

## Trivalent Lanthanide Interactions with a Terdentate Bis(dialkyltriazinyl)pyridine Ligand Studied by Electrospray Ionization Mass Spectrometry

Sonia Colette,<sup>\*,†</sup> Badia Amekraz,<sup>\*,†</sup> Charles Madic,<sup>‡</sup> Laurence Berthon,<sup>§</sup> Gérard Cote,<sup>||</sup> and Christophe Moulin<sup>†</sup>

CEA-DEN/DPC/SCPA/LAS<sub>2</sub>O, 91191 Gif-sur-Yvette Cedex, France, CEA-Saclay, DEN/Sac-dir, 91191 Gif-sur-Yvette Cedex, France, CEA-Valrhô, DEN/DRCP/SCPS/LCSE, B. P. 171, 30207 Bagnols-sur-Cèze, France, and ENSCP, UMR CNRS 7575, 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France

Received July 23, 2002

The 2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridines (DATPs) belong to a new family of extracting agents recently developed in the framework of nuclear fuel reprocessing. These molecules exhibit exceptional properties to separate actinides(III) from lanthanides(III) in nitric acid solutions. A previous work showed that electrospray ionization mass spectrometry (ESI-MS) is a reliable technique to provide solution data such as stoichiometries and conditional stability constants of various DATP complexes with europium and evidenced the unusual capability of DiPTP [bis-(di-*iso*-propyltriazinyl)pyridine] ligand to form 1:3 complexes in nitric acid solution. This latter result is further investigated by considering DiPTP complexation features with the complete lanthanide family. As a starting point of the experimental procedure used for stability constant evaluation, the intensity distribution of ions detected by ESI-MS is studied for solutions containing Ln(NO<sub>3</sub>)<sub>3</sub> in water/methanol (1:1 v/v) with the pH value set at 2.8 and 4.6 by HNO<sub>3</sub> additions. At pH 2.8, the nitrate anions are found to prevent lanthanides from processes occurring within the ion source: redox phenomena or gas-phase reactions with methanol which give species such as [Ln(MeO)<sub>2</sub>]<sup>+</sup>. Thus, the total intensity of MS signals from [Ln(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>*p*</sub>(MeOH)<sub>*n*</sub>]<sup>+</sup> ions is found proportional to the metal ion concentration. At pH 4.6, with lower nitrate concentration, the nature of the species identified on mass spectra depends on the electronic properties of the lanthanide elements. It is shown that Ln(III) complexation with DiPTP leads to the exclusive formation of 1:3 complexes with the whole lanthanide series which may be due not only to the hydrophobic exterior of the ligand but also to the unusual electronic density distribution in DATP ligands as compared with other aza-aromatic ligands. The conditional stability constants of the 1:3 lanthanide(III) complexes with DiPTP have been determined at pH 2.8 and are found to increase almost regularly from La (log β<sub>3<sup>app</sup></sub> = 11.7 ± 0.1) to Lu (log β<sub>3<sup>app</sup></sub> = 16.7 ± 0.8). Moreover, the kinetic stability of the gas-phase 1:3 complexes obtained by electrospray has been investigated by energy-resolved collision-induced dissociation and provides useful information on the bonding and structure.

### 1. Introduction

The interactions between trivalent actinide (An(III)) and lanthanide (Ln(III)) ions and polydentate nitrogen ligands have attracted great attention in recent years because of the

important task of actinide/lanthanide separation in highly acidic effluents for the management of the radioactive wastes coming from spent nuclear fuel reprocessing.<sup>1,2</sup> The An(III)/Ln(III) separation process is intended to take place after the PUREX and DIAMEX processes, which involve concen-

\* Authors to whom correspondence should be addressed. Telephone: + 33-1-6908-7751. Fax: + 33-1-6908-5411. E-mail: colette@carnac.cea.fr (S.C.); amekraz@cea.fr (B.A.).

<sup>†</sup> CEA-DEN/DPC/SCPA/LAS<sub>2</sub>O.

<sup>‡</sup> CEA-Saclay.

<sup>§</sup> CEA-Valrhô.

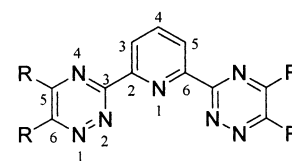
<sup>||</sup> ENSCP.

(1) *Proceedings of the 5th Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation*, Mol, Belgium, November 25–27, 1998; EUR-18898, Paris: OECD/NEA 1999.

(2) Madic, C.; Hudson, M. J.; Liljenzin, J. O.; Glatz, J. P., Nannicini, R.; Facchini, A.; Kolarik, Z.; Odoj, R. *New Partitioning Techniques for Minor Actinides* – Final Report, EUR 19149, Nuclear Science and Technology 2000.

trated nitric acid solutions.<sup>1–3</sup> A future goal is to transmute the long-lived minor actinides, such as americium, into short-lived or stable nuclides by irradiation with neutrons. An(III)/Ln(III) separation is an essential step to achieve prior to the transmutation of actinides; otherwise Ln nuclides, which absorb neutrons very effectively, may prevent neutron capture by the transmutable actinides.<sup>1</sup> The trivalent ions of the 4f and 5f series are known to be hard acids in the Pearson classification of acids and bases.<sup>4</sup> As a consequence, hard donor ligands such as oxygen ligands are preferred to soft N or S donor ligands. Thereby, these 4f and 5f trivalent ions are strongly solvated in aqueous solutions;<sup>5</sup> eight to nine water molecules are bound in the inner coordination sphere of these trivalent metal ions.<sup>6,7</sup> Furthermore, separation of lanthanides from actinides by liquid–liquid extraction has been revealed as a difficult task to achieve because of the great chemical similarity between these two cation families.<sup>8</sup> However, it has been proven that the use of soft multidentate nitrogen ligands makes it possible to separate the two groups of elements.<sup>8</sup> In both families of trivalent f elements, the inner f orbitals are largely or completely unavailable for bond formation and interactions between ligands and trivalent f ions are mainly electrostatic.<sup>6</sup> The nonparticipation of 4f electrons and the implication of the 5d orbitals to the Ln–N bonding in Ln(NH<sub>2</sub>)<sub>3</sub> has been demonstrated recently by theoretical calculations.<sup>9</sup> The better affinity of the soft nitrogen ligands for 5f vs 4f trivalent ions is commonly attributed to the weakly basic nature of these ligands, which results in the formation of stronger actinide–nitrogen bonds with some covalent character thanks to a 5f orbital contribution.<sup>8</sup> This is likely due to the slightly less hard character of An(III) compared to Ln(III). Thus, various aza-aromatic ligands have been shown to selectively extract actinides in preference to lanthanides from a concentrated nitric acid solution.<sup>2,10–14</sup>

Chart 1. Ligand Codes



| L     | R   |
|-------|---|
| DMTP  | CH <sub>3</sub>                                   |
| DnPTP | CH <sub>3</sub> –CH <sub>2</sub> –CH <sub>2</sub> |
| DiPTP | (CH <sub>3</sub> ) <sub>2</sub> –CH               |

Recent studies have shed light on a remarkable new family of extracting agents, the bis(dialkyltriazinyl)pyridines (DATPs) (Chart 1).<sup>2,15–22</sup> The alkyl moieties confer to these molecules hydrophobic properties required to prevent the solubility of the ligand in the aqueous phase, which may be responsible for dramatic lowering in extraction efficiency. The DnPTP [bis(di-*n*-propyltriazinyl)pyridine] ligand is able to selectively extract Am(III) toward Eu(III) from 0.3–0.9 M HNO<sub>3</sub> with a separation factor (SF<sub>Am/Eu</sub>) of 130–140 and a distribution ratio *D*<sub>Am</sub> between 20 and 60,<sup>19,23</sup> other ligands, such as terpyridine, tri(pyridyl)triazine, and aminobis(pyridyl)triazine, necessitate the use of a synergist to extract Am(III) from 0.1–0.13 M HNO<sub>3</sub> with an SF<sub>Am/Eu</sub> between 9 and 12 and *D*<sub>Am</sub> ≤ 1.<sup>13,14,24</sup> The DATP extractants act as terdentate ligands to form metal complexes with the coordination site constituted by the nitrogen atom of the central pyridine ring and the nitrogen atoms at the 2-position of the triazinyl rings. It has been suggested from solvent extraction slope analysis<sup>19,20</sup> that the formula of the complexes with M = Am or

- (3) *Solvent Extraction and Ion Exchange in the Nuclear Fuel Cycle*; Logsdail, D. H., Mills, A. L., Eds.; Ellis Horwood: Chichester, UK, 1985.
- (4) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533–3539.
- (5) (a) Marcus, Y. *Ion Solvation*; Wiley: New York, 1985. (b) Marcus, Y. *Ion Properties*; Marcel Dekker: New York, 1997.
- (6) Choppin, G. R.; Rizkalla, E. N. *Solution Chemistry of Actinides and Lanthanides*. In *Handbook on the Physics and Chemistry of Rare Earths. Lanthanides/Actinides: Chemistry*; Gschneidner, K. A., Jr., Eyring, L., Choppin, G. R., Lander, G. H., Eds.; Elsevier Science: Amsterdam, 1994; Vol. 18, pp 559–590.
- (7) Rizkalla, E. N.; Choppin, G. R. *Lanthanides and Actinides Hydration and Hydrolysis*. In *Handbook on the Physics and Chemistry of Rare Earths. Lanthanides/Actinides: Chemistry*; Gschneidner, K. A., Jr., Eyring, L., Choppin, G. R., Lander, G. H., Eds.; Elsevier Science: Amsterdam, 1994; Vol. 18, pp 529–558.
- (8) (a) Nash, K. L. *Separation Chemistry for Lanthanides and Trivalent Actinides*. In *Handbook on the Physics and Chemistry of Rare Earths. Lanthanides/Actinides: Chemistry*; Gschneidner, K. A., Jr., Eyring, L., Choppin, G. R., Lander, G. H., Eds.; Elsevier Science: Amsterdam, 1994; Vol. 18, pp 197–238. (b) Nash, K. L. *Solvent Extr. Ion Exch.* **1993**, *11*, 729–768.
- (9) Maron, L.; Eisenstein, O. *J. Phys. Chem. A* **2000**, *104*, 7140–7143.
- (10) Drew, M. G. B.; Iveson, P. B.; Hudson, M. J.; Liljenzin, J. O.; Spjuth, L.; Cordier, P.-Y.; Enarsson, Å.; Hill, C.; Madic, C. *J. Chem. Soc., Dalton Trans.* **2000**, 821–830.
- (11) Drew, M. G. B.; Hudson, M. J.; Iveson, P. B.; Madic, C.; Russel, M. L. *J. Chem. Soc., Dalton Trans.* **2000**, 2711–2720.
- (12) Hagström, I.; Spjuth, L.; Enarsson, Å.; Liljenzin, J. O.; Skålberg, M.; Hudson, M. J.; Iveson, P. B.; Madic, C.; Cordier, P.-Y.; Hill, C.; François, N. *Solv. Extr. Ion Exch.* **1999**, *17*, 221–242.

- (13) Cordier, P.-Y.; Hill, C.; Baron, P.; Madic, C.; Hudson, M. J.; Liljenzin, J. O. *J. Alloys Compd.* **1998**, *271/273*, 738–741.
- (14) Boubals, N.; Drew, M. G. B.; Hill, C.; Hudson, M. J.; Iveson, P. B.; Madic, C.; Russel, M. L.; Young, T. G. A. *J. Chem. Soc., Dalton Trans.* **2002**, 55–62.
- (15) Case, F. H. *J. Heterocycl. Chem.* **1971**, *8*, 1043–1046.
- (16) Drew, M. G. B.; Guillauneux, D.; Hudson, M. J.; Iveson, P. B.; Russel, M. L.; Madic, C. *Inorg. Chem. Commun.* **2001**, *4*, 12–15.
- (17) Drew, M. G. B.; Guillauneux, D.; Hudson, M. J.; Iveson, P. B.; Madic, C. *Inorg. Chem. Commun.* **2001**, *4*, 462–466.
- (18) Iveson, P. B.; Rivière, C.; Guillauneux, D.; Nierlich, M.; Thuéry, P.; Ephritikhine, M.; Madic, C. *Chem. Commun.* **2001**, 1512–1513.
- (19) Kolarik, Z.; Müllich, U.; Gassner, F. *Solv. Extr. Ion Exch.* **1999**, *17*, 23–32.
- (20) Kolarik, Z.; Müllich, U.; Gassner, F. *Solv. Extr. Ion Exch.* **1999**, *17*, 1155–1170.
- (21) Hill, C.; Guillauneux, D.; Berthon, L. *Proceedings of International Solvent Extraction Conference ISEC 2002*; Sole, K. C., Cole, P. M., Preston, J. S., Robinson, D. J., Eds.; South African Institute of Mining and Metallurgy, Chris van Rensburg Publications (Pty) Ltd.: Johannesburg, 2002; Vol. 2, pp 1205–1209.
- (22) Colette, S.; Amekraz, B.; Madic, C.; Berthon, L.; Cote, G.; Moulin, C. *Inorg. Chem.* **2002**, *41*, 7031–7041.
- (23) The DATP ligands extract trivalent actinides and lanthanides (M<sup>3+</sup>) from nitric acid medium as described by the following equilibrium: (M<sup>3+</sup>)<sub>aq</sub> + 3(NO<sub>3</sub><sup>-</sup>)<sub>aq</sub> + 3(DATP)<sub>org</sub> ⇌ (M(DATP)<sub>3</sub>(NO<sub>3</sub>)<sub>3</sub>)<sub>org</sub>. The reported DnPTP SF<sub>Am/Eu</sub> and *D*<sub>Am</sub> values are obtained for extraction of Am(III) and Eu(III) nitrates by 0.0344 M of ligand in modified TPH from 1.90 M (H<sub>4</sub>N)<sub>2</sub>NO<sub>3</sub> at room temperature.
- (24) The synergistic extraction of trivalent actinides and lanthanides (M<sup>3+</sup>) observed when combining tridentate planar ligands (L) such as terpyridine, tri(pyridyl)triazine or aminobis(pyridyl)triazine with α-bromodecanoic acid (α-HBrC<sub>10</sub>) in TPH can be described by the following equilibrium: (M<sup>3+</sup>)<sub>aq</sub> + 3(α-HBrC<sub>10</sub>)<sub>org</sub> + L<sub>org</sub> ⇌ (ML(α-BrC<sub>10</sub>)<sub>3</sub>)<sub>org</sub> + 3(H<sup>+</sup>)<sub>aq</sub>. The SF<sub>Am/Eu</sub> and *D*<sub>Am</sub> values reported here were measured for the synergistic systems: For organic solution: [α-HBrC<sub>10</sub>]<sub>initial</sub> = 1 M, [L]<sub>initial</sub> = 0.02 M, TPH; for aqueous solution: [HNO<sub>3</sub>]<sub>equilibrium</sub> = 0.10–0.13 M, T = 22 °C.

Eu has to be written as  $\text{ML}_3(\text{NO}_3)_3 \cdot \text{HNO}_3$ . However, no Am(III) or Cm(III) complex with DATP ligands has been isolated and characterized. In 2001, Drew et al.<sup>16</sup> demonstrated that addition of lanthanide(III) nitrates (Sm–Lu) to the extracting agent 2,6-bis(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine (DnPTP) in a 1:1 ratio in ethanol resulted in the crystallization of complexes containing  $[\text{Ln}(\text{DnPTP})_3]^{3+}$  cations in which the lanthanide ions were shown to be 9-coordinated. However, it proved impossible to obtain crystals of complexes with  $[\text{Ln}(\text{DATP})_3]^{3+}$  cations when ligands with methyl, ethyl, and *iso*-butyl substituents were allowed to react with lanthanide nitrates (La–Sm).<sup>17</sup> The lanthanide ionic radius decreases regularly along the series because of the increasing nuclear electric field: the effective ionic radius of  $\text{La}^{3+}$  is 1.216 Å for a coordination number (CN) of 9 and that of  $\text{Lu}^{3+}$  is 0.977 Å for CN = 8.<sup>6</sup> Thus, it has been suggested that the formation of 1:3 complexes was limited to the later lanthanides (Sm–Lu) as a result of their smaller ionic radii, which make them more prone to form 9-coordinate complexes, and thereby the three terdentate ligands could complete the coordination sphere of the metal ion.<sup>17</sup> It will be shown below that this assumption will not be valid in the results presented here.

Recently, we reported the results of a study of Eu(III) complexation with three DATPs—methyl- (DMTP), *n*-propyl- (DnPTP), and *iso*-propyl- (DiPTP)—by electrospray ionization mass spectrometry (ESI-MS).<sup>22</sup> Previous studies have proved the potential of ESI-MS for determining the speciation of dissolved metal species.<sup>25,26</sup> More recently, studies have been carried out on the speciation of uranium<sup>27</sup> and thorium<sup>28</sup> by ESI-MS. DATP/Eu(III) mixtures with a molar ratio in the range 0.2–5 have been prepared in nitric acid water/methanol (1:1 v/v) solutions, and ESI-MS has been used to provide solution data such as stoichiometries and stability constants for Eu(III)/DATP complexes. Because the DATP ligands are little soluble or not soluble in water, the use of methanol as an organic cosolvent was necessary. However, in a 50:50 mixture of water and methanol, Eu is mostly surrounded by water molecules in inner sphere and so the solution equilibrium should reflect that of an aqueous solution.<sup>6,7,29</sup>

Investigations have shown the existence of stable  $\text{Eu}(\text{L})_3^{3+}$  ions with  $\text{L} \equiv \text{DnPTP}$  ( $\log \beta_3^{\text{app}} = 12.0 \pm 0.5$ ) and DiPTP ( $\log \beta_3^{\text{app}} = 14.0 \pm 0.6$ ) in the pH range 2.8–4.6. The 1:3 stoichiometry obtained by ESI-MS is consistent with the conventional solvent extraction slope analysis. Other complexes are observed, such as  $\text{Eu}(\text{L})_2^{3+}$  only for DnPTP ( $\log \beta_2^{\text{app}} = 6.7 \pm 0.5$ ) and DMTP ( $\log \beta_2^{\text{app}} = 6.3 \pm 0.1$ ) and  $\text{Eu}(\text{L})^{3+}$  only for DMTP ( $\log \beta_1^{\text{app}} = 2.9 \pm 0.2$ ). The  $\log$

$\beta_n^{\text{app}}$  values for the  $\text{Eu}(\text{L})_n^{3+}$  ( $n = 1-3$ ) complexes were determined at pH 2.8. Further, ESI-MS measurements have been validated by giving evidence that the stability constants values are similar to that obtained by a complementary technique. Indeed, the TRLIF values reported in the previous study ( $\log \beta_3 = 14.3 \pm 0.6$  at pH 2.8 for DiPTP ligand and  $\log \beta_1 = 3.0$  at pH 4 for DMTP ligand) are in good agreement with those obtained by ESI-MS, providing some support for the reliability of the ESI-MS measurements. These data, together with different observations made previously either in extraction experiments<sup>2,19-21</sup> or in solid state,<sup>2,16,18</sup> evidenced a mode of complexation leading to unusual aqueous  $\text{Eu}(\text{DATP})_3^{3+}$  ions whereby the hydrophobic exterior, i.e., alkyl substituents, play a crucial role. This phenomenon is enhanced with *iso*-propyl substituents making the complexation of DiPTP remarkably restricted to 1:3 complex in the pH range 2.8–4.6 whatever the ligand-to-metal ratio between 0.2 and 5.<sup>22</sup> It is thought that in the structure of the type  $\text{Eu}(\text{DiPTP})_3^{3+}$  the complex core is an environment which excludes itself from the solvent molecules probably due to the alkyl chains at the triazinyl rings.

It appeared then quite interesting to check if the DiPTP complexation features were maintained within the whole lanthanide series and to investigate the electronic complexation mechanism leading to 1:3 complex formation. To date, several rare-earth complexes of nitrogen terdentate ligands of interest in liquid–liquid extraction have been characterized by X-ray diffraction.<sup>2,10,11,14,30-34</sup> Although crystallographic studies provide precious structural data on lanthanide and actinide complexes, they give little information about the mode of complexation. A theoretical donor–acceptor model of Ln(III) complexation with nitrogen ligands based on both ab initio calculations and thermodynamic data has recently been proposed<sup>35</sup> for the 1:1 complexes of Ln(III) with nitrogen terdentate ligands.

In this work, lanthanide complexes with DiPTP ligand were studied by the same experimental procedure as previously described.<sup>22</sup> It was decided to carry out experiments at one value of the ligand-to-metal ratio since the study was devoted to the DiPTP ligand with the whole lanthanide series. A molar ratio of DiPTP over the lanthanide ions < 3 was chosen (2-fold) to better establish the restricted 1:3 stoichiometry for lanthanide complexation by the DiPTP ligand. First, full-scan simple ESI-MS spectra have been used to investigate (i) the composition of the solutions at pH 4.6 and 2.8 and (ii) the conditional stability constant  $\log \beta_3^{\text{app}}$  for each 4f element trivalent ion at pH 2.8. The “free” Ln(III) (i.e.,  $[\text{Ln}(\text{NO}_3)_2(\text{H}_2\text{O})_p(\text{MeOH})_n]^+$ ) equilibrium con-

(25) Ross, A. R. S.; Ikonou, M. G.; Thompson, J. A. J.; Orians, K. J. *Anal. Chem.* **1998**, *70*, 2225–2235.

(26) Agnes, G. R.; Horlick, G. *Appl. Spectrosc.* **1992**, *46*, 401–406. Moulin, C.; Amekraz, B.; Hubert, S.; Moulin, V. *Anal. Chim. Acta* **2001**, *441*, 269–279.

(27) Moulin, C.; Charron, N.; Plancque, G.; Virelizier, H. *Anal. Spectrosc.* **2000**, *54*, 843–848.

(28) Moulin, C.; Amekraz, B.; Hubert, S.; Moulin, V. *Anal. Chim. Acta* **2001**, *441*, 269–279.

(29) Tanaka, F.; Kawasaki, Y.; Yamashita, S. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 1083–1090.

(30) Berthet, J. C.; Rivière, C.; Miquel, Y.; Nierlich, M.; Madic, C.; Ephritikhine, M. *Eur. J. Inorg. Chem.* **2002**, *6*, 1439–1446.

(31) Drew, M. G. B.; Hudson, M. J.; Iveson, P. B.; Madic, C.; Russel, M. L. *J. Chem. Soc., Dalton Trans.* **1999**, 2433–2440.

(32) Wietzke, R.; Mazzanti, M.; Latour, J.-M.; Pécaut, J.; Cordier, P.-Y.; Madic, C. *Inorg. Chem.* **1998**, *37*, 6690–6697.

(33) (a) Drew, M. G. B.; Hudson, M. J.; Iveson, P. B.; Madic, C. *Acta Crystallogr., Sect. C* **2000**, *C56*, 434–435. (b) Wietzke, R.; Mazzanti, M.; Latour, J.-M.; Pécaut, J. *Inorg. Chem.* **1999**, *38*, 3581–3585.

(34) Mazzanti, M.; Wietzke, R.; Pécaut, J.; Latour, J.-M.; Maldivi, P.; Remy, M. *Inorg. Chem.* **2002**, *41*, 2389–2399.

(35) Ionova, G.; Rabbe, C.; Guillaumont, R.; Ionov, S.; Madic, C.; Krupa, J.-C.; Guillaumont, D. *New J. Chem.* **2002**, *26*, 234–242.

centrations are deduced from the total signal response for all complexes coming from the “free” Ln(III) observed in the ESI mass spectra. Consequently, as required by this experimental procedure, preliminary determination of the Ln(III) speciation in nitric acid water/methanol (1:1 v/v) solutions as detected by ESI-MS has been investigated. Second, the kinetic stability of the gas-phase  $[\text{Ln}(\text{DiPTP})_3]^{3+}$  and  $[\text{Ln}(\text{DiPTP})_3(\text{NO}_3)]^{2+}$  ions generated by electrospray has been studied by monitoring the fragments obtained from variable-energy collision-induced-dissociation (CID) experiments, the so-called energy-resolved mass spectrometric (ERMS) technique.<sup>36,37</sup> CID experiments of Ln(III) complexes with ligands have been successfully used by Hopfgartner et al. to provide information on the bonding and structure.<sup>38</sup>

## 2. Experimental Section

**2.1. Materials.** The DiPTP ligand was provided by CEA/DEN/DRCP (Bagnols-sur-Cèze, France). Stock solutions ( $2 \times 10^{-4}$  M) of DiPTP ( $M = 405$  g/mol) were prepared by dissolution of a weighed amount in HPLC grade methanol. Stock solutions ( $10^{-4}$  M) of lanthanide(III) in nitric acid were prepared at pH 4.6 and 2.8 by dissolving high-purity crystals of  $\text{Ln}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$  ( $n = 5$  or 6) (Sigma) in appropriate solutions of nitric acid (Sigma). All chemicals used were of reagent grade, and Millipore water was used throughout the procedure. The study was carried out with nitrates since the An(III)/Ln(III) separation process takes place in nitric acid solutions.

The water/methanol (1:1 v/v) solutions ( $[\text{Ln}] = 5 \times 10^{-5}$  M) for the ESI-MS measurements were prepared from 5 mL of stock metal ion solution mixed with either 5 mL of methanol or 5 mL of stock DiPTP solution (the ligand-to-metal molar ratio of these solutions was 2 in order to check the exclusive formation of 1:3 complexes even at a molar ratio lower than 3). Experiments were directly performed in nitric acid with the ionic strength fixed mainly by the nitric acid and lanthanide nitrate concentrations. The pH was first fixed at 4.6 in order to avoid formation of lanthanide hydroxide species which may occur at higher pH values and also to limit competition between ligand protonation and Ln/DATP complexation; then, the pH was lowered at 2.8 to get closer to the process conditions. Among a series of samples, where the pH was adjusted to a given value by addition of nitric acid, the ionic strength remained roughly constant at around  $3.2 \times 10^{-4}$  M for pH 4.6 and  $1.9 \times 10^{-3}$  M at pH 2.8.

**2.2. MS Apparatus and Conditions.** The mass spectrometric measurements were recorded in positive ion mode using a Quattro II triple-quadrupole spectrometer equipped with an ESI interface (Micromass, Manchester, UK). The spray needle voltage was set to 3.5 kV, and nitrogen operating at 300 L/h was employed as both the drying and nebulizing gas. Freshly prepared samples were analyzed by flow injection ESI-MS using the sample solvent as the carrier. A syringe infusion pump (Harvard Apparatus, Cambridge, MA) delivered solvent at 15  $\mu\text{L}/\text{min}$  to a Rheodyne 9725 multiport rotary valve (20- $\mu\text{L}$  loop) connected to the ESI probe by a fused silica tubing. Samples were introduced using a 50- $\mu\text{L}$  glass syringe with a stainless steel needle (Hamilton Co., Reno, NV). The source temperature was set to 80 °C, and the sample cone

voltage was set at 30 or 40 V. Spectra were acquired at 6 s/scan over a mass range of  $m/z$  50–1800 with an acquisition time of 3 min. For ERMS measurements, collision-induced dissociation of cluster ions was performed with argon; the collision gas pressure was  $2 \times 10^{-3}$  mbar. Spectra were obtained at different collision energies ranging from 0 to 60 eV. Lanthanide species are seen in their natural abundance. In the data given and for simplification purposes, only the  $m/z$  peaks corresponding to the most abundant isotopic mass have been given.

**2.3. Measurement Procedure.** The pH values of the solutions were measured with a conventional pH meter (Model PHN 81, Tacussel, 22 °C) equipped with a subminiature combined electrode (Model PH XC161) filled with an aqueous KCl + AgCl solution and calibrated with aqueous pH standards. No correction was made for the presence of methanol. Between each sample, the instrument was rinsed with appropriate diluted nitric acid solutions ( $10^{-3}$ – $10^{-5}$  M).

**2.4. Equilibrium Concentration Calculation.** The free lanthanide equilibrium concentration was derived directly from the total ion current of the complexes coming from the free lanthanide in solution; then the equilibrium concentrations of the free ligand and of the  $[\text{Ln}(\text{DiPTP})_3]^{3+}$  ions were calculated from the known amounts of ligand and Ln added to each solution (“T” is the total concentration):

$$[\text{Ln}(\text{DiPTP})_3]^{3+} = [\text{Ln}]_T - [\text{Ln}] \quad (1)$$

$$[\text{DiPTP}] = [\text{DiPTP}]_T - 3[\text{Ln}(\text{DiPTP})_3]^{3+} \quad (2)$$

## 3. Results and Discussion

**3.1. ESI-MS of Lanthanide Nitrates in Water/Methanol Medium.** It has been recognized that the lanthanide(III) aquo ions  $\text{Ln}(\text{H}_2\text{O})_n$  ( $n = 8$ –9) undergo changes in the transition from the condensed phase to the gas phase for their detection by mass spectrometry:<sup>39</sup> they enter the gas phase with a solvation shell, and then desolvation process in the ESI interface<sup>40</sup> as well as redox reactions (at the ESI needle or the counter electrode) may produce ions different from those present in the solution. Van Berkel and Zhou<sup>41</sup> showed that the ESI source can be considered as a controlled-current electrolytic cell. Thus, hydrated trivalent metal ions have not been observed in ESI spectra, so that only species such as  $[\text{Ln}(\text{OH})(\text{H}_2\text{O})_n]^{2+}$  ( $M = \text{La}, \text{Ce}, \text{Nd}, \text{Sm}$ )<sup>42</sup> and  $[\text{Ln}(\text{MeO})(\text{MeOH})_n]^{2+}$  ( $M = \text{La}, \text{Ce}, \text{Pr}, \text{Tm}, \text{Yb}, \text{Lu}$ )<sup>43</sup> have been reported for methanolic (1%–5% water) solutions. Besides, it has been proved that, as the ion-source energy was increased,  $[\text{Ln}(\text{MeO})(\text{MeOH})_n]^{2+}$  ions decomposed to give species such as  $[\text{Ln}(\text{OH})]^{+}$  and  $[\text{Ln}(\text{MeO})_2]^{+}$ . These results illustrate that lanthanide cations behave as Lewis acids and bind most strongly to hard bases such as oxygen, and thereby lanthanide–oxygen bonds are readily observed. Recently, ESI-MS was used in negative mode for acidic methanol–water (1:1 v/v) solutions of  $M^{3+}$  metal cations such as  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Y}^{3+}$ , with an excess of nitrate or chloride.<sup>44</sup> These

(36) Harrison, A. G. *Rapid Commun. Mass Spectrom.* **1999**, *13*, 1663–1670.

(37) Gabelica, V.; De Pauw, E. *J. Mass Spectrom.* **2001**, *36*, 397–402.

(38) Hopfgartner, G.; Piguet, C.; Henion, J. D. *J. Am. Soc. Mass Spectrom.* **1994**, *5*, 748–756.

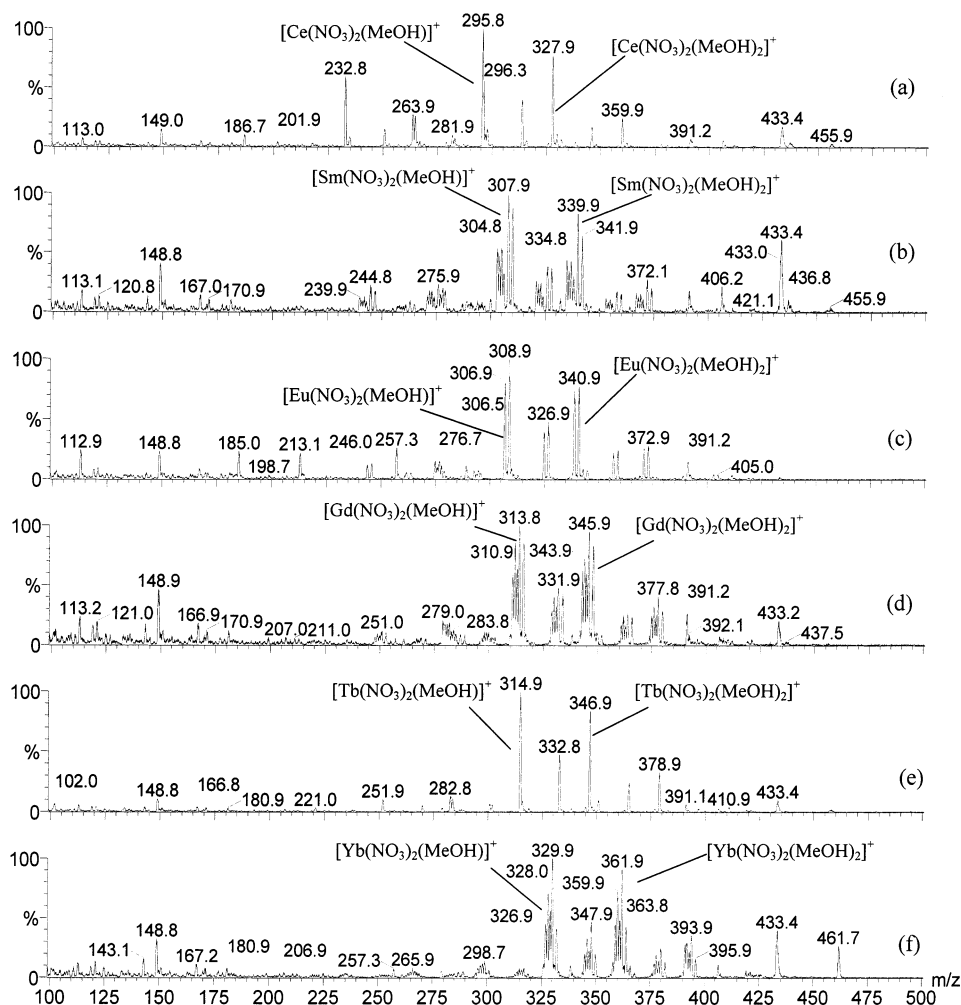
(39) Colton, R.; D’Agostino, A.; Traeger, J. C. *Mass Spectrom. Rev.* **1995**, *14*, 79–106.

(40) Kebarle, P. *J. Mass Spectrom.* **2000**, *35*, 804–817.

(41) Van Berkel, G. J.; Zhou, F. *Anal. Chem.* **1995**, *67*, 2916–2923.

(42) Blades, A. T.; Jayaweera, P.; Ikononou, M. G.; Kebarle, P. *Int. J. Mass Spectrom. Ion Process.* **1990**, *101*, 325–336.

(43) Stewart, I. I.; Horlick, G. *Anal. Chem.* **1994**, *66*, 3983–3993.



**Figure 1.** ESI-MS spectra of  $5 \times 10^{-5}$  M  $\text{Ln}(\text{NO}_3)_3$  in water/methanol (1:1 v/v) at pH 2.8, aqueous nitrate medium, cone voltage 40 V. Ln = Ce (a), Sm (b), Eu (c), Gd (d), Tb (e), and Yb (f).

latter anions, which were found to prevent reduction reactions, were used to produce  $[\text{M}(\text{NO}_3)_4]^-$  and  $[\text{M}(\text{Cl})_4]^-$  negative ions, thus allowing the speciation of metal ions.

The mass spectra of  $5 \times 10^{-5}$  M  $\text{Ln}(\text{NO}_3)_3$  in nitric acid water/methanol (1:1 v/v) at pH 4.6 and 2.8 have been obtained for the whole lanthanide series (except for radioactive Pm). It could be noticed that the mixed aqueous–organic solvents used in this work can yield mixed-solvent clusters  $\text{Ln}(\text{H}_2\text{O})_x(\text{MeOH})_y^{n+}$  in the early stages of ion evaporation in the ESI interface.<sup>40</sup> The extent of solvation and fragmentation observed are selected by using voltage differences in the ESI interface of 30 or 40 V. Representative spectra taken at 40 V are shown in Figure 1 to illustrate the ions observed at pH 2.8 for the lighter (Ce), intermediate (Sm, Eu, Gd, Tb), and heavier (Yb) lanthanides. At pH 2.8, the spectra taken at either 30 or 40 V are quite similar throughout the series, and the main peaks are singly charged ions involving two nitrate anions in which the central cation is in its initial +3 oxidation state. The likely cations  $[\text{Ln}(\text{NO}_3)_2(\text{MeOH})_n]^+$  ( $n = 1-3$ ) and  $[\text{Ln}(\text{NO}_3)_2(\text{H}_2\text{O})(\text{MeOH})_n]^+$  ( $n = 1-2$ ) can be identified when a voltage difference of 30 V is used (data not shown); the main peaks are from  $[\text{Ln}(\text{NO}_3)_2(\text{MeOH})_n]^+$

( $n = 2-3$ ). For a 40 V voltage difference, the signal distribution for the various peaks is  $[\text{Ln}(\text{NO}_3)_2(\text{MeOH})_n]^+$  ( $n = 0-3$ )  $>$   $[\text{Ln}(\text{NO}_3)_2(\text{H}_2\text{O})(\text{MeOH})_n]^+$  ( $n = 1-2$ )  $>$   $[\text{Ln}(\text{NO}_3)(\text{MeO})(\text{MeOH})_n]^+$  ( $n = 0-1$ ), these latter ions being more abundant for Ln = La–Sm (Table 1). Thus, there is an apparent predominance of the solvate  $[\text{Ln}(\text{NO}_3)_2(\text{MeOH})_n(\text{H}_2\text{O})_m]^+$  while, as stressed above, one can expect  $\text{H}_2\text{O}$  to be the primary solvating species in water/methanol (1:1 v/v).

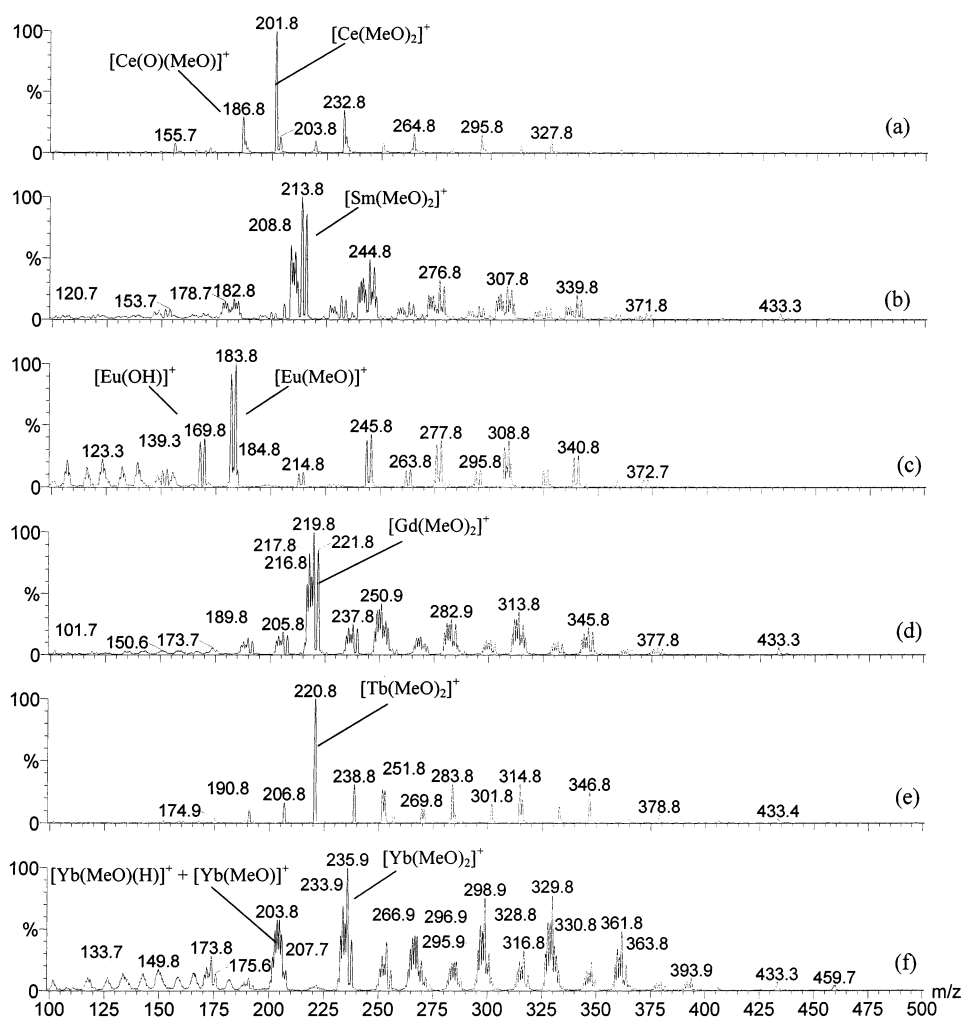
Previous measurements from solutions at pH 2.8 containing  $2 \times 10^{-5}$  to  $4 \times 10^{-4}$  M europium showed that the total ion abundance of  $[\text{Eu}(\text{NO}_3)_2(\text{MeOH})_n]^+$  ( $n = 0-3$ ) and  $[\text{Eu}(\text{NO}_3)_2(\text{H}_2\text{O})(\text{MeOH})_n]^+$  ( $n = 1-2$ ) species is proportional to the europium concentration (correlation coefficient 0.99).<sup>22</sup> In the present work, for either 30 or 40 V voltage differences, it was found also possible to evaluate Ln(III) equilibrium concentrations of samples containing DiPTP ligands from the total signal response of these singly charged ions in spectra. Assuming that ion intensity is proportional to concentration, if we note  $[\text{Ln}]_{\text{T}}$  and  $[\text{Ln}]_{\text{eq}}$  the total ion concentration of the species corresponding to “free” Ln in the ESI spectra of solutions containing  $5 \times 10^{-5}$  M lanthanide and either 0 or  $10^{-4}$  M ligand, respectively,  $[\text{Ln}]_{\text{eq}}$  may be calculated from the observed ion intensity ratio  $I_{[\text{Ln}]_{\text{eq}}}/I_{[\text{Ln}]_{\text{T}}}$ . Then, the distribution of singly charged “free” Ln

(44) Mollah, S.; Pris, A. D.; Johnson, S. K.; Gwizdala III, A. B.; Houk, R. S. *Anal. Chem.* **2000**, *72*, 985–991.

**Table 1.** Complexes Detected by ESI-MS at a Cone Voltage of 40 V for  $5 \times 10^{-5}$  M  $\text{Ln}(\text{NO}_3)_3$  at pH 2.8 in Water/Methanol (1:1 v/v), Aqueous Nitrate Medium<sup>a</sup>

| complex   |            | La    | Ce    | Pr    | Nd    | Sm    | Eu    | Gd    | Tb    | Dy    | Ho    | Er    | Tm    | Yb    | Lu    |
|---|------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| [Ln(NO <sub>3</sub> )(MeO)] <sup>+</sup>  | <i>m/z</i> | 231.9 | 232.8 | 233.8 | 235   | 244.8 | 246.0 | 251.0 | 251.9 | 257.1 |       |       |       |       |       |
|   | %          | 49    | 60    | 63    | 39    | 25    | 15    | 11    | 10    | 10    |       |       |       |       |       |
| [Ln(NO <sub>3</sub> )(MeO)(MeOH)] <sup>+</sup>  | <i>m/z</i> | 263.9 | 264.9 | 266   | 266.8 | 277   | 277.9 |       | 284   | 288.9 | 289.9 |       | 294.1 | 298.7 | 300.0 |
|   | %          | 18    | 26    | 27    | 17    | 19    | 13    |       | 11    | 15    | 10    |       | 10    | 15    | 13    |
| [Ln(NO <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup>                                       | <i>m/z</i> | 263   | 263.9 | 265   | 265.8 | 275.9 | 276.9 | 281.7 | 282.8 | 287.9 | 288.9 |       |       |       |       |
|   | %          | 33    | 29    | 24    | 30    | 29    | 19    | 18    | 12    | 9     | 8     |       |       |       |       |
| [Ln(NO <sub>3</sub> ) <sub>2</sub> (MeOH)] <sup>+</sup>                                 | <i>m/z</i> | 294.9 | 295.8 | 296.9 | 298   | 307.9 | 308.9 | 313.8 | 314.9 | 319.9 | 320.9 | 321.8 | 324.9 | 329.9 | 331.0 |
|   | %          | 100   | 100   | 100   | 100   | 100   | 100   | 100   | 100   | 100   | 100   | 100   | 100   | 100   | 100   |
| [Ln(NO <sub>3</sub> ) <sub>2</sub> (MeOH) <sub>2</sub> ] <sup>+</sup>                   | <i>m/z</i> | 326.9 | 327.9 | 328.9 | 329.9 | 339.9 | 340.9 | 345.9 | 346.9 | 352   | 352.9 | 353.9 | 356.9 | 361.9 | 362.9 |
|   | %          | 84    | 74    | 78    | 80    | 81    | 80    | 87    | 76    | 79    | 84    | 89    | 93    | 93    | 100   |
| [Ln(NO <sub>3</sub> ) <sub>2</sub> (MeOH) <sub>3</sub> ] <sup>+</sup>                   | <i>m/z</i> | 358.8 | 359.9 | 360.9 | 362   | 372.1 | 372.9 | 377.8 | 378.9 | 384   | 384.9 | 386   | 388.9 | 393.9 | 394.9 |
|   | %          | 22    | 23    | 25    | 27    | 29    | 34    | 32    | 30    | 29    | 32    | 37    | 40    | 38    | 38    |
| [Ln(NO <sub>3</sub> ) <sub>2</sub> (MeOH)(H <sub>2</sub> O)] <sup>+</sup>               | <i>m/z</i> | 312.9 | 313.9 | 314.9 | 315.9 | 326.1 | 326.9 | 331.9 | 332.8 | 338   | 338.9 | 339.9 | 343   | 347.9 | 348.9 |
|   | %          | 43    | 39    | 43    | 46    | 38    | 62    | 48    | 46    | 48    | 42    | 47    | 44    | 41    | 42    |
| [Ln(NO <sub>3</sub> ) <sub>2</sub> (MeOH) <sub>2</sub> (H <sub>2</sub> O)] <sup>+</sup> | <i>m/z</i> | 345   | 346   | 347   | 347.9 | 357.7 | 358.8 | 363.8 | 365   | 370   | 370.9 | 372   | 374.8 | 379.8 | 381.0 |
|   | %          | 17    | 16    | 15    | 20    | 18    | 27    | 24    | 23    | 22    | 23    | 25    | 31    | 25    | 26    |

<sup>a</sup> The abundance of each species has been normalized relative to that of [Ln(NO<sub>3</sub>)<sub>2</sub>(MeOH)]<sup>+</sup>, which is always the dominant species.



**Figure 2.** ESI-MS spectra of  $5 \times 10^{-5}$  M  $\text{Ln}(\text{NO}_3)_3$  in water/methanol (1:1 v/v) at pH 4.6, aqueous nitrate medium, cone voltage 40 V. Ln = Ce (a), Sm (b), Eu (c), Gd (d), Tb (e), and Yb (f).

species was apparently unaffected by phenomena such as mass-dependent transmission by the quadrupole analyzer<sup>45</sup> and differences in the response factors.

The situation is somewhat different at pH 4.6 (Figure 2). The main lanthanide species identified on the ESI-MS spectra and their relative percentage with regard to the most abundant species are gathered in Table 2. For simplification purposes,

the data are detailed for the lanthanides for which ESI-MS speciation is representative of the variation of the ion abundance profiles across the series. Indeed, La, Pr, and Nd are close to Ce, and Dy, Ho, and Er are similar to Tb. At lower nitric acid concentration, the cluster ions involving two nitrate anions are much less abundant and triply charged metal cations react with the organic cosolvent (methanol

**Table 2.** Complexes Detected by ESI-MS at a Cone Voltage of 40 V for  $5 \times 10^{-5}$  M  $\text{Ln}(\text{NO}_3)_3$  at pH 4.6 in Water/Methanol (1:1 v/v), Aqueous Nitrate Medium<sup>a</sup>

| complex   |            | Ce    | Sm    | Eu               | Gd    | Tb    | Tm    | Yb    | Lu    |
|---|------------|-------|-------|------------------|-------|-------|-------|-------|-------|
|   |            |       |       | $\text{Ln}^{2+}$ |       |       |       |       |       |
| $[\text{Ln}(\text{OH})]^+$  | <i>m/z</i> |       |       | 169.8            |       |       |       |       |       |
|   | %          |       |       | 40               |       |       |       |       |       |
| $[\text{Ln}(\text{MeO})]^+$   | <i>m/z</i> |       | 182.8 | 183.8            |       |       |       | 204.8 |       |
|   | %          |       | 15    | 100              |       |       |       | 39    |       |
| $[\text{Ln}(\text{NO}_3)]^+$  | <i>m/z</i> |       |       | 214.8            |       |       |       |       |       |
|   | %          |       |       | 10               |       |       |       |       |       |
|   |            |       |       | $\text{Ln}^{3+}$ |       |       |       |       |       |
| $[\text{Ln}(\text{H})(\text{MeO})]^+$                                     | <i>m/z</i> |       |       |                  | 189.8 | 190.8 | 200.8 | 205.8 | 206.8 |
|   | %          |       |       |                  | 14    | 11    | 12    | 48    | 13    |
| $[\text{Ln}(\text{MeO})_2]^+$   | <i>m/z</i> | 201.8 | 213.8 | 214.8            | 219.8 | 220.8 | 230.8 | 235.9 | 236.9 |
|   | %          | 100   | 100   | 10               | 100   | 100   | 100   | 100   | 100   |
| $[\text{Ln}(\text{MeO})_2(\text{H}_2\text{O})]^+$                         | <i>m/z</i> | 219.8 | 231.8 |                  | 237.8 | 238.8 | 248.9 | 253.9 | 254.8 |
|   | %          | 10    | 20    |                  | 26    | 31    | 42    | 39    | 44    |
| $[\text{Ln}(\text{NO}_3)(\text{MeO})]^+$                                  | <i>m/z</i> | 232.8 | 244.8 | 245.8            | 250.9 | 251.8 | 261.8 | 266.9 | 267.9 |
|   | %          | 35    | 49    | 40               | 43    | 27    | 16    | 40    | 13    |
| $[\text{Ln}(\text{MeO})_2(\text{MeOH})]^+$                                | <i>m/z</i> | 233.9 | 245.8 |                  | 251.9 | 252.8 | 262.9 | 267.9 | 268.9 |
|   | %          | 14    | 25    |                  | 26    | 27    | 34    | 45    | 43    |
| $[\text{Ln}(\text{NO}_3)(\text{MeO})(\text{H}_2\text{O})]^+$              | <i>m/z</i> | 251   | 262.8 | 263.8            | 268.8 | 269.8 | 279.9 | 284.9 | 285.9 |
|   | %          | 8     | 15    | 13               | 10    | 11    | 8     | 10    | 7     |
| $[\text{Ln}(\text{MeO})_2(\text{MeOH})(\text{H}_2\text{O})]^+$            | <i>m/z</i> |       |       |                  | 269.8 | 270.9 | 280.9 | 285.9 | 286.9 |
|   | %          |       |       |                  | 9     | 11    | 21    | 24    | 31    |
| $[\text{Ln}(\text{NO}_3)(\text{MeO})(\text{MeOH})]^+$                     | <i>m/z</i> | 264.8 | 276.8 | 277.8            | 282.9 | 283.8 | 293.9 | 298.9 | 299.9 |
|   | %          | 15    | 32    | 35               | 29    | 31    | 37    | 74    | 47    |
| $[\text{Ln}(\text{NO}_3)(\text{MeO})(\text{MeOH})(\text{H}_2\text{O})]^+$ | <i>m/z</i> |       |       | 295.8            | 300.9 | 301.8 | 311.9 | 316.8 | 317.9 |
|   | %          |       |       | 13               | 12    | 15    | 22    | 31    | 26    |
| $[\text{Ln}(\text{NO}_3)_2(\text{MeOH})]^+$                               | <i>m/z</i> | 295.8 | 307.8 | 308.8            | 313.8 | 314.8 | 324.9 | 329.8 | 330.8 |
|   | %          | 14    | 27    | 35               | 37    | 30    | 35    | 74    | 41    |
| $[\text{Ln}(\text{NO}_3)(\text{MeO})(\text{MeOH})_2]^+$                   | <i>m/z</i> |       |       | 309.8            | 314.8 | 315.8 | 325.9 | 330.8 | 331.9 |
|   | %          |       |       | 19               | 17    | 19    | 25    | 36    | 35    |
| $[\text{Ln}(\text{NO}_3)_2(\text{MeOH})(\text{H}_2\text{O})]^+$           | <i>m/z</i> |       | 325.8 | 326.9            | 331.7 | 332.8 | 342.8 | 347.8 | 348.8 |
|   | %          |       | 10    | 13               | 11    | 12    | 14    | 23    | 16    |
| $[\text{Ln}(\text{NO}_3)_2(\text{MeOH})_2]^+$                             | <i>m/z</i> | 327.8 | 339.8 | 340.8            | 345.8 | 346.8 | 356.9 | 361.8 | 362.8 |
|   | %          | 10    | 19    | 23               | 21    | 24    | 30    | 47    | 39    |
|   |            |       |       | $\text{Ln}^{4+}$ |       |       |       |       |       |
| $[\text{Ln}(\text{O})(\text{MeO})]^+$                                     | <i>m/z</i> | 186.8 |       |                  |       |       |       |       |       |
|   | %          | 30    |       |                  |       |       |       |       |       |

<sup>a</sup> The abundance of each species has been normalized relative to the most abundant one.

molecules), so most of them produce mainly singly charged species  $[\text{Ln}(\text{MeO})_2]^+$ . These latter ions are the major peaks for  $\text{Ln} = \text{La} - \text{Sm}$  at voltage differences of either 30 or 40 V. For other lanthanides such as  $\text{Ln} = \text{Gd} - \text{Lu}$ , the  $[\text{Ln}(\text{MeO})_2]^+$  ions are observed along with signals from  $[\text{Ln}(\text{NO}_3)(\text{MeO})(\text{H}_2\text{O})_p(\text{MeOH})_n]^+$  ions which decompose as the ion-source energy is increased. The  $[\text{Ln}(\text{MeO})_2]^+$  ions are precisely the same as those reported by Stewart and Horlick from an ESI-MS spectrum of  $\text{Pr}(\text{NO}_3)_3$  in methanol.<sup>43</sup> These species have been identified by MS/MS (Table 3) in the case of Ce, Tb, and Yb.

At pH 4.6, the Eu spectrum differs from those of the other lanthanides in that the  $[\text{Ln}(\text{MeO})_2]^+$  ions are not the species induced by low nitrate concentration and high ion-source energy. Instead, two singly charged species  $[\text{Eu}(\text{MeO})]^+$  and  $[\text{Eu}(\text{OH})]^+$  are observed as previously noticed.<sup>22</sup> In fact, the presence of these ions, characteristic of charge reduction reaction at the ESI interface, could be attributed to the europium  $E_{3/2}$  redox potential value ( $E_{3/2} = -0.35$  V),<sup>46</sup> so the solvated ions are likely converted to charged reduced species by electrochemical reduction. The  $E_{3/2}$  redox potential

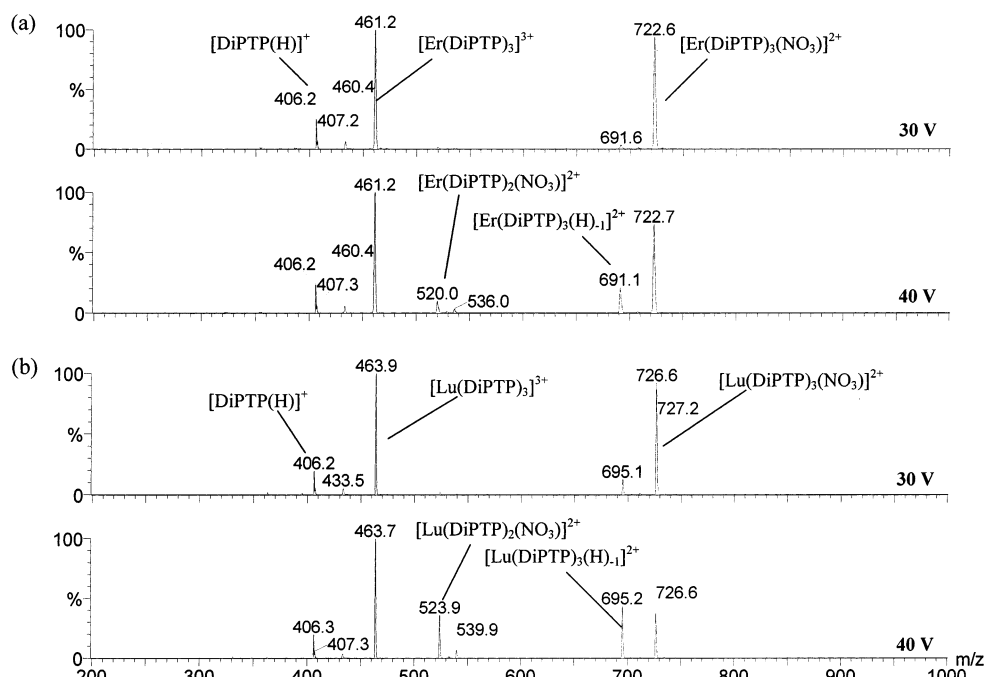
**Table 3.** Lanthanide Complex Characterization by MS/MS with a Cone Voltage Set at 30 V

| lanthanide complex   | <i>m/z</i> | daughter ion <i>m/z</i> | loss                   |
|--|------------|-------------------------|------------------------|
| $[\text{Ce}(\text{MeO})_2]^+$                              | 201.9      | 186.9                   | $\text{CH}_3$          |
|  |            | 171.8                   | $\text{CH}_2\text{O}$  |
|  |            | 169.9                   | $\text{CH}_3\text{OH}$ |
| $[\text{Tb}(\text{MeO})_2]^+$                              | 221        | 190.9                   | $\text{CH}_2\text{O}$  |
|  |            | 189                     | $\text{CH}_3\text{OH}$ |
| $[\text{Yb}(\text{MeO})_2]^+$                              | 235.9      | 205.9                   | $\text{CH}_2\text{O}$  |
|  |            | 204.9                   | $\text{CH}_3\text{O}$  |
|  |            | 173.9                   | $2\text{CH}_3\text{O}$ |
|  |            | 184.9                   | $\text{CH}_2\text{O}$  |
| $[\text{Eu}(\text{MeO})_2]^+ + [\text{Eu}(\text{NO}_3)]^+$ | 215        | 183.9                   | $\text{CH}_3\text{O}$  |
|  |            | 169                     | $\text{NO}_2$          |
|  |            | 152.9                   | $2\text{CH}_3\text{O}$ |
|  |            | 169                     | $\text{NO}_2$          |
|  |            | 169                     | $\text{NO}_2$          |
| $[\text{Eu}(\text{NO}_3)]^+^a$                             | 215        | 169                     | $\text{NO}_2$          |

<sup>a</sup> The cone voltage has been set at 60 V.

of europium is very close to zero, so the trivalent ion is readily reduced to the +2 oxidation state because this confers to the cation the very stable electronic configuration of  $\text{Gd}^{3+}$  with half-full 4f orbitals. Other  $\text{Ln}^{3+}$  ions such as  $\text{Yb}^{3+}$  and  $\text{Sm}^{3+}$  also produce the  $[\text{Ln}(\text{MeO})]^+$  species (Table 2) to a lesser degree as the ion-source energy is increased. One must keep in mind that, for the whole series, the lanthanide  $E_{3/2}$  redox potential is lower than  $-1.55$  V, except for Sm ( $E_{3/2} = -1.55$  V), Yb ( $E_{3/2} = -1.15$  V), and Eu ( $E_{3/2} = -0.35$

(45) Wang, G. D.; Cole, R. B. *J. Am. Soc. Mass Spectrom.* **1996**, *7*, 1050–1058.



**Figure 3.** ESI-MS spectra of  $5 \times 10^{-5}$  M  $\text{Ln}(\text{NO}_3)_3$  with a 2-fold molar ratio of DiPTP in water/methanol (1:1 v/v) at pH 2.8, aqueous nitrate medium. Cone voltage 30 and 40 V, Ln = Er (a), Lu (b).

V).<sup>46</sup> Also interesting is that the peak at  $m/z$  214.8, which is poorly observed in europium spectra, has been proven by MS/MS (Table 3) to result from both isobaric  $[\text{Eu}(\text{NO}_3)]^+$  and  $[\text{Eu}(\text{MeO})_2]^+$  species; the central cation is reduced from +3 to +2 oxidation state in the first species and remains at the +3 oxidation state in the second one. Hence, the fragmentation follows two major pathways: one leading to a loss of 30 amu ( $\text{CH}_2\text{O}$ ) and the other to a loss of 46 amu ( $\text{NO}_2$ ). At 60 V, formation of  $[\text{Eu}(\text{NO}_3)]^+$  is enhanced and thereby fragmentation of the complex leads to a unique loss of 46 amu.

Furthermore, it must be pointed out that, although the cerium mass spectrum taken at 40 V consists mainly of the peaks representative of the  $[\text{Ce}(\text{MeO})_2]^+$  complex, it differs from all other lanthanide spectra by exhibiting a complex  $[\text{Ce}(\text{O})(\text{MeO})]^+$  with Ce at the +4 oxidation state. The high  $E_{4/3}$  redox potential value of cerium compared to that of all other elements in the series<sup>46</sup> may account for the presence of an oxidized species only on the Ce MS spectrum. Indeed, all 4f elements have a  $E_{4/3}$  redox potential higher than 3.1 V except Ce, for which  $E_{4/3}$  is equal to 1.74 V.<sup>47</sup> In fact, it is well established that, although the lanthanide elements exhibit a marked trivalent oxidation state, the tetravalent ions  $\text{Ce}^{4+}$  and the divalent ions  $\text{Sm}^{2+}$ ,  $\text{Eu}^{2+}$ , and  $\text{Yb}^{2+}$  may exist in aqueous solutions as a consequence of small energy differences between the 4f and 5d electrons of these elements.<sup>6</sup> Then, at pH 4.6, the lower nitrate concentration as compared with pH 2.8 results in formation of species that depend on the electronic properties of the lanthanide elements, and this situation was found to make difficult quantitative measure-

ments as previously stressed.<sup>22</sup> Thus, it has been shown that ion current and concentration are linearly related in a much narrow range (i.e.,  $2 \times 10^{-5}$  to  $10^{-4}$  M) when measurements were made at pH 4.6 from the charge-reduced ions  $\text{Eu}(\text{MeO})^+$  and  $\text{Eu}(\text{OH})^+$ , as well as methoxide and hydroxide species containing one nitrate, such as  $[\text{Eu}(\text{NO}_3)(\text{MeO})(\text{MeOH})]^+$ .

**3.2. Complex Stability Constant Determination in Water/Methanol Medium.** Acidic solutions (pH 2.8 and 4.6) containing  $5 \times 10^{-5}$  M  $\text{Ln}(\text{NO}_3)_3$  and a 2-fold molar ratio of DiPTP have been analyzed by using voltage differences in the ESI interface of 30 or 40 V. The ESI mass spectra taken at an extraction cone voltage of 30 and 40 V and obtained with solutions at pH 2.8 that contain Er and Lu ions are depicted in Figure 3. At both pH values, the likely cations  $[\text{Ln}(\text{DiPTP})_3]^{3+}$  and  $[\text{Ln}(\text{DiPTP})_3(\text{NO}_3)]^{2+}$  can be identified in every spectrum throughout the series. For a voltage difference of 30 V, the doubly charged species  $[\text{Ln}(\text{DiPTP})_3(\text{H})_{-1}]^{2+}$  are also barely observed in the spectra of the later lanthanides Ln = Er–Lu (Table 4). As previously demonstrated in the case of Eu,  $[\text{Ln}(\text{DiPTP})_3(\text{NO}_3)]^{2+}$  ions readily lose  $\text{HNO}_3$  in the ESI source to lead to  $[\text{Ln}(\text{DiPTP})_3(\text{H})_{-1}]^{2+}$  complexes. Then, the 30 V setting appears as an optimum voltage difference strong enough to remove solvent molecules without abundant fragmentation reactions. The tendency of  $[\text{Ln}(\text{DiPTP})_3(\text{NO}_3)]^{2+}$  ions to fragment in the ESI source was illustrated by the data obtained for a voltage difference of 40 V (Figure 3, Table 4). Under such energetic conditions, it was found that complexes of the heavier lanthanides Ln = Tb–Lu show an increasing tendency across the series to produce both  $[\text{Ln}(\text{DiPTP})_3(\text{H})_{-1}]^{2+}$  and  $[\text{Ln}(\text{DiPTP})_2(\text{NO}_3)]^{2+}$  ions. Previous studies demonstrated that fast and moderately fast reactions may result in fragments formed in the ion source (the residence time in an ion source

(46) Nugent, L. J.; Baybarz, R. B.; Burnett, J. L.; Ryan, J. L. *J. Phys. Chem.* **1973**, *77*, 1528–1539.

(47) Nugent, L. J.; Baybarz, R. D.; Burnett, J. L.; Ryan, J. L. *J. Inorg. Nucl. Chem.* **1971**, *33*, 2503–2530.



**Table 4.** Complexes Detected by ESI-MS for  $5 \times 10^{-5}$  M  $\text{Ln}(\text{NO}_3)_3$  with  $[\text{DiPTP}]/[\text{Ln}] = 2$  at pH 2.8 in Water/Methanol (1:1 v/v), Aqueous Nitrate Medium

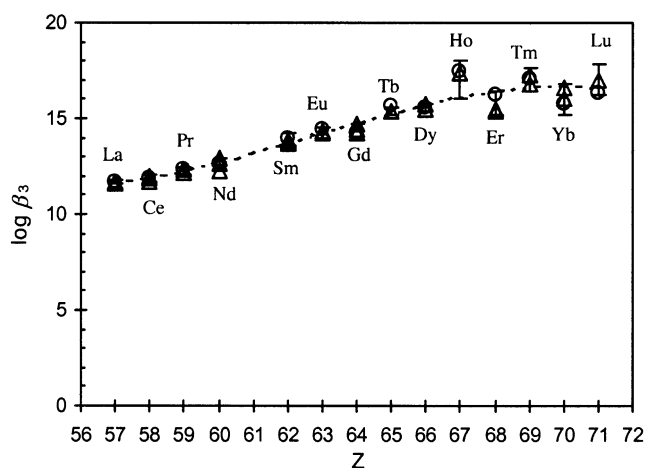
|    | 1:2   |    |  |   |                                    |    | 1:3   |       |   |       |    |    |
|----|---|----|--|---|------------------------------------|----|---|-------|---|-------|----|----|
|    | $[\text{Ln}(\text{DiPTP})_2(\text{NO}_3)]^{2+}$ |    | $[\text{Ln}(\text{DiPTP})_2(\text{NO}_3)(\text{MeOH})]^{2+}$ |   | $[\text{Ln}(\text{DiPTP})_3]^{3+}$ |    | $[\text{Ln}(\text{DiPTP})_3(\text{H})_{-1}]^{2+}$ |       | $[\text{Ln}(\text{DiPTP})_3(\text{NO}_3)]^{2+}$ |       |    |    |
|    | $m/z$   | %  | $m/z$  | % | $m/z$                              | %  | $m/z$   | %     | $m/z$   | %     |    |    |
| Pr |   |    |  |   | 452.4                              | 43 | 43  |       |   | 709.5 | 57 | 57 |
| Nd |   |    |  |   | 453.5                              | 47 | 47  |       |   | 710.6 | 53 | 53 |
| Sm |   |    |  |   | 456.2                              | 48 | 47  |       |   | 715.7 | 52 | 53 |
| Eu |   |    |  |   | 456.2                              | 49 | 50  |       |   | 715.5 | 51 | 50 |
| Gd |   |    |  |   | 457.8                              | 51 | 50  |       |   | 717.6 | 49 | 50 |
| Tb | 516.0   | 2  |  |   | 458.4                              | 47 | 45  | 687.1 | 3   | 718.5 | 53 | 50 |
| Dy | 517.9   | 2  |  |   | 459.6                              | 49 | 49  | 689.2 | 5   | 720.6 | 51 | 44 |
| Ho | 518.9   | 4  |  |   | 460.3                              | 49 | 49  | 690.1 | 7   | 721.5 | 51 | 40 |
| Er | 520.0   | 4  | 536.0  | 2 | 461.2                              | 52 | 49  | 691.1 | 2   | 722.7 | 46 | 36 |
| Tm | 520.9   | 8  | 536.9  | 2 | 461.9                              | 50 | 46  | 692.0 | 2   | 723.6 | 48 | 30 |
| Yb | 523.0   | 10 | 538.9  | 2 | 463.2                              | 57 | 53  | 694.3 | 4   | 725.8 | 39 | 20 |
| Lu | 523.9   | 15 | 539.9  | 3 | 463.7                              | 51 | 46  | 695.2 | 6   | 726.6 | 43 | 17 |

**Table 5.** Calculated Ln–N<sub>c</sub> and Ln–N<sub>i</sub> Bond Distances (in Å) in  $[\text{LnL}]^{3+}$  Complexes (Ln = La, Eu, Lu) in Vacuum (from Reference 35)

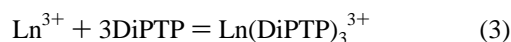
| ligand               | bond              | La   | Eu   | Lu   |
|----------------------|-------------------|------|------|------|
| Tpy                  | Ln–N <sub>c</sub> | 2.49 | 2.36 | 2.23 |
|                      | Ln–N <sub>i</sub> | 2.47 | 2.38 | 2.29 |
| Tptz                 | Ln–N <sub>c</sub> | 2.41 | 2.29 | 2.17 |
|                      | Ln–N <sub>i</sub> | 2.52 | 2.42 | 2.33 |
| Adptz                | Ln–N <sub>c</sub> | 2.42 | 2.29 | 2.17 |
|                      | Ln–N <sub>i</sub> | 2.52 | 2.43 | 2.33 |
| BTP                  | Ln–N <sub>c</sub> | 2.59 | 2.46 | 2.32 |
|                      | Ln–N <sub>i</sub> | 2.45 | 2.36 | 2.27 |
| Pyr <sub>2</sub> Pym | Ln–N <sub>c</sub> | 2.47 | 2.35 | 2.22 |
|                      | Ln–N <sub>i</sub> | 2.50 | 2.40 | 2.31 |
| Bzimpy               | Ln–N <sub>c</sub> | 2.57 | 2.44 | 2.30 |
|                      | Ln–N <sub>i</sub> | 2.45 | 2.35 | 2.26 |

is  $\sim 400 \mu\text{s}$ ).<sup>48</sup> This was confirmed by MS/MS experiments (discussed below) which showed that both  $[\text{Ln}(\text{DiPTP})_3(\text{H})_{-1}]^{2+}$  and  $[\text{Ln}(\text{DiPTP})_2(\text{NO}_3)]^{2+}$  ions can be formed by collision-induced dissociation of  $[\text{Ln}(\text{DiPTP})_3(\text{NO}_3)]^{2+}$  ions in the hexapole collision cell of the mass spectrometer.

Then, the stoichiometry of complexes in solution as deduced from the ESI spectra show that, while it proved possible to obtain crystals of 1:3 complexes only with the latter lanthanide nitrates (Sm–Lu),<sup>16,17</sup> the ligand DiPTP forms 1:3 complexes with trivalent lanthanide cations throughout the 4f series. The exclusive formation of the 1:3 complexes in nitric acid solution was surprising as previously noticed,<sup>11</sup> and no other examples could be found in the lanthanide literature. As already mentioned, changes in the alkyl substituents greatly affect solution complexation; thus, among substituents such as methyl, *n*-propyl, or *iso*-propyl, only *iso*-propyl substituents on DATP result in exclusive formation of 1:3 Ln/DATP complexes in nitric solutions at pH 2.8.<sup>22</sup> This was taken as reflecting an important role of the hydrophobic exterior of the DATP ligands in the complex formation. Presumably, a combination of hydrophobic, electrostatic, and stacking interactions are involved in the formation of the 1:3 complexes in solution, as noted for other noncovalent complexes.<sup>49</sup> Recently, *ab initio* calculations provided some insight into the electronic structures of 2,6-bis(pyridin-2-yl)-4-amino-1,3,5-triazine (Adptz) and 2,6-bis-

**Figure 4.** Conditional stability constants  $\log \beta_3^{\text{APP}}$  of the formation of  $\text{Ln}(\text{DiPTP})_3$  complexes in water/methanol (1:1 v/v) at pH 2.8, aqueous nitrate medium, cone voltage ( $\Delta$ ) 30 and ( $\circ$ ) 40 V, 25 °C.

(1,2,4-triazinyl)pyridine (BTP) and simple model systems corresponding to their 1:1 complexes with lanthanides.<sup>35</sup> The central ring appears negatively charged in the “free” Adptz ligand, but positively charged in BTP. Due to the positive charge borne by the central ring of BTP, the cation is pushed away from the nitrogen cavity of the ligand; consequently, the Ln–N<sub>c</sub> interatomic distance becomes larger relative to that observed with the Adptz ligand (Table 5). Then, in the nitrogen cavity of the BTP ligand, only the lateral rings appear to be donors relative to the Ln cation. It follows that  $[\text{Ln}(\text{BTP})]^{3+}$  was found to be less stable compared with the Adptz analogues. Therefore, 1:3 complex formation is thought to be promoted by either the hydrophobic exterior of the ligand or the unusual electronic density distribution in DATP ligands. Evidence of the electrostatic nature of the metal–ligand interaction in the 1:3 complexes is shown by the monotonic increase of the conditional stability constant  $\log \beta_3^{\text{APP}}$  with the metal ion atomic number (Figure 4). The values (Table 6) have been evaluated from the ESI data according to the method used previously.<sup>22</sup> Complexation of lanthanides by DiPTP ligand can be represented by the equation

(48) Kebarle, P.; Tang, L. *Anal. Chem.* **1993**, *65*, 972A–986A.(49) Loo, J. A. *Mass Spectrom. Rev.* **1997**, *16*, 1–23.

**Table 6.** Conditional Stability Constants  $\log \beta_3^{\text{app}}$  of  $\text{Ln}(\text{DiPTP})_3$  Complexes in Nitric Acid Water/Methanol (1:1 v/v) at pH 2.8, Average Values of Those Presented in Figure 4 at Cone Voltage 30 and 40 V, Temperature 22 °C

|                             |                |                |                |                |                |                |                |
|-----------------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Z (Ln)                      | 57 (La)        | 58 (Ce)        | 59 (Pr)        | 60 (Nd)        | 62 (Sm)        | 63 (Eu)        | 64 (Gd)        |
| $\log \beta_3^{\text{app}}$ | $11.7 \pm 0.1$ | $11.9 \pm 0.2$ | $12.3 \pm 0.2$ | $12.6 \pm 0.3$ | $13.9 \pm 0.3$ | $14.2 \pm 0.3$ | $14.5 \pm 0.2$ |
| Z (Ln)                      | 65 (Tb)        | 66 (Dy)        | 67 (Ho)        | 68 (Er)        | 69 (Tm)        | 70 (Yb)        | 71 (Lu)        |
| $\log \beta_3^{\text{app}}$ | $15.4 \pm 0.2$ | $15.6 \pm 0.2$ | $17.5 \pm 1$   | $15.8 \pm 0.6$ | $17.0 \pm 0.6$ | $16.0 \pm 0.6$ | $16.7 \pm 0.8$ |

The corresponding equilibrium constant is equivalent to the conditional stability constant of the complex:

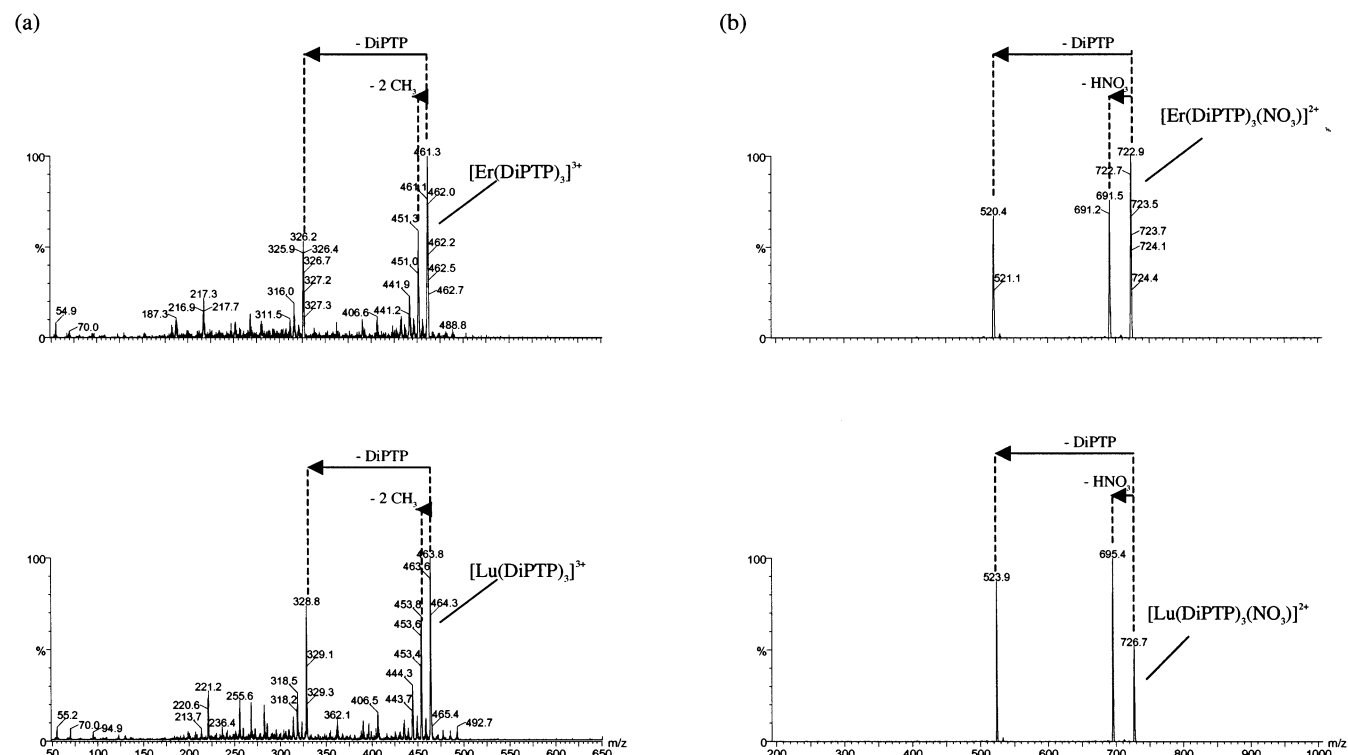
$$\beta_3^{\text{app}} = [\text{Ln}(\text{DiPTP})_3^{3+}] / [\text{Ln}^{3+}][\text{DiPTP}]^3 \quad (4)$$

where  $[\text{Ln}^{3+}]$  and  $[\text{DiPTP}]$  are the concentrations of uncomplexed metal and ligand, respectively. For solutions containing  $5 \times 10^{-5}$  M lanthanide nitrate and a 2-fold molar ratio of DiPTP, the free lanthanide equilibrium concentration was determined directly from the total ion current of the complexes coming from the free lanthanide in solution (see section 3.1). Then the equilibrium concentration of the free ligand and the  $\text{Ln}(\text{DiPTP})_3$  complex are deduced from the known amounts of ligand and Ln initially present in solution. The data presented in Figure 4 and Table 6 show that the  $\log \beta_3^{\text{app}}$  of the 1:3 lanthanide(III) complexes increases almost regularly from La ( $\log \beta_3^{\text{app}} = 11.7 \pm 0.1$ ) to Lu ( $\log \beta_3^{\text{app}} = 16.7 \pm 0.8$ ). Such an increase in stability of lanthanide complexes throughout the series is in agreement with an electrostatic bonding model in which the formation constants increase with the effective nuclear charge of the lanthanide ion. Further, one can expect that the Ln–N interatomic distances for 1:3 complexes decrease on traversing the lanthanide series as observed in  $\text{Ln}(\text{L})$  crystalline compounds (Table 5).

Recently, Charbonnel et al.<sup>50</sup> have determined the thermodynamic values linked to Eu(III) complexation with

DnPTP and DiPTP in octan-1-ol by using UV–vis spectroscopy and microcalorimetry. The two ligands were found to form 1:3 Eu/DATP complexes with  $\log \beta_3$  around 12; moreover, the enthalpy was shown to be the driving force for the complexation reaction. Furthermore, Orvig et al. reported the stability constants  $\log \beta_2$  of complexes in water with  $\text{N}_4\text{O}_3$  tripodal amine phenol ligand:<sup>51</sup> the values reported increased from  $12.75 \pm 0.03$  for Nd to  $18.26 \pm 0.03$  for Yb. Bünzli et al. determined, in anhydrous acetonitrile, the stability constants  $\log \beta_3$  of complexes with 2,2',6',2''-terpyridine ( $\log \beta_3 = 18.3 \pm 0.5$ ,  $18.4 \pm 0.9$ , and  $20.1 \pm 0.4$  for La, Eu, and Lu, respectively)<sup>52</sup> and its derivative with *tert*-butyl substituents in the 4-position of the pyridinyl ring ( $\log \beta_3 = 18.4 \pm 1.1$ ,  $19.1 \pm 0.4$ , and  $20.8 \pm 1.0$  for La, Eu, and Lu, respectively). In these systems, the increase in either the overall stability constant  $\log \beta_2$  or  $\log \beta_3$  in going from large to small lanthanide ions was attributed to the increased electrostatic attraction of the latter Ln(III) ions and steric effects were suggested to be of only minor importance. Interestingly, the values proposed by Orvig et al. and Bünzli et al. are in the range of those proposed for 1:3 complexes with DiPTP ligand.

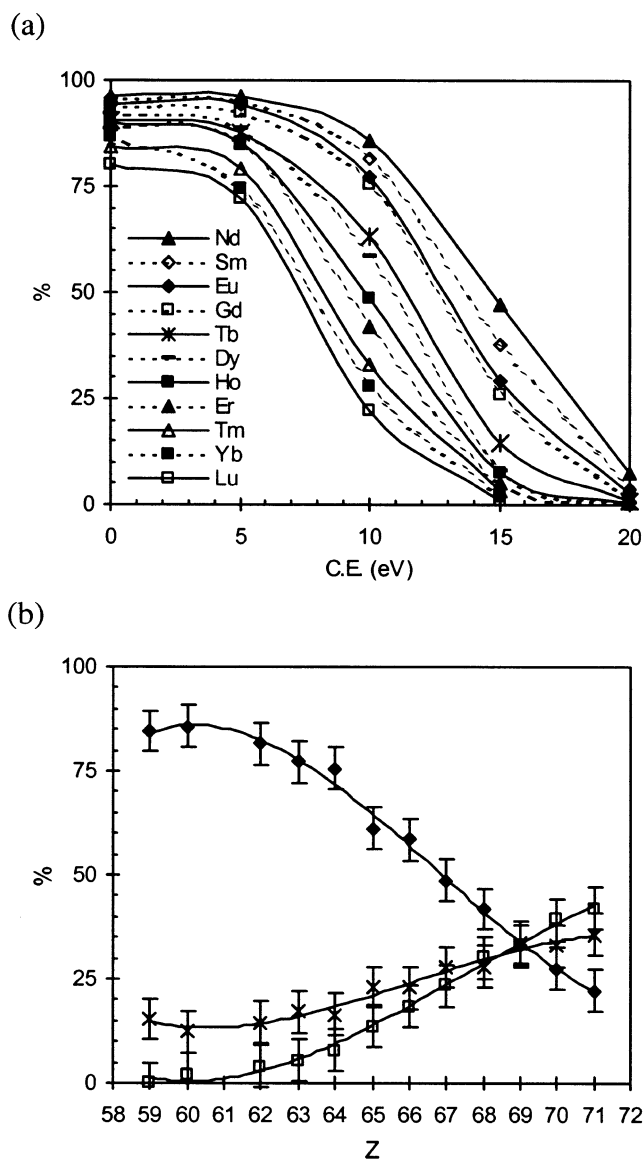
**3.3. Kinetic Stability of the Gas-Phase Complexes.** To investigate the gas-phase kinetic stability of the 1:3 complexes, energy-resolved CID experiments have been performed on the series of the  $[\text{Ln}(\text{DiPTP})_3]^{3+}$  and  $[\text{Ln}(\text{DiPTP})_3\text{NO}_3]^{2+}$



**Figure 5.** (a) MS/MS spectra of  $[\text{Ln}(\text{DiPTP})_3]^{3+}$  with a collision energy of 30 eV. Ln = Er, Lu. (b) MS/MS spectra of  $[\text{Ln}(\text{DiPTP})_3(\text{NO}_3)]^{2+}$  with a collision energy of 10 eV. Ln = Er, Lu.

(NO<sub>3</sub>)<sup>2+</sup> ions (Figure 5). In this approach, the studied complexes are selected by the first quadrupole mass analyzer, accelerated to kinetic energies in the 0–60 eV range and introduced into the rf-only collision cell containing argon collision gas at a pressure of  $2 \times 10^{-3}$  mbar. The ionic fragmentation products were detected using the final mass-analyzing quadrupole. The kinetic stability of the complexes should be considered instead of the gas-phase stability, because in MS/MS experiments the fragment ion abundances depend on both the time window of experiment and the rate constants of the fragmentation pathways which are dependent on either the internal energy of the ions or the activation barrier  $E_a$  of the fragmentation routes.<sup>37</sup> This is illustrated by the CID mass spectra presented in Figure 5.

Figure 5a shows, for example, the CID mass spectra of the [Ln(DiPTP)<sub>3</sub>]<sup>3+</sup> complexes (Ln = Er and Lu) obtained when the ions selected by the first quadrupole are accelerated at 30 eV kinetic energies. All the 1:3 gas-phase complexes were observed to be stable against dissociation, as suggested by the observation of fragmentations of the ligands with almost no complex dissociation. This would indicate the great strength of the interactions between the cations and the ligand. Furthermore, the CID mass spectra of the [Eu(DMTP)<sub>3</sub>]<sup>3+</sup> and [Eu(DnPTP)<sub>3</sub>]<sup>3+</sup> complexes showed that changes in the length of the alkyl substituents, although greatly affecting solution binding as previously noted, did not appear to affect the stability of the 1:3 gas-phase complexes (data not shown). As noted by Loo et al.,<sup>49,53</sup> the type of interactions that govern noncovalent binding in solution can be distinguished by the gas-phase stabilities of the complexes investigated by MS/MS studies. They stressed that electrostatic interactions are greatly strengthened in a solventless gas-phase environment, so complexes held together by such interactions are extremely stable in the gas phase. By contrast, interactions that are largely governed by hydrophobic interactions in solution appear to be weakened in a vacuum. Then, the noncovalent forces that hold 1:3 complexes together are likely to be largely governed by electrostatic interactions even if the hydrophobic exterior of the ligand may play a crucial role in the complexation mechanism. The presence of a nitrate anion as counteranion ([Ln(DiPTP)<sub>3</sub>(NO<sub>3</sub>)<sup>2+</sup> ions) in the cluster results in a decrease of the kinetic stability of the complex ion, and the metal center was found to drive the observed CID patterns. The CID mass spectra of the [Ln(DiPTP)<sub>3</sub>(NO<sub>3</sub>)<sup>2+</sup> complexes (Figure 5b) display two fragment ions, [Ln(DiPTP)<sub>2</sub>(NO<sub>3</sub>)<sup>2+</sup> and [Ln(DiPTP)<sub>3</sub>(H)<sub>-1</sub>]<sup>2+</sup>, and thus evidence that the complexes dissociate by losing one molecule of DiPTP or fragment by losing HNO<sub>3</sub>. Assuming that the nitrate anion is retained in the coordination outer sphere of the lanthanide, it does not influence the interactions between Ln(III) and



**Figure 6.** (a) Breakdown curves of [Ln(DiPTP)<sub>3</sub>(NO<sub>3</sub>)<sup>2+</sup>], cone voltage 30 V, Ln = Nd–Lu. (b) Fragmentation rate of [Ln(DiPTP)<sub>3</sub>(NO<sub>3</sub>)<sup>2+</sup> along the Ln series for a collision energy of 10 eV. (◆) [Ln(DiPTP)<sub>3</sub>(NO<sub>3</sub>)<sup>2+</sup>, (×) [Ln(DiPTP)<sub>2</sub>(NO<sub>3</sub>)<sup>2+</sup>, (□) [Ln(DiPTP)<sub>3</sub>(H)<sub>-1</sub>]<sup>2+</sup>.

the DiPTP molecules. However, it introduces new fragmentation pathways with energy barriers that are accessible from the internal energy of the ions.

Figure 6a shows the [Ln(DiPTP)<sub>3</sub>(NO<sub>3</sub>)<sup>2+</sup> complex percentage in the spectra plotted as a function of kinetic energy of the selected ions before their introduction into the collision cell. In Figure 6b are plotted the percentage of the ion abundances versus the atomic number of the lanthanide; these values are measured in spectra obtained for a kinetic energy value of 10 eV. The rate of one DiPTP loss increases on going from Nd(III) to Yb(III) (Figure 6a and 6b). This is certainly due to a steric effect, if this can be interpreted as a change in Ln<sup>3+</sup> inner sphere coordination. The nitrate anion may act as a bidentate ligand, so the [Ln(DiPTP)<sub>2</sub>(NO<sub>3</sub>)<sup>2+</sup> formation should lower the coordination number of lanthanide ions from 9 to 8. This can be correlated with the coordination number change of the Ln(III) aquo ions, as it

(50) Giroux, S.; Charbonnel, M. C., Scientific Report Atalante 2002, CEA/DEN-Valrhô France, to be published.

(51) Caravan, P.; Hedlund, T.; Liu, S.; Sjöberg, S.; Orvig, C. *J. Am. Chem. Soc.* **1995**, *117*, 11230–11238.

(52) Mürner, H. R.; Chassat, E.; Thummel, R. P.; Bünzli, J.-C. G. *J. Chem. Soc., Dalton Trans.* **2000**, 2809–2816.

(53) Sannes-Lowery, K. A.; Mei, H.-Y.; Loo, J. A. *Int. J. Mass Spectrom.* **1999**, *193*, 115–122.

has been demonstrated that the preferred lanthanide coordination number evolves from 9 to 8 from the beginning to the end of the series due to the contraction of the ionic radii: the probable species is for the light cations  $\text{Ln}(\text{H}_2\text{O})_9^{3+}$  and for the heavy ones  $\text{Ln}(\text{H}_2\text{O})_8^{3+}$ .<sup>5-7</sup> Consequently, the increase in  $\log \beta_3$  across the Ln series was taken as reflecting purely electrostatic effects with little evidence for a steric factor<sup>54</sup> associated with the contraction of the ionic radii, also indicating the capability of the Ln(III) ions to expand their coordination shell when required.<sup>55</sup>

Further fragments produced by cleavage of a carbon–hydrogen bond of the ligand with a neutral loss of  $\text{HNO}_3$  are observed. It is proposed that the lanthanide center stabilizes the anionic  $[\text{DiPTP}(\text{H})_{-1}]^-$  ligand in the transition state corresponding to the resulting ion  $[\text{Ln}(\text{DiPTP})_3(\text{H})_{-1}]^{2+}$  through its empty 5d orbitals. Thus, the increasing rate of  $\text{HNO}_3$  loss across the lanthanide series can be linked to the electronegativity of the lanthanide ions, and thereby the activation energy of this fragmentation pathway is expected to decrease across the series.

#### 4. Conclusion

Electrospray ionization mass spectrometry has provided quantitative analysis of uncomplexed lanthanide(III) metal ions in nitric acid solutions. At pH 2.8, complexation with nitrate anions prevents redox phenomena and the total intensity of signals from ions  $[\text{Ln}(\text{NO}_3)_2(\text{H}_2\text{O})_p(\text{MeOH})_n]^+$  was found to be proportional to the lanthanide concentration.

(54) Ishiguro, S.; Umebayashi, Y.; Komiya, M. *Coord. Chem. Rev.* **2002**, *226*, 103–111.

(55) Bünzli, J.-C. G.; André, N.; Elhabiri, M.; Muller, G.; Piguet, C. *J. Alloys Compd.* **2000**, *303/304*, 66–74.

At pH 4.6, the lower nitrate concentration compared to that at pH 2.8 results in formation of species that depend on the electronic properties of the lanthanide elements. Moreover, ESI-MS has allowed acquisition of solution data such as stoichiometries and conditional stability constants of Ln(III) complexes for the entire lanthanide family. By use of ESI-MS, it has been shown that the DiPTP ligand likely acts as a multidentate ligand toward lanthanide ions in nitric acid solutions, binding through the soft N atoms to form 1:3 complexes. The formation of 1:3 complexes is likely to be exclusive, and this is thought to be due either to the hydrophobic exterior of the ligand or to the unusual electronic density distribution in DATP ligands as compared with other aza-aromatic ligands. ESI-MS also allowed confident determination of the conditional stability constant  $\log \beta_3^{\text{app}}$  for the whole lanthanide series. Then, the DiPTP was found to be selective for the heavier lanthanides, which has been proposed to stem from the electrostatic nature of Ln(III) bonding. In addition, the kinetic stability of the gas-phase complexes  $[\text{Ln}(\text{DiPTP})_3]^{3+}$  and  $[\text{Ln}(\text{DiPTP})_3(\text{NO}_3)]^{2+}$  has been correlated with the predominantly ionic character of the bonding in these complexes. The resulting better understanding of the metal ion complexation mechanism should assist in the design of more efficient and specific self-assembling ligand–metal complexes.

**Acknowledgment.** We thank the Direction du Développement et de l'Innovation Nucléaire/Réduction Quantité et Nocivité des Déchets for financial support (A-SEPOU-03-03-02).

IC025894Y