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Use of Electrospray Mass Spectrometry (ESI-MS) for the Study of Europium(III) Complexation with Bis(dialkyltriazinyl)pyridines and Its Implications in the Design of New Extracting Agents

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ESI mass spectrometry was used to investigate the europium complexation by tridentate ligands L 2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)-pyridines (DATP) that have shown unique separation properties of actinides(III) from lanthanides(III) in nitric acid solutions. Complexes of three ligands, namely methyl (DMTP), *n*-propyl (DnPTP), and *iso*-propyl (DiPTP), have been investigated in acidic solutions to check the aqueous-phase stability of $Eu(L)_3^{3+}$ ions identified previously in the solid state. The data obtained show, first, the presence of stable $Eu(L)_3^{3+}$ ions with DnPTP (log $\hat{a}_3^{app}$) 12.0 ± 0.5) and DiPTP (log $\hat{a}_3^{app}$) 14.0 ± 0.6) in methanol/water (1:1 v/v) solutions under pH range 2.8−4.6 and, second, a mechanism whereby alkyl moieties contribute to a self-assembling process leading to the formation of $Eu(L)_3^{3+}$ ions. Other complexes such as $Eu(L)_2^{3+}$ ions are only observed for DnPTP (log $\hat{a}_2^{app}$) 6.7 ± 0.5) and DMTP (log $\hat{a}_2^{app}$) 6.3 ± 0.1) and $Eu(L)^{3+}$ only for DMTP (log $\hat{a}_1^{app}$) 2.9 ± 0.2). The log $\hat{a}_n^{app}$ values for the $Eu(L)_n^{3+}$ (n) 1−3) complexes were determined at pH 2.8. Better insight was given in this study concerning the role of the hydrophobic exterior of the ligands for the design of a new range of extracting agents.

Introduction

In the framework of nuclear waste reprocessing, research for new efficient extracting molecules is still of great interest. Hence, in the last years, several possible chelating agents have been tested in liquid−liquid extraction experiments to separate the trivalent minor actinides (An(III)) from the trivalent lanthanides (Ln(III)) for nuclear waste partitioning purposes.[1] The design of extracting agents has to overcome two difficulties. The first arises from the high nitric acid concentration (3−4 M) of the aqueous effluents that contain the actinides (americium and curium) and fission lanthanides to be partitioned. The second comes from the similarity of the ionic radii and the relevant chemical properties of the An(III) and Ln(III) ions in solution.[2]

Azaaromatic bases, including the 2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridines (DATP) are among the most extensively studied chelating agents[3−8] since they have shown

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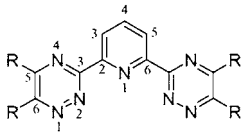
Chart 1. Ligand Codes



L	R
DMTP	CH_3
DnPTP	CH_3-CH_2-CH_2
DiPTP	$(CH_3)_2$-CH

unique capabilities to extract americium over europium (representative of the fission lanthanides) from acidic solutions into an organic phase. Extractants such as DATP (Chart 1) act as tridentate ligands to give metal complexes with the internal cavity formed by the nitrogen atom of the central pyridine and the nitrogen atoms at the 2 position of the triazinyl rings. These multiple interactions contribute to the ability of the azaaromatic base to compete with the water molecules for binding the strongly solvated 4f and 5f metal ions. An(III)/Ln(III) selectivity originates from the fact that An(III)'s have a somewhat higher affinity for the "soft" donor nitrogen atoms due to their slightly less hard character compared to the lanthanide ions.[9] The extraction properties and separation factors (SF) of many DATP ligands toward An/Ln have been thoroughly investigated regarding the effects of the size of the alkyl substituents at the triazinyl rings, the ligand concentration, the nature of the diluent, and also the synergistic combination of DATP with 2-bromohexanoic acid.[7,8] Hence, the DATP ligands are actually further developed to find the nature and position of substituents for optimum extractant properties and chemical stability of the compounds. For example, effort has been made to suppress the aqueous solubility of the protonated ligands by introduction of alkyl moieties at the triazinyl rings to increase thus the hydrophobicity of the resulting ligand.[8] As stressed by Nash[9] in a comprehensive review of Ln(III)/An(III) separation, the most effective ligands for solvent extraction are those with minimal solubility in the aqueous phase. Thereby, complex formation reaction can be considered to occur in or near the interfacial zone and, thus, the study of complex formation in the aqueous phase is needed even if the ligands are designed to be lipophilic.[9] The compounds with alkyl substituents at the 5,6 positions of the triazinyl rings, such as methyl (DMTP), *n*-propyl (DnPTP), and *iso*-propyl (DiPTP), have been synthesized.[10,11]

Considerable progress have been made in the extraction experiments, but the nature of the An(III) and Ln(III) complexes formed in acidic aqueous solutions with these ligands is still not elucidated. To date, a large number of rare-earth complexes of the most useful multidentate ligands have been crystallized and characterized by X-ray diffraction. Several reports[5,12−15] have reviewed the subject and recent studies were carried out with the DMTP and DnPTP ligands.[11,16−17] With DnPTP, $Ln(L)_3$ complexes of the elements Ln = Sm, Tm, and Yb have been obtained when crystallization was performed from ethanol solutions with nitrates as counterions.[11] The complexes containing Ce(DMTP)$_3^{3+}$, Ce(DnPTP)$_3^{3+}$, and U(DnPTP)$_3^{3+}$ cations have also been crystallized from pyridine solutions with iodides as anions.[16] In the case of DMTP, neodymium and praseodymium nitrates give structures of the type $[Ln_2(DMTP)_2(NO_3)_6]$ as well as two complexes $([Nd(DiBTP)_2(NO_3)_2]^{3+})_2[Nd(NO_3)_5]^-$ and $[Nd(DETP)(NO_3)_3(HOEt)]$ that have been crystallized from alcoholic solutions.[17] As already seen in the case of the previously published analysis of Ln(III) complexes with model ligands, the $Ln(L)_2^{3+}$ ions and even better the $Ln(L)_3^{3+}$ ions are quite unusual either in solution and in solid state.[12,14,18,19]

To date, the $Ln(L)_3^{3+}$ ions have only been observed in anhydrous conditions, e.g. acetonitrile, with weakly coordinating counterions such as perchlorate or triflate;[20−23] they have never been observed in the presence of more strongly coordinating ligands such as nitrate anions. Madic et al.,[14] in discussing the differences between the structures found for the Ln(III) complexes of the azaaromatic bases, made the point that the striking ability of the DATP ligands to form $Ln(L)_3^{3+}$ ions is probably due not only to the electronic properties of the nitrogen atoms but also to the hydrophobic exterior of these ligands. However, it should be noted that Bünzli et al. have recently made efforts to enhance the formation of $Ln(L)_3^{3+}$ ions (Ln = La, Eu and Lu) seen for the tridentate ligands 2,2′;6′,2"-terpyridine (terpy)[21] and 2,6-bis(1-methylbenzimidazol-2-yl)pyridine (mbzimpy)[22] in anhydrous acetonitrile by the introduction of *tert*-butyl moieties at the 4, 4′ and 4″ positions for the former and (*S*)-neopentyl N-substituents for the latter.[23] Nevertheless, the authors found that the stability constants log β_3 of complexes with terpy

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and its derivatives bearing substituents were similar,[21] while, for the mbzimpy ligands, the bulky alkyl moieties hindered the formation of tris complexes.[23]

The aim of our study is the understanding of the mechanisms governing the An(III)/Ln(III) separation process in acidic medium by liquid−liquid extraction using azaaromatic ligands. As the systems involved are very complexed, it was attempted to simplify the problem by considering the metal complexation by the ligands in acid aqueous solution. The ligands are little or not soluble in water so it was decided to use an organic cosolvent which physicochemical properties would not affect the metal−ligand interactions. There are typically two possible cosolvents, i.e. methanol and acetonitrile. Methanol was chosen because its dipolar moment (1.71 D) is similar to that of water (1.85 D) while that of acetonitrile (3.92 D) is much greater.[24] Moreover, in 50:50 mixture of water and methanol, Eu is mostly surrounded by water molecules in inner-sphere[25] and so the solution equilibrium should reflect that of an aqueous solution.

The coordination chemistry of Eu with three DATP ligands, namely methyl (DMTP), *n*-propyl (DnPTP), and *iso*-propyl (DiPTP), in nitric acid water/methanol (1:1 v/v) solutions is investigated in this study to check the solution stability of the $Ln(L)_3^{3+}$ ions identified in the solid state. This paper also focuses on the applicability of electrospray ionization mass spectrometry (ESI-MS) as a rapid screening method that may assist in the design of useful extracting agents. Europium(III) was chosen because, first, it possesses ionic radii and chemical properties that closely share features with those of the An(III) and Ln(III) of interest in the nuclear fuel reprocessing and, second, to take advantage of the luminescent properties of this ion for comparison purposes between data obtained by ESI-MS and time-resolved laser-induced fluorescence (TRLIF).[26] ESI-MS has been previously applied to the study of Ln complexation by a variety of ligands providing the structures, stoichiometries, and oxidation states of ligand−metal complexes[18,19,23,27] as well as for studies on the speciation of actinides[28,29] and lanthanides[30] in solution. It appears also that ESI-MS can be used as a reliable technique for direct determination of solution binding constants for noncovalent complexes.[31−33] Here, by studying Eu(III) complexes as a function of pH (pH range 2.8−4.6) and ligand-to-metal ratio, it was possible to show not only the competition occurring between protonation and complexation but also the role of the alkyl substituents at the triazinyl rings on the Eu(III) complexation in nitric acid water/methanol solutions. The stoichiometries and stability constants of europium(III) complexes with the different DATP (DMTP, DnPTP, and DiPTP) ligands are reported for the first time.

Experimental Section

Materials. The DMTP, DnPTP, and DiPTP ligands were provided by CEA/DEN/DRCP (Bagnols-sur-Cèze, France). Stock solutions (10^{-3} M) of DMTP (M = 293 g/mol), DnPTP (M = 405 g/mol), and DiPTP (M = 405 g/mol) were prepared by dissolution of a weighed amount in HPLC grade methanol. Stock solutions (2×10^{-4} or 10^{-4} M) of europium(III) in nitric acid were prepared at pH 4.6 by dissolving high-purity crystals of $Eu(NO_3)_3 \cdot 6H_2O$ (M = 446 g/mol) (Sigma) in appropriate solution of nitric acid (Sigma). All chemicals used were reagent grade, and Millipore water was used throughout the procedure. The study was carried out with nitrates since the extraction process takes place in nitric acid solutions.

Solutions for the ESI-MS measurements were prepared from 2.5 mL of stock metal ion solution mixed with a precise volume of stock ligand (L) solution required to give ligand-to-metal ratios L/Eu in the range 0.1 to 5. Then, the appropriate amount of methanol was added to obtain water/methanol (1:1 v/v) mixtures. Experiments were directly performed in nitric acid with the ionic strength fixed mainly by the nitric acid and europium nitrate concentrations. Hence, among a series of samples, where the pH was adjusted to the same value by addition of nitric acid, the ionic strength remained roughly constant. For solutions containing 10^{-4} M of europium and a fixed ligand-to-metal ratio, the ionic strength varied from 6.2×10^{-4} M at pH 4.6 to 2.2×10^{-3} M at pH 2.8.

MS Apparatus and Conditions. The mass spectrometric measurements were recorded in positive ion mode using a QuattroII triple-quadrupole spectrometer equipped with an ESI interface (Micromass, Manchester, U.K.). 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 μL/min to a Rheodyne 9725 multiport rotary valve (20-μL loop) connected to the ESI probe by a fused silica tubing. Samples were introduced using a 50-μL 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 within the range 25−60 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 MS/MS measurements, collision-induced dissociation of cluster ions was performed with argon; the collision gas pressure was 2×10^{-3} mbar. Spectra were obtained at different collision energies ranging from 10 to 40 eV. Europium species are seen in their natural abundance, i.e. 52.2% ^{153}Eu and 47.8 ^{151}Eu. The isotopic distributions are not well resolved for the triply and doubly charged complexes because the quadrupole mass spectrometer only allows nominal unit resolution. High-resolution mass spectral data were obtained by using a Q-Tof II mass spectrometer (Micromass, Manchester, U.K.) that was operating in the electrospray mode. In the data given, and for simplification purposes, only the m/z peaks corresponding to the most abundant isotopic mass have been indicated.

Measurement Procedure. The pH of the solutions were measured with a conventional pH meter (model PHN 81, Tacussel,

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22 °C) equipped with a subminiature combined electrode (model PH XC161) filled with an aqueous solution and calibrated with aqueous pH standards. No correction was made for the presence of methanol. Solutions were introduced in the spectrometer by increasing order of ligand concentration. Between each sample, the instrument was rinsed with appropriate diluted nitric acid solutions ($10^{-3}-10^{-5}$M).

Equilibrium Concentration Calculation. The free Eu equilibrium concentration was derived directly from the total ion current of the complexes coming from the free Eu in solution; then, the equilibrium concentrations of the free ligand and each of the three $Eu(DATP)_n^{3+}$ ions were calculated from the known amounts of ligand and Eu added to each solution (T is the total concentration):

$$(\sum_{n=1}^{3}[Eu(DATP)_n^{3+}]) = [Eu]_T - [Eu] \quad (1)$$

$$[Eu(DATP)_n^{3+}] = \%(Eu(DATP)_n^{3+}) \times (\sum_{n=1}^{3}[Eu(DATP)_n^{3+}]) \quad (2)$$

$$[DATP] = [DATP]_T - \sum_{n=1}^{3} n[Eu(DATP)_n^{3+}] \quad (3)$$

Results and Discussion

The methods traditionally employed for determining stability constants of Ln(III) complexes rely on a change in the physicochemical properties of the ligand upon complexation, as in spectrophotometry or NMR experiments, or take advantage of the luminescent properties of the Ln(III), mainly Eu and Tb.[23,34] By contrast, ESI-MS reveals directly the complexes as well as free europium or protonated ligand free of complexation. After passage through the electrospray ion source, species exist in the form of isolated ions swiftly detected by MS analysis.[35] However, there is increasing acceptance[36] that noncovalent interactions in solution can be maintained on the time scale of the ESI process (~400 μs).[35] Recently, Vottéro et al.[19] have analyzed by ESI-MS the complexes coming from the attachment of nitrates as well as triflates with the $Eu(L)_n^{3+}$ ($n = 1-2$) ions of cyclohexanetriol in methanol and noticed that species observed on the spectra were in agreement with the solution equilibrium deduced from ^{1}H NMR investigations.

Further, several studies have shown good agreement between solution-phase and gas-phase ionic abundance for metal complexes present in thermodynamic equilibrium in solution.[37−39] The difficulty in making ESI measurement stems from two steps in the electrospray process (i.e. electrolytic pH change and increased solute concentrations due to the evaporation of solvent from the droplets) which could be suspected to induce possible shift in the equilibrium position for the complexation reactions.[38,39] For the special case of kinetically labile species, Wang and Agnes[38,39] made a very interesting investigation on the equilibrium shift toward complex formation induced by the ESI process. The authors illustrated possible application of ESI-MS to assess the solution-phase concentration of the Sr^{2+}−EDTA complex which is governed by a fast formation ($k_f \sim 10^9$ M^{-1} s^{-1}) and slow dissociation ($k_r \sim 1.6$ s^{-1}) rates.[38] Moreover, as noticed by Saito et al.,[40] lanthanide(III) complexes are usually classified as kinetically labile on the basis of the large rate constants for water exchange (~10^8-10^7 M^{-1} s^{-1})[41] and the dissociation processes for monodentate or bidentate complexes. There are no reports yet dealing with the formation and dissociation kinetics of DATP complexes with lanthanide ions. In fact, little is known about kinetics of multidentate ligands containing nitrogen donors alone, while the formation and dissociation kinetics of Ln(III) complexes with polyaminocarboxylate ligands have attracted much interest because of the application of these ligands in biomedical analyses.[42−45] Thus, it has been shown by Choppin[46] that bulk steric effects in multidentate coordination lead to slower complex formation as well as slower decomposition and, hence, greater kinetic stability. Recently, the "chelate effect" contribution to the inertness in solvolysis was illustrated by the dissociation kinetics for Ln(III) complexes with polyaminocarboxylates in aqueous solutions.[40] Furthermore, in the case of DATP ligands which contain only nitrogen donors, the reaction rates could be expected to be several orders of magnitude lower than for the polyaminocarboxylates ligands as a consequence of the oxophilicity of the Ln(III) aquo ions. It has also been reported that the basicity of macrocyclic ligands as well as the longer lifetimes for Ln−N bonds relative to Ln−O bonds govern inertness in the proton-assisted dissociation of the Ln complexes.[46] Therefore, the systems such as DATP + Ln(III) are unlikely to undergo extensive change in species distribution in the evaporating droplet prior to desorption. Thus, it would be possible to assess an image of the speciation by ESI-MS with a sufficient reliability to justify the calculation of equilibrium constants.

The analytical strategy presented herein involves Eu speciation, i.e. determination of all free and complexed species. Eu complexation by DATP ligands can be schematically described by the following reaction, where for simplification purposes, solvation and anion coordination have been omitted:

$$Eu^{3+} + nL = Eu\ (L)_n^{3+} \qquad n = 1-3 \quad (4)$$

Europium speciation was divided into two categories: (A) Eu complexes coming from the $Eu(L)_n^{3+}$ ($n = 1-3$) ions

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Table 1. Complexes Detected by ESI-MS for 10^{-4} M $Eu(NO_3)_3$ with $[DATP]_T/[Eu]_T = 0.1-5$ under pH Range 2.8−4.6 in Water/Methanol (1:1 v/v) and Aqueous Nitrate Medium

complexes	DiPTP		DnPTP		DMTP	
$Eu(L)_3^{3+}$	$[Eu(L)_3]^{3+}$	*m/z* 456.2	$[Eu(L)_3]^{3+}$	*m/z* 456.2	$[Eu(L)_3]^{3+}$	*m/z* 344.1
	$[Eu(L)_3(NO_3)]^{2+}$	*m/z* 715.3	$[Eu(L)_3(NO_3)]^{2+}$	*m/z* 715.3	$[Eu(L)_3(NO_3)]^{2+}$	*m/z* 547.3
	$[Eu(L)_3(H)_{-1}]^{2+}$	*m/z* 684.0	$[Eu(L)_3(H)_{-1}]^{2+}$	*m/z* 683.9	$[Eu(L)_3(H)_{-1}]^{2+}$	*m/z* 515.8
$Eu(L)_2^{3+}$			$[Eu(L)_2(NO_3)]^{2+}$	*m/z* 512.7	$[Eu(L)_2(NO_3)_2]^{+}$	*m/z* 863.1
					$[Eu(L)_2(NO_3)]^{2+}$	*m/z* 400.5
					$[Eu(L)_2]^{2+}$	*m/z* 369.5
$Eu(L)_1^{3+}$					$[Eu(L)(NO_3)_2]^{+}$	*m/z* 569.9

and (B) Eu species coming from the "free" Eu in solution. As already mentioned, in water/methanol (1:1 v/v), the first coordination sphere of Eu is mostly constituted of water molecules;[25] moreover, at the experimental concentrations and pH range, Eu complexation by nitrate (NO_3^-), a bidentate oxygen-donating ligand, was considered negligible via calculation in water.[47] Using the measured distribution of total metal speciation between A and B, it was possible to quantify the percentage of the different europium species, i.e. Eu^{3+}, $Eu(L)^{3+}$, $Eu(L)_2^{3+}$, and $Eu(L)_3^{3+}$, and thereby to calculate complexation constants.

ESI-MS Measurements. ESI mass spectra were recorded with a constant Eu(III) concentration fixed at 10^{-4} M under pH range 2.8−4.6. It should be noted that, within these conditions, europium precipitation is not likely to occur. The experiments were carried out in the presence of the DATP ligands at ligand-to-metal ratios up to 5. The setting voltage of the first orifice encountered by the sample ions in the ESI source (cone voltage) was kept at 40 V; lower settings led to loss of the spray stability due to the salt content of the solutions as well as reduction of the overall sensitivity, and higher settings led to fragmentation of the ions coming from the complexes.

The ESI-MS spectra generated from solutions containing a 1-fold molar ratio of DiPTP and 3-fold molar ratio of DnPTP over Eu at pH 2.8 are respectively shown in Figure 1a,b. They are typical of ESI-MS in that they reveal an array of species, i.e. free protonated ligands, free Eu species, and metal-bounded ligands, which have different ESI response factors. All the complexes coming from the different $Eu(L)_n^{3+}$ ($n = 1-3$) ions with L = DiPTP, DnPTP, and DMTP have been identified by high-resolution ESI utilizing a Q-Tof mass spectrometer and are summarized in Table 1.

It can be noted that the basicity of DATP ligands is highlighted by the presence of great intensities of the protonated molecules in the ESI spectra (here DiPTP − H^+ or DnPTP − H^+ at *m/z* 406), since one would expect that, in both cases (3 ligands being expected to be associated with 1 europium), most of the DATP would be associated with europium.

Concerning free europium, the inset zoom scan (*m/z* 200−400) in Figure 1a shows 6 main species assigned to $[Eu(NO_3)_2(MeOH)_n]^+$ ($n = 0-3$) and $[Eu(NO_3)_2(MeOH)_n(H_2O)]^+$ ($n = 1-2$) complexes. Other complexes identified as $[Eu(MeO)(NO_3)]^+$ are weakly observed at pH 2.8. The same species are identified in the mass spectrum for a 10^{-4} M Eu solution at pH 2.8 prepared without DATP addition (Table 2).

Concerning Eu−DATP complexes, monomeric species $[Eu(DATP)_n(NO_3)_m]^{(3-m)+}$ ($n = 1-3$; $m = 0-2$) are observed. The high nitrate content of the solutions promotes formation of complexes that retain either one nitrate anion, such as the $[Eu(DATP)_3(NO_3)]^{2+}$ (Figure 1a,b) and $[Eu(DATP)_2(NO_3)]^{2+}$ (Figure 1b) complexes, or two nitrate anions, such as those seen for the complexes coming from the $Eu(DMTP)_n^{3+}$ ($n = 1-2$) ions (Table 1). Typical examples of the specific pattern obtained with high-resolution ESI for the multiply charged complexes are presented in the Figure 1b inset for $[Eu(DnPTP)_3]^{3+}$ at *m/z* 456 and $[Eu(DnPTP)_3(NO_3)]^{2+}$ at *m/z* 715. The complexes identified as $[Eu(DnPTP)_3(H)_{-1}]^{2+}$ at *m/z* 684 originate from the desolvation of the $[Eu(DnPTP)_3(NO_3)]^{3+}$ complexes (HNO_3 release) in the ESI source (MS/MS spectra confirmed that the HNO_3 release is the predominant fragmentation pathway of these complexes). Unlike in DnPTP mass spectra, the peaks from the $[Eu(DATP)_3(H)_{-1}]^{2+}$ complexes are barely observed in the case of DiPTP (Figure 1a). Vottero et al.[19] have previously illustrated that $[Eu(L)_n(NO_3)_2]^+$ ($n = 1-2$) complexes readily lost HNO_3 in the ESI source to lead to $[Eu(L)_n(H)_{-1}(NO_3)]^+$ complexes with trihydroxycyclohexane ligands.

For DMTP, ESI-MS spectra obtained are much more complexed since 7 different complexes are observed (see Table 1). Furthermore, the complexes coming from the $Eu(DATP)_3^{3+}$ species are observed with a strong contribution of the $[Eu(DMTP)_3(H)_{-1}]^{2+}$ ions, suggesting that the presence of labile hydrogen atoms on methyl substituents (see Chart 1) makes the HNO_3 release more favorable. Interestingly, these results have been correlated to the relative chemical stability of the DATP in extraction experiments.[48] For DMTP, desolvation in the ESI source was also found to promote formation of small amounts of the charge-reduced ions $[Eu(DMTP)_2]^{2+}$. MS/MS experiments confirmed that these species are the result of the predominant fragmentation pathway of the $[Eu(DMTP)_2(NO_3)]^{2+}$ complexes.

MS/MS experiments have also been used to assess that the 1:1 complexes as well as the 1:2 complexes detected by

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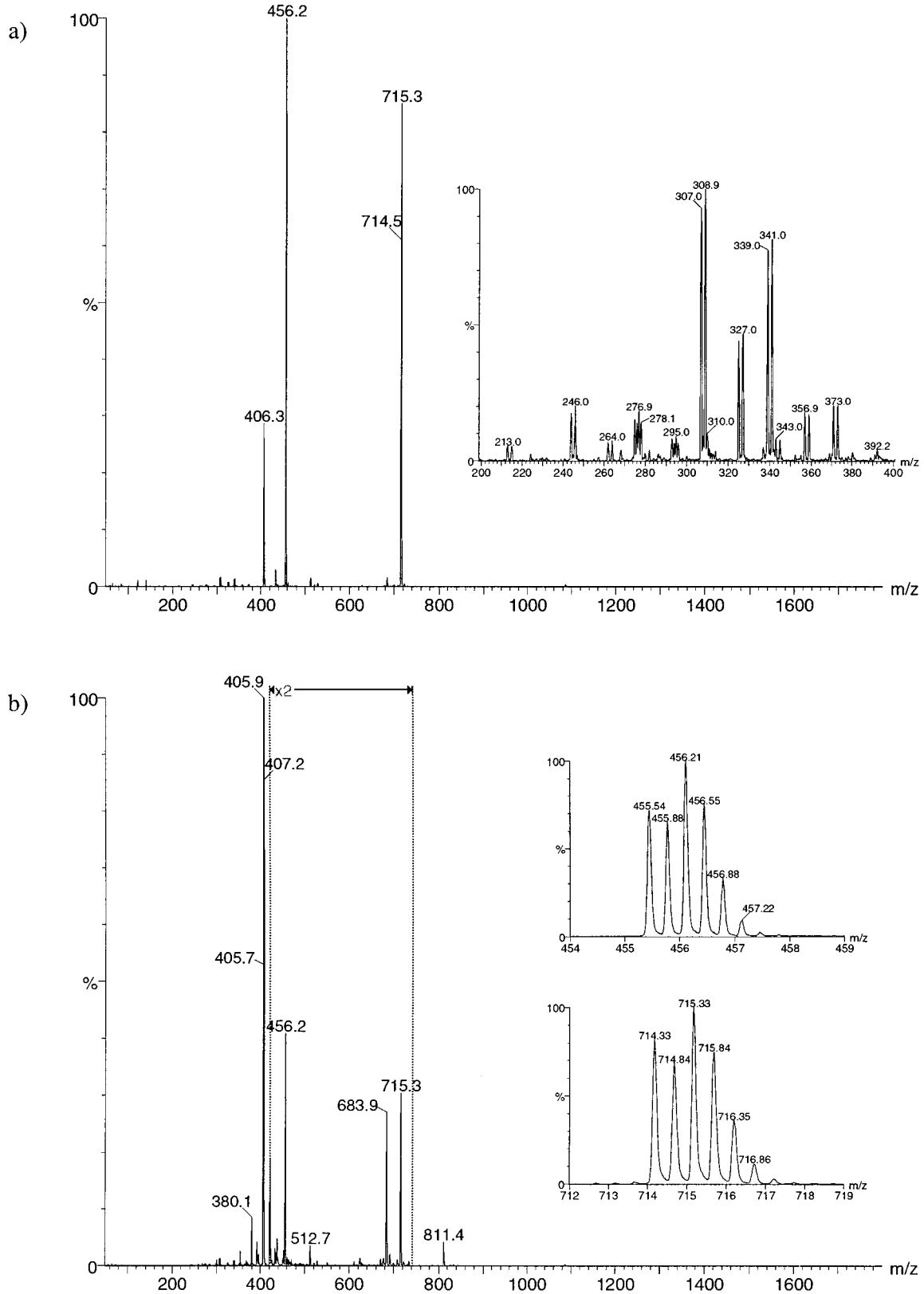

Figure 1. (a) ESI-MS spectrum of an equimolar mixture of DiPTP and $Eu(NO_3)_3$. Inset: region from m/z = 200 to 400. (b) ESI-MS spectrum with $[DnPTP]_T/[Eu]_T = 3$. Inset: High-resolution ESI-MS signals from $[Eu(DnPTP)_3]^{3+}$ and $[Eu(DnPTP)_3(NO_3)]^{2+}$ species. $[Eu(NO_3)_3] = 10^{-4}$ M in water/methanol (1:1 v/v) at pH 2.8 and aqueous nitrate medium.

ESI are present in solution and not formed by fragmentation in the gas phase of the related higher coordinated complexes. Similar experiments have been recently reported by Vottéro et al.[19] to validate the relative abundance of the nitrate and triflate complexes coming from the $Eu(L)^{3+}$ and $Eu(L)_2^{3+}$ ions of L ≡ cyclohexanetriol.

The $Eu(DATP)_n^{3+}$ ($n = 1-3$) distribution was obtained by summing the intensities of all related complexes singly

Table 2. Complexes Detected by ESI-MS for 10^{-4} M $Eu(NO_3)_3$ under pH Range 2.8−4.6 in Water/Methanol (1:1 v/v) and Aqueous Nitrate Medium

complexes	pH 2.8		pH 3.7−4.6	
Eu^{3+}	$[Eu(NO_3)_2(MeOH)_n]^+$, $n = 0-3$	*m/z* 276.9, 308.8, 340.9, 372.9	$[Eu(NO_3)_2(MeOH)_n]^+$, $n = 0-3$	*m/z* 276.9, 308.8, 340.9, 372.9
	$[Eu(NO_3)_2(MeOH)_n(H_2O)]^+$, $n = 1-2$	*m/z* 326.9, 358.9	$[Eu(NO_3)_2(MeOH)_n(H_2O)]^+$, $n = 1-2$	*m/z* 326.9, 358.9
	$[Eu(MeO)(NO_3)]^+$	*m/z* 245.8	$[Eu(MeO)(NO_3)(MeOH)_n]^+$, $n = 0-2$	*m/z* 245.9, 277.9, 309.8
			$[Eu(OH)(NO_3)(MeOH)_n]^+$, $n = 1-2$	*m/z* 263.9, 295.8
			$[Eu(MeO)_2]^+$	*m/z* 214.9
Eu^{2+}			$[Eu(NO_3)]^+$	*m/z* 214.9
			$[Eu(MeO)]^+$	*m/z* 183.8
			$[Eu(OH)]^+$	*m/z* 169.8

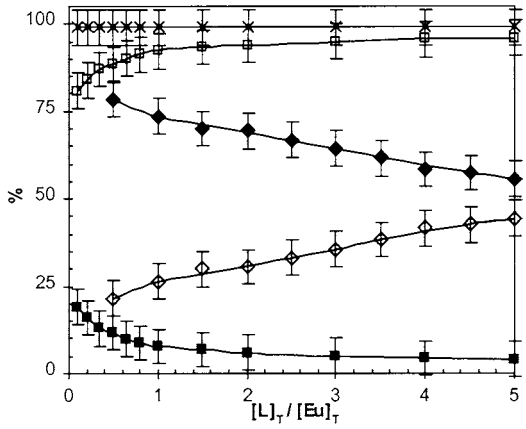

Figure 2. ESI-MS speciation diagram of $Eu(L)_n^{3+}$, $n = 1-3$, species in solution, with L = DiPTP, DnPTP, and DMTP. $[Eu(NO_3)_3] = 10^{-4}$ M with $[L]/[Eu]_T = 0.1-5$ in water/methanol (1:1 v/v) at pH 2.8 and aqueous nitrate medium. Relative abundance varied (±5%) from run to run. (×) $Eu(DiPTP)_3^{3+}$; (■) $Eu(DnPTP)_2^{3+}$; (□) $Eu(DnPTP)_3^{3+}$; (◆) $Eu(DMTP)^{3+}$; (◇) $Eu(DMTP)_2^{3+}$.

and doubly charged at each ligand-to-metal ratio. By doing so, it was possible to assess the general trends in the complexation of each DATP group ligand. The distribution plots for the different complexes at pH 2.8 as a function of DATP/Eu molar ratio are shown in Figure 2. The first assumption is that the relative amounts of complexed ligand can be measured by assuming equal signal responses for triply and doubly charged complexes containing the same ligand and metal. The second is that a measurement of ion current in the gas phase quantitatively represents the solution equilibrium. It is worth noticing that these assumptions have already been discussed in the literature.[49] Each set of data acquisition was carried out three times, and the conclusions are that the percent relative abundance of the $Eu(DATP)_n^{3+}$ ions are reproducible within 5% from different sample preparations run several weeks apart. Moreover, it is worth noting that, for each 1:*n* ($n = 1-3$) complex, the relative abundance of the related ions changed by no more than 20% for slight variations in instrumental conditions as the flow rate of either the drying or nebulizing gas. This phenomenon is likely to be due to changes in the desolvation of the complex ions which exert an influence on the appearance of the ESI mass spectrum.

Data shown in Figure 2 indicate that DiPTP added to 10^{-4} M Eu forms exclusively complexes coming from $Eu(DATP)_3^{3+}$ ions whatever the ligand-to-metal ratio. Moreover, decreasing the total Eu and ligand concentrations by a factor of 2 does not change the complexation observed in the ESI spectra. Thus, at least for strong bindings such as the ones occurring between Eu and terdentate DiPTP ligands, dissociation linked with desolvation does not occur. With *n*-propyl moieties as substituents, the species coming from the $Eu(DnPTP)_3^{3+}$ ions are again predominant whatever the ligand-to-metal ratio, but complexes coming from $Eu(DnPTP)_2^{3+}$ ions are also observed at low ligand-to-metal ratio (<2). This 1:2 complex evolves from 5% for a 2-fold molar ratio of ligand over Eu to 20% for a 0.1-fold ratio. Although it is small, the 1:2 contribution to Eu complexation by DnPTP suggests that *n*-propyl moieties induce some changes in the complexation properties compared to *iso*-propyl moieties. The *n*-propyl moieties seem thus to favor the stability of the $Eu(DATP)_3^{3+}$ ions but lead to a slightly lesser degree of specificity for the 1:3 stoichiometry compared to the bulky *iso*-propyl moieties. Concerning interactions between europium and DMTP, the two complexes obviously present in solution come from the $Eu(DATP)^{3+}$ and $Eu(DATP)_2^{3+}$ ions with this time no $Eu(DATP)_3^{3+}$ at pH 2.8. The 1:1 species is the major complex in solution that evolves from 75% at equimolarity to 55% at a 5-fold molar ratio (the 1:2 complex percentage being complementary).

Evidence is given from the ESI-MS data for the presence of stable $Eu(DATP)_3^{3+}$ ions with DnPTP and DiPTP ligands in nitric acid solution at pH 2.8, consistent with the structure isolated in solid phase for Ln complexes of DnPTP ligand.[11] Under such acidic conditions, 1:3 complexes are not detected at all for the DMTP derivative bearing methyl moieties though $U(L)_3^{3+}$ and $Ce(L)_3^{3+}$ structures prevail in solid state.[16] The anhydrous conditions used for crystals preparation may account for the difference noticed in structures.

Stability Constants. Assuming an equivalence between concentrations and thermodynamic activities, the following equation can be used:

$$\beta_n = [Eu(DATP)_n^{3+}]/[Eu^{3+}][DATP]^n \qquad (5)$$

The values of K_n, which are the constants for the formation of individual complexes, may be assessed by mean of the equilibrium constants β_n. Thus, it is possible, for exemple, to compare the log K_n values or the magnitude of log β_n/n with one another. The latter gives the mean free energy of addition of each ligand.[50]

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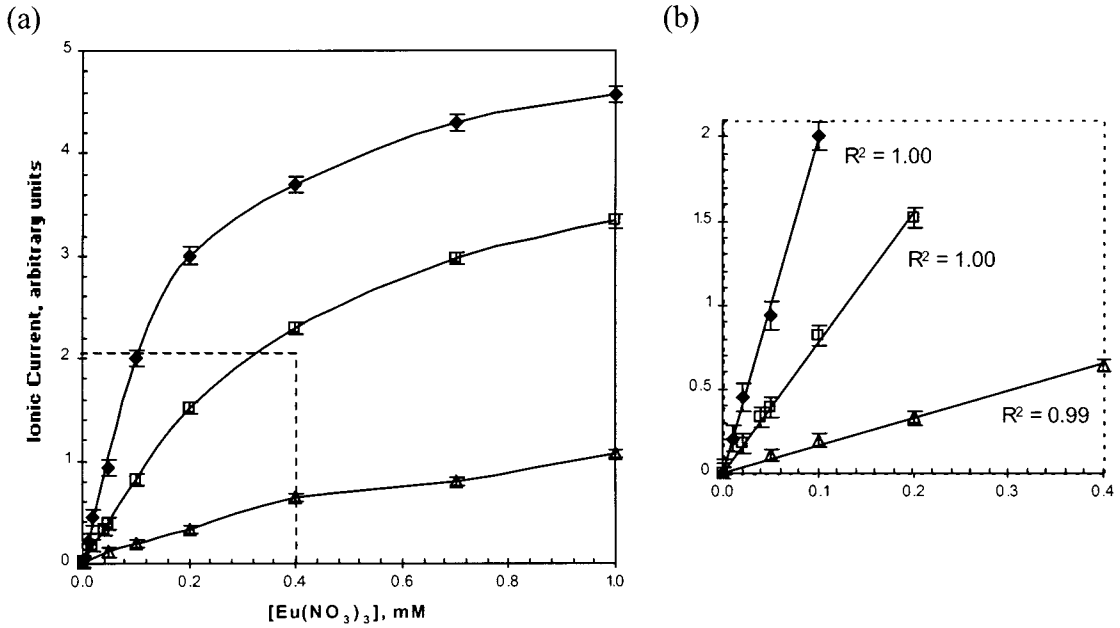

Figure 3. Calibration curves for solutions containing $2 \times 10^{-5}-10^{-3}$ M $Eu(NO_3)_3$ in water/methanol (1:1 v/v) under pH range 2.8−4.6 and aqueous nitrate medium: (a) wide range concentration plots, including nonlinear region; (b) plots of the lower concentration region of (a). (◆) pH 4.6; (□) pH 3.7; (△) pH 2.8.

It was not recommended, with the different observations made above, to determine the equilibrium concentration by using methods that solely involves direct comparison of either the relative intensities of both free Eu and Eu−ligand complexes or the intensities of both ligand species, i.e. free protonated ligands and metal-bound ligands. Instead, by using the Eu concentration free of complexation and the percent relative abundance of the $Eu(DATP)_n^{3+}$ ions, it was possible to reach the conditional stability constants thanks to eq 5. In the present study, the free Eu equilibrium concentration was derived directly from the total ion current of the complexes coming from the free Eu in solution (see Experimental Section).

It should be mentioned that the use of ESI-MS for the analysis of Ln(III) has been previously reported[27,30] but none on europium and all in methanolic (1−5% water) solutions. These studies have indicated that the transfer of the solvated ions from the liquid to the gas phase led to a variety of ion species which were dependent on the properties of the lanthanide metal, the solvent, and the counterion of the salt used as well as the electrospray interface setup. In particular, the above studies outlined that the lanthanides are strong oxides formers and further exhibit high ionization potential values, and, thus, charge-reduced species are favored. Kebarle et al.[27] have found that no triply charged hydrates $Ln(H_2O)_n^{3+}$ could be produced by ESI-MS; the species seen in the mass spectra were the charge-reduced complexes $Ln(OH)(H_2O)_n^{2+}$. Stewart and Horlick[30] found that a variety of ion species, bare metal ions (Ln^+ or Ln^{2+}), oxides (LnO^+), and hydroxides ($LnOH^+$) as well as charge-reduced clusters such as $[Ln(MeO)(MeOH)_n]^{2+}$ and $[Ln(MeO)(X)(MeOH)_n]^+$ ($X = Cl^-$ or NO_3^-) as a result of ion pairing are produced and demonstrated that ESI-MS can be used for the analysis of uncomplexed lanthanides in solution.

All free europium species observed for 10^{-4} M Eu solutions at pH 2.8−4.6 are listed in Table 2. The species observed at pH 2.8 are those previously identified as free europium in the mass spectrum (Figure 1a) generated from a solution containing a 1-fold molar ratio of DiPTP over Eu at pH 2.8. These complexes are mainly singly charge ions having a metal−nitrate core $Eu(NO_3)_2$ with solvent molecules attached: $[Eu(NO_3)_2(MeOH)_n]^+$ ($n = 0-3$); $[Eu(NO_3)_2(MeOH)_n(H_2O)]^+$ ($n = 1-2$). At pH 3.7, can be seen important contributions from methoxide and hydroxide species, $[Eu(MeO)(NO_3)(MeOH)_n]^+$ and $[Eu(OH)(NO_3)(MeOH)_n]^+$, as well as charge-reduced ions $Eu(MeO)^+$ and $Eu(OH)^+$. At pH 4.6, the dominant ions observed in the spectrum are the charge-reduced 1+ ions $Eu(MeO)^+$ and $Eu(OH)^+$; methoxide and hydroxide species containing one nitrate such as $[Eu(MeO)(NO_3)(MeOH)_n]^+$ are also detected, while the contribution of clusters having a metal−nitrate core, $Eu(NO_3)_2$, becomes much smaller.

The total signal responses for the previously mentioned complexes were plotted for each pH as a function of the europium added to water/methanol (1:1 v/v) mixtures (Figure 3) together with the linear region of the calibration curve (Figure 3b). At pH 2.8, the total ion current and the Eu concentration are linearly related (correlation coefficient of 0.99) in a range of $2 \times 10^{-5}-4 \times 10^{-4}$ M Eu concentration, while when the pH is increased, these two data are linearly related in a much narrow range (i.e. $2 \times 10^{-5}-10^{-4}$ M at pH 4.6). These results may be connected to the electrolytic effects evidenced above. Therefore, it was decided to carry out quantitative measurements at pH 2.8 within the linear range, and studies at higher pH were restricted to the investigation of the pH-dependent differences in the binding stoichiometries of the three DATP ligands.

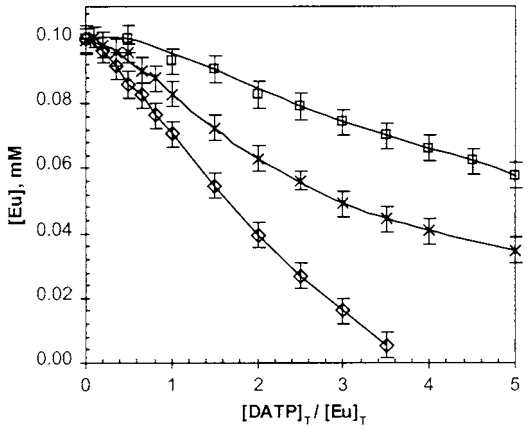

Figure 4. Calculated fraction of free Eu concentration vs $[DATP]_T/[Eu]_T$ for the ligands studied in solutions water/methanol (1:1 v/v) containing 10^{-4} M $Eu(NO_3)_3$ and $[DATP]_T/[Eu]_T = 0.1-5$ at pH 2.8 and aqueous nitrate medium. (□) DMTP; (×) DnPTP; (◇) DiPTP.

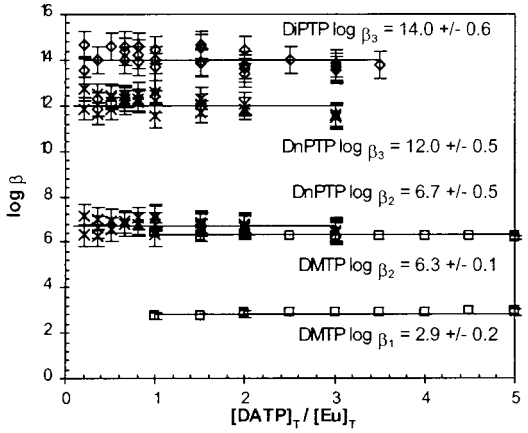

Figure 5. Stability constants at pH 2.8 obtained by undertaking multiple measurements of solutions containing 10^{-4} M (and 5×10^{-5} M for DiPTP) $Eu(NO_3)_3$ and $[DATP]_T/[Eu]_T = 0.2-5$ in water/methanol (1:1 v/v) and aqueous nitrate medium.

Figure 4 compares the variation of free europium as a function of DATP/Eu molar ratio at pH 2.8 for 10^{-4} M Eu. The error bars represent a $\pm 4 \times 10^{-6}$ M variation in the Eu concentration free of complexation. Several comments should be made: At a 3.5-fold molar ratio of DiPTP, it could be directly observed that no free Eu remains in solution, and total Eu added in solution is in the $Eu(L)_3^{3+}$ form. Under the same conditions, there is still 45% of Eu free of complexation in the presence of DnPTP, while 52% and 3% of Eu is complexed in the 1:3 and 1:2 complexes, respectively. For DMTP, still 70% of Eu is free, while 19% and 11% of Eu is complexed in the 1:1 and 1:2 complexes, respectively. Further, when up to 5-fold ratios of DnPTP and DMTP ligands are added in solution, there is still 35% and 58% of Eu free, respectively. These results combined with the restricted 1:3 stoichiometry for Eu complexation of DiPTP contend that *iso*-propyl moieties induce unusual changes in the complexation properties of the ligand compared to *n*-propyl and methyl moieties. It is interesting to notice that the first protonation constant of DMTP was found to be around $pKa_1 = 1.5$ in mixed water and methanol (1:1 v/v);[51] thus, DMTP is likely to be partially protonated at pH 2.8, which may inhibit its complexation with Eu(III). Nevertheless, propyl moieties having a greater inductor donor effect than methyl substituents, DnPTP and DiPTP are expected to have nitrogen atoms more basic than DMTP and thus to interact more efficiently not only with H^+ but also with Eu^{3+} ions. Hence, in the case of DnPTP and DiPTP, the competition between protonation and complexation appears to turn in favor of complexation.

The conditional stability constants extracted from ESI data are presented in Figure 5. The reproducibility is quite good as is evident from the small discrepancies seen for the log β_i values determined by performing multiple measurements of solutions containing 10^{-4} M $[Eu]_T$ and $[DATP]_T/[Eu]_T = 0.2-5$. As shown in Figure 5, the average values for the log of the stability constants show standard deviation values range between ±0.1 to 0.6. These relatively small uncertainties on log β_i values highlight the gas-phase stability of the multiple interactions between Eu and the terdentate ligands. It is important to point out that, with DiPTP, it has been found that measurements performed with total Eu and ligand concentrations twice lower led to calculated log β_3 values (Figure 5) lying within the standard deviation of those evaluated with $[Eu]_T = 10^{-4}$ M.

Stability constants determined by ESI-MS show that the $Eu(DiPTP)_3^{3+}$ ion (log $\beta_3 = 14.0 \pm 0.6$) is somewhat more stable than its counterpart with the DnPTP ligand (log $\beta_3 = 12.0 \pm 0.5$). It is important to notice that a TRLIF study of europium complexation with DiPTP is now underway and has provided a log β_3 value of 14.3 ± 0.6 at pH 2.8.[26] The gap between DnPTP and DiPTP log β_3 values is unexpected as *n*-propyl and *iso*-propyl moieties are unlikely to induce large differences in the basicity of the coordinating nitrogen atoms or the ligands internal cavity size. Thus, the alkyl substituents may influence the degree of π-stacking interactions[23,52−56] between the ligand units and, thereby, probably assist in the assembly process. However, it is also possible, since solvent coordination is important to the ligand exchange process, that bulky *iso*-propyl substituents interfere to a greater extent with solvent coordination, affording a more hydrophobic environment around the complex core as compared with the $Eu(DnPTP)_n^{3+}$ ion. The enhancement of this phenomenon with the *iso*-propyl moieties thus makes the complexation of DiPTP remarkably restricted to 1:3 complexes, while a contribution from 1:2 species (log $\beta_2 = 6.7 \pm 0.5$) is seen for DnPTP. These results are likely to support the assumption made by Drew et al.[14] from solid-

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state studies that the ability to form $Eu(DATP)_n^{3+}$ ions is due not only to the different electronic properties of the nitrogen atoms in the DATP ligands but also to the hydrophobic exterior of the ligands. The phenomenon provided here by the ESI-MS data may contribute to the high stability of the $Eu(DiPTP)_3^{3+}$ ions at low pH condition and, hence, would have a significant effect on the extraction properties.[7,8,14]

For the DnPTP ligand, the 1:1 complex was not detected and thereby the K_n values ($n = 1, 2$) could not be evaluated. However, it is possible to compare the magnitude of $\log \beta_2/2$ and $\log \beta_3/3$. The mean free energy of addition for the second ligand is found to be lower than for the third ligand ($\log \beta_2/2 < \log \beta_3/3$). This trend may probably be connected with DnPTP mechanism of complexation, but the link has not been established yet.

The complexation constants calculated for the two equilibria of DMTP are $\log \beta_1 = 2.9 \pm 0.2$ and $\log \beta_2 = 6.3 \pm 0.1$. It is interesting to notice that the only other binding constant value previously reported for the DATP group ligand was $\log \beta_1 = 3$ for DMTP ligand obtained by TRLIF titration[51] in perchlorate aqueous medium at pH = 4; the two values are in very good agreement.

The stability constants of the 1:2 complexes containing DnPTP or DMTP ligands are thus quite similar. However, DnPTP ligand favors formation of $Eu(DATP)_3^{3+}$ species, while for DMTP it is not seen at all on the ESI spectra. These results suggest that $Eu(DATP)_3^{3+}$ ions arise from specific interactions and, hence, give strong support for a mechanism whereby the propyl substituents play an important role. The 1:1 complexes found only for the DMTP ligand ($\log \beta_1 = 2.9 \pm 0.1$) may probably be due to the lesser hydrophobic character of the DMTP ligand exterior compared to DnPTP and DiPTP. It has been reported that the tridentate ligands 2,6-bis(5-alkyl-1,2,4-triazol-3-yl)pyridine[12] and 4-aminobis-(2,6-(2-pyridyl))-1,3,5-triazine[14] led only to 1:1 complexes and probably failed to form $Eu(L)_n^{3+}$ ions ($n = 2-3$) since they contain NH and NH_2 groups respectively that can form extensive hydrogen bonding, the net effect being further stabilization of 1:1 complexes.[14] Clearly, the role of the alkyl substituents is important in terms of the maximum stoichiometry. On the other hand, it was found from solid-state studies that distances in the coordination sphere occupied by the two ligands DnPTP and DMTP in the analogous $Ce(DATP)_3^{3+}$ ions are quite similar arguing that the alkyl substituents do not have significant effect on the metal coordination sphere.[16]

The overall stability constants obtained for the DMTP ligand are indicative of stepwise equilibria in which $\log K_1 = 2.9 \pm 0.2$ and $\log K_2 = 3.4 \pm 0.3$; the $\log \beta_n$ values ($n = 1, 2$) are also indicative of a trend in the mean free energy of the addition of the first and the second ligand with $\log \beta_1/1 < \log \beta_2/2$. The trend $K_2 > K_1$ is unexpected; the formation constants for consecutive addition of ligands to the same metal ion usually decrease with increasing substitution due to statistical, electrostatic, and steric factors.[57,58] The observation that $K_2 > K_1$ probably arises from a gain in entropy due to a lowering of coordination number on going from the 1:1 to the 1:2 complex. Hence, such an exception in lanthanide complexation has been reported by Caravan et al.[57] on a water-soluble N_4O_3 tripodal amine phenol ligand equilibrium where $K_2 > K_1$. The trend was attributed to an entropic effect due to the desolvation of the 1:1 complex because of steric hindrance. The coordination number of Ln(III) aquo ions has been the subject of numerous investigations, with 8 or 9 being the generally accepted number. Caravan et al.[57] have shown that, when a first tripodal ligand binds to a lanthanide(III) ion in a tridentate fashion, 3 water molecules are displaced from the aquo ion, while a second ligand displaces 5 water molecules due to a steric effect. The authors stated that the second equilibrium likely increases the entropy of the system more than the first, as determined by calorimetric measurements, and thereby leads to a larger K_2 value.

pH Dependence of the Complex Stoichiometry. The pH dependence of the stoichiometries of the complexes of great importance in the framework of further extraction experiments has been investigated. Figures 6 show the pH-dependent differences for $Eu(DATP)_n^{3+}$ species of DnPTP and DMTP ligands as a function of the ligand-to-metal ratio. The resulting data outline a strong effect due to alkyl substituents with striking differences in the DATP group ligands under pH 2.8−4.6. First, with the *iso*-propyl chains as substituents, the only complex observed by ESI-MS whatever the pH is $Eu(DiPTP)_3^{3+}$. Second, with *n*-propyl moieties as substituents, Eu is always bounded predominantly to three DnPTP, but the trend when the pH goes from 2.8 to 4.6 is the increase of complexes coming from the $Eu(DnPTP)_2^{3+}$ ions at ligand-to-Eu ratios < 2 (Figure 6a). For example, at a 1-fold molar ratio, the abundance of $Eu(DnPTP)_2^{3+}$ reaches the value of 8% at pH 2.8, 13% at pH 3.7, and 26% at pH 4.6. These results are in agreement with the assumption made above that the *n*-propyl moieties lead to a slightly lesser degree of specificity for the 1:3 stoichiometry compared to the *iso*-propyl moieties. Moreover, in contrast to the formation of $Eu(DnPTP)_3$ complexes, formation of $Eu(DnPTP)_2$ complexes is likely to be pH-dependent, probably because of a competition between complexation and protonation. This gives further support for a structure of the type $Eu(DATP)_3^{3+}$ where the complex core is an environment which excludes itself from the solvent thanks to the alkyl chains at the triazinyl rings.

With methyl moieties as substituents, the distribution of the complexes coming from the $Eu(DMTP)_n^{3+}$ ions ($n = 1-3$) is highly dependent on both solution pH and ligand-to-metal molar ratios. Under pH 3.7 and 4.6 (Figure 6b,c), there is a mixture of complexes coming from the three $Eu(DMTP)_n^{3+}$ ions ($n = 1-3$) unlike pH 2.8 where complexes coming from $Eu(DMTP)_3^{3+}$ ions are not observed at all

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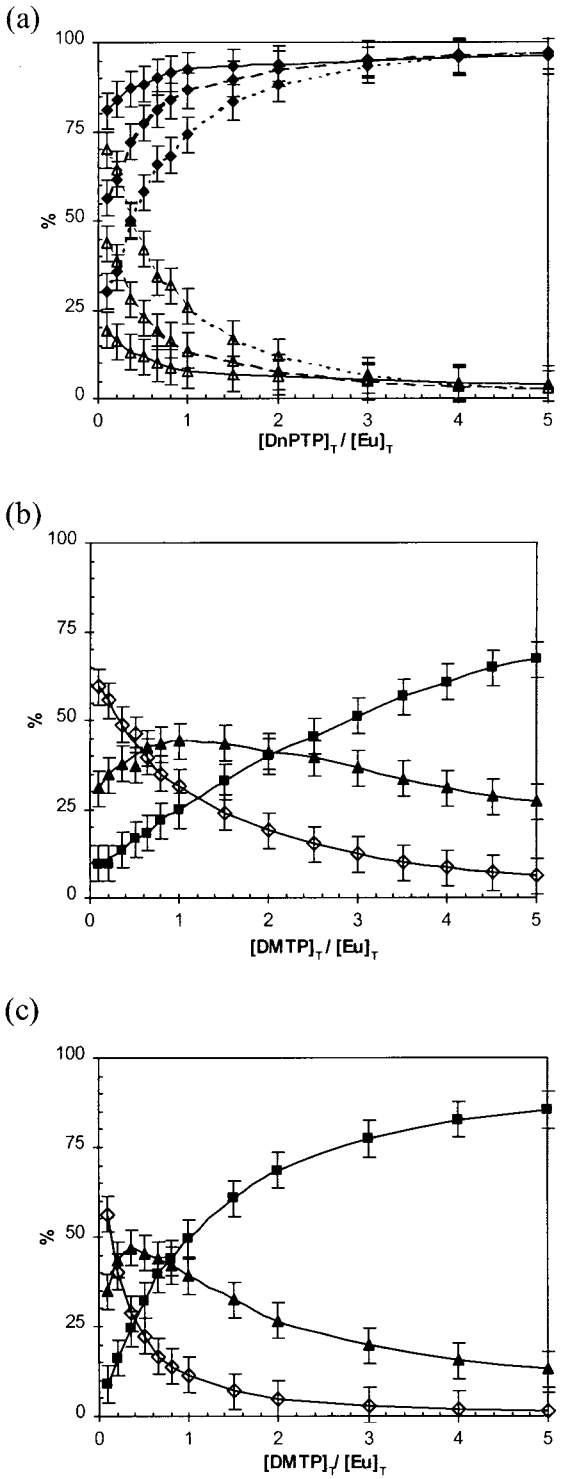

Figure 6. ESI-MS speciation diagrams of $Eu(DATP)_n^{3+}$, $n = 1-3$, species in solutions of water/methanol (1:1 v/v) containing 10^{-4} M $Eu(NO_3)_3$ and $[DATP]_T/[Eu]_T = 0.1-5$: (a) DnPTP ((△) $Eu(DnPTP)_2^{3+}$; (◆) $Eu(DnPTP)_3^{3+}$) at pH 2.8 (−), 3.7 (- - -) and 4.6 (···); solutions with DMTP ((◇) $Eu(DMTP)^{3+}$; (▲) $Eu(DMTP)_2^{3+}$; (■) $Eu(DMTP)_3^{3+}$) at pH 3.7 (b) and pH 4.6 (c). Relative abundance varied (±5%) from run to run.

(Figure 2). Furthermore, the $Eu(DMTP)_n^{3+}$ ($n = 1-3$) ions are formed in acidic aqueous/methanol solution with relative percentage depending on the ligand-to-metal ratios. Hence, at pH 3.7 (Figure 6b), the 1:2 species reach a maximum of 45% at 1-fold molar ratio while the 1:3 ions reach a maximum of 67% at 5-fold molar ratio, whereas the 1:1 ions diminish from 60% to 6% of the total. A significant shift in the $Eu(DMTP)_n^{3+}$ distribution toward species $Eu(DMTP)_2^{3+}$ and $Eu(DMTP)_3^{3+}$ is observed with increasing pH from 2.8 to 4.6 (Figure 6c). Indeed, at pH 4.6, the 1:2 ions reach a maximum of 45% at 0.4-fold molar ratio while the 1:3 ions reach a maximum of 85% for a 5-fold molar ratio whereas the 1:1 ions diminish from 56% to 5% of the total at a 2-fold molar ratio.

In summary, these different features reflect a shift in the $Eu(DMTP)_n^{3+}$ distribution toward 1:2 and 1:3 complexes across the ligand-to-metal molar ratios range when increasing the pH from 2.8 to 4.6. This behavior suggests that the presence of methyl moieties results in lower stabilization of the $Eu(DATP)_n^{3+}$ ($n = 2-3$) ions at low pH conditions while the lesser hydrophobic character of the DMTP ligand exterior increases the stability of the 1:1 complexes that can form hydrogen bonds with solvent molecules unlike their counterparts with the DnPTP or DiPTP ligands.

Conclusion

It is the first time to our knowledge that metal ion complexes of DATP group extracting agents have been studied in aqueous/methanol acidic solutions. The ability of ESI-MS to provide solution data such as stoichiometries and stability constants for these complexes has been demonstrated. An unusual role of the hydrophobic exterior in the action of a new range of extracting agents has been evidenced by ESI-MS, and strong support for these results comes from the different observations made previously either in solid-state or in extraction experiments. The data obtained for the DATP group ligands are the first to implicate a mechanism whereby alkyl substituents make a contribution to a self-assembling process leading to unusual aqueous $Eu(DATP)_3^{3+}$ ions. This phenomenon is enhanced with *iso*-propyl substituents making the complexation of DiPTP remarkably restricted to 1:3 complex under pH range 2.8−4.6. Furthermore, the pH dependence of the stoichiometries contends that, in the structure of the type $Eu(DATP)_3^{3+}$, the complex core is an environment which excludes itself from the solvent molecules probably thanks to the alkyl chains at the triazinyl rings. Hence, the DiPTP ligand can be expected to exhibit good kinetic stabilization against decomplexation, which for the partitioning purposes represents a significant advantage over simple chelating ligands. 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. Further efforts are being directed toward quantification of factors such as ligand basicity and steric hindrance.

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Supporting Information Available: Figure F1, giving ESI-MS spectra at pH (a) 2.8, (b) 3.7, and (c) 4.6 of 10^{-4} M $Eu(NO_3)_3$ in water/methanol (1:1 v/v) and aqueous nitrate medium.