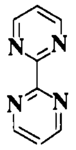
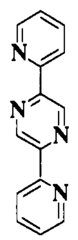
the complex $[Ru(o\text{-}phen)_2(py)_2]^{2+}$ (I) into the optical isomers.[7] We followed the literature procedure with good results. Reactions of I with the two bridging ligands bpym (II) or 2,5-dpp (III) yield dinuclear complexes $[(Ru(o\text{-}phen)_2)_2bpym]^{4+}$ and $[(Ru(o\text{-}phen)_2)_2(2,5\text{-}dpp)]^{4+}$, respectively. The 360-MHz ^1H NMR spectra (Figure 1a and Figure 2a) are recorded from solutions obtained with *rac*-$Ru(o\text{-}phen)_2Cl_2$, and the traces in Figure 1b and Figure 2b, from solutions obtained with Λ-$[Ru(o\text{-}phen)_2(py)_2]^{2+}$, respectively. The spectra reveal clearly the stereospecific route of the reaction[8] leading to the dinuclear complexes. Λ,Λ-$[(Ru(o\text{-}phen)_2)_2bpym]^{4+}$ and Λ,Λ-$[(Ru(o\text{-}phen)_2)_2(2,5\text{-}dpp)]^{4+}$ are obtained in ca. 95% and 90% isomeric purity, respectively. Recrystallization yields further separation of the isomers. Full assignment of pure Λ,Λ-$[(Ru(o\text{-}phen)_2)_2bpym]^{4+}$ has been given by COSY ^1H NMR as illustrated in Figure 3. There are signals of 10 different protons present with the coupling constants values $J_{23} = J_{89} = 5.2$ Hz, $J_{24} = J_{79} = 1.2$ Hz, $J_{34} = J_{78} = 8.3$ Hz, $J_{56} = 9.0$ Hz, and $J_{ab} = 5.7$ Hz. The spectrum of the dinuclear complex prepared from the racemic building block shows 20 different protons (10 from the Δ,Λ meso form).



bpym (II)



2,5-dpp (III)

The use of inert and enantiomerically pure building blocks for the synthesis of isomerically pure polynuclear complexes is a necessary prerequisite for the production of species with a well-defined identity. Such well-defined species are of interest in highly organized supramolecular structures containing several metal centers and also for studies of the interactions of metal complexes with biomolecules.

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(8) The relative abundance of the meso form and of the enantiomeric pair in the dinuclear complex is somewhat different if *rac*-$[Ru(o\text{-}phen)_2(py)]^{2+}$ or *rac*-$Ru(o\text{-}phen)_2Cl_2$ is used for its synthesis. The exact course of the reaction in the formation of the dinuclear complexes is the subject of further investigations. The first results indicate retention of configuration if the two pyridine ligands in $[Ru(o\text{-}phen)_2(py)]^{2+}$ are substituted by a dinuclear chelate. CD spectra indicate, e.g., clearly that the substitution of the two py ligands in Λ-$[Ru(o\text{-}phen)_2(py)_2]^{2+}$ by bpy yields Λ-$[Ru(o\text{-}phen)_2(bpy)]^{2+}$ with complete retention of configuration.

Articles

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Luminescent Eu^{3+}, Tb^{3+}, and Gd^{3+} Complexes of a Branched-Triazacyclononane Ligand Containing Three 2,2′-Bipyridine Units

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The Eu^{3+}, Tb^{3+}, and Gd^{3+} complexes of the branched-triazacyclononane ligand **1**, which contains three 2,2′-bipyridine coordinating units, have been prepared and their absorption spectra, luminescence spectra, luminescence decays, and transient absorption spectra and decays have been investigated. The three complexes show intense absorption bands at 243 nm ($\epsilon \cong 14000$ M^{-1} cm^{-1}) and 311 nm ($\epsilon \cong 22000$ M^{-1} cm^{-1}), which are considerably red-shifted and weaker compared with the bands of the free ligand. The free ligand and the Gd^{3+} complex show ligand-centered (LC) fluorescence and phosphorescence, as well as triplet–triplet transient absorption. The transient absorption can also be observed for the Tb^{3+} complex but not for the Eu^{3+} complex. For the Tb^{3+} and the Eu^{3+} complexes excitation in the LC bands causes the characteristic luminescence of the lanthanide ion. The excitation spectra match closely the absorption spectra in the region of LC absorption. Measurements carried out in H_2O and D_2O at 77 and 300 K show that, when coordinated to **1**, the metal ion is almost completely shielded from interaction with solvent molecules, in agreement with expectations based on molecular models. The emission lifetime at 77 K in D_2O for $[Tb(\mathbf{1})]^{3+}$ is considerably shorter than that of analogous complexes. This may be due either to a high radiative rate constant or, more likely, to radiationless deactivation via coupling with the very close lying CH_2 groups of the triazacyclononane ring. For $[Tb(\mathbf{1})]^{3+}$ no temperature effect is observed on the luminescence decay, because of the relatively high energy gap between the luminescent $^5D_4$ level and the upper lying $^3\pi\pi^*$ LC level. For $[Eu(\mathbf{1})]^{3+}$, the lifetime in D_2O at 77 K is again rather short, and furthermore, it decreases with increasing temperature. The latter effect is presumably caused by an activated radiationless decay via a low-lying CT excited state, related to the presence of the aliphatic amine groups (intramolecular electron-transfer quenching). Because of its high luminescence quantum yield (0.37 in H_2O at 300 K), $[Tb(\mathbf{1})]^{3+}$ can be an excellent luminescence label.

Introduction

Molecular species capable of exhibiting strong luminescence are quite interesting not only from a fundamental point of view but also because of their potential use for a variety of applications. Some lanthanide ions possess strongly emissive and long-lived excited states but do not exhibit intense absorption bands.[2] Therefore, considerable effort is currently devoted to the design

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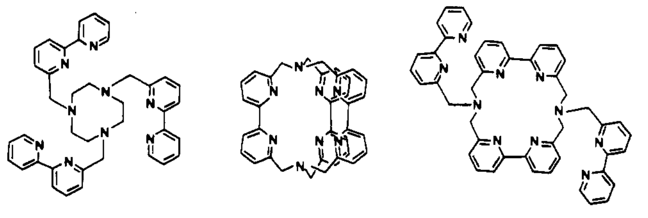
Table I. Ligand-Centered Absorption and Emission Maxima[a]

	absorption				emission			
	ground state[b]		$^3\pi\pi^*$ level[c]		$^1\pi\pi^*$ level[d]		$^3\pi\pi^*$ level[e]	
compd	λ_{max},[f] nm	ϵ_{max}, M^{-1} cm^{-1}	λ_{max}, nm	τ,[a] μs	λ_{max}, nm	τ, ns	λ_{max}, nm	τ, ms
1	286	41 000[b]	340		360	10, 24	470	1000
$[Gd(\mathbf{1})]^{3+}$	311	23 400	347	110	340	<1, 10	480	1.2[i]
$[Tb(\mathbf{1})]^{3+}$	311	20 400	355	4				
$[Eu(\mathbf{1})]^{3+}$	311	24 500						

[a] Aqueous solutions at room temperature (300 K), unless otherwise noted. [b] Ground-state absorption spectrum. [c] Transient absorption spectrum. [d] Fluorescence. [e] Phosphorescence in EtOH/MeOH rigid matrix at 77 K. [f] Lowest energy band (see also Figure 2). [g] Deaerated solution. [h] CH_2Cl_2 solution. [i] 110 μs in H_2O at 300 K.



1 **2** **3**

Figure 1. Schematic representation of the ligands.

of lanthanide complexes where light is absorbed by the ligands and electronic energy is then transferred to the emitting metal ion (antenna effect).[3-6] Recent investigations have shown that bipyridine-type units are suitable building blocks to design macrocyclic,[7,8] macrobicyclic,[3,4,9-11] and podand-type[12] ligands capable of giving highly stable and strongly luminescent Eu^{3+} (and, in some cases, Tb^{3+}) complexes.[13,14] A combined study of the Gd^{3+}, Tb^{3+}, and Eu^{3+} complexes of the same ligand can give important pieces of information on the behavior of the ligand-centered (LC) and metal-centered (MC) levels and on the efficiency of the ligand-to-metal energy-transfer processes.[4] As will be discussed in detail later, the energy level diagrams for Gd^{3+}, Tb^{3+}, and Eu^{3+} are quite different.[12] The lowest excited state of Gd^{3+} lies *above* the LC levels of bpy-type ligands. Therefore, in the Gd^{3+} complexes, the LC fluorescence, phosphorescence, and triplet–triplet transient absorption can be observed, and one can thus obtain information on the behavior of the LC levels under the perturbation caused by a paramagnetic metal ion. In the Tb^{3+} complexes, the lowest (luminescent) MC level lies below the lowest energy LC level. Upon excitation in the LC bands, ligand-to-metal energy transfer takes place and MC luminescence can occur, but in some cases the energy gap between the lowest LC and MC levels is small and back energy transfer can also take place. This may compromise the luminescence efficiency and lead to a complicated kinetic behavior. Finally, in Eu^{3+} complexes the lowest (luminescent) excited state lies at considerably lower energy than the lowest LC level. In these complexes ligand-to-metal energy transfer is therefore irreversible, but complications may arise from the presence of low-energy ligand-to-metal charge-transfer (LMCT) levels, since Eu^{3+} can be easily reduced.

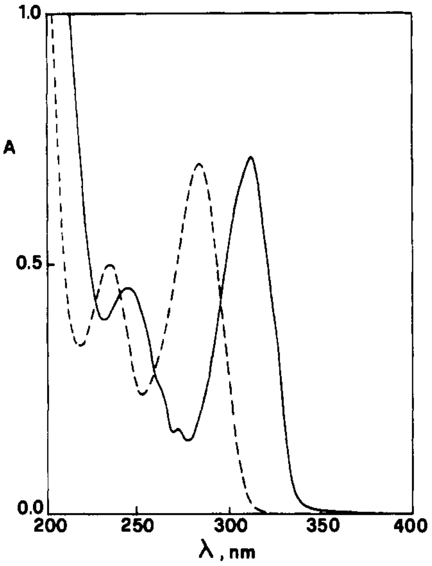


Figure 2. Absorption spectra of free ligand **1** (---) and of the $[Eu(\mathbf{1})]^{3+}$ complex (—).

Another topic of considerable interest in this field is the extent to which the ligand shields the metal ion from interaction with solvent (H_2O) molecules, which would cause nonradiative decay of the luminescent MC level. Such a shielding effect is also of the greatest relevance in the design of lanthanide-based contrast agents for magnetic resonance imaging.[15]

In order to better understand the role played by the various factors that determine the luminescence properties, we have synthesized and studied the Gd^{3+}, Tb^{3+}, and Eu^{3+} complexes of the branched-triazacyclononane ligand **1** (Figure 1), which contains three 2,2′-bipyridine coordinating units. The structures of two other bpy-based ligands (**2** and **3**), whose Eu^{3+} and Tb^{3+} complexes have been recently investigated,[4,8] are also shown in Figure 1.

Experimental Section

The 1,4,7-tris(2,2′-bipyridinyl)-1,4,7-triazacyclononane ligand, **1**, was obtained as previously described.[16] $[Gd(\mathbf{1})]Cl_3 \cdot 3H_2O$, $[Tb(\mathbf{1})]Cl_3 \cdot 4H_2O$, and $[Eu(\mathbf{1})]Cl_3 \cdot 4H_2O$ were prepared by the following procedure. To a solution of the ligand (0.158 mM in 3 mL of CH_2Cl_2) was added an equimolar quantity of the lanthanide salt ($MCl_3 \cdot 6H_2O$, M = Gd, Tb, Eu) dissolved in 3 mL of methanol. On being heated at 60 °C, the solution became highly fluorescent when irradiated with 365-nm light. After 1 h the solution was cooled to room temperature and the solvent was removed under vacuum. The pale yellow residue was dissolved in ethanol, and the complex was crystallized by slow diffusion of diethyl ether into the solution.

The complexes were characterized by FAB^+, absorption, and luminescence spectra, as well as by elemental analysis. $[Gd(\mathbf{1})]Cl_3 \cdot 3H_2O$:

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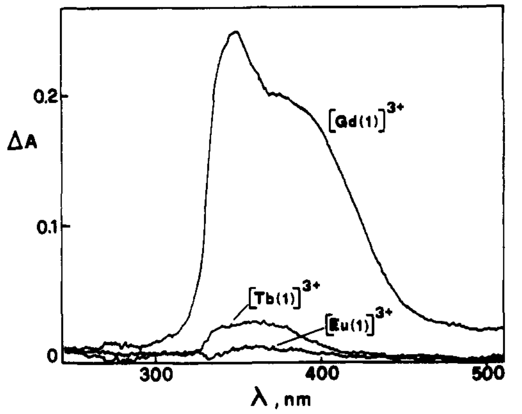

Figure 3. Transient absorption spectra of [Gd(**1**)]$^{3+}$, [Tb(**1**)]$^{3+}$, and [Eu(**1**)]$^{3+}$ in H_2O at 300 K.

FAB$^+$ (nitrobenzyl alcohol (NBA) matrix) *m/z* 861.0 (M − Cl), 825.0 (M − 2Cl + H). Anal. Calcd for $C_{39}H_{39}N_9GdCl_3{\cdot}3H_2O$: C, 49.23; H, 4.13; N, 13.25. Found: C, 49.19; H, 3.99; N, 13.18. [Tb(**1**)]$Cl_3{\cdot}4H_2O$: FAB$^+$ (NBA) *m/z* 862.0 (M − Cl), 827.0 (M − 2Cl), 792.1 (M − 3Cl). Anal. Calcd for $C_{39}H_{39}N_9TbCl_3{\cdot}4H_2O$: C, 48.23; H, 4.05; N, 12.98. Found: C, 48.19; H, 3.72; N, 12.75. [Eu(**1**)]$Cl_3{\cdot}4H_2O$: FAB$^+$ (NBA) *m/z* 856.0 (M − Cl), 821.0 (M − 2Cl), 786.1 (M − 3Cl). Anal. Calcd for $C_{39}H_{39}N_9EuCl_3{\cdot}4H_2O$: C, 48.58; H, 4.91; N, 13.07. Found: C, 48.53; H, 4.78; N, 13.09.

The solvents used were triply distilled water, 99.5% isotopically pure D_2O (Carlo Erba), and fluorescence grade methanol and ethanol.

The absorption spectra were recorded with a Kontron Uvikon 860 spectrophotometer. The luminescence spectra were measured with Perkin-Elmer LS5 and 650-40 spectrofluorometers. Luminescence decays were measured with a Perkin-Elmer LS5 spectrofluorometer or with a Nd:YAG DLPY4 JK laser. Luminescence quantum yields were obtained with a Perkin-Elmer 650-40 spectrofluorometer following the method described by Haas and Stein[17] using as standards Ru(bpy)$_3^{2+}$ (Φ = 0.028 in aerated water)[18] for the Eu^{3+} complex and quinine sulfate (Φ = 0.546 in 1 N H_2SO_4)[19] for the Tb^{3+} complex. Transient absorption spectra were obtained with an EG&G PARC 1460 optical multichannel analyzer (OMA III). Transient absorption decays were acquired by using a Tektronic 466 storage oscilloscope.

Results

The [Gd(**1**)]$^{3+}$, [Tb(**1**)]$^{3+}$, and [Eu(**1**)]$^{3+}$ complexes are stable in aqueous solution for several days, as shown by the lack of changes in the absorption and luminescence spectra.

The free ligand **1** is not much soluble in aqueous solution, where it shows absorptions bands with maxima at 238 and 286 nm (Table I, Figure 2). The absorption spectrum of [Eu(**1**)]$^{3+}$ (λ_{max} = 243 and 311 nm) is also shown in Figure 2. The spectra of [Gd(**1**)]$^{3+}$ and [Tb(**1**)]$^{3+}$ are quite similar to that of [Eu(**1**)]$^{3+}$ (Table I). The absorption spectra of the three complexes are the same in H_2O and MeOH.

The free ligand **1** in aqueous solution exhibits a fluorescence band with maximum at 360 nm and biexponential decay (Table I). In rigid glass at 77 K a long-lived phosphorescence band (λ_{max} = 470 nm) can also be observed.

[Gd(**1**)]$^{3+}$ shows the same emission and transient absorption bands as **1** but with maxima at slightly different wavelength and with different decay times (Table I). The zero–zero energy of the phosphorescence band is estimated to be 22 700 cm^{-1}. The transient absorption spectrum is quenched by dioxygen with k_q = 1.1×10^9 M^{-1} s^{-1}. For the [Tb(**1**)]$^{3+}$ complex the luminescence bands shown by the Gd^{3+} complex are no longer observed, but a weak transient absorption spectrum can still be seen (Figure 3). The Tb^{3+} complex shows a strong, structured luminescence in the visible region (highest energy band, 475 nm; highest intensity band, 540 nm), characteristic of the Tb^{3+} ion. [Eu(**1**)]$^{3+}$ does not show the luminescence and transient absorption bands of the Gd^{3+} complex but exhibits a strong, structured luminescence characteristic of the Eu^{3+} ion (highest energy band, 577 nm, highest intensity band, 617 nm). Corrected excitation spectra for [Tb(**1**)]$^{3+}$ and [Eu(**1**)]$^{3+}$ match closely the corresponding absorption spectra over the UV spectral region.

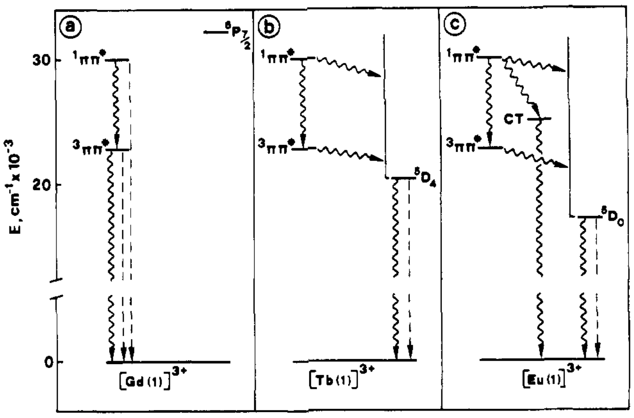

Figure 4. Schematic energy-level diagrams for the [Gd(**1**)]$^{3+}$, [Tb(**1**)]$^{3+}$, and [Eu(**1**)]$^{3+}$ complexes. Only the most important deactivation paths are indicated.

Table II. Metal-Centered Luminescence

	lifetimes, ms^{a,b}				quantum yield^c	
compd	$\tau^{77K}_{D_2O}$	$\tau^{77K}_{H_2O}$	$\tau^{300K}_{D_2O}$	$\tau^{300K}_{H_2O}$	$\Phi^{300K}_{D_2O}$	$\Phi^{300K}_{H_2O}$
[Tb(**1**)]$^{3+}$	1.5	1.4	1.5	1.5	0.38	0.37
[Tb⊂**2**]$^{3+\,d}$	3.8	1.7	0.63^e	0.45^e	0.03^e	0.03^e
[Tb(**3**)]$^{3+\,f}$	2.9	2.0	1.2	1.1	0.35	0.14
[Eu(**1**)]$^{3+}$	1.1	0.87	0.57	0.50	0.07	0.05
[Eu⊂**2**]$^{3+\,d}$	1.7	0.81	1.7	0.34	0.1	0.02
[Eu(**3**)]$^{3+\,g}$	1.9	1.8	1.9	1.5	0.2	0.1

[a] Measured in correspondence with the most intense emission band ($^5D_4 \rightarrow {}^7F_5$ for Tb^{3+} and $^5D_0 \rightarrow {}^7F_2$ for Eu^{3+}). [b] Experimental error ≤10%. [c] Experimental error ≤30%. [d] From ref 4. [e] Deaerated solution. [f] From ref 8, MeOH/MeOD solution. [g] From ref 8.

The luminescence behavior of the Tb^{3+} and Eu^{3+} complexes has been investigated in H_2O and D_2O at 77 and 300 K. The data obtained (luminescence lifetimes and quantum yields) are summarized in Table II, where analogous data of the previously investigated Tb^{3+} and Eu^{3+} complexes of ligands **2** and **3** are also shown for comparison purposes.

The decay of the [Tb(**1**)]$^{3+}$ luminescence was strictly monoexponential when measured with the Perkin-Elmer LS5 fluorometer; under laser excitation, a complex decay was observed. The bimolecular/biphotonic processes that take place at high light intensities and concentrations and the energy transfer observed in preliminary experiments from *[Gd(**1**)]$^{3+}$ to [Tb(**1**)]$^{3+}$ are currently under investigation and will be reported elsewhere.

Discussion

Looking at a space-filling model of **1**, one can see that the metal ion cannot be lodged in the small cavity of the triazacyclononane ring, but it must lay on the ring.[20] The model also shows that the three appended bpy units can wrap themselves around the metal ion. It follows that (i) the metal ion can be completely shielded from solvent interaction, (ii) the aliphatic nitrogen atoms of the ring are very close to the metal ion, (iii) the hydrogens of some CH_2 groups lie very close to the metal, and (iv) the bpy units are very close to one another. As we will see later, such an intimate molecular structure is fully consistent with the experimental results.

Free Ligand 1. The ligand **1** contains three 2,2′-bipyridine (bpy) chromophoric groups. For each bpy unit, the spectroscopically relevant excited states are the lowest $^1\pi\pi^*$ level, responsible for the absorption band (λ_{max} = 281 nm, ϵ = 13 000 M^{-1} cm^{-1}) and for the fluorescence band (λ_{max} = 324 nm, τ = 7 ns), and the lowest $^3\pi\pi^*$ level, responsible for the phosphorescence band (λ_{max} = 456 nm, τ = 0.94 s in MeOH/EtOH at 77 K) and the trip-

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Table III. Decay Rate Constants (s^{-1}) for the MC Luminescent Level and Related Quantities[a]

compd	k_r[b]	k_{nr}(OH)	$k_{nr}(T)$	Σk	η_r	Φ_{exp}	η_{et}	$n(H_2O)$[c]
$[Tb(\mathbf{1})]^{3+}$	670[d]	<50	<50	670	0.5	0.37	0.8	0
$[Tb\subset\mathbf{2}]^{3+}$[e]	260	630	2100	3000		0.03	1	2.6
$[Tb(\mathbf{3})]^{3+}$[f]	350	70	490	910	0.4	0.14	0.3	
$[Eu(\mathbf{1})]^{3+}$	910	≅250	840	2000	0.2[g]	0.05	0.25	0.3
$[Eu\subset\mathbf{2}]^{3+}$[e]	590	2350	<100	2940	0.2	0.02	0.10	2.5
$[Eu(\mathbf{3})]^{3+}$[h]	530	140	<100	670	0.8	0.10	0.13	0

[a] Aqueous solution at 300 K, unless otherwise noted; for the definition of the various quantities, see text. [b] The reported values have been obtained from eq 3 on the assumption that k_{nr}(other vibr) is negligible; see text. [c] Average number of coordinated water molecules, ±0.5; see ref 21. [d] A more correct value is ≅350 s^{-1}; see text. [e] Reference 4. [f] EtOH/MeOH; see ref 8. [g] Taking $k_r \cong 450$ s^{-1}; see text. [h] Reference 8.

let-triplet transient absorption band (λ_{max} = 350 nm).[4] The absorption and emission properties of **1** (Table I) are similar to but not identical with those of free bpy. Particularly worth noting are the red-shifted maximum and the biexponential decay observed for the fluorescence of **1**, which suggests the presence of bpy–bpy interactions (in the ground and/or excited state).

$[Gd(\mathbf{1})]^{3+}$. Since Gd^{3+} does not possess energy levels below the $^1\pi\pi^*$ and $^3\pi\pi^*$ LC levels (Figure 4a), the $[Gd(\mathbf{1})]^{3+}$ complex allows us to investigate the behavior of LC levels in a structure identical with that of the Tb^{3+} and Eu^{3+} complexes. The LC absorption bands are considerably red-shifted and strongly weakened upon metal coordination (Table I). In the previously studied case of the $[Gd\subset\mathbf{2}]^{3+}$ cryptate, both effects were considerably smaller.[4] This suggests that in $[Gd(\mathbf{1})]^{3+}$ the bpy units are much more perturbed than in $[Gd\subset\mathbf{2}]^{3+}$, presumably because **1** is more flexible and the bpy units can approach the metal ion more closely in the case of this ligand. It can also be observed that the molar extinction coefficient of the 311-nm band in the $[M(\mathbf{1})]^{3+}$ complexes (Table I) decreases slightly in the series Eu^{3+} > Gd^{3+} > Tb^{3+}, i.e. with the increasing radius of the metal ion.[2] Such an effect was not observed in the previously studied $[M\subset\mathbf{2}]^{3+}$ cryptates, presumably because of the rather large and rigid cavity of the cryptand **2**.

Contrary to the $^1\pi\pi^*$ absorption band, the LC fluorescence band is shifted to higher energy compared with the fluorescence band of the free ligand. This could again indicate that the free-ligand fluorescence has an excimeric-type character. It should be noted, however, that also in $[Gd(\mathbf{1})]^{3+}$ the fluorescence decay is biexponential (Table I), suggesting again some type of bpy–bpy interaction. The LC phosphorescence (at 77 K) is slightly red-shifted and much shorter lived compared to the free-ligand phosphorescence, as expected because of the influence of the paramagnetic metal ion.[14] From the phosphorescence spectrum, the zero–zero energy of the $^3\pi\pi^*$ LC levels results to be 22 700 cm^{-1} with a lifetime of 1.2 ms in EtOH/MeOH rigid matrix at 77 K. At room temperature, a phosphorescence band can still be observed but with a much shorter lifetime (110 μs). The same lifetime is exhibited by the transient absorption spectrum (Figure 3, Table I), which can thus be assigned to the absorption of the $^3\pi\pi^*$ level. Both the phosphorescence and the transient absorption signals are quenched by dioxygen with $k_q = 1.1 \times 10^9$ M^{-1} s^{-1}, indicating again that they originate from the same excited state.

$[Tb(\mathbf{1})]^{3+}$. The relative energy position of the LC and MC levels for this complex is schematized in Figure 4b. The LC fluorescence and phosphorescence bands cannot be observed but it is reasonable to assume that the $^1\pi\pi^*$ and the $^3\pi\pi^*$ levels have the same energies as in the Gd^{3+} complex. The weak, transient absorption spectrum (Figure 3) is quite similar to that of the Gd^{3+} complex and can thus be assigned to the $^3\pi\pi^*$ level. The small differences between the two spectra may be due to the presence of CT transitions in the excited Tb^{3+} complex. The transient spectrum recorded immediately after the laser pulse is considerably less intense than that found for the Gd^{3+} complex (Figure 3). This suggests that a substantial fraction of $^1\pi\pi^*$ excited states undergoes energy transfer to the MC manifold in competition with intersystem crossing to $^3\pi\pi^*$ (Figure 4b). The transient spectrum is also considerably shorter lived than that of the Gd^{3+} complex, as expected because of the occurrence of energy transfer from $^3\pi\pi^*$ to the metal-centered levels.

In the Tb^{3+} complex, ligand-centered excitation causes strong metal-centered luminescence. From the luminescence lifetimes gathered in Table II, it is possible to estimate the values of the radiative and nonradiative rate constants of the luminescent $^5D_4$ Tb^{3+} level. As previously discussed,[4,21,22] the overall rate constant $\sum k$ can be expressed by the following equation:

$$\sum k = 1/\tau = k_r + k_{nr} \qquad (1)$$

Here k_r is the (temperature independent) radiative rate constant and k_{nr} is the nonradiative rate constant. The nonradiative rate constant receives contribution from a temperature-independent term, k_{nr}', which accounts for the phonon-assisted deactivation to the ground state, and a temperature-dependent term, $k_{nr}(T)$, which can play an important role when short-lived, upper lying excited states are thermally accessible. In turn, the temperature-independent term, k_{nr}', receives the most important contribution from the decay through coupling with high-energy vibrations (O–H vibrations, in aqueous solution), while the contribution coming from the coupling with other vibrations, k_{nr}(other vibr), is usually small:

$$\sum k = 1/\tau = k_r + k_{nr}(T) + k_{nr}(\mathrm{OH}) + k_{nr}(\text{other vibr}) \qquad (2)$$

At 77 k in D_2O, $k_{nr}(T)$ and k_{nr}(OH) may be neglected so that

$$k_r + k_{nr}(\text{other vibr}) = 1/\tau(D_2O)^{77K} \qquad (3)$$

If k_{nr}(other vibr) is also neglected, the radiative rate constant is approximately given by $1/\tau(D_2O)^{77K}$. The values of k_{nr}(300 K) and k_{nr}(OH) can be obtained from the experimentally determined luminescence lifetimes (Table II) through the following relationships:[4,21,22]

$$k_{nr}(300\ \mathrm{K}) = 1/\tau(D_2O)^{300K} - 1/\tau(D_2O)^{77K} \qquad (4)$$

$$k_{nr}(\mathrm{OH}) = 1/\tau(H_2O)^{300K} - 1/\tau(D_2O)^{300K} \qquad (5)$$

The values of the rate constants for $[Tb(\mathbf{1})]^{3+}$ and other complexes are gathered in Table III. It is clear that for $[Tb(\mathbf{1})]^{3+}$ both k_{nr}(OH) and $k_{nr}(T)$ are negligible, indicating that (i) the ligand **1** fully protects the metal ion from interaction with solvent molecules (which is not the case for $[Tb\subset\mathbf{2}]^{3+}$[4]) and (ii) back energy transfer from $^5D_4$ to $^3\pi\pi^*$ does not take place (which is not the case for $[Tb\subset\mathbf{2}]^{3+}$[4] and $[Tb(\mathbf{3})]^{3+}$[8]). It is interesting to note (Table III) that the value of k_r for $[Tb(\mathbf{1})]^{3+}$ is considerably larger than that found for the other two Tb^{3+} complexes. Other available data for k_r are those concerning Tb_{aq}^{3+},[10] $[Tb\subset 2.2.1)]^{3+}$,[10] and $[Tb\subset 2.2.1)]^{3+}\cdot 2F^-$.[10] In all these cases k_r is around 350 s^{-1}. It seems unlikely that in $[Tb(\mathbf{1})]^{3+}$ the value of k_r is about twice that found in other five complexes of quite different ligands. Rather, we believe that such an anomalously high value of k_r is due to the approximation introduced when k_{nr}(other vibr) is neglected in eq 3. For $[Tb(\mathbf{1})]^{3+}$, the term k_{nr}(other vibr) may be not negligible because of the presence of nine $-CH_2-$ groups, each of which is directly linked to the aliphatic nitrogens coordinated to the metal ion. Molecular models show that in the complexes of **1** some H atoms must indeed be very close

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(21) Horrocks, W. DeW., Jr.; Sudnick, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 334.

(22) Horrocks, W. Dew., Jr.; Sudnick, D. R. *Acc. Chem. Res.* **1981**, *14*, 384.

to the metal, so that some coupling with C–H vibrations may be effective. Assuming a radiative rate constant similar to that of the other complexes ($\cong$350 s^{-1}), k_{nr}(other vibr) results to be around 300 s^{-1}.

Upon LC excitation, $[\mathrm{Tb}(\mathbf{1})]^{3+}$ exhibits a quite high (Table II) luminescence quantum yield, Φ_{exp}, that can be expressed as

$$\Phi_{exp} = \eta_{et}\eta_{r} \tag{6}$$

In eq 6 η_{et} is the energy-transfer efficiency from $^1\pi\pi^*$ to $^5D_4$ (regardless of the actual path; see later) and η_r is the luminescence efficiency of $^5D_4$ defined as

$$\eta_r = k_r/\sum k \tag{7}$$

Taking k_r = 350 s^{-1} and k_{nr}(other vibr) $\cong$ 300 s^{-1} (see above), η_r is about 0.5. This means that the energy-transfer efficiency is not far from unity, as previously found for $[\mathrm{Tb}\subset\mathbf{2}]^{3+}$, where, however, Φ_{exp} is very low because of back metal-to-ligand energy transfer (high $k_{nr}(T)$).[4] If our interpretation concerning k_{nr}(other vibr) is correct, the use of a C-deuterated ligand would lead to a highly luminescent ($\Phi_{exp} \cong 0.75$) $[\mathrm{Tb}(\mathbf{1})]^{3+}$ species.

Finally, we would like to notice that in $[\mathrm{Tb}(\mathbf{1})]^{3+}$ ligand-to-metal energy transfer seems to take place from both the $^1\pi\pi^*$ level (as indicated from the low "initial" $^3\pi\pi^*$ concentration; Figure 3) and the $^3\pi\pi^*$ level (as shown by the short lifetime of the transient spectrum compared to that of $[\mathrm{Gd}(\mathbf{1})]^{3+}$; Table I).

$[\mathrm{Eu}(\mathbf{1})]^{3+}$. The energy-level diagram from this complex is schematized in Figure 4c. Again, LC fluorescence and phosphorescence cannot be observed, but it is reasonable to assume that the $^1\pi\pi^*$ and $^3\pi\pi^*$ levels have the same energy as in the Gd^{3+} complex. The transient absorption signal is negligible, and a strong MC luminescence is observed upon LC excitation. From the luminescence lifetimes gathered in Table II one can see that there are small temperature and solvent effects. Using the same procedure outlined above for the Tb^{3+} complex (eqs 1–5),[4,21,22] we obtain the values collected in Table III for the various rate constants. The value estimated for k_r is again higher than that obtained for other complexes (beside those shown in Table III, we may consider the following k_r values: $\mathrm{Eu_{aq}}^{3+}$, 300 s^{-1}; $[\mathrm{Eu}\subset 2.2.1]^{3+}$, 830 s^{-1}; $[\mathrm{Eu}\subset 2.2.1]^{3+}\cdot 2F^-$, 550 s^{-1}).[4] It is therefore likely that k_{nr}(other vibr) contributes to reduce substantially $\tau(D_2O)^{77K}$ (eq 3). From Table III, it results that k_{nr}(OH) is small (notice the high uncertainty on its value, which derives from the difference of two very close quantities; eq 5) and that $k_{nr}(T)$ is not negligible. Since the energy gap between the luminescent $^5D_0$ level and the lowest $^3\pi\pi^*$ LC level is very high (>5000 cm^{-1}), the temperature effect cannot be due to back energy transfer. Such an effect is likely associated to the presence of ligand-to-metal charge-transfer excited states that involve the electron pairs of the aliphatic nitrogens. Assuming that k_{nr}(other vibr) $\cong k_r$, from eq 7 it follows that η_r is about 0.2, so that η_{et} is about 0.25. This suggests that the originally excited $^1\pi\pi^*$ LC level can undergo efficient decay to the ground state via CT levels, as already discussed for $[\mathrm{Eu}\subset\mathbf{2}]^{3+}$.[4] Finally, we would like to note that **1** shields Eu^{3+} from solvent interactions much better that the analogous 1,4,7-triazacyclononane-*N,N',N''*-triacetate (also called NOTA) ligand. In the Eu(NOTA) complex, the average number of coordinated water molecules is 3.3,[20] whereas in $[\mathrm{Eu}(\mathbf{1})]^{3+}$ the average number of coordinate water molecules is about 0.3,[21] which means that there is at most only a small effect caused by water molecules distant from the metal ion.

Conclusions

The bpy-branched triazacyclonane ligand **1** shows intense absorption bands in the near-UV region and shields almost completely the Tb^{3+} and Eu^{3+} metal ions from solvent interactions. The $[\mathrm{Eu}(\mathbf{1})]^{3+}$ complex, however, does not exhibit good luminescence properties because of a poor ligand-to-metal energy-transfer efficiency and an activated radiationless decay of the luminescent $^5D_0$ level. It seems likely that such drawbacks are both associated with the presence of LMCT levels at relatively low energies, which involve the aliphatic nitrogens. For the Tb^{3+} complexes, where low-energy CT levels are not present, the luminescent quantum yield is very high (0.37). A further increase of the quantum yield (approximately, by a factor of 2) is expected upon deuteration of the $-CH_2-$ groups of the ligand.

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Registry No. **1**, 131294-89-8; $[\mathrm{Gd}(\mathbf{1})]\mathrm{Cl_3}$, 135733-36-7; $[\mathrm{Tb}(\mathbf{1})]\mathrm{Cl_3}$, 135733-37-8; $[\mathrm{Eu}(\mathbf{1})]\mathrm{Cl_3}$, 135733-38-9.