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Article

# Europium(III) Interaction with a Polyaza-Aromatic Extractant Studied by Time-Resolved Laser-Induced Luminescence: A Thermodynamical Approach

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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. In a previous work, the use of electrospray ionization mass spectrometry (ESI-MS) provided 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 has then been further investigated by considering DiPTP complexation features with the complete lanthanide family. Moreover, a complementary study of equilibria in solution with a non intrusive technique such as time-resolved laser-induced luminescence (TRLIL) seemed quite promising to determine thermochemical data such as enthalpy and entropy variations associated with the complexation reaction between Eu(III) and DiPTP. Furthermore, this TRLIL study may also allow ensuring that the observations made on mass spectra actually reflected the equilibrium in solution and not an intermediate state between liquid phase and gaseous phase. The investigation of europium(III) complexation with DiPTP by TRLIL described in this paper first led to highlight the exclusive formation of a 1:3 complex between europium(III) and the DiPTP ligand, specificity already pointed out by ESI-MS. Two different calculation methods, using either luminescence spectra and luminescence decay curves, have then been used to measure the conditional stability constant of the $[Eu(DiPTP)_3]^{3+}$ complex. Both methods gave similar results (log $\beta_3^{app} = 14.3 \pm 0.6$ at pH 2.8) in good agreement with the one previously reported in ESI-MS studies (log $\beta_3^{app} = 14.0 \pm 0.6$ at pH 2.8). Moreover, while considering the influence of temperature on the value of the stability constant, it was possible to estimate the enthalpy ($\Delta H_{\beta 3} = -29 \pm 3$ kJ mol$^{-1}$ at pH 2.8) and entropy variations ($\Delta S_{\beta 3} = 173 \pm 10$ J K$^{-1}$ mol$^{-1}$ at pH 2.8) associated with the $[Eu(DiPTP)_3]^{3+}$ complex formation.

## 1. Introduction

The interactions between polyaza-aromatic ligands and trivalent actinides (An(III)) and lanthanides (Ln(III)) are of great interest 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.[1,2] The An(III)/Ln(III) separation process is intended to take place after the PUREX and DIAMEX processes, which involve concentrated nitric acid solutions.[1−3] The final aim being to transmute the long-lived minor

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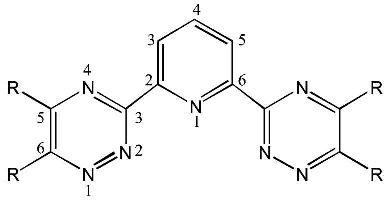
**Chart 1.** Ligands Code



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

actinides, such as americium, into short-lived or stable nuclides by irradiation with neutrons, An(III)/Ln(III) separation constitutes a crucial step as Ln nuclides absorb neutrons very effectively and may then prevent neutron capture by the transmutable actinides.[1] Various aza-aromatic ligands have been shown to selectively extract actinides in preference to lanthanides from concentrated nitric acid solution.[2,4−8] Recent studies have shed light upon a remarkable new family of extracting agents: the bis(dialkyltriazinyl)pyridines (DATPs) (Chart 1).[2,9−17] These 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 of the two positions of the triazinyl rings. The alkyl moieties confer to the DATP molecules, hydrophobic properties required to prevent the solubility of the ligands in the aqueous phase, which may dramatically lower extraction efficiency. It has been suggested from the initial solvent extraction studies[13,14] that the enhanced separation factor values for the DATP (L) is due to the formation of the extracted species $ML_3(NO_3)_3{\cdot}HNO_3$. Previously, we reported the results of a study of Eu(III) complexation with three DATPs—methyl (DMTP), *n*-propyl (DnPTP), and isopropyl (DiPTP)—by electrospray ionization mass spectrometry (ESI-MS).[16] It appeared that europium complexation by DiPTP was remarkably restricted to 1:3 complex, whatever the ligand-to-metal ratio. Further investigations led to check that the DiPTP complexation features with europium were maintained within the whole lanthanide series and to study the electronic complexation mechanism leading to 1:3 complex formation.[17]

In this work, coordination chemistry of Eu with DiPTP ligand in nitric acid water/methanol (1:1 v/v) solutions is investigated by TRLIL in order to estimate upon the conditional stability constant of the $[Eu(DiPTP)_3]^{3+}$ complex as a function of temperature and to reach for the first time by this technique enthalpy and entropy of that reaction. It will also lead to compare the TRLIL data with those obtained by ESI-MS at 25 °C. Indeed, time-resolved laser-induced luminescence is well suited for the study of such interactions and has been successfully applied for the determination of the stability constants of various ligands with lanthanide ions as well as first coordination sphere environment through lifetime measurements.[18−27] Even if several studies have already shown that ESI-MS spectra could roughly reflect solution for coordination complexes, the reliability of this technique for the determination of the binding constants of species in solution is not always clear-cut. This paper contributes to demonstrate capacity of ESI-MS for coordination chemistry investigations once it has been previously ensured that experimental conditions (solvent, electrolyte, ESI parameters, ...) are well suited for the examination of complexes initially present in solution.

## 2. Experimental Section

**Materials.** The DiPTP ligand was provided by CEA/DEN/DRCP/ (Bagnols-sur-Cèze, France). Stock solutions ($10^{-3}$ M) of DiPTP ($M = 405$ g/mol) were prepared by dissolution of a weighed amount in HPLC grade methanol. Stock solutions ($2 \times 10^{-4}$ 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

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the procedure. The study was carried out with nitrate ions since the extraction process takes place in nitric acid solutions.

Solutions for the TRLIL measurements were prepared from 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 0.1−5. 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 $6.2 \times 10^{-4}$ M at pH 4.6 to $2.2 \times 10^{-3}$ M at pH 2.8.

**Time-Resolved Laser-Induced Luminescence.** A Nd:YAG laser (model Minilite, Continuum) operating at 532 nm (doubled) and delivering about 15 mJ of energy in a 4 ns pulse with a repetition rate of 15 Hz was used as the excitation source. The excitation wavelength was fixed at 532 nm in order to, on one hand, prevent complex destruction under UV−visible excitation and, on the other hand, to avoid energy transfer phenomena thanks to europium direct excitation. The laser beam was directed into the 4 mL quartz cell of the spectrofluorimeter “Fluo 2001” (Dilor, France). The radiation coming from the cell was focused on the entrance slit of the polychromator (focal length 50 cm and 1 mm slit widths). Taking into account dispersion of the holographic grating (300 g/mm, blaze 500 nm) used in the polychromator, the measurement range extends to approximately 200 nm into the visible spectrum with a resolution of 1 nm. The detection was performed by an intensified photodiode (1024) array cooled by the Peltier effect (−20 °C) and positioned at the polychromator exit. Recording of spectra was performed by integration of the pulsed light signal given by the intensifier. The integration time, adjustable from 1 to 99 s, allows us to vary the detection sensitivity. Logic circuits, synchronized with the laser shot, allow the intensifier to be active with determined time delay (from 0.1 to 999 $\mu$s) and during a determined duration time from 0.5 to 999 $\mu$s.

**pH Measurements.** The pH 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 solution and calibrated with aqueous pH standards. No correction was made for the presence of methanol.

## 3. Results and Discussion

**3.1. Preliminary Studies.** The ESI-MS complexation studies between europium and DiPTP ligand previously reported had been performed in MeOH/$H_2O$ mixtures and in aqueous nitrate medium. Methanol was used to allow sufficient solubility of both organic and inorganic species in an homogeneous medium as close as possible to pure water and nitrate have been used as counterions in order to approach the process conditions. The same medium was chosen for TRLIL investigations so as preliminary studies, the influence of either methanol and nitrate ions on europium luminescence have been checked and compared to results obtained in the “noncomplexing” perchlorate medium. Hence, perchlorate anions are currently used because they do not complex Ln(III) in internal sphere,[19] the cation is then considered as “free” when it is in solution in the presence of this only counterion, which means that it is directly linked exclusively to water molecules and that its primary hydration number is around 9. A luminescence spectrum of uncomplexed europium presents characteristic peaks (Figure 1a, gray line) at 618 nm ($^5D_0 \rightarrow {}^7F_2$ hypersensitive transition, electric dipole), at 592 nm ($^5D_0 \rightarrow {}^7F_1$ transition, magnetic dipole), at 700 nm ($^5D_0 \rightarrow {}^7F_4$ transition, electric dipole, sensitive to Eu environment), and 650 nm ($^5D_0 \rightarrow {}^7F_3$ transition, electric dipole, forbidden) with specific ratios. Lifetime measured for the cation in water in perchlorate medium is $\tau = 110 \pm 10$ $\mu$s. Lifetime of the $^5D_0$ europium emitting level depends on the number of OH oscillators directly linked to the cation. This is due to a nonradiative desexcitation phenomenon through OH bonds vibrations, which does not occur when hydrogen atoms are replaced by their deuterium isotope.[20,21] Kimura and Kato[22] proposed an extension of the method described by Horrocks and Sudnick[23] in order to link the lifetime of the $^5D_0$ europium emitting level and the primary hydration number of the cation. They obtained a linear relation between the inverse of the lifetime measured in $H_2O/D_2O$ mixtures of variable proportions and the volume percentage of $H_2O$ in the mixture. Following this procedure, a correlation between primary hydration number of europium ($N_{H2O}$) and the lifetime of its $^5D_0$ emitting level ($\tau$) has been established for this system: $N_{H2O} = 1.06/\tau - 0.19$ (eq 1). This result in is good agreement with that reported by Kimura and Kato[22] ($N_{H2O} = 1.05/\tau - 0.44$) as the hydration number is determined with an uncertainty of ±0.4.

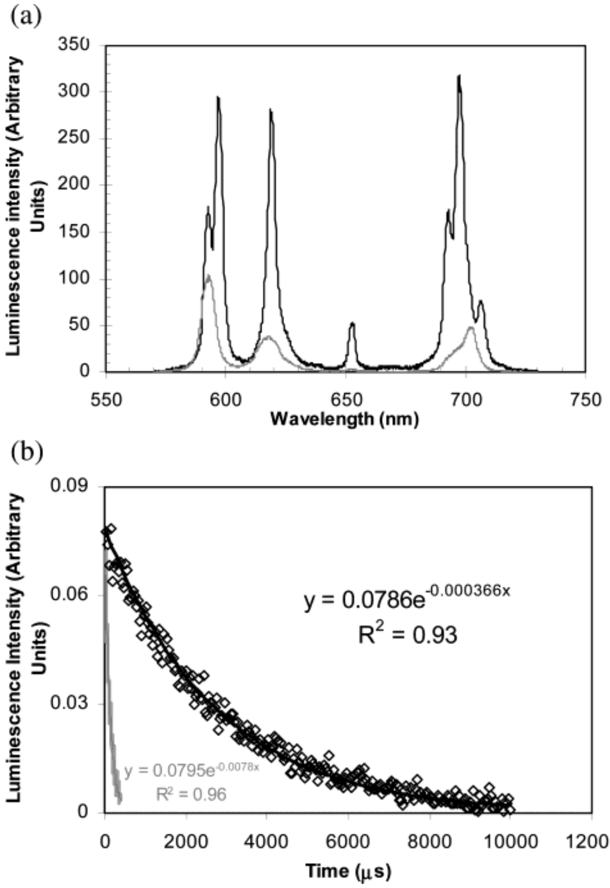

**Figure 1.** TRLIL spectra (a) and luminescence decay curves (b) obtained with solutions containing $10^{-4}$ M Eu($NO_3$)$_3$ (gray) or $10^{-4}$ M Eu($NO_3$)$_3$ + $5 \times 10^{-4}$ M DiPTP (dark) in MeOH/$H_2O$ (1:1 v/v), aqueous nitrate medium at pH 3.7, $\lambda_{exc} = 532$ nm, delay = 10 $\mu$s, duration = 100 $\mu$s.

Luminescence spectra and lifetimes of the $^5D_0$ europium emitting levels in various MeOH/$H_2O$ mixtures have then been measured. While increasing methanol proportion, absolute luminescence intensity enhances for each wavelength and the 592/618 ratio significantly decreases compared to the one measured in water. However, if the methanol proportion in water does not exceed 50% (v/v), the lifetime of the $^5D_0$ europium emitting level is around 105 ± 10 μs, with larger methanol proportion the lifetime value increases. Hence, it would seem like for MeOH/$H_2O$ mixtures containing up to 50% methanol in volume, methanol molecules are almost absent in the internal coordination sphere of europium. However, the evolution of luminescence spectra tends to show an influence of methanol molecules which may be present in the external coordination sphere of europium likely thanks to hydrogen bonds with water molecules from the primary hydration sphere of the cation.

Several works have shown an increase in the lifetime of the $^5D_0$ europium emitting level with an increase in nitrate ions concentration[24−26] tending to evidence the formation of complexes in internal sphere between $Eu^{3+}$ and $NO_3^-$ when the cation is in the excited state. Sadowski and Majdan[27] showed the existence of nitrato complexes in internal sphere of lanthanide cations, a stability constant of 1.9 has been determined by UV−visible spectrophotometry for samarium. While measuring the lifetime of the $^5D_0$ europium emitting level, Tanaka and Yamashita[26] reported the disappearance of complexation in internal sphere between $Eu^{3+}$ and nitrate anions for a concentration in water of these latter lower than $10^{-3}$ M and only a weak rate of complexation for a concentration of $10^{-2}$ M. The luminescence spectrum obtained for a solution of europium nitrate in aqueous nitrate medium in MeOH/$H_2O$ (1:1 v/v) is close to that obtained with a solution of europium in water in perchlorate medium. Moreover, the lifetime of the $^5D_0$ europium emitting level in nitrate medium is 125 ± 10 μs (Figure 1b, gray line), close to the one obtained in water, i.e., 110 μs, certainly due to the presence of at most one nitrate anion in the coordination sphere of the lanthanide cation.

**3.2. $Eu^{3+}$ Complexation with DiPTP Ligand.** In Figure 1a appears the TRLIL spectrum obtained with a solution of $Eu^{3+}$ in the presence of an excess of DiPTP ligand in MeOH/$H_2O$ (1:1 v/v) in aqueous nitrate medium at pH 3.7 (dark line). The lifetime measured from the luminescence decay curve (Figure 1b, dark line) is about 2700 ± 150 μs, which, accordingly to eq 1, means that no more water molecule is present in the first coordination sphere of the cation. Hence, as DiPTP is expected to be a terdentate ligand, each molecule entering the internal coordination sphere of europium is likely to exclude three water molecules from the primary hydration sphere of the cation. Therefore, the spectrum in Figure 1a (dark line) can be considered as characteristic of the $[Eu(DiPTP)_3]^{3+}$ complex as the initial species in solution was $[Eu(H_2O)_{8-9}]^{3+}$. It is noteworthy that, whatever the ligand-to-metal ratio considered, only one europium species except aquo-ion seems to exist in solution as luminescence spectra remain unchanged while the time delay of the measurement aperture increases beyond 400 μs, i.e., after extinction of the luminescence signal emitted by uncomplexed europium. This result confirms the observation made with ESI-MS: the exclusive formation of $[Eu(DiPTP)_3]^{3+}$ complex in solution.

The luminescence spectrum obtained for the $[Eu(DiPTP)_3]^{3+}$ complex is very close to those obtained with $[Eu(DnPTP)_3]^{3+}$ and $[Eu(DMTP)_3]^{3+}$ complexes, which indicates strong similarities in the structure of these different species as it has been shown by crystallography. Indeed, it is possible to correlate luminescence spectra with the geometry of the species insofar as the rising of europium $^7F_J$ levels degeneration under crystal field effect depends on the symmetry of the environment in which the cation is. Hart et al.[28] deduced from the luminescence spectrum characteristic of $Eu(Tpy)_3(ClO_4)_3$ complex a slightly distorted $D_3$ geometry consistent with the structure determined by crystallography.[29] The luminescence spectra obtained for $[Eu(DATP)_3]^{3+}$ complexes are less resolved than the one presented by Hart et al. for europium complex with terpy because it was recorded at low temperature. However, it is possible to consider that the different peaks observed on $[Eu(DATP)_3]^{3+}$ luminescence spectra (double at 592 nm and triple at 650 nm) are reflecting a $D_3$ symmetry around the metal ion which is consistent with the X-ray diffraction studies reported for $[Ln(DATP)_3]^{3+}$ complexes.[12,30]

Two distinct methods have been designed to determine the conditional stability constant of $[Eu(DiPTP)_3]^{3+}$ complex: the one by linear combination of luminescence spectra and the other by adjustment of the luminescence decay curves.

The evolution of TRLIL spectrum and luminescence decay curve for solutions containing $10^{-4}$ M $Eu(NO_3)_3$ and increasing amounts of DiPTP (ligand-to-metal ratio = 0, 1, 2, and 5) in MeOH/$H_2O$ (1:1 v/v) in aqueous nitrate medium at pH 4.6 are presented in Figure 2, parts a and b, respectively.

For a given europium species, luminescence intensity at a fixed wavelength is proportional to the concentration of this species in solution. As a consequence, the luminescence spectrum of a solution containing europium nitrate in MeOH/$H_2O$ (1:1 v/v) in aqueous nitrate medium has, at each emission wavelength, an intensity fixed by the initial europium concentration, taking all other parameters constant. When 5 molar equivalents of DiPTP ligand are added, no uncomplexed europium remains in solution so the only Eu species present in solution are the $[Eu(DiPTP)_3]^{3+}$ complexes. The luminescence spectrum obtained for a given ligand-to-metal ratio can be adjusted with a linear combination of the spectra of uncomplexed europium and of $[Eu(DiPTP)_3]^{3+}$ complex, these two spectra being perfectly known. The coefficients of the linear combination allow us to determine the relative proportions and then the concentration of the two species (europium free of complexation and

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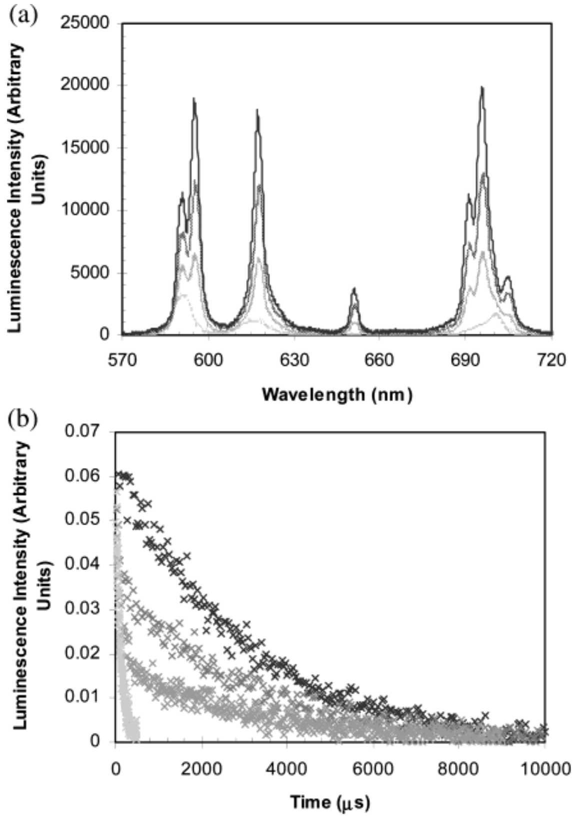

**Figure 2.** Evolution of TRLIL spectra (a) and luminescence decay curve (b) for solutions containing $10^{-4}$M of $Eu(NO_3)_3$ and increasing amounts of DiPTP (ligand-to-metal ratio = 0, 1, 2 and 5) in $MeOH/H_2O$ (1:1 v/v) in aqueous nitrate medium at pH 4.6, $\lambda_{exc} = 532$ nm.

$[Eu(DiPTP)_3]^{3+}$) present in solution at thermodynamic equilibrium. Knowing the amount of ligand initially added, it is possible to calculate the remaining free ligand concentration and then to evaluate the conditional stability constant of the $[Eu(DiPTP)_3]^{3+}$ complex ($\beta_3^{app} = [Eu(DiPTP)_3{}^{3+}]/([Eu]\times[DiPTP]^3)$). An example of TRLIL spectral adjustment is presented in Figure 3a for an equimolar mixture of Eu(III) and DiPTP, and the proportion of complex is found around 29%. As the total europium concentration is $10^{-4}$ M, the concentration of $[Eu(DiPTP)_3]^{3+}$ complex is $2.9 \times 10^{-5}$ M which leads to a conditional stability constant of about $\log \beta_3^{app} = 14.2 \pm 0.6$.

By the same token, for a solution containing various europium species, noted n, the luminescence decay curve follows the equation: $I(t) = \sum(I_n \exp(-t/\tau_n))$, where $I_n$ is the luminescence intensity at time origin which is directly proportional to the concentration of the species noted *n*, and $\tau_n$ is the lifetime of the $^5D_0$ europium emitting level of the species noted *n*. In Eu/DiPTP solutions, only two europium species are present, aquo-ion and $[Eu(DiPTP)_3]^{3+}$ complex; therefore, the luminescence decay curves follow the equation $I(t) = I_{Eu3+} \exp(-t/\tau_{Eu3+}) + I_{[Eu(DiPTP)3]3+} \exp(-t/\tau_{[Eu(DiPTP)3]3+})$. The method consists first in adjusting the luminescence decay curve for europium in the presence of 5 molar equivalents of DiPTP ligand, i.e., when the totality of europium is present as $[Eu(DiPTP)_3]^{3+}$ complex. This leads to the proportionality coefficient resulting from the dependence of luminescence intensity measured at time origin ($I_{[Eu(DiPTP)3]3+}$) and the complex concentration. The luminescence decay curve obtained for a given ligand-to-metal ratio is then adjusted with the sum of exponentials written below; the $I_{[Eu(DiPTP)3]3+}$ coefficient hence calculated leads to the $[Eu(DiPTP)_3]^{3+}$ concentration in solution at thermodynamic equilibrium. In the example presented in Figure 3b are plotted the luminescence decay curves for $10^{-4}$ M Eu(III) solutions with 1 and 5 molar equivalents of DiPTP ligand, respectively. The adjustment obtained for a ligand-to-metal ratio equal to 1 is $I(t) = 0.054 \exp(-t/130) + 0.024 \exp(-t/2770)$ and that for a ratio of 5 is $I(t) = 0.084 \exp(-t/2770)$. It is then possible to deduce the concentration of $[Eu(DiPTP)_3]^{3+}$ complex $= 0.024 \times 10^{-4}/0.084 = 2.86 \times 10^{-5}$ M. This result leads to a conditional stability constant $\log \beta_3^{app} = 14.2 \pm 0.6$, which is in good agreement with the result obtained using the spectral combination method. An example of $\log \beta_3^{app}$ values as a function of ligand-to-metal ratio determined at pH 4.6 is presented in Figure 4a. It appears a good agreement between the results obtained by both TRLIL methods.

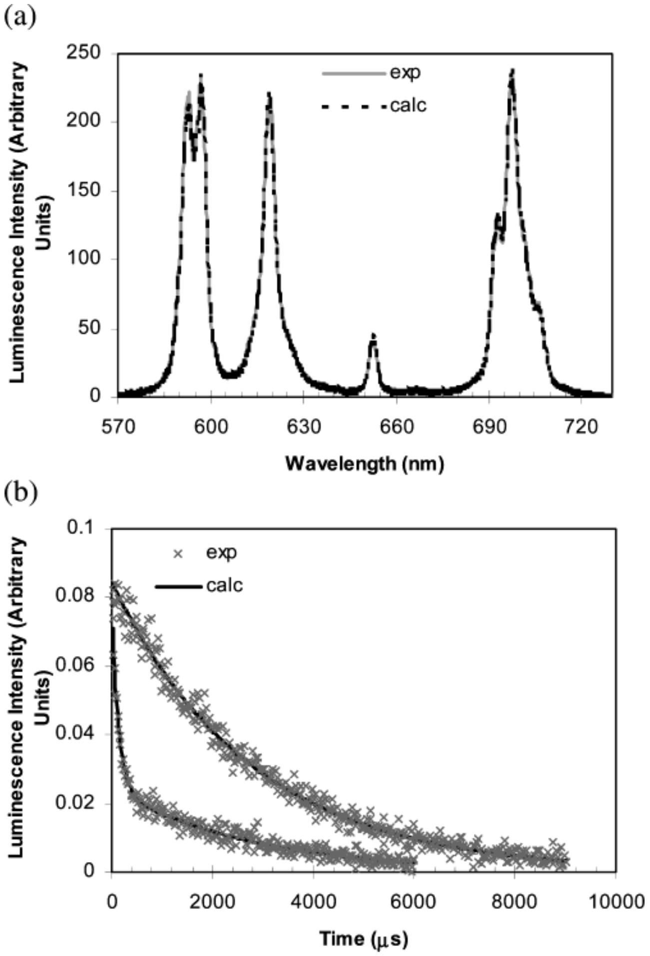

**Figure 3.** Determination of the proportions of uncomplexed europium and $[Eu(DiPTP)_3]^{3+}$ complex using linear combination of luminescence spectra (a) and adjustment of luminescence decay curves (b).

Conditional stability constant of the $[Eu(DiPTP)_3]^{3+}$ complex measured using both methods in $MeOH/H_2O$ (1:1 v/v) in aqueous nitrate medium at pH 2.8, 3.7, and 4.6 are reported in Table 1. As it had been previously noticed

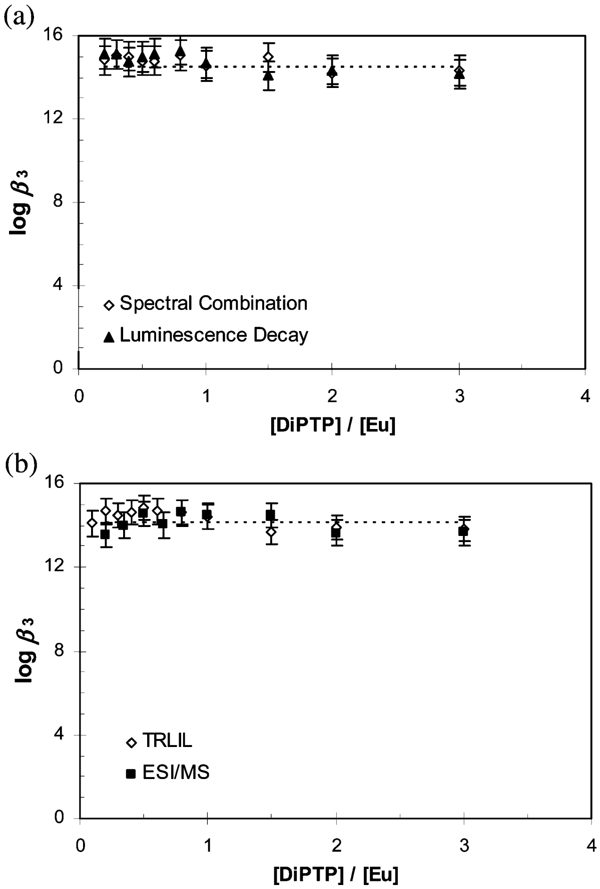

**Figure 4.** Conditional stability constant (log $\beta_3^{\mathrm{app}}$) measurement for the $[\mathrm{Eu(DiPTP)_3}]^{3+}$ complex in $\mathrm{MeOH/H_2O}$ (1:1 v/v) in aqueous nitrate medium. (a) Comparison of the two TRLIL methods: spectral linear combination and luminescence decay curves adjustment at pH 4.6. (b) Comparison between TRLIL and ESI-MS measurements at pH 2.8.

**Table 1.** Conditional Stability Constants log $\beta_3^{\mathrm{app}}$ of $[\mathrm{Eu(DiPTP)_3}]^{3+}$ Complex Measured by TRLIL[a]

| | spectrum | lifetime |
|---|---|---|
| pH = 4.6 | 14.7 ± 0.6 | 14.4 ± 0.5 |
| pH = 3.7 | 14.4 ± 0.8 | 14.2 ± 0.6 |
| pH = 2.8 | 14.3 ± 0.6 | 14.3 ± 0.6 |

[a] $\mathrm{Eu(NO_3)_3}$ $10^{-4}$ M + DiPTP in $\mathrm{MeOH/H_2O}$ (1:1 v/v), aqueous nitrate medium. $T$ = 21 °C.

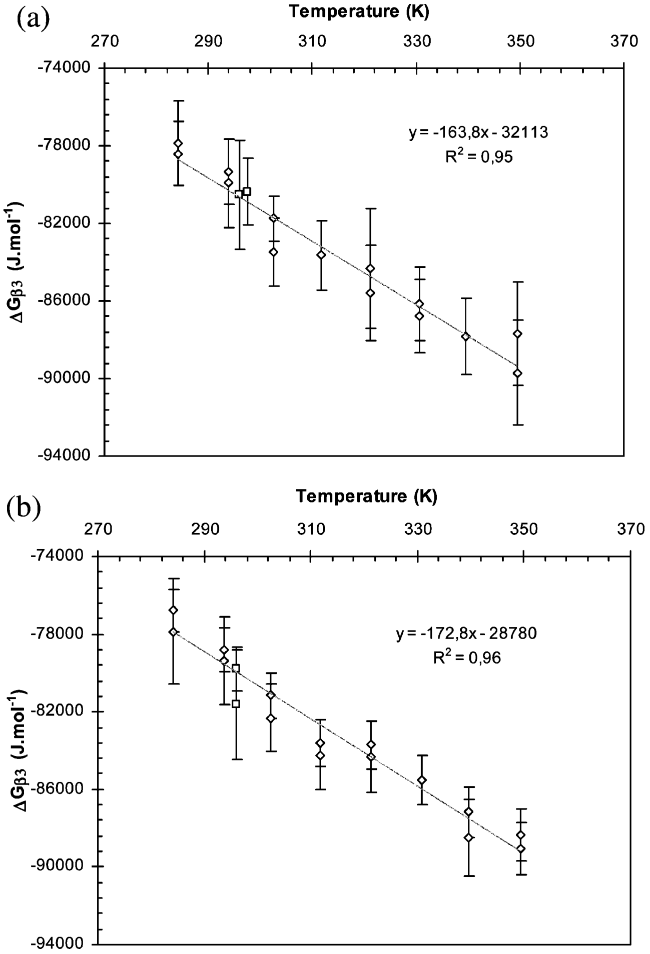

**Figure 5.** Enthalpy and entropy variations associated to the $[\mathrm{Eu(DiPTP)_3}]^{3+}$ complex formation measured in $\mathrm{MeOH/H_2O}$ (1:1 v/v) in aqueous nitrate medium at pH 4.6 (a) and 2.8 (b).

by ESI-MS investigations, pH variation between 2.8 and 4.6 does not significantly affect $\mathrm{Eu^{3+}}$ complexation with DiPTP.

Figure 4b shows a comparison of the results obtained either by ESI-MS and TRLIL for the measurement of the conditional stability constant of the $[\mathrm{Eu(DiPTP)_3}]^{3+}$ complex in $\mathrm{MeOH/H_2O}$ (1:1 v/v) in aqueous nitrate medium at pH 2.8. The consistency between data obtained by the two techniques tends to confirm that ESI-MS is a reliable technique to observe thermodynamic equilibria in solution.

**3.3. Enthalpy and Entropy of Reaction.** The reaction to be considered is that leading to the formation of the $[\mathrm{Eu(DiPTP)_3}]^{3+}$ complex: $\mathrm{Eu^{3+} + 3DiPTP \rightarrow [Eu(DiPTP)_3]^{3+}}$. The thermodynamic constant that characterizes that equilibrium is the conditional stability constant log $\beta_3^{\mathrm{app}}$ which measurement is reported above. Hence, the Gibbs free energy variation ($\Delta G_{\mathrm{r}}$) associated to this complexation reaction is: $\Delta G_{\beta 3} = -RT \ln \beta_3^{\mathrm{app}}$ (eq 2), where $R = 8.3144$ J mol$^{-1}$ K$^{-1}$ and $T$ is the temperature in Kelvin.

According to the van't Hoff equation, the thermodynamic equilibrium constant of a chemical reaction is linked to the enthalpy variation occurring during that reaction as mentioned hereafter: $\mathrm{d}(\ln K)/\mathrm{d}T = \Delta H_{\mathrm{r}}/RT^2$ (eq 3). From eqs 2 and 3 can be deduced the following relation: $\Delta G_{\mathrm{r}} = \Delta H_{\mathrm{r}} - RT \times \mathrm{cst}$. Enthalpy, entropy and free energy variations dependence is given by the equation: $\Delta G_{\mathrm{r}} = \Delta H_{\mathrm{r}} - T\Delta S_{\mathrm{r}}$ (eq 4).

Therefore, assuming that enthalpy and entropy variations associated to the formation of the $[\mathrm{Eu(DiPTP)_3}]^{3+}$ complex are constant in the temperature range here considered (284−350 K), the measurement of log $\beta_3^{\mathrm{app}}$, and then that of $\Delta G_{\beta 3}$, at different temperatures allows to determine the thermodynamic quantities $\Delta H_{\beta 3}$ and $\Delta S_{\beta 3}$ insofar as $\Delta G_{\beta 3}$ variation as a function of temperature follows a straight line with a slope equal to $-\Delta S_{\beta 3}$ and an ordinate at the origin equal to $\Delta H_{\beta 3}$ (according to eq 4).

The measurement of the enthalpy and entropy variations has been performed by using the TRLIL method of luminescence decay curve adjustment for the determination of the conditional stability constant of the $[\mathrm{Eu(DiPTP)_3}]^{3+}$ complex. The $\Delta G_{\beta 3}$ variations as a function of temperature measured in MeOH/$H_2O$ (1:1 v/v) in aqueous nitrate medium at pH 4.6 and 2.8 are presented in Figure 5, parts a and b, respectively. For each pH value considered, the different data are roughly situated on a straight line. The enthalpy and entropy variations associated to the $[Eu(DiPTP)_3]^{3+}$ complex formation are

$$\Delta H_{\beta 3} = -32 \pm 3 \text{ kJ mol}^{-1} \quad \text{and} \quad \Delta S_{\beta 3} = 164 \pm 10 \text{ J K}^{-1} \text{ mol}^{-1} \text{ at pH 4.6}$$

$$\Delta H_{\beta 3} = -29 \pm 3 \text{ kJ mol}^{-1} \quad \text{and} \quad \Delta S_{\beta 3} = 173 \pm 10 \text{ J K}^{-1} \text{ mol}^{-1} \text{ at pH 2.8}$$

The thermodynamic quantities determined at pH 4.6 and 2.8 are similar, which shows the great selectivity of DiPTP toward $Eu^{3+}$ compared with $H^+$, as it has been also observed by ESI-MS. Enthalpy and entropy variations are both favorable to $[Eu(DiPTP)_3]^{3+}$ formation reaction. The fact that the enthalpy variation is exothermic necessitates each of the three ligands to be multidentate so that the energy formation of the multiple Eu−N bonds manages to compensate dehydration enthalpy of the cation. Moreover, a positive variation of entropy indicates that mobility reduction of the ligands, due to their complexation with $Eu^{3+}$, is compensated by the departure in solution of water molecules initially present in the primary hydration sphere of the metal, and this observation is also in agreement with a multidentate way of coordination for DiPTP ligands.

Enthalpy variation associated to Eu complexation by three DiPTP determined in MeOH/$H_2O$ (1:1 v/v) by TRLIL is less exothermic than the one measured using UV−Vis and microcalorimetry in octanol by Charbonnel et al. ($\Delta H° \sim -70 \pm 3$ kJ $mol^{-1}$).[31] This can be explained by desolvation energy for the cation less important in octanol than in water. Besides, entropy variation reported in octanol is unfavorable to complex formation, which is consistent with a number of solvent molecules initially present in internal coordination sphere of the cation smaller in octanol than in water. Indeed, mobility loss for the ligand during $[Eu(DiPTP)_3]^{3+}$ complex formation in octanol is not compensated, as it is the case in water, by the departure of sufficient solvent molecules in the bulk.

## 4. Conclusion

As it had been evidenced in ESI-MS investigations, TRLIL studies of $Eu^{3+}$ complexation with DiPTP shows the exclusive formation of a $[Eu(DiPTP)_3]^{3+}$ complex. The conditional stability constant of this latter has been determined with two methods: the one using linear combination of luminescence spectra and the other based on luminescence decay curves adjustment. The results obtained with both methods are quite consistent and the value found at pH 2.8 ($\log \beta_3^{app} = 14.3 \pm 0.6$) is in agreement with that measured by ESI-MS ($\log \beta_3^{app} = 14.0 \pm 0.6$). These results confirm and stress the potential of ESI-MS as a reliable technique for the study of equilibria in solution.

Study of the variation of $\log \beta_3^{app}$ as a function of temperature allowed to determine, thanks to van't Hoff equation, thermodynamic quantities $\Delta H_{\beta 3}$ and $\Delta S_{\beta 3}$ associated with $[Eu(DiPTP)_3]^{3+}$ complex formation. It appears that enthalpic and entropic terms are both favorable to complex formation and that the driving force of the reaction is enthalpy.

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