189. Luminescence Properties of Eu^{3+} Complexes of Tripode and Tetrapode Ligands Containing 2,2′-Bipyridine Units

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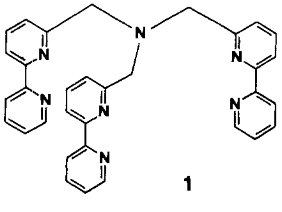
The Eu^{3+} complexes of the tripode and tetrapode ligands **1** and **2**, respectively, containing 2,2′-bipyridine coordinating units have been prepared. The UV absorption and luminescence spectra, lifetimes, and quantum yields have been measured under a variety of experimental conditions. The contributions of different paths to the decay of the luminescent excited state are evaluated, and the structures of the complexes are discussed on the basis of spectroscopic and photophysical data.

In the last few years, there has been a growing interest in the luminescence properties of Eu^{3+} species because of their potential use as probes and labels for a variety of chemical and biological applications [1–5]. To make use of the excellent emitting properties of the Eu^{3+} ion, one has to remedy for the lack of intense metal-centered absorption bands. Current research [6–14] is, therefore, oriented towards the use of ligands that exhibit intense absorption bands in the near-UV spectral region and have their lowest excited state sufficiently high in energy to be able to transfer excitation to the luminescence $^5D_0$ Eu^{3+} level. The 2,2′-bipyridine (bpy) chromophoric unit satisfies this requirements, since it exhibits an intense $^1\pi\pi^*$ absorption band around 280 nm and has its lowest excited state ($^3\pi\pi^*$) at *ca.* 23000 cm^{-1} (both the absorption band and the lowest excited state are somewhat displaced to lower energies upon metal coordination) [10] [15]. Eu^{3+}, however, exhibits a stronger coordinating ability for H_2O than for bpy so that in aqueous solution, Eu^{3+} complexes of the simple bpy ligand are not stable. Preorganized multidentate ligands made up by two ore more bpy units (*e.g.*, the bpy·bpy·bpy cryptand [6] [16]) are, therefore, used to obtain kinetically inert complexes which exhibit good luminescent properties.

Continuing our studies in this field, we have prepared the Eu^{3+} complexes of the tripode and tetrapode ligands **1** and **2** (which contain three and four bpy units, respectively), and we have studied their luminescence behavior.



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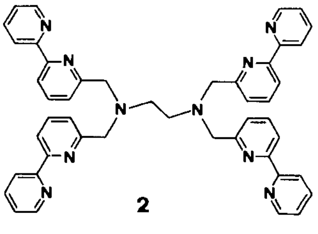

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Experimental. – *General.* The solvents used were triply distilled H_2O, spectroscopic grade MeOH (*Merck*), D_2O 99.5% (*Carlo Erba*), and MeOD 99.9% (*Carlo Erba*). UV spectra: *Kontron-Uvicon-860* spectrophotometer. Luminescence spectra: *Perkin-Elmer-LS5* spectrofluorimeter. Luminescence decays: *Perkin-Elmer-LS5* spectrofluorimeter or *Nd:YAG DLPY4 JK* laser. Luminescence quantum yields were obtained by the method described by *Haas* and *Stein* [18] using $[Ru(bpy)_3]^{2+}$ as a standard ($\Phi = 0.028$ in aerated soln.) [19].

Syntheses. The ligands **1** and **2** were obtained as previously described [17]. $[Eu(\mathbf{1})]Cl_3 \cdot 4\,H_2O$ and $[Eu(\mathbf{2})]Cl_3 \cdot H_2O$ were prepared by the following procedure: A suspension of the ligand (0.055 mM in 30 ml of CH_2Cl_2/MeOH 5:1) was added to an equimolar amount of $EuCl_3 \cdot 6\,H_2O$ dissolved in 2 ml of MeOH. All the solid was dissolved after heating for 1 h at 80°. The soln. was cooled to r.t. and the solvent evaporated. The pale yellow residue was dissolved in EtOH and the complex precipitated by slow diffusion of Et_2O.

{Tris[(2,2'-bipyridin-6-yl)methyl]amine}europium(III) Trichloride-Water(1/4) ($[Eu(\mathbf{1})]Cl_3 \cdot 4\,H_2O$): FAB-MS (positive mode; nitrobenzyl alcohol matrix): 744.0 ($[M - Cl]^+$), 709.0 ($[M - 2\,Cl]^+$). Anal. calc. for $C_{33}H_{27}Cl_3EuN_7 \cdot 4\,H_2O$: C 46.52, H 4.14, N 11.50; found: C 46.31, H 4.22, N 11.24.

{N,N,N',N'-Tetrakis[(2,2'-bipyridin-6-yl)methyl]ethylenediamine}europium(III) Trichloride-Water(1/1) ($[Eu(\mathbf{2})]Cl_3 \cdot H_2O$): FAB-MS (positive mode; NBA + acetone): 955.1 ($[M - Cl]^+$), 920.2 ($[M - 2\,Cl]^+$). Anal. calc. for $C_{46}H_{40}Cl_3EuN_{10} \cdot H_2O$: C 54.74, H 4.19, N 13.88; found: C 54.55, H 4.17, N 13.75.

Results and Discussion. – *Stability.* Both $[Eu(\mathbf{1})]^{3+}$ and $[Eu(\mathbf{2})]^{3+}$ are quite stable in MeOH solution. In aqueous solution, however, both compounds undergo decomposition as shown by changes in the UV spectra and, eventually, by the precipitation of free ligand. The decomposition is very slow for $[Eu(\mathbf{2})]^{3+}$, spectral changes becoming appreciable only after 1 h so that it has been possible to obtain data on the luminescence emission and the luminescence decay in aqueous solution. For $[Eu(\mathbf{1})]^{3+}$, the reaction is much faster: spectral variations already occur within a few min so that meaningful luminescence data could not be obtained for aqueous solutions. However, in MeOH/H_2O 4:1 (*v*/*v*), $[Eu(\mathbf{1})]^{3+}$ is much more stable, and lifetime data could be obtained.

UV Absorption Spectra. The UV spectrum of $[Eu(\mathbf{2})]Cl_3 \cdot H_2O$ in MeOH solution is shown in *Fig. 1*. As one can see, two absorption maxima are present at 243 and 301 nm (molar absorption coefficients 37000 and 42000 $M^{-1} \cdot cm^{-1}$, resp.), and there is a shoulder at *ca.* 310 nm. The UV spectrum of $[Eu(\mathbf{1})]Cl_3 \cdot 4\,H_2O$ in MeOH is identical to that of $[Eu(\mathbf{2})]Cl_3 \cdot H_2O$, except for somewhat lower absorption coefficients (24000 and 32000

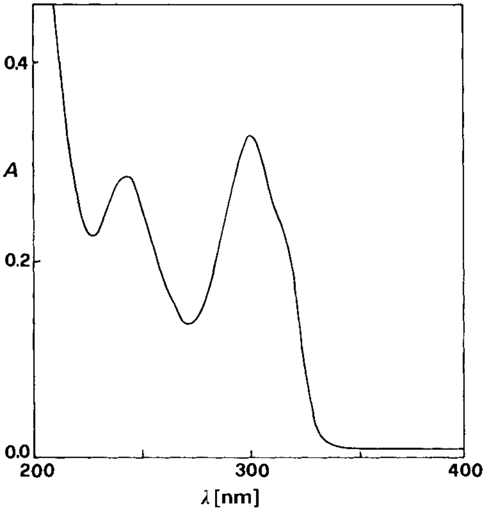

Fig. 1. *UV spectrum* (MeOH) *of* $[Eu(\mathbf{2})]Cl_3 \cdot H_2O$

$\mathrm{M}^{-1}\cdot\mathrm{cm}^{-1}$), as expected because of the smaller number of bpy units. In aqueous solution, the two maxima of [Eu(**2**)]Cl$_3$·H$_2$O are displaced to higher energies, $\lambda_{\max}$ 235 (ε = 35000 $\mathrm{M}^{-1}\cdot\mathrm{cm}^{-1}$) and 283 nm ($\varepsilon$ = 39500 $\mathrm{M}^{-1}\cdot\mathrm{cm}^{-1}$), and the shoulder disappears. The spectrum of [Eu(**1**)]Cl$_3$·4 H$_2$O immediately after dissolution in H$_2$O shows maxima at 237 and 285 nm and a shoulder at *ca.* 300 nm. Thus, for both complexes, there is a strong displacement of the ligand-centered bands towards higher energy in passing from MeOH to H$_2$O solutions. It can be noticed that such an effect is not observed for the $[\mathrm{Eu} \subset \mathrm{bpy}\cdot\mathrm{bpy}\cdot\mathrm{bpy}]^{3+}$ cryptate ($\lambda_{\max}$ 244 and 304 nm, both in H$_2$O and in MeOH) where the bpy units make a rigid cage around the metal ion.

It is known that the displacement towards lower energies of the $^1\pi\pi^*$ bpy band is related to the degree of perturbation induced by the coordinated metal ion [10]. Therefore, the above results indicate that the bpy chromophoric units are more affected by the presence of Eu^{3+} in MeOH solution than in aqueous solution. This may be due to a change in the structure of the complex in the two different solvents or, simply, to the decrease in the effective charge of the metal ion when H$_2$O replaces MeOH in the coordination positions left free by the bpy units. It should be noticed that, at least in the case of [Eu(**2**)]$^{3+}$, from the shape of the absorption bands there is no evidence of different types of bpy units (*e.g.*, 'coordinated' and 'dangling').

Luminescence Spectra. Excitation in the bpy absorption band around 300 nm causes the well known, structured emission of the Eu^{3+} ion, showing that energy transfer from ligand-centered to metal-centered levels takes place. The emission spectra of [Eu(**2**)]Cl$_3$·H$_2$O in H$_2$O and MeOH solutions at 300 K are shown in *Fig. 2*. Although the equipment used did not allow us to obtain high-resolution spectra, some interesting

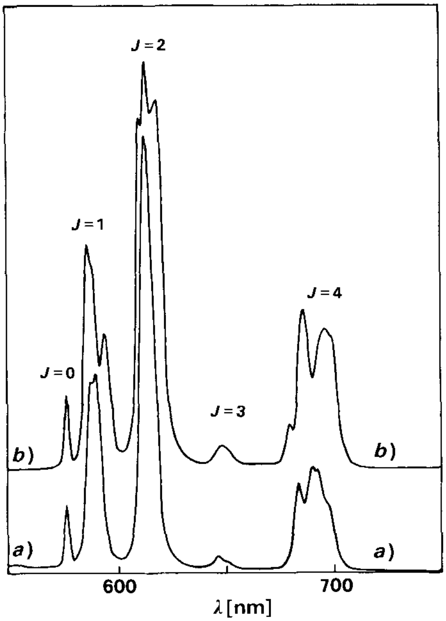

Fig. 2. *Luminescence spectra of [Eu(**2**)]Cl$_3$·H$_2$O in* a) *water and* b) *methanol.* The assignments of the various $0 \rightarrow J$ transitions of the $^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_J$ manifold are indicated.

conclusions can be drawn. The relatively high intensity of the O→O transition indicates that the Eu^{3+} ion does not lie in a centrosymmetric coordination site. The splitting of the components of the various O→J transitions is definitely more pronounced in MeOH than in H_2O, indicating that the Eu^{3+} ion experiences a lower-symmetry environment in the former solvent. The luminescence spectrum of the solid $[Eu(\mathbf{2})]Cl_3 \cdot H_2O$ is quite similar to that in MeOH solution, indicating again a lower symmetry with respect to the aqueous solution. The luminescence spectrum of $[Eu(\mathbf{1})]Cl_3 \cdot 4\,H_2O$ in MeOH solution shows 1, 2, and 2 components for $J = 1, 2$, and 3, respectively, which is consistent with the approximate C_{3v} symmetry expected on the basis of the ligand structure.

Excited-State Lifetimes and Luminescence Quantum Yields. The lifetimes of the luminescent excited states and the luminescence quantum yields have been measured under several experimental conditions. The results are summarized in the *Table* where some pertinent data previously obtained for the $[Eu \subset bpy \cdot bpy \cdot bpy]^{3+}$ cryptate are also shown for comparison purposes. As mentioned above, data for $[Eu(\mathbf{1})]^{3+}$ in aqueous solution are not available because of the instability of the complex. However, the data obtained in H_2O/MeOH 1:4 (v/v) (where the complex is sufficiently inert to be studied carefully) are likely very close to those that would have been obtained in H_2O since Eu^{3+} has a stronger coordination affinity for H_2O than for MeOH. For the bare Eu^{3+} ion under the same experimental conditions, the mole fraction of H_2O in the first solvation sphere is *ca.* 0.80 [20].

Table. *Luminescence Data*[a])

	$[Eu(\mathbf{1})]^{3+}$			$[Eu(\mathbf{2})]^{3+}$			$[Eu \subset bpy \cdot bpy \cdot bpy]^{3+}$[b])		
	77 K	300 K		77 K	300 K		77 K	300 K	
	τ [ms]	τ [ms]	Φ	τ [ms]	τ [ms]	Φ	τ [ms]	τ [ms]	Φ
H_2O				[c])	0.34	0.003	0.81	0.34	0.02
D_2O				[c])	1.8	0.014	1.7	1.7	0.10
H_2O/MeOH[d])	0.65	0.45		0.56					
D_2O/MeOD[d])	1.9	1.6		2.0					
MeOH	0.94	0.95	0.06	1.1	0.81	0.07			
MeOD	2.0	1.8	0.10	1.8	1.7	0.20			

[a]) Excitation at 300 nm; experimental errors: ±10% on lifetimes, ±30% on quantum yields.

[b]) From [10] [21] and unpublished results.

[c]) The measurement in water was prevented by the opacity of the matrix and the weak luminescence signal.

[d]) H_2O/MeOH 1:4 (v/v). Because of preferential solvation effects [20], the behavior in this mixed solvent is expected to be close to that in H_2O (see text).

In order to discuss the data shown in the *Table*, we need to recall [10] [21] that the $^5D_0$ luminescent excited state of Eu^{3+} can decay *via* radiative and radiationless transitions. The rate constant of the radiative transition, k_r, is usually temperature-independent, whereas the nonradiative decay may take place by a temperature-independent path (phonon-assisted conversion to the ground state), k_{nr}, and by a temperature-dependent path (activated crossing of the emitting level to short-lived excited states belonging to other electronic configurations), $k_{nr}(T)$. The lifetime of the luminescent excited state can thus be expressed by the following equation:

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

The main contribution to the phonon-assisted radiationless decay comes from coupling with high-energy vibrations of the ligands coordinated to Eu^{3+}. A particular role is, therefore, played by coordinated H_2O and MeOH solvent molecules, since they possess high-energy O–H vibrations. *Eqn. 1* can, thus, be rewritten as follows:

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

It should be noted that k_{nr}(OH) may indirectly depend on temperature since the number of coordinated solvent molecules (*i.e.*, the composition of the first coordination sphere) may be temperature-dependent. The contribution of the various terms which appear in *Eqn. 2* can be evaluated comparing the results obtained in non-deuterated and deuterated solvents, and at low and high temperature. In deuterated solvents, k_{nr}(OH) vanishes and k_{nr}(OD) is negligible, so that the value of k_{nr}(OH) can be evaluated from *Eqn. 3*

$$k_{nr}(\mathrm{OH}) = 1/\tau_{\mathrm{OH}} - 1/\tau_{\mathrm{OD}} \tag{3}$$

where τ_{OH} and τ_{OD} are the luminescence lifetimes in the non-deuterated and deuterated solvent, respectively. On the other hand, at 77 K, $k_{nr}(T)$ is negligible, so that k_{nr}(300 K) can be evaluated from *Eqn. 4*

$$k_{nr}(300\,\mathrm{K}) = 1/\tau_{\mathrm{OD}}^{300\,\mathrm{K}} - 1/\tau_{\mathrm{OD}}^{77\,\mathrm{K}} \tag{4}$$

From the *Table* one can see that for each compound, the luminescence lifetime in deuterated solvent is the same (within the experimental error) at 77 and 300 K. On the basis of *Eqn. 4*, we can conclude that at 300 K, $k_{nr}(T)$ is negligible. This is an expected result, since the lowest ligand-centered level lies more than 4000 cm^{-1} above the luminescent $^5D_0$ level [10], and the charge-transfer levels in the Eu-bpy compounds lie at even higher energies [10] [21]. Comparison of the data obtained in non-deuterated and deuterated solvents shows that k_{nr}(OH) plays an important role in the excited-state decay. The values of k_{nr}(OH) obtained from *Eqn. 3* under various experimental conditions are consistently 30–50% higher for $[Eu(\mathbf{2})]^{3+}$ than for $[Eu(\mathbf{1})]^{3+}$, indicating that the smaller ligand **1** leaves less room for solvent accessibility in the first coordination sphere. Using the empirical equation proposed by *Horrocks* and *Sudnick* [22] and the lifetime values in H_2O and D_2O at room temperature, the average number of coordinated H_2O molecules is calculated to be 2.5(±0.5) for $[Eu(\mathbf{2})]^{3+}$ which is the same value as obtained for the $[Eu \subset bpy \cdot bpy \cdot bpy]^{3+}$ cryptate [21]. Introducing in the *Horrocks* and *Sudnick* equation the lifetime values obtained in H_2O/MeOH and D_2O/MeOD, the number of coordinated H_2O molecules for $[Eu(\mathbf{1})]^{3+}$ results to be 1.7(±0.5). It is also interesting to note that for $[Eu(\mathbf{2})]^{3+}$, k_{nr}(OH) is 3.7 times higher in H_2O than in MeOH, and that for $[Eu(\mathbf{1})]^{3+}$, k_{nr}(OH) is 3.2 times higher in H_2O/MeOH than in pure MeOH. A higher deactivating effect by H_2O as compared to MeOH is indeed expected not only because each H_2O molecule carries two O–H oscillators, but also because the H_2O molecules, being smaller, can better fit the coordination sites left free by the bpy units. The very close values (3.7 and 3.2) of the above mentioned rate ratios support the hypothesis that the photophysical behavior in H_2O/MeOH solution is close to that in pure H_2O.

In MeOH solution, the values of the luminescence quantum yields are not very different for $[Eu(\mathbf{1})]^{3+}$ and $[Eu(\mathbf{2})]^{3+}$ if we consider the large experimental errors involved (±30%). For $[Eu(\mathbf{2})]^{3+}$, the luminescence quantum yield was measured also in H_2O, and it was found to be more than 25 times lower than in MeOH. This very strong solvent effect cannot be attributed to different k_{nr}(OH) values (which, as we have seen, only differ by a factor of *ca.* 4). In fact, a decrease of the quantum-yield value by a factor of *ca.* 10 is observed in going from MeOD to D_2O solution. Comparison with the data previously obtained for $[Eu \subset bpy \cdot bpy \cdot bpy]^{3+}$ (*Table*) shows that in H_2O, the quantum yield for [Eu(**2**)]$^{3+}$ is *ca.* 7 times lower in spite of the fact that the two complexes exhibit the same lifetime. These comparisons indicate that for [Eu(**2**)]$^{3+}$ the energy-transfer efficiency from the ligand-centered levels to the $^5D_0$ luminescent level is much smaller in aqueous solution than in MeOH solution.

Conclusions. – The results obtained indicate that the Eu^{3+} complexes of tripode and tetrapode bipyridine-type ligands undergo dissociation in aqueous solution. This confirms that the light-absorbing heterocyclic ligands have to be incorporated in macrocyclic [14] or macrobicyclic [4] [6] [16] structures to obtain really stable Eu^{3+} complexes. As it happens for other Eu^{3+} complexes of bpy-type ligands [10], the temperature-dependent path for deactivation of the luminescent $^5D_0$ level is negligible for both [Eu(**1**)]$^{3+}$ and [Eu(**2**)]$^{3+}$. Deactivation by coupling with the high-energy O–H vibrations is very efficient, and it plays a more important role for [Eu(**2**)]$^{3+}$ than for [Eu(**1**)]$^{3+}$, indicating that the smaller ligand **1** leaves less room for solvent accessibility in the first coordination sphere.

It has also been found that in [Eu(**2**)]$^{3+}$, the energy of the ligand-centered (bpy) band, the coordination symmetry of the Eu^{3+} ion, and the efficiency of energy transfer from the ligand-centered to the metal-centered excited states depend on the nature of the solvent (H_2O or MeOH). This may be due to a change in the number of solvent molecules participating to the first coordination sphere in the two different solvents or simply to a change in the properties of the Eu^{3+}-bpy bonds as a consequence of the different properties of the Eu^{3+}–MeOH and Eu^{3+}–H_2O bonds. The smaller perturbation of the ligand-centered band and the lower ligand→metal energy transfer efficiency seem to indicate that in aqueous solution, the bpy–Eu^{3+} distance is higher than in MeOH.

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