also their complexes with synthetic ionophores, generally stabilized by the macrocyclic effect.<sup>13</sup> In the absence of strongly stabilizing ligands, the complex formation is often precluded by the competition for the coordination sites from the solvent molecules and the counteranions.

The use of N-donor ligands in the Ln(III) complex formation has rarely been considered. Previous works mention that in water a few thermodynamically stable complexes were obtained by using weakly basic amines.<sup>14</sup> The use of strongly basic amines led to the formation of lanthanide(III) oxides or hydroxides.<sup>14</sup>

Nonaqueous solvents with weak basic properties offer, however, a powerful means for the synthesis of Ln(III) complexes with neutral ligands with N (or even S) as donor atoms.<sup>14,15</sup> Some results obtained by  $^{139}\text{La}$  NMR,<sup>16</sup>  $^1\text{H}$  NMR,<sup>17</sup> calorimetry,<sup>15</sup> and IR measurements<sup>18</sup> clearly report that ethylenediamine (en), and diethylenediamine (dien) form inner sphere complexes with Ln(III) in acetonitrile. Similarly, although 2,2'-bipyridyl and 1,10-phenanthroline are relatively less basic than en, some of their Ln(III) complexes were characterized in solution and in the solid state.<sup>11,19-23</sup> It has also been shown that, depending on the counteranion used, the complex structures can largely vary in solution as well as in the solid state, thus affecting the number of ligands bound and the coordination number in the resulting Ln(III) complexes.<sup>13,18,24</sup>

In a stepwise attempt to better understand the role played by the ligand, the counteranion, and the solvent in the stability of the Ln(III) complexes in solution, the complexation of La(III) with 1,10-phenanthroline in acetonitrile was first considered. By means of a multinuclear magnetic resonance analysis combining  $^{139}\text{La}$ ,  $^{17}\text{O}$ ,  $^{13}\text{C}$ , and  $^1\text{H}$  NMR data, information on the interactions between the La(III) ions and the various potentially coordinating compounds in solution were obtained from chemical shift and line-width analysis.

### Experimental Section

**Materials and Samples.**  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Aldrich, 99.99%) and 1,10-phenanthroline (phen) (Aldrich, 99%) were kept in a desiccator over drierite and used as received. Acetonitrile (BDH) was dried as previously reported.<sup>25</sup> Acetonitrile- $d_3$  (Aldrich, 99% D) was used as received.

The metal ion concentration in the stock solution was checked by complexometric titrations with a standard EDTA solution at pH = 4.6 using xylenol orange as the metal indicator.<sup>26</sup> Results confirmed that

- (1) Riker, L. W.; Gschneidner, Jr., K. A. Eds. *Industrial Applications of the Rare Earth Elements*; American Chemical Society: Washington, DC, 1981.
- (2) Niinistö, L. *Inorg. Chim. Acta* **1987**, *140*, 339-343.
- (3) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 219-223.
- (4) Kagan, H. B.; Namy, J. L. *Tetrahedron* **1986**, *42*, 6573.
- (5) Evans, C. H. *Biochemistry of the Lanthanides*; Plenum Press: New York, 1990.
- (6) Meares, C. F.; Wensel, T. G. *Acc. Chem. Res.* **1984**, *17*, 202.
- (7) Inagaki, F.; Miyazawa, T. *Prog. Nucl. Magn. Reson. Spectrosc.* **1981**, *14*, 67.
- (8) Cox, J. P. L.; Jankowski, K. J.; Katakay, R.; Parker, D.; Beeley, N. R. A.; Boyce, B. A.; Eaton, M. A. W.; Millar, K.; Millican, A. T.; Harrison, A.; Walker, C. *J. Chem. Soc., Chem. Commun.* **1989**, 797-798.
- (9) Anderson-Berg, W. T.; Squire, R. A.; Strand, M. *Cancer Res.* **1987**, *47*, 1905.
- (10) (a) Bednorz, J. G.; Muller, K. A. *Z. Phys.* **1986**, *B64*, 189. (b) *Superconductivity and its Applications*; Kwok, H. S., Shaw, D. T., Eds.; Elsevier: New York, 1988.
- (11) Sinha, S. P. *Complexes of the Rare Earths*; Pergamon Press Ltd.: Toronto, Canada, 1966; pp 36-81.
- (12) Ducommun, Y.; Helm, L.; Laurency, G.; Merbach, E. A. *Magn. Reson. Chem.* **1988**, *26*, 1023.
- (13) Bünzli, J. C. G. *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Jr., Eyring, L., Eds.; Elsevier Science Publishers B. V.: Amsterdam, 1987; pp 321-394.
- (14) (a) Sinha, S. P. *Complexes of the Rare Earths*; Pergamon Press Ltd.: Toronto, Canada, 1966; pp 24-36. (b) Forsberg, J. H. *Coord. Chem. Rev.* **1973**, *10*, 195.
- (15) Forsberg, J. H.; Wathen, C. A. *Inorg. Chem.* **1971**, *10*, 1379.
- (16) Evans, D. F.; Missen, P. H. *J. Chem. Soc., Dalton Trans.* **1982**, 1929.
- (17) Birnbaum, E. R.; Statton, S. *Inorg. Chem.* **1973**, *12*, 379.
- (18) Forsberg, J. H.; Moeller, T. *Inorg. Chem.* **1969**, *8*, 883.
- (19) Bukietynska, K.; Thuy, P. N. *Polyhedron* **1988**, *7*, 641.
- (20) Bukietynska, K.; Thuy, P. N. *Inorg. Chim. Acta* **1987**, *132*, 21.
- (21) Ermolaev, V. L.; Gruzdev, V. P. *Inorg. Chim. Acta* **1983**, *94*, 179.
- (22) Selbin, J.; Ahmad, N.; Bhacca, N. *Inorg. Chem.* **1971**, *10*, 1383.
- (23) Al-Karaghoul, A. R.; Wood, J. S. *Inorg. Chem.* **1972**, *11*, 2293.
- (24) Forsberg, J. H.; Moeller, T. *Inorg. Chem.* **1969**, *8*, 889.
- (25) Graves, H. P.; Detellier, C. *J. Am. Chem. Soc.* **1988**, *110*, 6019.

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**Table I.** Crystallographic Data for  $\text{La}(\text{NO}_3)_3(\text{phen})_2$ 

formula	$\text{LaC}_{24}\text{H}_{16}\text{N}_7\text{O}_9$	$a$ , Å	11.2252 (8)
fw	685.34	$b$ , Å	18.1844 (14)
cryst syst	monoclinic	$c$ , Å	13.1278 (8)
space group	$C2/c$	$\beta$ , deg	100.416 (5)
radiation ( $\lambda$ , Å)	Mo $K\alpha$ (0.709 30)	$Z$	4
$d_{\text{calc}}$ , $\text{g cm}^{-3}$	1.727	$T$ , °C	20
$R_f = R_f(F_o)^a$	0.031	$V$ , Å <sup>3</sup>	2635.5 (3)
$R_w = R_w(F_o)^b$	0.032	trans coeff	0.501928–0.708698
		$\mu$ (Mo $K\alpha$ ), $\text{cm}^{-1}$	16.9

$$^a R_f = \sum(F_o - F_c) / \sum F_o \quad ^b R_w = (\sum w(F_o - F_c)^2 / \sum w(F_o)^2)^{1/2}$$

the lanthanum salt contained, as indicated, six water molecules per mole of lanthanum. All solutions and NMR samples were prepared and kept under argon and sealed with Parafilm. The spectra were recorded within 6 h after the preparation of samples because precipitation occurred on standing, especially if  $\rho = [\text{phen}]_0 / [\text{La}(\text{III})]_0 \geq 1.0$ .

**NMR Measurements.**  $^{139}\text{La}$ ,  $^{17}\text{O}$ , and  $^{13}\text{C}$  NMR spectra were recorded at  $298.0 \pm 0.5$  K on a Varian XL-300 spectrometer using a 10-mm probe. No lock was used, the field drift being negligible during the time of the acquisition.

$^{139}\text{La}$  NMR spectra were obtained at 42.37 MHz. A delay of 40  $\mu\text{s}$  between the end of the pulse and the start of the acquisition was chosen to minimize baseline distortion. Chemical shifts were measured relative to external 0.10 M  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in  $\text{H}_2\text{O}-\text{D}_2\text{O}$  (80:20). Intensities ( $I$ ), line widths ( $\nu_{1/2}$ ), and chemical shifts ( $\delta$ ) of the decomposed Lorentzian lines were obtained from a curve-fitting analysis. Because of small residual baseline distortion, the Lorentzian decompositions were performed on several spectra of the same sample after the phase parameter values were varied. A series of 20 different  $\text{La}(\text{III})$ -phen solutions were prepared and fifty-four decomposition curves were considered. From 25 to 42 °C no temperature dependence on the  $^{139}\text{La}$  NMR line widths obtained from the decomposition procedure was observed, in the limits of the experimental errors.

Natural abundance  $^{17}\text{O}$  NMR spectra were obtained at a resonance frequency of 40.66 MHz. Chemical shifts were referenced to external 100%  $\text{D}_2\text{O}$ .

$^{13}\text{C}$  NMR spectra were obtained at 75.43 MHz. Chemical shifts were reported relative to external dioxane in  $\text{C}_6\text{D}_6$  (60:40) and converted to the TMS reference scale using  $\delta_{\text{TMS}} = \delta_{\text{diox}} + 67.40$  ppm. The  $^{13}\text{C}$  off-resonance spectrum and the hetero-correlated shift 2D spectrum were also recorded to assist signal assignment.

Proton NMR spectra were obtained at room temperature on a Gemini 200 spectrometer operating at 199.97 MHz using a 5-mm probe. Chemical shifts were measured relative to internal acetonitrile and converted to the TMS reference scale using  $\delta_{\text{TMS}} = \delta_{\text{AN}} + 2.00$  ppm.

**Crystallographic Analysis of  $\text{La}(\text{NO}_3)_3(\text{phen})_2$ .** Crystalline  $\text{La}(\text{NO}_3)_3(\text{C}_{12}\text{H}_8\text{N}_2)_2$  was precipitated from the NMR samples when  $\rho = [\text{phen}]_0 / [\text{La}(\text{III})]_0 \geq 2.0$ . The crystals were isolated by decantation and dried with a stream of argon.

A colorless crystal of dimensions  $0.35 \times 0.30 \times 0.07$  mm was selected by examination under a microscope. The crystal was mounted on a glass fiber and was then studied by X-ray diffraction with a monochromatic Mo  $K\alpha$  radiation on a Rigaku AFC65 diffractometer controlled by the TEXRAY system of programs.<sup>27a</sup>

Details on crystal structure determination and relevant parameters on molecular geometry are reported respectively in Tables I and II; atomic parameters  $x$ ,  $y$ ,  $z$ , and  $B_{\text{eq}}$  are reported in Table III.

Cell dimensions were obtained from 25 reflections with  $2\theta$  in the range  $36.0$ – $42.0^\circ$ . Intensity data were collected for 2459 reflections using the  $\theta/2\theta$  scan method to a maximum  $2\theta$  value of  $49.9^\circ$ . On data reduction, 2335 unique reflections were obtained of which 2059 were considered significant with  $I_{\text{net}} > 2.5\sigma(I_{\text{net}})$ . Absorption correction was made from four  $\psi$  scans using the scattering factors given in ref 27b. The structure was solved by direct methods followed by a difference Fourier map and refined by least-squares methods. The space group was determined by systematic absences. The space group  $C2/c$ , with  $Z = 4$ , requires that La is on a 2-fold axis, and N(1) and O(2) also sit on special positions. All non-hydrogen atoms were refined anisotropically together with the scale and extinction parameter. Hydrogen atom positions were calculated

**Table II.** Selected Bond Lengths and Bond Angles<sup>a,b</sup>

Bond Distances			
La–O(1)	2.580 (3)	La–N(3)	2.701 (3)
La–O(3)	2.599 (3)	La–N(4)	2.646 (3)
La–O(4)	2.611 (3)		
Bond Angles			
O(1)–La–O(1)*	49.05 (13)	O(3)–La–O(3)*	144.34 (10)
O(1)–La–O(3)	74.27 (11)	O(3)–La–O(4)	48.95 (10)
O(1)–La–O(3)*	73.38 (11)	O(3)–La–O(4)*	128.32 (10)
O(1)–La–O(4)	69.14 (11)	O(3)–La–N(3)	74.51 (10)
O(1)–La–O(4)*	104.31 (11)	O(3)–La–N(3)*	141.14 (10)
O(1)–La–N(3)	139.10 (11)	O(3)–La–N(4)	118.32 (10)
O(1)–La–N(3)*	139.83 (12)	O(3)–La–N(4)*	74.53 (10)
O(1)–La–N(4)	87.14 (12)	O(4)–La–O(4)*	173.15 (10)
O(1)–La–N(4)*	131.84 (12)	O(4)–La–N(3)	70.52 (10)
N(3)–La–N(3)*	66.69 (10)	O(4)–La–N(3)*	115.68 (10)
N(3)–La–N(4)	85.01 (10)	O(4)–La–N(4)	69.39 (10)
N(3)–La–N(4)*	61.33 (10)	O(4)–La–N(4)*	113.12 (10)
N(4)–La–N(4)*	140.35 (10)		

<sup>a</sup> Atoms flagged with an asterisk are symmetry equivalents. <sup>b</sup> Complete listings of bond lengths and bond angles are included in the supplementary material.

**Table III.** Atomic Parameters  $x$ ,  $y$ ,  $z$  and  $B_{\text{iso}}$  Where Esds Refer to the Last Digit Printed

	$x$	$y$	$z$	$B_{\text{iso}}$ , Å <sup>2</sup>
La	$1/2$	0.328235 (18)	0.25000	2.564 (16)
O(1)	0.4879 (4)	0.45734 (20)	0.1672 (3)	6.39 (21)
O(2)	$1/2$	0.5598 (3)	0.25000	12.6 (6)
O(3)	0.2782 (3)	0.37200 (17)	0.24280 (23)	4.08 (14)
O(4)	0.3179 (3)	0.33682 (18)	0.09546 (22)	4.13 (15)
O(5)	0.1389 (3)	0.37630 (25)	0.1060 (3)	7.11 (22)
N(1)	$1/2$	0.4934 (3)	0.25000	7.1 (5)
N(2)	0.2420 (4)	0.36162 (21)	0.1468 (3)	4.05 (18)
N(3)	0.3663 (3)	0.20417 (17)	0.24144 (24)	3.07 (15)
N(4)	0.5628 (3)	0.27889 (18)	0.07761 (23)	3.15 (15)
C(1)	0.3327 (4)	0.16745 (25)	0.1535 (3)	3.94 (21)
C(2)	0.2898 (5)	0.0951 (3)	0.1504 (4)	5.2 (3)
C(3)	0.2814 (5)	0.0604 (3)	0.2402 (4)	5.4 (3)
C(4)	0.3132 (4)	0.09766 (24)	0.3350 (3)	4.09 (22)
C(5)	0.3569 (4)	0.16993 (23)	0.3319 (3)	3.05 (17)
C(6)	0.3009 (6)	0.0663 (3)	0.4316 (4)	5.7 (3)
C(7)	0.6718 (5)	0.1046 (3)	–0.0198 (4)	5.4 (3)
C(8)	0.6266 (4)	0.1781 (3)	–0.0201 (3)	3.65 (20)
C(9)	0.6093 (4)	0.21066 (22)	0.0732 (3)	2.89 (18)
C(10)	0.5982 (4)	0.2212 (3)	–0.1110 (3)	4.35 (25)
C(11)	0.5555 (5)	0.2904 (3)	–0.1050 (3)	4.61 (24)
C(12)	0.5371 (4)	0.3170 (3)	–0.0103 (3)	3.96 (20)

<sup>a</sup>  $B_{\text{iso}}$  is the mean of the principal axes of the thermal ellipsoid.

assuming  $\text{C–H} = 1.08$  Å, and  $B_{\text{iso}}(\text{H})$  was obtained assuming  $U(\text{H}) = U_{\text{iso}}(\text{C}) + 0.01$ . The last least-squares cycle was calculated with 30 atoms, 188 parameters, and 2059 out of the unique 2335 reflections. Weights based on counting statistics were used. The residuals on significant reflections were  $R_f = 0.031$  and  $R_w = 0.032$  with  $\text{GoF} = 1.30$ , and for all reflections  $R_f = 0.039$  and  $R_w = 0.032$ . The instrument instability factor  $k$  was 0.0001. The maximum shift/ $\sigma$  ratio in the final least-squares cycle was 0.011. In the last  $E$ -map the deepest hole was  $-0.450$   $\text{e}/\text{Å}^3$  and the top peak was  $0.540$   $\text{e}/\text{Å}^3$ . The top peak was located 1.10 Å from the lanthanum atom, indicating the absence of solvent molecules. All calculations were done using the NRCVAX system of crystal structure solving programs.<sup>27c</sup>

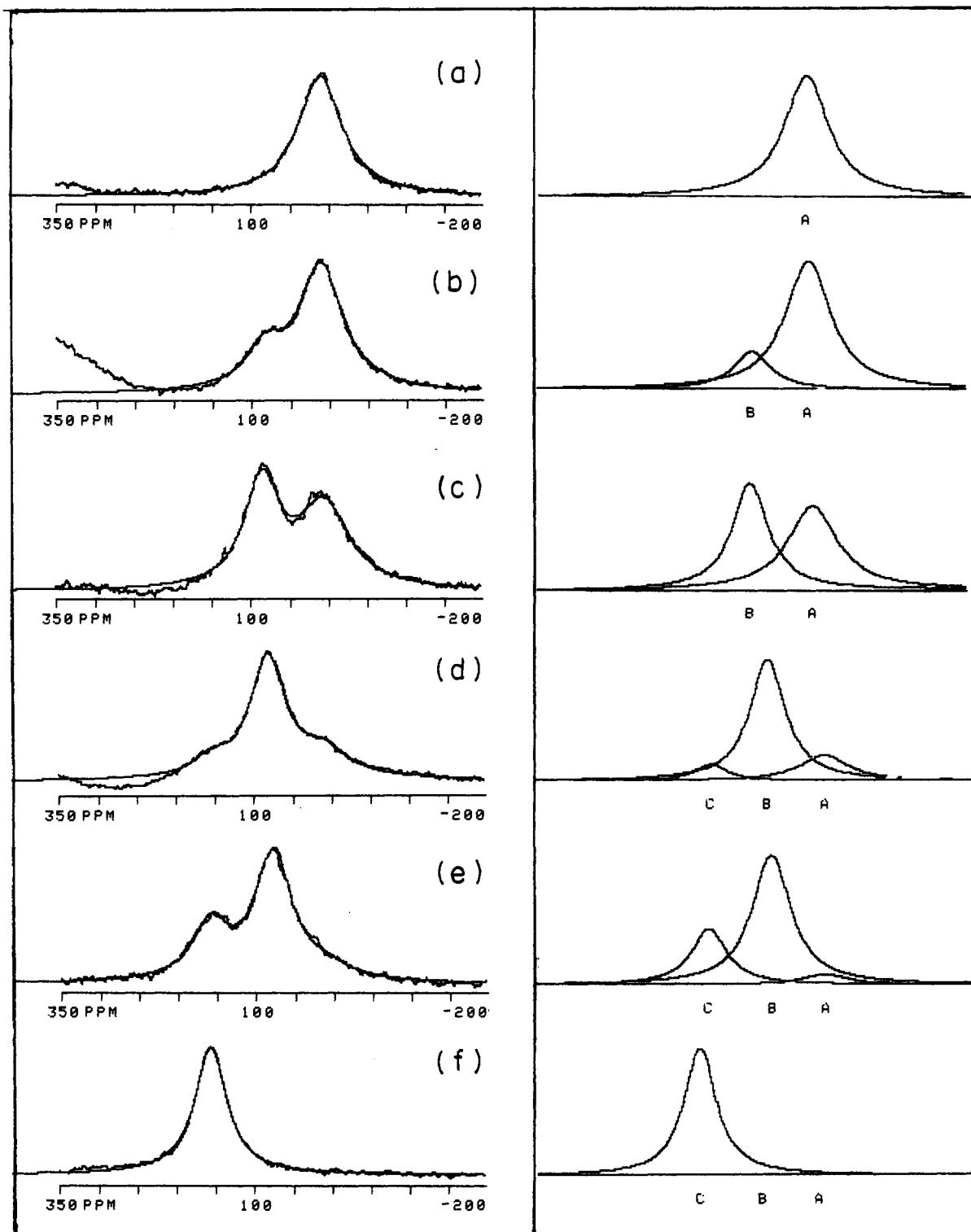
## Results

**$^{139}\text{La}$  NMR Data.** Figure 1 shows the  $^{139}\text{La}$  NMR spectra of a  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  solution ( $5.14 \times 10^{-3}$  M) in acetonitrile, in the presence of various amounts of 1,10-phenanthroline. In the absence of phen, the observed  $^{139}\text{La}$  NMR spectrum exhibits a single Lorentzian line characterized by a chemical shift of 10 ppm and a line width of 2.9 kHz. Increasing amounts of phen to the  $\text{La}(\text{III})$  solution causes the appearance of up to two additional signals resonating at higher frequencies (Figure 1).

The experimental spectra were decomposed in three Lorentzian signals. The resulting decomposition plots are also represented in Figure 1. The chemical shift ( $\delta$ ) and line-width ( $\nu_{1/2}$ ) values

(26) Lyle, S. J.; Rahman, M. M. *Talanta*, 1963, 10, 1177.

(27) (a) TEXRAY. Diffractometer Control Program. Molecular Structure Corp., Houston, TX. (b) *The International Tables for X-Ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV. (c) Gabe, E. J.; Lepage, Y.; Charland, J. P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* 1989, 22, 384.



**Figure 1.**  $^{139}\text{La}$  NMR spectra, at 42.37 MHz, of  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in  $\text{CH}_3\text{CN}$  in the presence of increasing concentration of phen;  $\rho = [\text{phen}]_0/[\text{La}(\text{III})]_0$  with  $[\text{La}(\text{III})]_0 = 5.14 \times 10^{-3}$  M. The decomposition plots characterizing each species are given on the right part side. Key: (a)  $\rho = 0$ ; (b)  $\rho = 0.27$ ; (c)  $\rho = 0.69$ ; (d)  $\rho = 1.06$ ; (e)  $\rho = 1.38$ ; (f)  $\rho = 2.42$ .

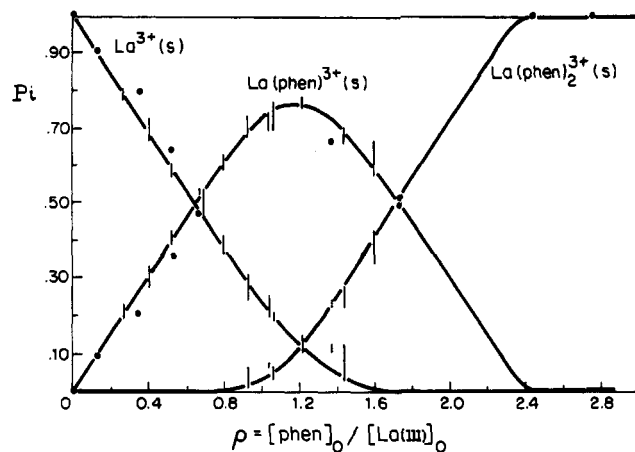
of the three Lorentzian lines obtained by the decomposition procedure are given in Table IV. Their respective populations ( $p_i$ ;  $i = 1-3$ ) are shown in Figure 2. The only assumption made in the building of Figure 2 is the La(III) monomeric nature of the three species. Since the second species ( $\delta = 80$  ppm) is major for  $\rho = [\text{phen}]_0/[\text{La}(\text{III})]_0 = 1.2$ , and the third species ( $\delta = 150$  ppm) is major for  $\rho \geq 2.4$ , it is reasonable to assign the stoichiometries  $(\text{phen})\text{La}^{\text{III}}$  and  $(\text{phen})_2\text{La}^{\text{III}}$  to the second and the third species respectively. This will be borne out by the  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{17}\text{O}$  NMR results, as well as by the X-ray crystallographic structure of the  $(\text{phen})_2\text{La}^{\text{III}}$  species. The first species ( $\delta = 10$

**Table IV.** Chemical Shift  $\delta$ , and Line Width,  $\nu_{1/2}$  of the  $^{139}\text{La}$  Resonances and the Formation Constant of the Phen Complexes

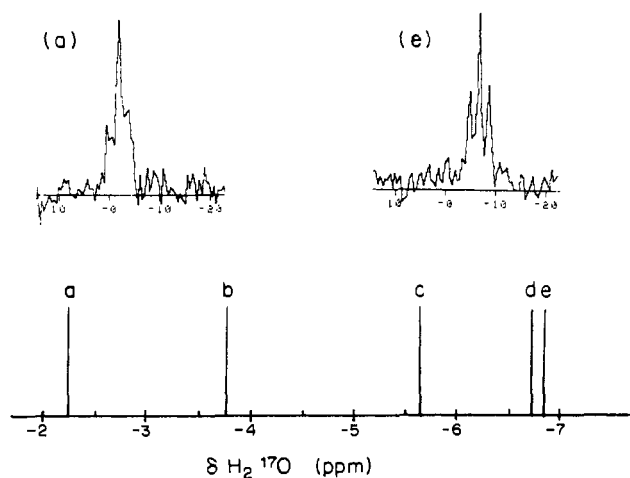
species	$\delta$ , ppm	$\nu_{1/2}$ , kHz	$\log K_f$
$\text{La}^{3+}(\text{s})$	$10 \pm 4$	$2.9 \pm 0.2$	
$\text{La}(\text{phen})^{3+}(\text{s})$	$80 \pm 5$	$2.35 \pm 0.15$	$3.3 \pm 0.2$
$\text{La}(\text{phen})_2^{3+}(\text{s})$	$150 \pm 6$	$2.06 \pm 0.09$	$2.2 \pm 0.2$

ppm) is attributed to a solvated trinitratolanthanum complex (as will be shown below).

**$^{17}\text{O}$  NMR Data.** The  $^{17}\text{O}$  NMR spectrum of a  $5.24 \times 10^{-3}$  M solution of  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in acetonitrile is characterized by a



**Figure 2.** Distribution of the three La(III) species as a function of  $\rho$ . The bars represent the error range on populations values averaged on a set of experimental data. The dots represent a population value obtained from a single experiment.

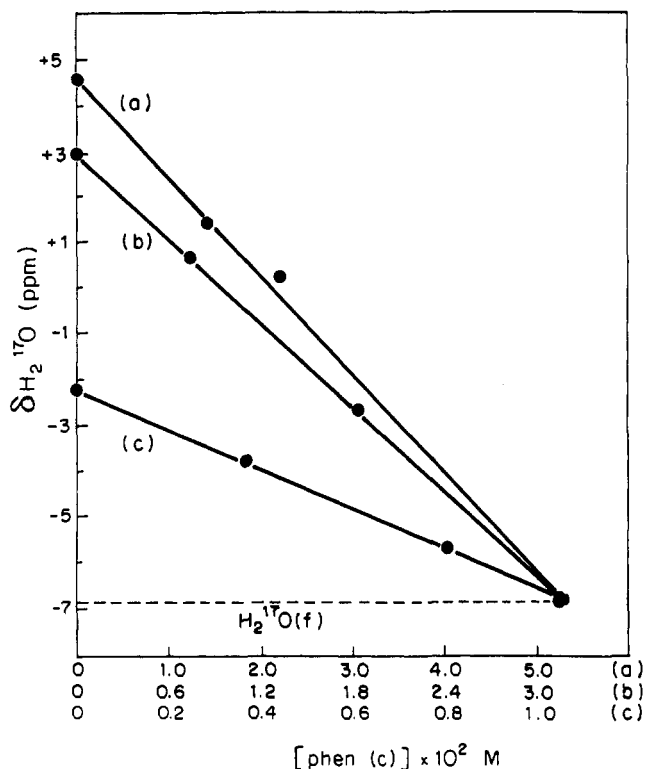


**Figure 3.**  $^{17}\text{O}$  NMR spectra (a,e) and chemical shift variations (a-e) of  $\text{H}_2^{17}\text{O}$  in  $\text{CH}_3\text{CN}$  for different values of  $\rho$ . The population percentages for each species are given according to the data obtained from Figure 2.  $\rho = [\text{phen}]_0/[\text{La(III)}]_0$  with  $[\text{La(III)}]_0 = 5.24 \times 10^{-3}$  M. Key: (a)  $\rho = 0$ , 100%  $\text{La}^{3+}(\text{s})$ ; (b)  $\rho = 0.88$ , 31%  $\text{La}^{3+}(\text{s})$ , 68%  $\text{La}(\text{phen})^{3+}(\text{s})$ , 1%  $\text{La}(\text{phen})_2^{3+}(\text{s})$ ; (c)  $\rho = 1.76$ , 46%  $\text{La}(\text{phen})^{3+}(\text{s})$ , 54%  $\text{La}(\text{phen})_2^{3+}(\text{s})$ ; (d)  $\rho = 2.64$ , 100%  $\text{La}(\text{phen})_2^{3+}(\text{s})$ ; (e)  $5 \times 10^{-2}$  M  $\text{H}_2\text{O}$  in  $\text{CH}_3\text{CN}$ .

triplet associated with the  $^{17}\text{O}$  water resonance at  $-2.26$  ppm ( $^1J_{^{17}\text{O}-\text{H}} = 82 \pm 6$  Hz). Similar  $^{17}\text{O}$  NMR water spectra were observed in nonhydroxylic solvents.<sup>28</sup> The addition of increasing amounts of phen to the solution moves the triplet resonance at lower frequencies, to reach the limit value of  $-6.76$  ppm ( $^1J = 80 \pm 9$  Hz). These values are very close to the chemical shift and the  $^1J_{^{17}\text{O}-\text{H}}$  coupling constant of free water in acetonitrile ( $\delta = -6.88$  ppm;  $^1J = 78 \pm 2$  Hz; see Figure 3).

The  $^{17}\text{O}$  chemical shift variation indicates the presence of free and coordinated water molecules in variable proportions in solution. The phen ligand molecules added to a solution of La(III) substitute the water molecules in the inner sphere of La(III). The result is an increase of the population of free water and consequently in the shielding of the  $^{17}\text{O}$  NMR water signal. With a sufficient addition of phen, the displacement of the coordinated water molecules is total, and only free water is present in solution.

Figure 4 shows the  $\delta(\text{H}_2^{17}\text{O})$  values as a function of the total concentration of coordinated phen,  $[\text{phen}(\text{c})]$ , for three different values of  $[\text{La(III)}]_0$  ( $[\text{phen}(\text{c})] = (P_B + 2P_C)[\text{La(III)}]_0$ , calculated from the population curves shown in Figure 2). The three linear relationships are illustrated in Figure 4. Remarkably, they in-



**Figure 4.**  $^{17}\text{O}$  NMR chemical shift of  $\text{H}_2\text{O}$  in  $\text{CH}_3\text{CN}$  as a function of the total concentration of coordinated phen,  $[\text{phen}(\text{c})]$  and for various  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  concentrations. Key: (a)  $[\text{La(III)}]_0 = 2.62 \times 10^{-2}$  M; (b)  $[\text{La(III)}]_0 = 1.57 \times 10^{-2}$  M; (c)  $[\text{La(III)}]_0 = 5.24 \times 10^{-3}$  M.

tersect at a point whose coordinates are  $\delta = -6.8$  ppm (the chemical shift of uncoordinated water in acetonitrile) and  $[\text{phen}(\text{c})]/[\text{La(III)}]_0 = 2.0$ . This clearly indicates that all water molecules are free in solution for  $[\text{phen}(\text{c})] = 2[\text{La(III)}]_0$ , which corresponds to the exclusive presence of the 1:2 La(III) complex in the media. These results point out the presence of water in the coordination spheres of both the free La(III) and the 1:1 La(III) complexes, whereas the inner coordination sphere of the 1:2 complex is water-free. Furthermore, the low-frequency shift of the  $^{17}\text{O}$  NMR chemical shift of water as the  $[\text{La(III)}]_0$  values decrease is the indication of an equilibrium between various species of hydrated La(III) in acetonitrile. The study of these complex equilibria will be published separately.<sup>29</sup>

A broad band at 426 ppm, assigned to the  $\text{NO}_3^-$  resonance,<sup>30</sup> can also be detected in solutions containing high enough concentrations of  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ . The chemical shift remains unchanged with the addition of phen, as well as with dilution, indicating that the nature of the  $\text{NO}_3^-$  species in solution does not depend on the coordination of La(III) by phen. In agreement with the crystal structure of the 1:2 La(III) complex (see below), the  $^{17}\text{O}$  NMR data indicate that all three  $\text{NO}_3^-$  groups belong to the first coordination sphere of the three La(III) species detected by  $^{139}\text{La}$  NMR. In strong contrast with the water molecules, they are not substituted during the stepwise complexation process of La(III) by phen.

**$^{13}\text{C}$  NMR Data.** Carbon-13 NMR spectra of  $9.2 \times 10^{-3}$  M phen solutions were recorded in the presence of increasing  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  concentrations, so that  $R = [\text{La(III)}]_0/[\text{phen}]_0$  varied between 0 and 2.0.

For  $0 < R < 0.5$ , the observed chemical shift was a weighted average of the chemical shifts of free and complexed phen. For  $R > 0.5$ , a plateau was observed, indicating that very similar chemical shifts characterize both the 1:1 and the 1:2 complexes. Table V summarizes the  $^{13}\text{C}$  NMR spectral data obtained for phen and its La(III) complexes in acetonitrile.

(28) Kintzinger, J. P. In *NMR. Basic Principles and Progress. Oxygen-17 and Silicon-29*; Diehl, P., Fluck, E., Kosfeld, R. Eds.; Springer: New York, 1981; pp 4, 37.

(29) Fréchet, M. To be submitted for publication.

(30) Rehder, D. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987; pp 483-486.

Table V.  $^{13}\text{C}$  and  $^1\text{H}$  NMR Spectral Data<sup>a</sup>

	chem shift					
	2,9-position	3,8-position	4,7-position	5,6-position	11,12-position	13,14-position
A. $^{13}\text{C}$ NMR Data						
phen(s)	151.24	124.43	137.24	127.96	147.42	130.12
phen(c) <sup>b</sup>	150.93	125.75	140.82	128.52	145.69	131.05
B. $^1\text{H}$ NMR Data						
phen(s)	9.17	7.77	8.45	7.98		
1:1 complex	9.26	8.02	8.75	8.16		
1:2 complex <sup>c</sup>	8.91	7.82	8.70	8.15		

<sup>a</sup>Chemical shift, in ppm ( $\pm 0.03$  ppm). <sup>b</sup>The  $^{13}\text{C}$  chemical shifts of complexed phen in the 1:1 and in the 1:2 complexes are undistinguishable. <sup>c</sup>Calculated from the measured  $^1\text{H}$  NMR chemical shift value for  $p < 0.5$ , in considering the populations and the chemical shifts of the phen species present in solution.

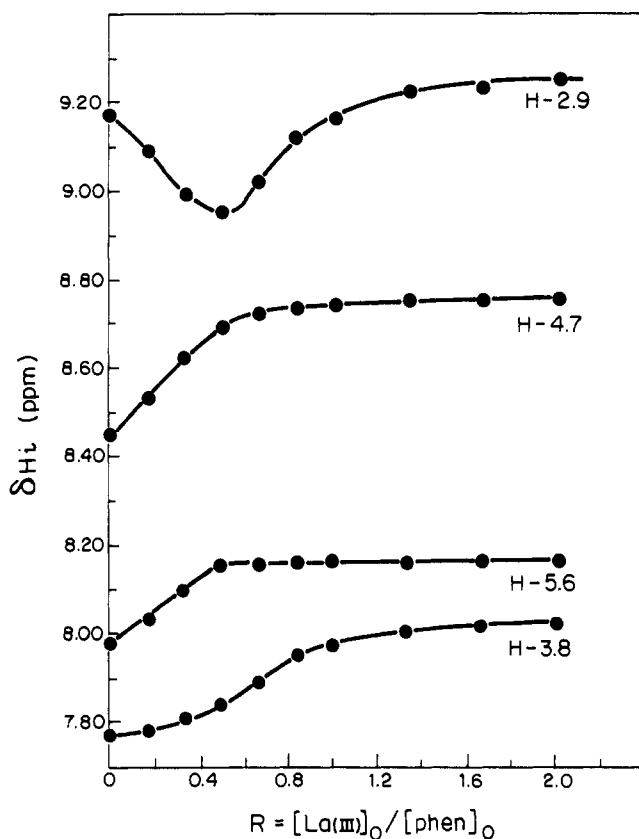


Figure 5.  $^1\text{H}$  NMR chemical shifts of phen in  $\text{CH}_3\text{CN}$  as a function of  $[\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$ .  $R = [\text{La}(\text{III})]_0 / [\text{phen}]_0$  with  $[\text{phen}]_0 = 2.26 \times 10^{-3}$  M.

**$^1\text{H}$  NMR Data.** Proton NMR spectra of phen were recorded over a range of La(III) concentrations so that  $0 < R = [\text{La}(\text{III})]_0 / [\text{phen}]_0 < 2.02$ , with  $[\text{phen}]_0 = 2.26 \times 10^{-3}$  M. The NMR spectra consisted of four resonances, three quadruplets and one singlet. The proton assignment agrees with previous literature data.<sup>31</sup> The addition of  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  to the phen solution causes chemical shift variations which are given in Figure 5. The curves indicate the successive formation of the 1:2 and 1:1 complexes in solution with different chemical shift values for coordinated phen in both complexes. The difference is particularly large for H-2,9 and H-3,8. This behavior suggests that an additional factor, nonobservable in the  $^{13}\text{C}$  NMR spectra (carbons of both 1:1 and 1:2 complexes had similar chemical shifts), affects the proton NMR chemical shifts. The close proximity of two phen ligands in the first coordination sphere of the 1:2 complex, as it is the case in the crystal structure (see below), should result in shielding effects due to mutual diamagnetic anisotropy of the aromatic rings. These effects should be absent in the 1:1 complex. This anisotropic contribution should be more effective with a

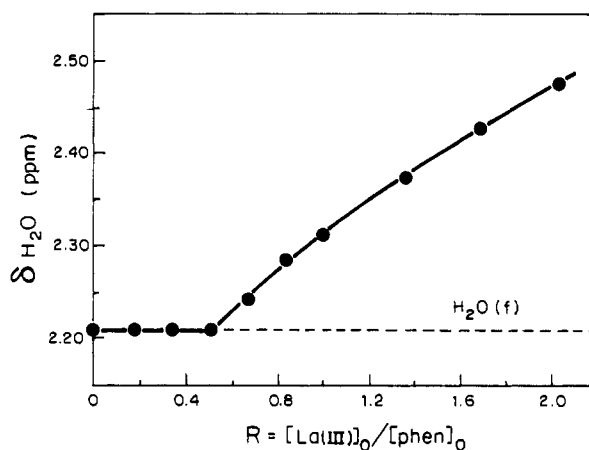


Figure 6.  $^1\text{H}$  NMR chemical shifts of  $\text{H}_2\text{O}$  as a function of  $R = [\text{La}(\text{III})]_0 / [\text{phen}]_0$ .

decrease in the distance between the two phen moieties, so that the corresponding contribution for each proton would be in the order  $\text{H-2,9} > \text{H-3,8} > \text{H-4,7} > \text{H-5,6}$ . This is exactly what is experimentally observed. The results and the experimental data are given in Table V.

The  $^1\text{H}$  NMR spectra were also useful in following the chemical shift variation of water during the complexation. As indicated in Figure 6, the water molecules are not coordinated up to  $R = 0.5$ , confirming the absence of water in the inner coordination sphere of the 1:2 La(III) complex, as previously shown by  $^{17}\text{O}$  NMR spectroscopy. For  $R < 0.5$ , the observed chemical shift of water ( $2.209 \pm 0.003$  ppm) is identical to the chemical shift of the residual  $\text{H}_2\text{O}$  in the phen solution (for  $R = 0$ ,  $\delta_{\text{H}_2\text{O}} = 2.207 \pm 0.003$  ppm) and very close to that of free water in  $\text{CD}_3\text{CN}$  ( $\delta_{\text{H}_2\text{O}} = 2.199$  ppm). For  $R > 0.5$ , a downfield shift of the water signal is observed, corresponding to higher concentrations of the 1:1 complex and of the solvated La(III) in solution, both species containing some water molecules in the La(III) first coordination sphere.

**X-ray Data.** Figure 7 shows an ORTEP drawing of the complex  $\text{La}(\text{NO}_3)_3(\text{phen})_2$ . Some bond lengths and angles of interest are given in Table II. The structure of  $\text{La}(\text{NO}_3)_3(\text{phen})_2$  shows similarities with the complex trinitratobis(2,2'-bipyridyl)lanthanum(III), previously reported.<sup>23</sup>

The lanthanum atom is 10-coordinate with four nitrogen and six oxygen donors from two phen and three chelating  $\text{NO}_3^-$  ligands. The averaged La-N and La-O bond distances in  $\text{La}(\text{NO}_3)_3(\text{phen})_2$  are 2.67 (3) and 2.60 (1) Å, in excellent agreement with the values of 2.66 (1) and 2.60 (2) Å previously found for the corresponding La-N and La-O bond distances in the  $\text{La}(\text{bpy})_2(\text{NO}_3)_3$  complex. This is also in agreement with the sum of the ionic radius of La(III) and of the van der Waals radius of N or O, giving 2.67 and 2.57 Å, respectively.<sup>32</sup>

- (31) Miller, J. D.; Price, R. H. *J. Chem. Soc.* **1965**, 4706.  
 (32) (a) Mackay, K. M.; Mackay, R. A. *Introduction to Modern Inorganic Chemistry*, 3rd ed.; International Textbook Co.: London, 1981; p 25.  
 (b) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley & Sons: Toronto, Canada, 1988; p 956.

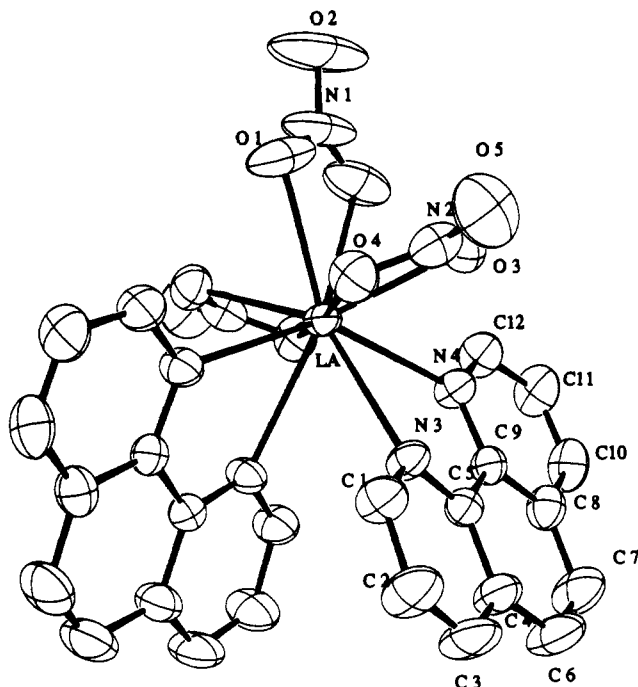


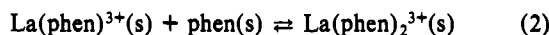
Figure 7. ORTEP drawing and numbering scheme of the  $\text{La}(\text{NO}_3)_3(\text{phen})_2$  complex.

The N–La–N chelate angle in the  $(\text{phen})_2$  complex is  $61.33 (10)^\circ$ , comparable to the corresponding angle of  $60.1^\circ$  in the  $(\text{bpy})_2$  complex. All other N–La–N angles are smaller in the  $(\text{phen})_2$  complex than in the  $(\text{bpy})_2$  complex by at least  $5^\circ$ . Concerning the geometry of the whole polyhedron, a 2-fold axis of symmetry,  $C_2$ , joins O(2), N(1), and La and on the basis of the angle values, the geometry of the 10-coordinated polyhedron should be closest of the idealized geometry of the bicapped dodecahedron.<sup>23</sup>

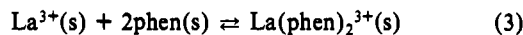
**Formation Constants.** The “apparent” formation constants for the 1:1 and 1:2 complexes were calculated from the respective populations of the three La(III) species (Figure 2) (coordinated  $\text{NO}_3^-$  not indicated). These values were obtained according to eqs 1–3, in which all species are solvated. Here  $[\text{phen}] = [\text{phen}]_0$



$$K_1 = \frac{[\text{La}(\text{phen})^{3+}(\text{s})]}{[\text{La}^{3+}(\text{s})][\text{phen}(\text{s})]} = \frac{P_B}{P_A[\text{phen}(\text{s})]}$$



$$K_2 = \frac{[\text{La}(\text{phen})_2^{3+}(\text{s})]}{[\text{La}(\text{phen})^{3+}(\text{s})][\text{phen}(\text{s})]} = \frac{P_C}{P_B[\text{phen}(\text{s})]}$$



$$\beta_2 = \frac{[\text{La}(\text{phen})_2^{3+}(\text{s})]}{[\text{La}^{3+}(\text{s})][\text{phen}(\text{s})]^2} = \frac{P_C}{P_A[\text{phen}(\text{s})]^2}$$

$-P_B[\text{La}(\text{III})]_0 - 2P_C[\text{La}(\text{III})]_0$ .  $P_A$ ,  $P_B$ , and  $P_C$  are the respective populations of  $\text{La}^{3+}$  ( $\text{La}(\text{NO}_3)_3(\text{s})$ ),  $\text{La}(\text{phen})^{3+}$  ( $\text{La}(\text{NO}_3)_3(\text{phen})(\text{s})$ ), and  $\text{La}(\text{phen})_2^{3+}$  ( $\text{La}(\text{NO}_3)_3(\text{phen})_2(\text{s})$ ).  $[\text{phen}]_0$  and  $[\text{La}(\text{III})]_0$  are the total concentrations of phen and of the La(III) cation, respectively.

The mean values of  $\log K_1$ ,  $\log K_2$ , and  $\log \beta_2$  with their corresponding standard deviations are respectively  $3.3 \pm 0.3$  (obtained from 38 independent values),  $2.2 \pm 0.2$  (13 values), and  $5.8 \pm 0.2$  (11 values).

## Discussion

The addition of each phenanthroline ligand in the inner coordination sphere of  $^{139}\text{La}(\text{III})$  results in a constant high frequency shift of 70 ppm (Table IV). Similar monotonic relationships

between  $\delta$  and the number of coordinated ligands with N or O atoms have been previously observed with ethylenediamine and diethylenediamine<sup>16</sup> and with several polycarboxylates.<sup>12</sup> This constancy of the  $^{139}\text{La}$  NMR chemical shift variation when passing from  $\text{La}^{\text{III}}$  to  $\text{La}^{\text{III}}(\text{phen})$  and then to  $\text{La}^{\text{III}}(\text{phen})_2$  suggests that either the same ligands are substituted by phen during the first and second complexation steps or the ligands displaced have the same shielding effect. However, if the character of the possibly substituted species  $\text{NO}_3^-$ ,  $\text{H}_2\text{O}$ , and  $\text{CH}_3\text{CN}$  is considered, and because substantial differences are observed in the  $\delta$   $^{139}\text{La}$  of the unmixed complexes  $\text{La}(\text{NO}_3)_6^{3-}$ ,  $\text{La}(\text{H}_2\text{O})_9^{3+}$ , and  $\text{La}(\text{CH}_3\text{CN})_9^{3+}$ , respectively, of  $-60$ ,  $0$ , and  $-129$  ppm,<sup>16</sup> the first hypothesis is far more reasonable and was borne out by the  $^{17}\text{O}$  results as will be shown below.

The results in Table IV also show decreasing values of  $\nu_{1/2}$  when passing from  $\text{La}^{\text{III}}$  to  $\text{La}^{\text{III}}(\text{phen})$  and then to  $\text{La}^{\text{III}}(\text{phen})_2$ . For a quadrupolar nucleus such as  $^{139}\text{La}$ , in the absence of exchange-broadening effects that was checked by a temperature study, the line-width variation should result essentially from two factors: a change in the symmetry of the first coordination shell, and a change in the size of the La(III) species,<sup>16</sup> with higher symmetry and smaller size leading to narrower resonances. Thus, because an increase of the complex size is expected with the addition of phen in the inner sphere of La(III), the decrease of  $\nu_{1/2}$  results from a greater local electronic symmetry at the  $^{139}\text{La}$  nucleus. This is in agreement with a  $C_2$  structure for the 1:2 complex, as shown in Figure 7.

On the basis of the  $^{17}\text{O}$  NMR data, two important conclusions can be reached and are helpful to determine which other ligands than phen belong to the first coordination sphere of the La(III) species. First, each La(III) species has three nitrate groups bound in its coordination sphere. This is indicated by the presence of three coordinated nitrate molecules in the crystalline  $(\text{phen})_2$  complex and by the constant  $^{17}\text{O}$   $\delta$  value of  $\text{NO}_3^-$  obtained when phen was increasingly added to the La(III) solutions. The presence of the three nitrate groups in the inner sphere of free La(III) is supported by the results of Evans and Missen who, by adding  $\text{NBu}_4\text{NO}_3$  to a solution of  $\text{La}(\text{ClO}_4)_3$  in  $\text{CH}_3\text{CN}$ , showed that the chemical shift varied linearly by 54 ppm for the three first equivalents of  $\text{NO}_3^-$  added.<sup>16</sup> This indicates a full addition of the three  $\text{NO}_3^-$  ions in the inner sphere of La(III) based on the additivity hypothesis. Furthermore, in a recent study, Bunzli et al.<sup>33</sup> mentioned significant inner sphere interactions between La(III) and the anion  $\text{NO}_3^-$  in  $\text{CH}_3\text{OH}$  with probably two  $\text{NO}_3^-$  ions belonging to the La(III) inner sphere. In  $\text{CH}_3\text{CN}$ , a less effective donor solvent, the interactions between La(III) and  $\text{NO}_3^-$  should be even stronger, so that all three  $\text{NO}_3^-$  groups should logically be bound. Finally, the presence of three coordinated  $\text{NO}_3^-$  in the inner sphere of the free and of the complexed La(III) species is in agreement with the calorimetric study of Forsberg and Moeller<sup>24</sup> who reported the absence of competition between nitrate ions and en for the coordination sites before the addition of the first two en molecules. In the present study, the NMR results show that there is no such competition between nitrate ions and phen. This is reasonable, due to the weaker basicity of phen compared to en.

The second conclusion deduced from the  $^{17}\text{O}$  NMR data is the participation of water in the inner sphere of  $\text{La}^{\text{III}}$  and  $\text{La}^{\text{III}}(\text{phen})$  whereas  $\text{La}^{\text{III}}(\text{phen})_2$  is water-free. The absence of water in the 1:2 complex agrees very well with the corresponding crystal structure and indicates a strong similarity between the 1:2 complexes in solution and in the solid state.

At this point, the stoichiometry of the La(III) species can be determined on the basis of both the crystal structure data and the  $^{139}\text{La}$  and  $^{17}\text{O}$  NMR results. The indication of the presence of two phen molecules and three  $\text{NO}_3^-$  groups and the absence of water in the inner sphere of the 1:2 complex suggests identical molecular formulas for the solvated and the crystalline complexes,  $[\text{La}(\text{NO}_3)_3(\text{phen})_2]$ . The coordination number would be 10, which

(33) Bunzli, J. C. G.; Merbach, A. E.; Nielson, R. M. *Inorg. Chim. Acta* 1987, 139, 151.

results from two chelating phen moieties and three bidentate  $\text{NO}_3^-$  ions. These results are in excellent agreement with data previously reported for the corresponding complexes of heavier Ln(III) ions which were isolated in the solid state.<sup>11,34</sup> Concerning the two other species,  $\text{La}^{\text{III}}$  and  $\text{La}^{\text{III}}(\text{phen})$ , the chemical formulas should include undetermined amounts of  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{CN}$ , in addition to the three  $\text{NO}_3^-$  ions and the phen molecule (1:1 complex). Accordingly, one should formulate them as  $[\text{La}(\text{NO}_3)_3(\text{H}_2\text{O})_x(\text{CH}_3\text{CN})_y]$  and  $[\text{La}(\text{NO}_3)_3(\text{phen})(\text{H}_2\text{O})_w(\text{CH}_3\text{CN})_z]$ , respectively.

By addition of hydrated lanthanum(III) nitrate and phen in  $\text{CH}_3\text{CN}$ , a competition is established between phen,  $\text{NO}_3^-$ ,  $\text{H}_2\text{O}$ , and  $\text{CH}_3\text{CN}$  for the occupancy of the coordination sites on La(III). During the course of the complexation of La(III) by phen, the three coordinated  $\text{NO}_3^-$  groups remain bound to La(III) whereas water and  $\text{CH}_3\text{CN}$  are substituted. No NMR spectral evidence of competition between phen and  $\text{NO}_3^-$  was noted, indicating that  $\text{NO}_3^-$  is a much stronger stabilizing species than phen. The  $^{17}\text{O}$  NMR results show that some water is coordinated to La(III) in both  $\text{La}^{\text{III}}$  and  $\text{La}^{\text{III}}(\text{phen})$  even though its total concentration in solution is much lower than that of the solvent  $\text{CH}_3\text{CN}$ . From these results, it comes that the decreasing coordinating strength for La(III) is  $\text{NO}_3^- > \text{phen} > \text{H}_2\text{O} > \text{CH}_3\text{CN}$ .

An analysis of  $\log K_i$  for the successive coordination of phen to La(III) (see Table IV) shows a decrease when going from  $\log K_1$  to  $\log K_2$ . This decrease is in good agreement with other studies and results from statistical factors.<sup>35</sup> On the basis of this statistical factor only,  $\log K_3$  should not be higher than 1.0. This estimation is valid only if the ligands expelled are the same throughout the

complexation steps. Since the addition of a third phen ligand could be done only at the expense of a much stronger ligand than  $\text{CH}_3\text{CN}$  or  $\text{H}_2\text{O}$ , namely  $\text{NO}_3^-$ , the resulting  $\log K_3$  value should be much smaller than 1.0.

Since water is also substituted during the course of the complexation, the actual equilibrium processes involved in the complexation of La(III) with phen are not as simple as it appears above. To write a complete thermodynamic scheme of the complexation processes in solution would necessitate the exact knowledge of the water content in the coordination sphere of  $\text{La}^{\text{III}}$  and of  $\text{La}^{\text{III}}(\text{phen})$ . From the  $^{17}\text{O}$  NMR data, one knows that very small amounts of water are coordinated to the inner sphere of  $\text{La}^{\text{III}}$  and  $\text{La}^{\text{III}}(\text{phen})$ . For this first study of the system, this validates the simplification of considering only the displacement of  $\text{CH}_3\text{CN}$  in the equations describing the complexation process. A more complete thermodynamic treatment based on  $^{17}\text{O}$  and  $^{139}\text{La}$  NMR data as well as on potentiometric methods will be published later.<sup>29</sup>

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**Registry No.**  $\text{La}(\text{NO}_3)_3(\text{phen})_2$ , 139758-78-4.

**Supplementary Material Available:** Table S-I-S-V, listing respectively crystallographic data, calculated hydrogen atom parameters, anisotropic temperature factors, bond distances, and bond angles (4 pages); Table S-VI, listing structure factors (13 pages). Ordering information is given on any current masthead page.

(34) Lobanov, N. I.; Smirnova, V. A. *Russ. J. Inorg. Chem. (Engl. Transl.)* 1963, 8, 1154.

(35) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; 5th ed.; John Wiley & Sons: Toronto, Canada, 1988; pp 41-45.

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## Resolved and Unresolved Crystallographic Disorder between $\{\eta^3\text{-HB}(3\text{-Bu}^i\text{pz})_3\}\text{ZnCN}$ and $\{\eta^3\text{-HB}(3\text{-Bu}^i\text{pz})_3\}\text{ZnX}$ (X = Cl, Br, I)

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Crystallographic disorder between structurally inequivalent groups has been investigated by X-ray diffraction studies. By use of a technique in which a crystal is doped with an impurity, the disorder at a single site was varied in a controlled fashion. Specifically, single crystals of composition  $\{\eta^3\text{-HB}(3\text{-Bu}^i\text{pz})_3\}\text{Zn}(\text{CN})_x\text{X}_{1-x}$  ( $3\text{-Bu}^i\text{pz} = 3\text{-C}_3\text{N}_2\text{H}_2\text{Bu}^i$ ; X = Cl, Br, I;  $0 \leq x \leq 1$ ) were obtained by cocrystallization of  $\{\eta^3\text{-HB}(3\text{-Bu}^i\text{pz})_3\}\text{ZnCN}$  and  $\{\eta^3\text{-HB}(3\text{-Bu}^i\text{pz})_3\}\text{ZnX}$ . Although disorder between (i) CN and Cl and (ii) CN and Br was not resolved, the disorder between CN and I in  $\{\eta^3\text{-HB}(3\text{-Bu}^i\text{pz})_3\}\text{Zn}(\text{CN})_{0.9}\text{I}_{0.1}$  was readily apparent, and the individual groups could be refined with surprising success. However, the bond lengths obtained from the disordered structure were incorrect, as judged by comparison with the pure structures. Thus, although satisfactory refinement of a disordered structure may be taken as good evidence for the nature of the disorder, and therefore a good indication of the molecular structure, attempts to extract the true bond lengths from such a structure must be treated with caution. Crystal data are as follows.  $\{\eta^3\text{-HB}(3\text{-Bu}^i\text{pz})_3\}\text{ZnCN}$ : orthorhombic, *Pnma* (No. 62),  $a = 16.315$  (3) Å,  $b = 15.852$  (3) Å,  $c = 9.757$  (2) Å,  $V = 2523$  (1) Å<sup>3</sup>,  $Z = 4$ .  $\{\eta^3\text{-HB}(3\text{-Bu}^i\text{pz})_3\}\text{Zn}(\text{CN})_{0.8}\text{Cl}_{0.2}$ : orthorhombic, *Pnma* (No. 62),  $a = 16.235$  (2) Å,  $b = 15.871$  (3) Å,  $c = 9.760$  (1) Å,  $V = 2514$  (1) Å<sup>3</sup>,  $Z = 4$ .  $\{\eta^3\text{-HB}(3\text{-Bu}^i\text{pz})_3\}\text{Zn}(\text{CN})_{0.95}\text{Br}_{0.05}$ : orthorhombic, *Pnma* (No. 62),  $a = 16.303$  (4) Å,  $b = 15.847$  (6) Å,  $c = 9.752$  (3) Å,  $V = 2519$  (1) Å<sup>3</sup>,  $Z = 4$ .  $\{\eta^3\text{-HB}(3\text{-Bu}^i\text{pz})_3\}\text{Zn}(\text{CN})_{0.9}\text{I}_{0.1}$ : orthorhombic, *Pnma* (No. 62),  $a = 16.315$  (6) Å,  $b = 15.841$  (8) Å,  $c = 9.751$  (4) Å,  $V = 2520$  (1) Å<sup>3</sup>,  $Z = 4$ .

### Introduction

Our recent investigations have demonstrated that the original report of "distortional"<sup>1</sup> or "bond-stretch"<sup>2</sup> isomerism is an artifact

due to crystallographic disorder.<sup>3</sup> The observation of "isomers" of *cis-mer*- $\text{MoOCl}_2(\text{PMe}_2\text{Ph})_3$ , with apparently different  $\text{Mo}=\text{O}$  bond lengths, is due to cocrystallization with small quantities of

(1) (a) Chatt, J.; Manojlovic-Muir, L.; Muir, K. W. *Chem. Commun.* 1971, 655-656. (b) Manojlovic-Muir, L. *J. Chem. Soc. A* 1971, 2796-2800. (c) Manojlovic-Muir, L.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* 1972, 686-690. (d) Haymore, B. L.; Goddard, W. A., III; Allison, J. N. *Proc. Int. Conf. Coord. Chem.*, 23rd 1984, 535.

(2) (a) Jean, Y.; Lledos, A.; Burdett, J. K.; Hoffmann, R. *J. Am. Chem. Soc.* 1988, 110, 4506-4516. (b) Jean, Y.; Lledos, A.; Burdett, J. K.; Hoffmann, R. *J. Chem. Soc., Chem. Commun.* 1988, 140-142. (3) (a) Yoon, K.; Parkin, G.; Rheingold, A. L. *J. Am. Chem. Soc.* 1991, 113, 1437-1438. (b) Yoon, K.; Parkin, G.; Rheingold, A. L. *J. Am. Chem. Soc.* 1992, 114, 2210-2218.