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Luminescent Lanthanide Complexes of a Bis-bipyridine-phosphine-oxide Ligand as Tools for Anion Detection

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Abstract: The Gd^{3+}, Tb^{3+}, and Eu^{3+} complexes of a bis-bipyridine-phenylphosphine oxide ligand PhP(O)-$(bipy)_2$ **1** (bipy for 6-methylene-6′-methyl-2,2′-bipyridine) have been synthesized. In acetonitrile solutions at room temperature, the Tb^{3+} and Eu^{3+} complexes show a metal-centered luminescence, indicative of an efficient energy transfer from the two bipy subunits to the Ln center. The photophysical properties drastically depend on the nature of the anions present in solution. In particular, addition of 2 equiv of nitrate anions to a solution containing the $[Ln\cdot\mathbf{1}](OTf^-)_3$ leads to an 11-fold increase of the luminescence intensity for the Eu^{3+} and a 7-fold increase for the Tb^{3+} complexes. Similar effects are provided with Cl^-, F^-, and CH_3COO^- anions. UV−vis titration experiments were used to determine association constants for binding of, respectively, one, two, and three anions. Stepwise anion addition has also been investigated on the molecular level using quantum mechanical (QM) calculations for the Eu complexes. These calculations reproduce the experimental findings, especially if solvent molecule addition is taken into account. The X-ray crystal structure of the nitrate salt of the Tb complex, as well as QM calculation of a similar Eu complex, demonstrates the coordination of three nitrate anions in a bidentate mode and the step-by-step relegation of the bipy subunits in the second coordination sphere. These features give valuable insights into the mechanism of the overall light amplification process.

Introduction

Luminescent Ln complexes are being used in numerous analytical applications, ranging from water proton relaxation agents for NMR imaging[1] to luminescent probes in time-resolved fluoroimmunoassays.[2] In the past decade, thanks to the development of supramolecular chemistry[3] and supported by the enhanced sensitivity offered by luminescence spectroscopy, the synthesis, characterization, and application of such luminescent labels and sensors have been the focus of much attention.[4] Their use has opened up a lot of opportunities for solving complex analytical problems in growing fields of large social and economical impact, such as environmental sciences, medical diagnostics, and cell biology.[5−8]

In photoluminescence analysis, autofluorescence and light scattering cause the most relevant interferences, particularly when biological material is involved. Time-resolved spectroscopy, that requires the use of luminophores with a very long luminescence lifetime, can efficiently exclude this kind of background light. For this reason, there has been a great interest in the design of luminescent complexes containing the Eu^{3+} and Tb^{3+} ions,[9] which possess luminescence lifetimes in the microsecond−millisecond range. Some of them have actually found applications as labels or sensors.[1,9−13] To obtain an efficient luminescent frame, the ligand is expected (i) to form stable complexes with the Ln ions in coordinating solvents, (ii) to shield the ion from deactivating solvent molecules, and (iii)

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to absorb light effectively and to transfer this excitonic energy to the metal center with high efficiency. This latter feature is of particular importance to overcome the intrinsic drawback of low absorption coefficients of the Ln ions.[10−12]

In environmental sciences, almost all of the sensors used to analyze, for example, nitrates in food, fertilizers, and plant tissues are based on ion exchanger and have a limited sensitivity.[14] Undoubtedly, the development and improvement of highly selective ionophores that will allow measurements of, for example, nitrate traces remain a central issue in analytical chemistry. In this context, an increasing interest is centered on the design of luminescent sensors containing Ln ions, which possess outstanding optical properties.[15−17] In previous work, we demonstrated that stable Ln complexes could be generated from phosphinate esters attached to macrocyclic bipy scaffoldings.[18] Unfortunately, we were unable to produce at that time derivatives that function as anion sensors. The main reason for this was the saturation of the Eu coordination sphere by six nitrogen atoms and two P═O bonds. It was therefore tempting to design a hybrid ligand bearing a phosphineoxide group and bipy fragments. Herein, we describe Ln complexes engineered from a ligand consisting of a single P═O fragment and two methylene linked bipy subunits that represents our rational attempt to provide complexes possessing long lifetimes, pronounced absorption in the near UV, and tunable emission depending on the presence of anions.

Our choice is based on the expectation that in ligand **1** the P═O bond will provide relatively stable complexes because of the strong coordination ability of the P═O group[19] and that the bipy fragments will coordinate to the Ln and effectively act as photon antenna able to transfer energy to Eu^{3+} and Tb^{3+} ions with high efficiency. The ligand and coordination pocket provided by Ln complexation are sketched in Chart 1.

As a first step, we have investigated the photophysical properties of the ligand and of its Eu^{3+} complex with NO_3^- and TfO^- anions in different solvents.[20] This revealed a strong effect of the counterion on the photophysical properties of the complexes, and this feature was auspicious for the use of [Ln·**1**]$(OTf)_3$ complexes as chemosensors for anions. Results are reported here for the full characterization of the complexes, together with an X-ray structure analysis of the Tb species with nitrate anions, generated in methanol solution. Combined with QM calculations, these investigations clarify the nature of the binding site and provide insight into both the structural aspects of anion binding and the luminescence enhancement behavior.

Chart 1

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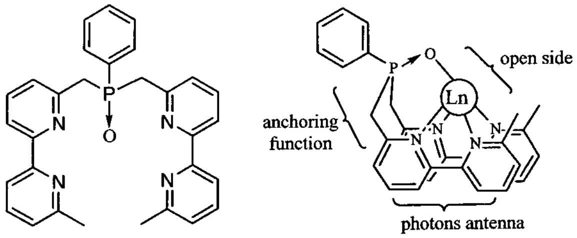

Experimental Section

Synthesis and Characterization of the Complexes. General Procedure for [Ln·1]$(NO_3)_3 \cdot xH_2O$. To a solution of $Ln(NO_3)_3 \cdot 6H_2O$ (0.1 mmol) dissolved in 2 mL of MeOH was added a solution of **1**[21] (49 mg, 0.1 mmol) in 2 mL of CH_2Cl_2. The solution is stirred for 15 min and evaporated to dryness. The residue was dissolved in a minimum amount of MeOH, and Et_2O was added, resulting in the precipitation of a solid. The mother liquor was decanted, the solid was washed twice with 5 mL of Et_2O, and dried under vacuum, affording the analytically pure complexes.

[Eu·1]$(NO_3)_3 \cdot 6H_2O$. (65%) ^1H NMR (CD_3OD): 2.59 (s, 6H), 3.65 (d, br, 4H), 7.18−7.55 (m, 9H), 7.67−7.89 (m, 6H), 8.13 (d, 2H, $^3J = 8.4$ Hz). Anal. Calcd for $C_{30}H_{39}EuN_7O_{16}P$: C, 38.47; H, 4.20; N, 10.47. Found: C, 38.30; H, 4.05; N, 10.25. FAB$^+$MS: 765.2; 767.2 [Eu·**1**·$(NO_3)_2$]$^+$, 491.2 [**1**·H]$^+$. IR (KBr pellets, cm^{-1}): 1619, 1572 ($\nu_{C=C}$, $\nu_{C=N}$), 1480 (ν_{NO}), 1440, 1384 (ν_{CH_2}), 1311 (ν_{NO}), 1182 (ν_{PO}).

[Tb·1]$(NO_3)_3 \cdot 5H_2O$. (53%) Anal. Calcd for $C_{30}H_{37}TbN_7O_{15}P$: C, 38.93; H, 4.03; N, 10.59. Found: C, 38.76; H, 3.89; N, 10.38. ES$^+$/MS: 835.3 (([**1**·Tb]$(NO_3)_3$ + H)$^+$, 12%), 490.9 ((1 + H)$^+$, 100%). IR (KBr pellets, cm^{-1}): 1620, 1572 ($\nu_{C=C}$, $\nu_{C=N}$), 1480 (ν_{NO}), 1439, 1384 (ν_{CH_2}), 1291 (ν_{NO}), 1173 (ν_{PO}).

[Gd·1]$(NO_3)_3 \cdot 5H_2O$. (37%) Anal. Calcd for $C_{30}H_{37}GdN_7O_{15}P$: C, 39.00; H, 4.04; N, 10.61. Found: C, 39.16; H, 4.01; N, 10.45. IR (KBr pellets, cm^{-1}): 1610, 1572 ($\nu_{C=C}$, $\nu_{C=N}$), 1478 (ν_{NO}), 1439, 1384 (ν_{CH_2}), 1293 (ν_{NO}), 1175 (ν_{PO}).

General Procedure for [Ln·1]$(CF_3SO_3)_3 \cdot xH_2O$. Forty-nine milligrams of **1** (0.1 mmol) and $Ln(CF_3SO_3)_3$[22] (0.1 mmol) were dissolved in 10 mL of dry acetonitrile under an argon atmosphere. The solution was stirred for 15 min at room temperature leading to a light yellow solution. The solvent was removed under reduced pressure, the resulting yellow oil was dissolved in 1 mL of dry acetonitrile, and anhydrous Et_2O was added to precipitate the compound. The mother liquor was decanted, the solid washed twice with 2 mL of dry Et_2O, and dried under vacuum, leading to the analytically pure complexes.

[Eu·1]$(CF_3SO_3)_3 \cdot 3H_2O$. (42%) Anal. Calcd for $C_{33}H_{33}F_9EuN_4O_{13}PS_3$: C, 34.66; H, 2.91; N, 4.90. Found: C, 34.35; H, 2.74; N, 4.70.

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FAB$^+$MS: 941.2 [Eu$\cdot$**1**$\cdot$(OTf)$_2$]$^+$). IR (KBr pellets, cm^{-1}): 1619, 1596, 1575 ($\nu_{C=C}$, $\nu_{C=N}$), 1454, 1441 (ν_{CH_2}), 1285 (broad, ν_{SO}), 1182 (ν_{PO}).

[Tb$\cdot$1](CF$_3$SO$_3$)$_3\cdot$2H$_2$O. (85%) Anal. Calcd for $C_{33}H_{31}F_9TbN_4O_{12}PS_3$: C, 34.99; H, 2.76; N, 4.95. Found: C, 34.80; H, 2.56; N, 4.74. IR (KBr pellets, cm^{-1}): 1624, 1636, 1595 ($\nu_{C=C}$, $\nu_{C=N}$), 1453, 1441 (ν_{CH_2}), 1284 (broad, ν_{SO}), 1171 (ν_{PO}). FAB$^+$-MS: 947 ([TbL](CF$_3$SO$_3$)$_2$)$^+$ 24%.

[Gd$\cdot$1](CF$_3$SO$_3$)$_3\cdot$2H$_2$O. (57%) Anal. Calcd for $C_{33}H_{31}F_9GdN_4O_{12}PS_3$: C, 35.05; H, 2.76; N, 4.95. Found: C, 34.82; H, 2.42; N, 4.77. IR (KBr pellets, cm^{-1}): 1619, 1595, 1572 ($\nu_{C=C}$, $\nu_{C=N}$), 1451 (ν_{CH_2}), 1280 (broad, ν_{SO}), 1167 (ν_{PO}).

Crystal Structure of the Terbium Complex with Nitrate Anions. Slow diffusion of THF in a methanol solution of the Tb complex with nitrate anions afforded colorless crystals, suitable for X-ray diffraction analysis, with the generic formula [**Tb$\cdot$1**](NO$_3$)$_3\cdot$(MeOH)$_2$/{[**Tb$\cdot$1**](NO$_3$)$_3\cdot$(H$_2$O)(MeOH)}$\cdot$H$_2$O. Experimental data are given in the Supporting Information in Table S1; selected bond lengths and angles are given in Table S2.

Results

Complexation of 1 with Lanthanide Triflates. Complexation of **1** by Ln(III) cations was evidenced by UV−vis spectrophotometric titrations of the ligand by Ln(OTf)$_3$ (Ln = Eu or Tb) in acetonitrile containing 0.01 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. Upon addition of increasing amounts of the Eu or Tb salts, the $\pi \rightarrow \pi^*$ transitions centered on the bipy units gradually shift to lower energy from 291 nm for **1** to 313 nm for the emergent complex (Figure S1). Although less prononced, the complexation process can also be followed thanks to the variations observed in the 230−250 nm region. For the free ligand, two shoulders are present at 237 and 245 nm, wich can be ascribed to transitions centered on the phenyl ring (Figure S2). The complexation induces a broadening of these bands with a bathochromic shift, pointing to perturbation of the electronic cloud localized on the phenyl ring, as would be expected by coordination of the P═O function to the *Ln* center. The variations in absorbances were fitted according to eq 1 and gave the following association constants for the mononuclear complexes: log $K_{Eu} = 5.8 \pm 0.5$ and log $K_{Tb} = 5.9 \pm 0.3$. There is no indication for the formation of complexes with higher nuclearities, as also confirmed by the absence of oligomers in the mass analyses.

$$\mathrm{Ln}^{3+} + \mathbf{1} \rightleftharpoons [\mathrm{Ln}\cdot\mathbf{1}]^{3+} \qquad K_{\mathrm{Ln}} = [(\mathrm{Ln}\cdot\mathbf{1})^{3+}]/[\mathrm{Ln}^{3+}] \times [\mathbf{1}] \tag{1}$$

The [Ln$\cdot$**1**]X$_3$ (Ln = Gd, Eu, and Tb; X$^-$ = NO$_3^-$ or CF$_3$SO$_3^-$) complexes were prepared by mixing stoichiometric amounts of **1** with the Ln salt in a CH$_2$Cl$_2$/MeOH mixture for the nitrate or in acetonitrile for the triflate precursors. On the basis of elemental analysis and FAB-mass spectrometry, a one to one metal to ligand stoichiometry was established for both families of complexes. IR spectra for all complexes are similar and displayed features characteristic of the ligand ($\nu_{C=C}$, $\nu_{C=N}$, ν_{PO}) and of the used anion (ν_{NO} and ν_{SO}, respectively, for nitrate and triflate anions). In the case of the nitrate anion, the splitting between the two highest frequency bands attributed to the NO$_3^-$ vibrations ($\Delta\nu$ = 169, 185, and 189 cm^{-1}, respectively, for Eu, Gd, and Tb) is consistent with a chelating bidentate mode of coordination of approximate C_{2v} symmetry.[23] Coordination of the P(O) to the Eu is substantiated by a splitting of the P═O absorption band[24] with an average shift toward lower energy of 16 and 74 cm^{-1}, respectively, in the nitrate and triflate complexes, as compared to the free ligand (ν_{PO} = 1185 cm^{-1}).[21]

The ^{1}H NMR spectrum of [Eu$\cdot$**1**](NO$_3$)$_3$ in deuterated methanol displayed well-resolved signals in a diamagnetic window, indicating a weak interaction of the bipy subunits of the ligand with the paramagnetic Eu atom. For example, the chemical shift of the methyl groups on the terminal pyridine rings is totally unaffected, displaying a singlet at 2.59 ppm, that is exactly as for the free ligand.[21] The main perturbations are noted for the methylene bridges, which are shifted upfield and broadened upon complexation, so that the hyperfine coupling between P and H is lost in the spectrum of the complexes. For the aromatic protons, the complexation leads to minor changes in the pattern as compared to the free ligand. A significantly different situation was found in CD$_3$CN, where the peaks became very broad with a significant upfield shift for all of the aromatic protons. This is in keeping with a stronger interaction between the bipy arms of the ligand and the Ln cation.

Crystal Structure of the Terbium Complex with Nitrate Anions. The crystallographic cell is composed of two discrete and neutral complexes. ORTEP views, coordination polyhedron around the Tb atoms, and labeling of the atoms are given in Figure 1. In each complex, a Tb^{III} metal atom has a coordination number of nine provided by a single bond with the oxygen atom of the phosphine oxide, three bidentate nitrate anions, and two solvent molecules completing the first coordination sphere. For Tb1, the two solvent molecules are MeOH molecules, while for Tb2, one molecule of water and one of MeOH are present. In each case, the coordination polyhedron around the Tb atom is best described as a distorted tetradecahedron. The pentagonal base contains the oxygen atom of **1**, the oxygen atom of a MeOH molecule, a bidentate nitrate, and the oxygen atom of a second nitrate. The Tb atom is slightly out of the average plane defined by these five atoms, on the same side as the triangular base formed by the third bidentate nitrate anion and the remaining oxygen of the second nitrate anion. On the other side of the plane, the apical position is occupied by the oxygen atom of a MeOH molecule for Tb1 and of a water molecule for Tb2.

Within a complex, one of the bipy arms of the ligand is pointing away from the Tb atom and is in a transoïd conformation (N6−C20−C21−N7 = 157.8° for Tb1, N11−C39−C40−N12 = 155.1° for Tb2). The second bipy arm is in a distorted cisoïd conformation (N4−C8−C9−N5 = 53.7° for Tb1, N13−C51−C52−N14 = 60.2° for Tb2) with the two nitrogen atoms pointing toward the Tb cation. The two nitrogen atoms of this bipy fragment are connected to the two solvent molecules coordinated to the metal atom (respectively, O10, O11 for Tb1 and O22, O23 for Tb2) through H-bonds, so that this bipy can be considered as being coordinated to the second sphere of the Tb center.

Photophysical Properties of the Nitrate Salts. The absorption spectra of the nitrate salts of the Ln complexes with ligand **1** drastically depend on the solvent used (Figure 2a). In particular, the absorption spectra of the three complexes in acetonitrile display a band at 300 nm (Table 1), whereas in methanol the band maximum is at 290 nm (Table 2), and in water it is at 285 nm, with a higher absorption coefficient. A

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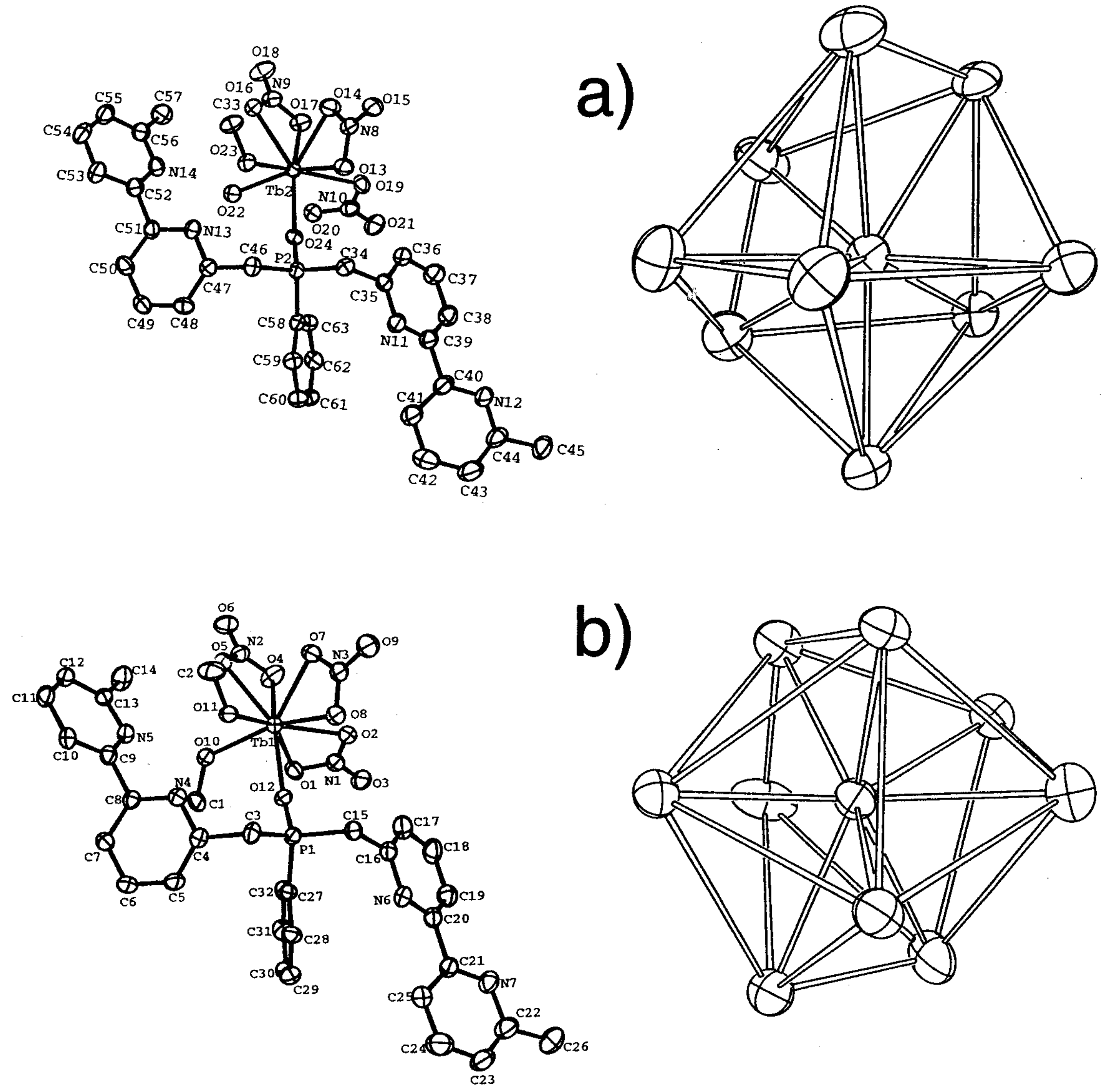

Figure 1. ORTEP view of (a) the [(Tb·**1**)$(NO_3)_3(H_2O)$(MeOH)] complex with coordination polyhedron (right-hand side) and (b) the [(Tb·**1**)$(NO_3)_3$$(MeOH)_2$] complex with coordination polyhedron (right-hand side).

shoulder in the 300−310 nm region is present in methanol, but absent in water.

Room-temperature excitation of acetonitrile, water, and methanol solutions of the Gd^{3+} complexes did not lead to any appreciable luminescence. At 77 K, in a methanol/ethanol transparent matrix, a weak, structured phosphorescence band, whose highest energy feature peaks at 440 nm, was observed with two lifetimes (3 ms and 1 s). Upon excitation in the absorption bands of the ligand in acetonitrile at room temperature, the Eu^{3+} and Tb^{3+} complexes showed a very intense metal-centered luminescence ($\Phi = 0.14$ and 0.30 for Tb^{3+} and Eu^{3+}). For both complexes, the excited state was strictly monoexponential (0.63 and 1.45 ms for Tb^{3+} and Eu^{3+}, Table 1). The metal-centered luminescence excitation spectra are very similar to the absorption spectra. Contrary to what is observed in acetonitrile, almost no metal-centered luminescence was observed when the complexes were dissolved in water ($\Phi < 1 \times 10^{-5}$).

An intermediate situation is found in methanol solution, where a metal-centered luminescence, although much weaker than in acetonitrile, can be observed for both complexes. In this solvent, the metal luminescence excitation spectra ($\lambda_{max} = 300$ nm, Figure 2b) are very similar in shape to those in acetonitrile solutions, even when the absorption spectra in these solvents were found to be remarkably different. The excited-state decay can only be conveniently fitted for the Eu^{3+} and Tb^{3+} complexes if two different lifetimes are taken into account (0.31 and 0.88 ms for Tb^{3+}, 0.30 and 0.77 ms for Eu^{3+}). It is worth noting that a double lifetime was also found for the Eu^{3+} (0.95 and 0.39 ms) and Tb^{3+} (0.68 and 0.18 ms) complexes when solid samples were excited in the 240−320 nm region.

Photophysical Properties of the Triflate Salts. In acetonitrile, the absorption maxima are shifted to lower energies, and, even more interestingly, the fluorescence quantum yields are drastically reduced (0.026 for both Eu^{3+} and Tb^{3+} complexes), and the excited-state lifetimes are shortened ($\tau = 0.81$ and 0.35 ms for the Eu^{3+} and Tb^{3+} complexes). As observed for the nitrate salts, almost no metal-centered luminescence was observed ($\Phi < 1 \times 10^{-5}$) when the triflate was dissolved in water. Again, an intermediate situation was observed in methanol solutions, although in this case the fluorescence quantum yields were substantially lower than those observed

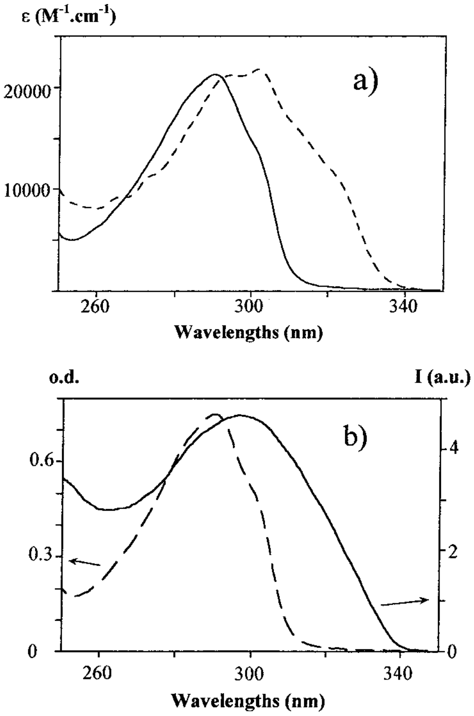

Figure 2. (a) Absorption spectra of [Eu·**1**](NO$_3$)$_3$ in methanol (−) and acetonitrile (- - -) solutions; (b) absorption (- - -) and excitation (−) (λ_{em} = 615 nm) spectra of [Eu·**1**](NO$_3$)$_3$ in methanol solution.

Table 1. Photophysical Properties of the Nitrate Complexes in Acetonitrile Solutions at Room Temperature

	absorption		luminescence		
	λ_{max} (nm)	ϵ_{max} (M^{-1} cm^{-1})	λ_{max} (nm)	τ (ms)	Φ
[Gd·**1**]$^{3+}$	300	21 200			
[Tb·**1**]$^{3+}$	300	20 500	545[a]	0.63	0.14
[Eu·**1**]$^{3+}$	300	21 000	615[b]	1.45	0.30

[a] $^5D_4 \rightarrow {}^7F_5$ transition. [b] $^5D_0 \rightarrow {}^7F_2$ transition.

Table 2. Photophysical Properties of the Nitrate Complexes in Methanol Solutions at Room Temperature

	absorption		luminescence		
	λ_{max} (nm)	ϵ_{max} (M^{-1} cm^{-1})	λ_{max} (nm)	τ_1 (ms)	τ_2 (ms)
[Gd·**1**]$^{3+}$	290	21 600			
[Tb·**1**]$^{3+}$	290	21 200	546[a]	0.31	0.88
[Eu·**1**]$^{3+}$	290	22 200	615[b]	0.30	0.77

[a] $^5D_4 \rightarrow {}^7F_5$ transition. [b] $^5D_0 \rightarrow {}^7F_2$ transition.

for the nitrate salts. Furthermore, a double lifetime was found for the Eu^{3+} (0.17 and 0.52 ms) and Tb^{3+} (0.12 and 0.41 ms) triflate salts when solid samples were excited in the 240−320 nm region. All lifetimes are shorter than those observed for the nitrate salts.

Influence of the Counterion on the Photophysical Properties of the Triflate Salts. A particularly straightforward effect was discovered by addition of tetrabutylammonium salts to an acetonitrile solution of the [Eu·**1**](OTf)$_3$ (Figure 3a) and [Tb·**1**](OTf)$_3$ (Figure 3b) complexes. A drastic change of their photophysical properties and an amplification of the Ln luminescence dependent on the nature of the counterion were observed. Noteworthy, addition of tetrabutylammonium triflate does not induce any change either in the absorption or in the luminescence spectra. However, a large increase of the luminescence intensity could be observed upon addition of up to 2 equiv of nitrate anions, while larger amounts of this species lead to a slight intensity decrease. After addition of 3 equiv of nitrate ions, we observed the same excited-state lifetimes and luminescence quantum yields as measured with the genuine nitrate complexes. This means that a 7-fold increase of the luminescence intensity of the Tb^{3+} complex and an 11-fold increase for the Eu^{3+} complex have been observed during the titration experiments. It is worth noting that the structure of the luminescence bands changes upon addition of the nitrate anion as well (Figure 3). A similar effect, but with a smaller increase of the luminescence intensity and excited-state lifetime, was observed upon addition of tetrabutylammonium chloride. In this case, a plateau was reached upon addition of 2 equiv of salt, and changes in the structure of the luminescence bands were also observed.

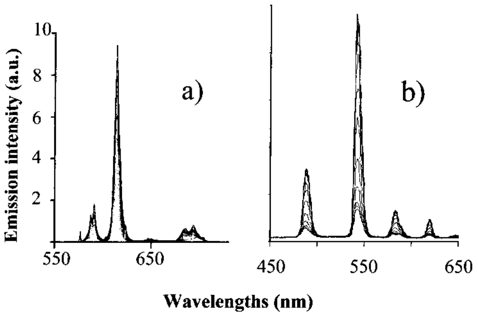

Figure 3. Luminescence intensity in acetonitrile solutions of (a) [Eu·**1**](OTf)$_3$, with increasing amounts of tetrabutylammonium nitrate anions from 0 to 4.2 equiv and by increments of 0.14 equiv until 2.25 equiv and by increments of 0.28 equiv until 4.2 equiv and (b) [Tb·**1**](OTf)$_3$ with increasing amounts of tetrabutylammonium nitrate anions from 0 to 4 equiv by increments of 0.25 equiv.

A different effect was observed upon addition of acetate or fluoride ions. In this case, after an initial increase of the luminescence intensity, a decrease was observed upon addition of more than 1 equiv of the anionic species. At the same time, large changes could be observed in the absorption spectrum, such as a decrease of the band at 300 nm and an increase of the absorbance at 285 nm.

Association Constants with Various Anions. To get as much possible data about the interactions of the anions with the complexes in acetonitrile solutions, we performed UV−vis titrations where the evolution of the UV−vis spectra of solutions containing [Ln·**1**](OTf)$_3$ (Ln = Eu and Tb) was monitored[25] as a function of added amounts of tetrabutylammonium salts of different anions (X$^-$ = NO$_3$$^-$, Cl$^-$, F$^-$, and AcO$^-$). In almost all cases, the titration can be conveniently fitted with a model in which the “naked” complex [Ln·**1**]$^{3+}$ is successively coordinated by one, two, and three anions:

$$[\mathrm{Eu}\cdot\mathbf{1}]^{3+} + \mathrm{X}^- \rightleftharpoons [\mathrm{Eu}\cdot\mathbf{1}\cdot\mathrm{X}]^{2+} \qquad \beta_1 = \frac{[(\mathrm{Eu}\cdot\mathbf{1}\cdot\mathrm{X})^{2+}]}{[(\mathrm{Eu}\cdot\mathbf{1})^{3+}] \times [\mathrm{X}^-]}$$

$$[\mathrm{Eu}\cdot\mathbf{1}]^{3+} + 2\mathrm{X}^- \rightleftharpoons [\mathrm{Eu}\cdot\mathbf{1}\cdot\mathrm{X}_2]^{+} \qquad \beta_2 = \frac{[(\mathrm{Eu}\cdot\mathbf{1}\cdot\mathrm{X}_2)^{+}]}{[(\mathrm{Eu}\cdot\mathbf{1})^{3+}] \times [\mathrm{X}^-]^2}$$

$$[\mathrm{Eu}\cdot\mathbf{1}]^{3+} + 3\mathrm{X}^- \rightleftharpoons [\mathrm{Eu}\cdot\mathbf{1}\cdot\mathrm{X}_3] \qquad \beta_3 = \frac{[(\mathrm{Eu}\cdot\mathbf{1}\cdot\mathrm{X}_3)]}{[(\mathrm{Eu}\cdot\mathbf{1})^{3+}] \times [\mathrm{X}^-]^3}$$

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(25) Charbonnière, L. J.; Balsiger, C.; Schenk, K. J.; Bünzli, J.-C. G. *J. Chem. Soc., Dalton Trans.* **1998**, 505.

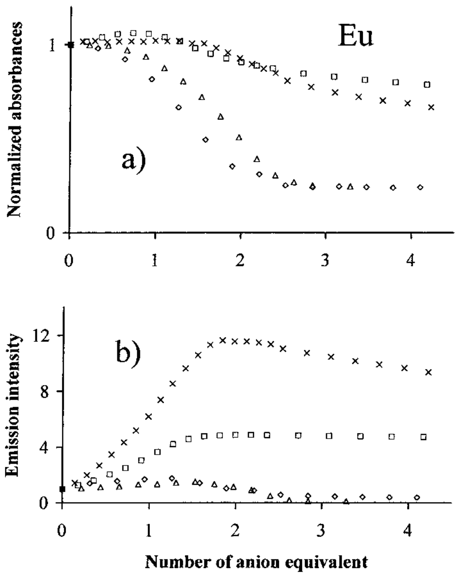

Figure 4. (a) Absorbance intensity at $\lambda_{abs} = 310$ nm of [Eu·**1**](OTf)$_3$ in acetonitrile solution with increasing amounts of tetrabutylammonium anions (×) for nitrates, (□) for chlorides, (△) for fluorides, (◇) for acetates; (b) emission intensity at $\lambda_{em} = 610$ nm of [Eu·**1**](OTf)$_3$ in acetonitrile solution with increasing amounts of tetrabutylammonium anions (×) for nitrates, (□) for chlorides, (△) for fluorides, (◇) for acetates.

Table 3. Cumulative Association Constants for Complex Formation with One, Two, and Three Coordinated Anions in Acetonitrile Solution (25 °C, 0.01 M TBAPF$_6$) Starting from [Ln·**1**](OTf)$_3$ Complexes

		log β_1	log β_2	log β_3
NO_3^-	Eu	6.1 ± 0.3	11.0 ± 0.2	14.4 ± 0.7
	Tb	6.0 ± 0.5	11.7 ± 0.8	15.4 ± 1.0
Cl^-	Eu	6.9 ± 0.2	12.0 ± 0.2	<14.5
	Tb	7.1 ± 0.8	12.1 ± 0.8	<14.6
F^-	Eu	7.8 ± 0.7	15.5 ± 1.1	21.2 ± 1.2
	Tb	6.7 ± 0.3	11.9 ± 0.6	17.8 ± 1.0
AcO^-	Eu	6.9 ± 0.6	13.2 ± 0.8	19.1 ± 1.1
	Tb	7.2 ± 0.3	13.5 ± 0.3	19.0 ± 0.3

A summary of the cumulative association constants obtained for titrations of Tb and Eu complexes is given in Table 3, and full experimental details are given in the Supporting Information. We were not able to obtain evidence for the formation of the [Ln·**1**·X$_3$] species in the case of the chloride anion only. This suggests that either the coordination of the third chloride anion is very weak or that the spectral changes from [Ln·**1**·X$_2$]$^+$ to [Ln·**1**·X$_3$] are too small to be fitted. On the basis of the results obtained for the other anions, the first hypothesis was retained and translated into an upper limit for the value of the third association constant K_3. A graphical representation of the absorption change versus the number of added equivalents of the anion is provided for the Eu and the Tb complexes, respectively, in Figures 4a and 5a.

In all cases, the titration shows a shift of the absorption maximum (at 312 nm in the starting solution) toward higher energy upon addition of the anion, finally reaching values from 285 to 300 nm in the presence of a large excess of anion, depending on the anion used. This hypsochromic shift can be correlated to the step by step decomplexation of the *bipy* moieties from the metal atom.[26] The coordinating anions compete with the aromatic fragments and gradually remove them from the first coordination sphere of the metal.

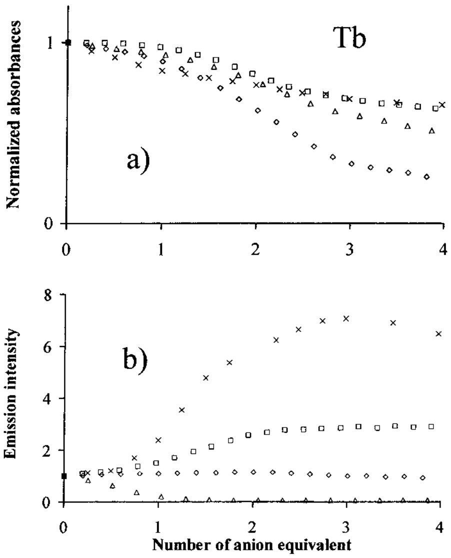

Figure 5. (a) Absorbance intensity at $\lambda_{abs} = 310$ nm of [Tb·**1**](OTf)$_3$ in acetonitrile solution with increasing amounts of tetrabutylammonium anions (×) for nitrates, (□) for chlorides, (△) for fluorides, (◇) for acetates; (b) emission intensity at $\lambda_{em} = 541$ nm of [Eu·**1**](OTf)$_3$ in acetonitrile solution with increasing amounts of tetrabutylammonium anions (×) for nitrates, (□) for chlorides, (△) for fluorides, (◇) for acetates.

In a parallel experiment, the emission spectra of the solutions were measured during the titrations ($\lambda_{exc} = 310$ nm, Figures 4b and 5b). The most dramatic influence was observed for addition of up to 2 equiv of nitrate anions to both the *Eu* and the *Tb* complexes, for which, respectively, an 11- and a 7-fold increase of the luminescence were observed. The same trends, but less pronounced, were observed with chloride anions, with 5- and 2.5-fold increases of the luminescence intensity for Eu and Tb complexes, respectively, while for fluoride and acetate anions, the changes are far less pronounced.

Discussion

The absorption spectra of the complexes reported here are dominated by the transitions centered on the bipy moieties, because the phenyl chromophore attached to the P-atom has a much lower molar absorption coefficient. Complexation of Gd^{3+}, Eu^{3+}, and Tb^{3+} ions typically causes a bathochromic shift in the lowest energy peak of the absorption spectrum of the bipy subunits from 285 nm (λ_{max} for the free ligand) to the 300–315 nm region.[10c] This is exactly what we observed for the Ln complexes of ligand **1** in acetonitrile solutions as the $\pi \rightarrow \pi^*$ transitions centered on the bipy moieties are displaced from 285 for the free ligand to 300 nm in the complexes. It indicates that, in this solvent, the bipy units are substantially coordinated to the central metal ion. For Eu^{3+} and Tb^{3+} complexes, excitation in the bipy absorption bands leads to the typical metal-centered luminescence, indicating that in these cases energy transfer from the bipy units to the metal ion occurs. The efficiency of this process, whose lower limit can be assumed to be the metal-centered luminescence quantum yield upon ligand excitation, is high as compared to that of other complexes containing the bipy units,[10c] and is in keeping with a strong electronic interaction of the bipy fragment with the Ln center

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(26) (a) Sabbatini, N.; Perathoner, S.; Lattanzi, G.; Dellonte, S.; Balzani, V. *J. Phys. Chem.* **1987**, *91*, 6136. (b) Sabbatini, N.; Perathoner, S.; Lattanzi, G.; Dellonte, S.; Balzani, V. *Inorg. Chem.* **1988**, *27*, 1628.

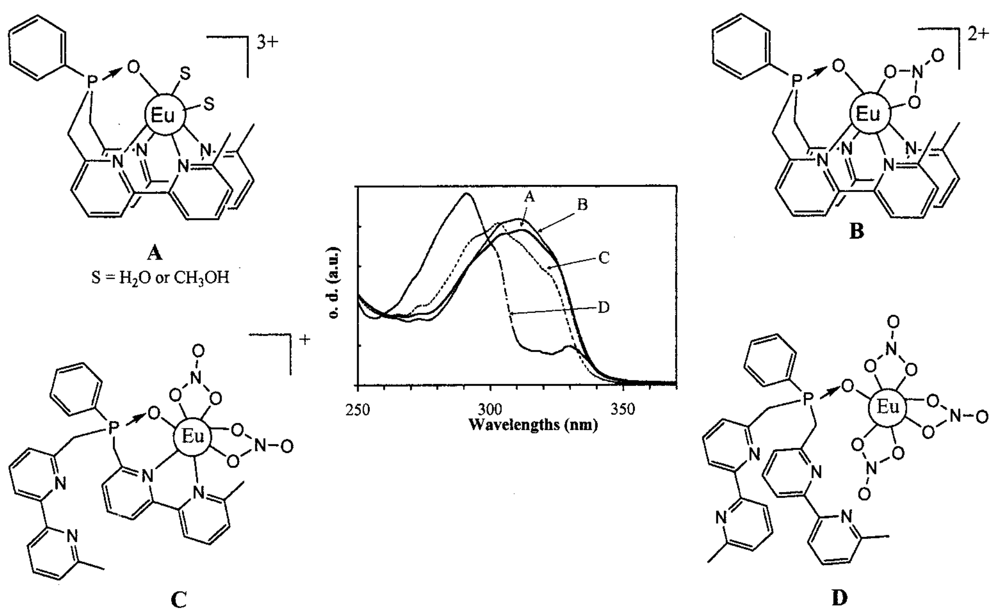


Figure 6. Proposed mechanism for the stepwise coordination of the nitrate anions to the [Eu·**1**](OTf)$_3$ complex and deconvoluted UV−vis spectra of the [Eu·**1**](NO$_3$)$_n$$^{(3-n)+}$ species. Solvent molecules such as methanol or water could complete the first coordination shell of the Ln and are not represented. For **D**, the X-ray crystal structure confirms the presence of either two coordinated methanol molecules or one molecule of methanol and one molecule of water. The central part of the figure exhibits the absorption spectra of all assumed intermediates.

in acetonitrile. Furthermore, the very good matching between the excitation and absorption spectra and the observation of only one excited-state lifetime indicate that in acetonitrile only one form is present.

In contrast, by means of X-ray diffraction on single crystals, two different forms are observed in the solid state, when crystals of the Tb^{3+} complex are obtained from a methanol solution. In these crystals, the existence of two different environments for the metal ion (Figure 1) causes, as expected, the observation of a double lifetime (0.18 and 0.68 ms). Similarly, a double lifetime (0.39 and 0.95 ms) was found for the Eu^{3+} complex, indicating that this metal ion also experiences two different coordination spheres in the solid state. The analysis of the preexponential terms indicates that the two forms are present in the same amount.

In methanol solution, the presence of a shoulder at 305 nm indicates that some bipy units are interacting with the Ln ion. However, the observation of the maximum at 290 nm for both the Eu^{3+} and the Tb^{3+} complexes indicates that other bipy units are not directly bounded to the metal ion. On the other hand, in the excitation spectra, the band at 285 nm is almost absent, clearly indicating that only the bipy units closer to the metal ion are able to transfer energy to it with good efficiency. By analogy with what was found in the solid state, the presence of a double lifetime again shows that the central ion is surrounded by two different coordination spheres. The analysis of the preexponential terms indicates that the two different systems are almost present in the same amount. In water solution, both the shape of the absorption spectrum and the lack of any metal-centered luminescence indicate that none of the bipy units are directly coordinated to the metal ions. The observed results can be explained by two different hypotheses: (i) the complete dissociation of the complex, and (ii) the metal ion is still coordinated to the PO groups, but the two bipy units are replaced in the coordination sphere by solvent molecules. Careful FT-IR measurements in water using CaF_2 cells seem to confirm that the PO remained coordinated to the Eu center ($\nu_{PO} = 1185$ cm^{-1} versus $\nu_{PO} = 1200$ cm^{-1} found for the free ligand in a mixture of methanol and water).

In acetonitrile solution, triflate salts show, as mentioned above, a lower luminescence quantum yield and a shorter lifetime than do the nitrate salts. In these conditions, triflate anions are not expected to coordinate the central metal ion or to form strong ionic couples with it. The changes in the spectra observed upon addition of nitrate and chloride ions, and in particular the different structures of the most symmetry-sensitive transitions ($^5D_0 \rightarrow {}^7F_2$ for Eu^{3+} and $^7F_5 \rightarrow {}^5D_4$ for Tb^{3+}), clearly indicate that these species in acetonitrile solution are able to enter the first coordination sphere of the metal ion. This feature gives to these complexes the interesting feature to change drastically their luminescence intensity in the presence of coordinating anions.

It can be surmised that the addition of the first nitrate anion to the starting material **A** provides a dicationic species **B** (Figure 6). This is corroborated by the fact that very slight modifications of the UV−vis absorption spectra are observed during the titration experiments. A first increase in the luminescence spectra was observed in this process, and this can be conveniently explained by the change of symmetry and by the shielding from solvent molecules experienced by the central metal ion. However, addition of the second equivalent of nitrates has a more drastic influence as probed by the absorption spectrum which, in particular, displays a hypsochromic shift (see insert in Figure 6). This shift is in agreement with the coordination of the second nitrate and concomitant release of a single bipy arm, leading to the monocationic species **C**. At a first glance, the large luminescence increase observed upon addition of the second equivalent of anion could seem in contrast with this proposed mechanism. However, if in this process a stronger electronic interaction among the metal ion and the bipy moiety that is still coordinated to it is established, it can strongly increase the overall efficiency of the ligand-to-metal energy

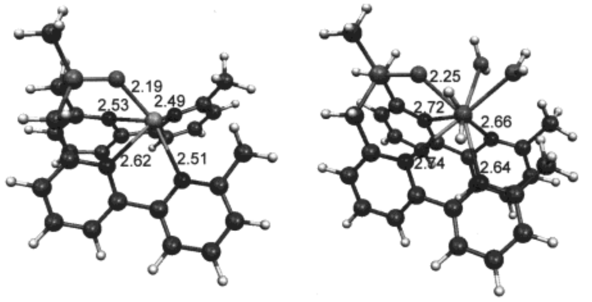
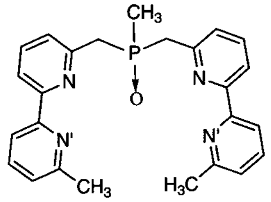


Figure 7. HF optimized structure of $[\mathrm{Eu}\cdot\mathbf{2}]^{3+}$ (left) and $[\mathrm{Eu}\cdot\mathbf{2}, (\mathrm{H_2O})_3]^{3+}$ (right). Distances are in Å.

Chart 2

2



transfer process and, as a consequence, the luminescence quantum yield. Indeed, quantum mechanical calculations (vide infra) confirm the strengthening of the coordination feature of one bipy subunit. The unparallel increase of the excited-state lifetime and of the luminescence quantum yield is in agreement with such a mechanism. Finally, addition of the third nitrate anion has the most spectacular effect with an additional 30 nm hypsochromic shift of the most intense absorption band because of decoordination of the second bipy arm and formation of the neutral species **D**. The decrease in the luminescence intensity during this process is also in agreement with this mechanism. This latter complex is similar to the one isolated from the nitrate starting material in methanol solution, the molecular structure of which, determined by X-ray crystallography (vide supra), showed that the first coordination sphere of the Ln is completed either by two methanol or by one methanol/one water molecules and that one bipy unit assumes a cis conformation because of some interaction with the metal atom, while the second bipy unit assumes a trans conformation to reduce electron repulsion of the nitrogen lone pairs. Similarly, the first coordination sphere in species **A** to **D** is expected to be completed to nine by solvent molecules.

The stepwise substitution of the bipy arms by nitrate anions outlined above is consistent with quantum mechanical (QM) calculations for the Eu complexes of ligand **2**, an analogue of ligand **1** bearing a methyl in place of the phenyl group to which water and/or anion have been gradually added forming $[\mathrm{Eu}\cdot\mathbf{2}\cdot(\mathrm{H_2O})_3]^{3+}$, $[\mathrm{Eu}\cdot\mathbf{2}\cdot\mathrm{X}_n]^{(3-n)+}$ ($\mathrm{X} = \mathrm{Cl}^-$, $\mathrm{NO_3}^-$; $n = 1-3$), and $[\mathrm{Eu}\cdot\mathbf{2}\cdot\mathrm{X}_3\cdot(\mathrm{H_2O})_2]$ complexes. In $[\mathrm{Eu}\cdot\mathbf{2}]^{3+}$ (Figure 7), without the presence of solvent molecules or counterions, ligand **2** is bonded via the P(O) oxygen atom and two sets of pyridine nitrogen atoms N and N′ (Chart 2). The Eu−O(P) bond is the shortest metal−ligand bond, leading to a nonoptimal coordination of the other binding sites and to asymmetric binding of the two pyridine units of a given bipy arm. The N binding sites form weaker bonds to Eu than do the N′ ones, as found in all complexes studied here. The O(P)−N repulsion also lets the Pyr(N) rings turn less toward Eu than the Pyr(N′) rings, and one bipy arm is bonded closer to the cation than is the other.

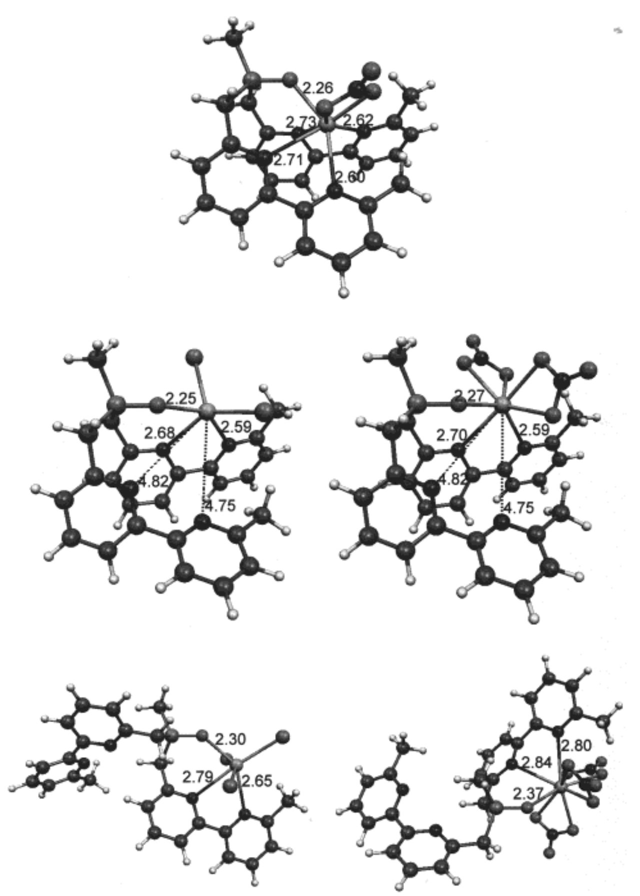


Figure 8. HF optimized structure of $[\mathrm{Eu}\cdot\mathbf{2}, \mathrm{X}_n]^{(3-n)+}$, with $n = 1$ (top) to 3 (bottom) and $\mathrm{X} = \mathrm{Cl}^-$ (left) or $\mathrm{NO_3}^-$ (right). Distances are in Å.

The addition of three water molecules to form $[\mathrm{Eu}\cdot\mathbf{2}\cdot(\mathrm{H_2O})_3]^{3+}$ leads to a lengthening of all bonds between **2** and Eu, but **2** still uses all five binding sites (Figure 7). The situation is different when counteranions are stepwise added to $[\mathrm{Eu}\cdot\mathbf{2}]^{3+}$ (Figure 8). The Eu charge decreases, the metal−ligand bonds weaken, and the repulsions between the ligands increase. We first examine the influence of chloride anions. Upon addition of the first Cl^-, all binding sites of **2** remain in contact with Eu but with the second Cl^- in $[\mathrm{Eu}\cdot\mathbf{2}\cdot\mathrm{Cl_2}]^+$, one bipy arm moves away from the first to the second coordination shell of the metal, while the other bipy arm moves closer to Eu, benefiting from the space freed by its counterpart. This is in perfect agreement with the luminescence increase observed after the addition of a second equivalent of anion, as discussed above. Finally, if a third chloride anion is added, and the neutral $[\mathrm{Eu}\cdot\mathbf{2}\cdot\mathrm{Cl_3}]$ complex is formed, the nonbonded bipy arm moves completely away from Eu, presumably because of its reduced attraction to the formally neutral $\mathrm{EuCl_3}$ unit.

Similar results are obtained with $\mathrm{NO_3}^-$ anions, which are bidentate and sterically more demanding than Cl^- anions. The most noticeable difference concerns the lengthening of the Eu−**2** distances (by less than 0.02 Å for one or two nitrates, and up to 0.15 Å with three nitrates (Figure 8)). In the presence of three nitrates, **2** retains, in addition to the phosphoryl binding site, one coordinated bipy arm, which notably differs from what was observed from the experimental results. The discriminating factor could be the coordination of solvent molecules to the cation in condensed phases. Therefore, we have added two water molecules to $[\mathrm{Eu}\cdot\mathbf{2}\cdot\mathrm{X}_3]$ forming $[\mathrm{Eu}\cdot\mathbf{2}\cdot\mathrm{X}_3\cdot(\mathrm{H_2O})_2]$-type com-

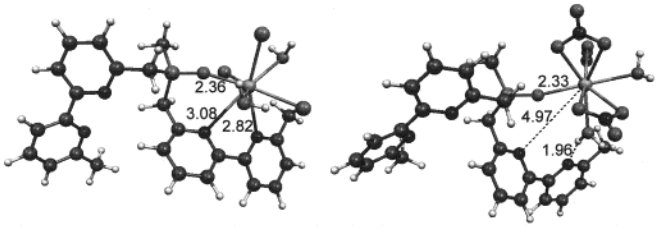


Figure 9. HF optimized structure of [Eu·**2**, $Cl_3(H_2O)_2$] (left) and [Eu·**2**, $(NO_3)_3(H_2O)_2$] (right). Distances are in Å.

plexes (Figure 9). With the chloride anions, two H_2O are still not enough to remove the second bipy from Eu, but with NO_3^- anions, the steric crowding of the first coordination shell of Eu leads to a structure similar to the crystal structure of [Tb·**1**]-$(NO_3)_3$,(H_2O)(MeOH), where **1** is only bound via O(P) to the cation.

As far as the other anions are concerned, the hard fluoride anions are known to coordinate efficiently Ln ions and were already found to replace water molecules in the coordination sphere of Eu complexes, with important changes in their luminescence properties.[26] It is thus not surprising that a similar effect can also be observed in the present case, especially considering that acetonitrile molecules form much weaker coordinative bonds with the central Ln ion than does water. Because of its stronger coordination ability toward Ln cations as compared to chloride and nitrate, fluoride can even better compete with the bipy units appended to **1**, especially when a molar excess has been added, therefore pushing the bipy moieties out of the first coordination sphere. This can be clearly seen looking at the absorption spectra, where a decrease of the band at 300 nm and an increase of the absorbance at 285 nm were observed. Finally, a similar behavior has been observed for both Eu and Tb complexes with acetate ions (Figures 4a,b and 5a,b, respectively).

Both the absorption and emission measurements and the QM calculations show that the Ln-**1** systems described here react to the addition of suitable anions by successively removing the bipy arms of **1** out of the first coordination shell of the cation. This leads to an increase in luminescence yield and lifetime, and opens up the possibility to use such complexes as luminescent chemosensors for anions, which are relatively rare[2−4,27,28] as compared to those for cations, but very interesting for practical applications.[2−4] The design of a more efficient sensor, able to work also in coordinating solvents, requires the coordination of the bipy units of ligand **1** to be strengthened, so that this binding could also be stable in water solution. The design and synthesis of a second generation of sensors bearing anionic bipy fragments are currently under way in our laboratories. Preliminary quantum mechanical calculations of an Eu^{3+} complex of $\mathbf{3}^{2-}$, an anionic analogue of ligand **2** with the methyl replaced by carboxylate groups, allow one to predict that the two carboxylate oxygen atoms O(CO) and the phosphoryl O(P) bind strongly to the metal cation (Chart 3, Figure 10). In [Eu·**3**]$^+$, one N looses coordination to the metal, but the three remaining Eu−N bonds, although somewhat longer than in [Eu·**1**]$^{3+}$ (2.49−2.89 Å with ligand $\mathbf{3}^{2-}$ as compared to 2.49−2.62 Å with ligand **1**), still allow for efficient energy transfer to the metal. It is also noteworthy that the Eu−O(CO) bonds are about 0.1 Å shorter than the Eu−O(P) bond, indicating that the carboxylate groups are even stronger bound than the phosphoryl group.

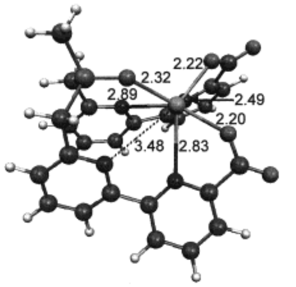
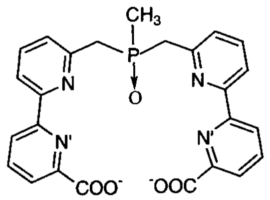


Figure 10. HF optimized structure of [Eu·**3**]$^+$. Distances are in Å.

Chart 3



$\mathbf{3}^{2-}$

Conclusions

Ligand **1** forms complexes with Gd^{3+}, Tb^{3+}, and Eu^{3+} whose photophysical properties depend drastically on the presence of anions. In particular, addition of nitrate anions to an acetonitrile solution containing [Ln·**1**]$^{3+}$ complexes as triflate salts results in an up to 7-fold increase of the luminescence intensity for the Tb^{3+} complex and an up to 11-fold increase for the Eu^{3+} complex. This increase is caused by the displacement of solvent molecules of the first coordination shell of the Ln cations by the competing nitrate anions and by important changes in the coordination features of the bipy moieties. In the same solvent, the nitrate salts show an intense metal-centered luminescence at room temperature, indicative of an efficient energy transfer from bipy subunits to the metal ion, suggesting that at least one of them remains close to the metal atom. In methanol and in solids obtained from methanol solutions, the luminescence is still present, but, in both cases, the excited-state decay can only be fitted with two exponential terms, suggesting that the central metal ion experiences two different environments. This is in perfect agreement with what is observed for the Tb^{3+} complex by means of X-ray diffraction on single crystals. For these complexes, the excitation spectra show that only the bipy unit that is closer to the metal ion can transfer energy to it. A key feature of these prototypes is that coordination of anions to the Ln provides an excellent shielding effect against detrimental nonradiative deactivation processes.

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Supporting Information Available: The crystallographic data (without the structure factors) for the structure described in this publication have been deposited as “supplementary publication no. CCDC-186916” with the Cambridge Crystallographic Data Centre. General methods, crystal data, spectroscopic measurement techniques, theoretical quantum mechanics methods, experimental data for association constants determination of ligand **1** with Eu and Tb, UV−vis titration experiments for each anion and each Ln complex (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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