Inorg. Chem. **1993**, *32*, 1237-1241 **1237**

Dinuclear Eu^{3+}, Tb^{3+}, and Gd^{3+} Complexes of a Branched Hexaazacyclooctadecane Ligand Containing Six 2,2′-Bipyridine Pendant Units

Raymond Ziessel,[*,1a] **Mauro Maestri,**[*,1b] **Luca Prodi,**[1b] **Vincenzo Balzani,**[1b] **and Alain Van Dorsselaer**[1c]

Groupe de Matériaux Inorganiques, Ecole Européenne des Hautes Etudes des Industries Chimiques de Strasbourg, 1 rue Blaise Pascal, BP 296, 67000 Strasbourg, France, Dipartimento di Chimica "G. Ciamician" dell'Università, via Selmi 2, 40126 Bologna, Italy, and Laboratoire de Spectrometrie de Masse Bio-Organique, Faculté de Chimie, 1 rue Blaise Pascal, BP 296, 67000 Strasbourg, France

Received July 15, 1992

The dinuclear Eu^{3+}, Tb^{3+}, and Gd^{3+} complexes of a branched hexaazacyclooctadecane ligand containing six 2,2′-bipyridine (bpy) pendant units (**1**) have been prepared and characterized as chloride salts. Elemental analysis and FAB^+ mass spectrometry show unambiguously that in the solid state two lanthanide ions are complexed by one molecule of **1**. In CH_3CN and alcohol (ethanol/methanol, 5:1 v/v) solution, **1** exhibits a bpy-centered absorption band at 285 nm and a bpy-centered phosphorescence (77 K, λ = 435 nm, τ = 1 s). The $[Gd_2(\mathbf{1})]Cl_6$ complex shows an absorption band at 305 nm and a phosphorescence band at 455 nm with τ = 1.8 ms (at 77 K) in CH_3CN solution, whereas in alcohol solution it displays an absorption band at 286 nm and two phosphorescence bands (λ = 435 nm, τ = 1.2 s; λ = 455 nm, τ = 3.9 ms). The $[Eu_2(\mathbf{1})]Cl_6$ and $[Tb_2(\mathbf{1})]Cl_6$ complexes show an absorption band at 306 nm in CH_3CN and at 285 in alcohol and H_2O. In all the solvents used the metal-centered luminescence, characteristic of the Eu^{3+} and Tb^{3+} metal ions, can be observed. The excitation spectra (recorded at the wavelength of the metal centered emission) of the Eu^{3+} and Tb^{3+} complexes show a maximum at 306 nm in all solvents, which coincides with the absorption maximum in CH_3CN but not in alcohol and H_2O solution. The results obtained indicate that in CH_3CN solution an average of almost five bpy units per molecule of **1** are coordinated to the two metal ions in the $[M_2(\mathbf{1})]Cl_6$ complexes (M = Eu^{3+}, Tb^{3+}, Gd^{3+}), whereas in alcohol and water most of the pendant bpy branches are not coordinated. High-resolution spectra show that three $^5D_0 \rightarrow {}^7F_0$ bands are present for the $[Eu_2(\mathbf{1})]Cl_6$ complex in acetonitrile solution suggesting the presence of Eu^{3+} ions with one, two, and three coordinated bpy units. In acetonitrile at room temperature the lifetime of the metal-centered luminescent level is 0.73 ms for $[Eu_2(\mathbf{1})]Cl_6$ and 1.36 ms for $[Tb_2(\mathbf{1})]Cl_6$, and the luminescence quantum yield is about 0.02 in both cases. Decay measurements carried out in H_2O and D_2O show that in aqueous solution the most strongly luminescent Eu^{3+} and Tb^{3+} species have between 3- and 4-coordinated water molecules. Measurements carried out at 77 and 300 K show that the effects of thermally activated decay processes are relatively unimportant for both the Eu^{3+} and Tb^{3+} complexes.

Introduction

Eu^{3+} and Tb^{3+} complexes of bipyridine-type ligands have attracted much attention in the last few years because of their luminescence properties.[2-16] Absorption in the intense UV bands of bipyridine-type ligands can be followed by energy transfer to the strongly luminescent and long-lived excited states of the metal ion (antenna effect),[2,3] giving rise to molecular species that can be used as probes and labels for a variety of chemical and biological applications.[17-21]

A further step along this direction, as well as toward the design of photochemical molecular devices[22] capable of performing other light-induced functions, is the preparation of species that contain two lanthanide ions. We have used a branched hexaazacyclooctadecane ligand which contains six pendant 2,2′-bipyridine (bpy) units (**1**)[23] to prepare the first dinuclear lanthanide complexes of polypyridine-type ligands.

As shown in previous investigations,[5,11] a combined study of the free ligand and of its Gd^{3+}, Tb^{3+}, and Eu^{3+} complexes can give important pieces of information on the role played by various factors in determining the luminescence efficiency, since the energy level diagrams for the Gd^{3+}, Tb^{3+}, and Eu^{3+} complexes are quite different. The lowest excited state of Gd^{3+} lies above the low-energy ligand-centered (LC) levels of the bpy-type ligands. Therefore, in the Gd^{3+} complexes the LC fluorescence, phos-

---

(1) (a) EHICS, Strasbourg. (b) Università di Bologna. (c) Faculté de Chimie.

(2) Alpha, B.; Lehn, J.-M.; Mathis, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 266.

(3) Alpha, B.; Balzani, V.; Lehn, J.-M.; Perathoner, S.; Sabbatini, N. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1266.

(4) Sabbatini, N.; Perathoner, S.; Balzani, V.; Alpha, B.; Lehn, J.-M. In *Supramolecular Photochemistry*; Balzani, V., Ed.; Reidel: Dordrecht, The Netherlands, 1987; p 187.

(5) Alpha, B.; Ballardini, R.; Balzani, V.; Lehn, J.-M.; Perathoner, S.; Sabbatini, N. *Photochem. Photobiol.* **1990**, *52*, 299.

(6) Balzani, V.; Ballardini, R. *Photochem. Photobiol.* **1990**, *52*, 409.

(7) Pietraszkiewicz, M.; Pappalardo, S.; Finocchiaro, P.; Mamo, A.; Karpiuk, J. *J. Chem. Soc., Chem. Commun.* **1990**, 1907.

(8) Lehn, J.-M.; Pietraszkiewicz, M.; Karpiuk, J. *Helv. Chim. Acta* **1990**, *73*, 106.

(9) Balzani, V.; Berghmans, E.; Lehn, J.-M.; Sabbatini, N.; Therorde, R.; Ziessel, R. *Helv. Chim. Acta* **1990**, *73*, 2083.

(10) Balzani, V.; Lehn, J.-M.; Van Loosdrecht, J.; Mecati, A.; Sabbatini, N.; Ziessel, R. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 190.

(11) Prodi, L.; Maestri, M.; Ziessel, R.; Balzani, V. *Inorg. Chem.* **1991**, *30*, 3798.

(12) Prodi, L.; Maestri, M.; Balzani, V.; Lehn, J.-M.; Roth, C. *Chem. Phys. Lett.* **1991**, *180*, 45.

(13) Bünzli, J.-C. G. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Jr., Eyring, L., Eds.; Elsevier: Amsterdam, 1987; Vol. 9, Chapter 60.

(14) Buonocore, G. E.; Li, H. *Coord. Chem. Rev.* **1990**, *99*, 55.

(15) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Horwood: Chichester, England, 1991.

(16) Sabbatini, N.; Guardigli, M.; Lehn, J.-M. *Coord. Chem. Rev.*, in press.

(17) Richardson, F. S. *Chem. Rev.* **1982**, *82*, 541.

(18) Horrocks, W. DeW., Jr.; Albin, M. *Prog. Inorg. Chem.* **1984**, *31*, 1.

(19) Hemmila, I. A. *Application of Fluorescence in Immunoassay*; Winefordner, J. D., Ed.; Wiley: New York, 1991.

(20) Lehn, J.-M. In *Supramolecular Photochemistry*; Balzani, V., Ed.; Reidel: Dordrecht, The Netherland, 1987; p 29.

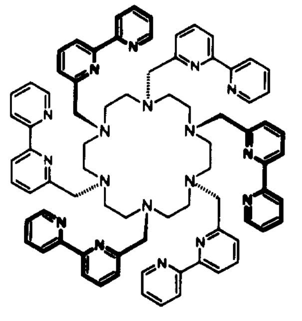
(21) Bünzli, J.-C. G. In *Lanthanide Probes in Life, Medical, and Environmental Sciences*; Choppin G. R., Bünzli, J.-C. G., Eds.; Elsevier: Amsterdam, The Netherland, 1989; Chapter 7.

(22) Reference 15, Chapter 12.

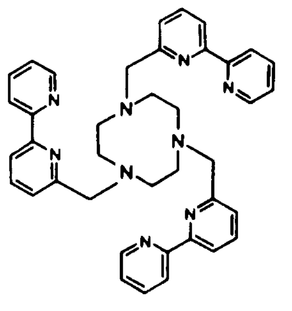
(23) Ziessel, R.; Lehn, J.-M. *Helv. Chim. Acta* **1990**, *73*, 1149.

0020-1669/93/1332-1237$04.00/0

Chart I



1



2

phorescence, and triplet–triplet absorption can usually be observed. By comparison with the corresponding data for the free ligand, one can thus obtain information on the behavior of the LC levels under the perturbation caused by metal coordination. In the Tb^{3+} complexes the lowest (luminescent) metal-centered (MC) level lies below the lowest LC level. Following excitation in the LC bands, ligand-to-metal energy transfer can occur and MC luminescence can be observed. In some cases, however, the energy gap between the lowest LC and MC levels is small and back energy transfer can take place.[5,16] Finally, in Eu^{3+} complexes the lowest (luminescent) MC level lies at considerably lower energy than the lowest LC level. Therefore, ligand-to-metal energy transfer is irreversible in these complexes, but complications may arise[11,16] from the presence of low-energy ligand-to-metal charge transfer (LMCT) levels since Eu^{3+} can be quite easily reduced.

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 facilitate the nonradiative decay of the luminescent MC level.[18] Such a shielding effect is also of the greatest importance in the design of lanthanide-based contrast agents for magnetic resonance imaging.[24]

In this paper, the results obtained for the dinuclear complexes of **1** (Chart I) are compared with those previously obtained[11] for the mononuclear complexes of the branched triazacyclononane ligand **2** which contains three pendant bpy units.

Experimental Section

The 1,4,7,10,13,16-hexakis[(2,2′-bipyridin-6-yl)methyl]-1,4,7,10,13,-16-hexaazacyclooctodecane ligand, **1**, was prepared in 70% yield from an adapted literature procedure.[23]

$[Gd_2(\mathbf{1})]Cl_6{\cdot}6H_2O$, $[Tb_2(\mathbf{1})]Cl_6{\cdot}8H_2O$, and $[Eu_2(\mathbf{1})]Cl_6{\cdot}8H_2O$ were prepared by the following procedure. A solution of ligand **1** (0.063 mM, 1 equiv in 15 mL of CH_2Cl_2) was dropwise added to a refluxing solution of the lanthanide salt ($MCl_3{\cdot}6H_2O$, M = Eu, Tb, Gd; 2.2 equiv in 15 mL of MeOH). After 1 h of heating, the solution was weakly fluorescent when irradiated with 365-nm light, whereas a strong fluorescence was observed after 15 h of reflux. The solution was cooled to room temperature and concentrated to one-third of its volume. Addition of EtOH caused the precipitation of free ligand as confirmed by ^{1}H-NMR and its UV absorption spectrum (in CH_2Cl_2, λ_{max} at 286 nm (ϵ = 82 400 M^{-1} cm^{-1}) and 239 nm (ϵ = 59 000 M^{-1} cm^{-1})). After recovery of the ligand by filtration, the resulting solution was evaporated to dryness. The solid was dissolved in ethanol and the complex recrystallized twice by slow diffusion of diethyl ether into the solution, giving the pure dinuclear complexes (yields: 20% for Eu, 28% for Tb, and 25% for Gd).

The complexes were characterized by FAB^+ spectroscopy and elemental analysis.

$[Eu_2(\mathbf{1})]Cl_6{\cdot}8H_2O$: FAB^+ (*m*-nitrobenzyl alcohol (*m*-NBA) matrix) *m/z* 1746.8 (M – Cl), 1711.8 (M – 2Cl), 1676.7 (M – 3Cl), 855.8 (M – 2Cl/2, doubly charged), 838.4 (M – 3Cl/2, doubly charged). Anal. Calcd for $C_{78}H_{78}N_{18}Eu_2Cl_6{\cdot}8H_2O$: C, 48.58; H, 4.91; N, 13.08; Cl, 11.03. Found: C, 48.43; H, 4.89; N, 12.97; Cl, 10.69.

$[Tb_2(\mathbf{1})]Cl_6{\cdot}8H_2O$: FAB^+ (*m*-NBA) *m/z* 1761.3 (M – Cl), 1726.3 (M – 2Cl), 1593.2 (M – Cl – CH_2bpy + H), 1557.3 (M – 2Cl – CH_2bpy), 1497.5 (M – 3Cl – Tb), 1327.5 (M – 3Cl – Tb – CH_2bpy – H), 863.2 (M – 2Cl/2, doubly charged). Anal. Calcd for $C_{78}H_{78}N_{18}Tb_2Cl_6{\cdot}8H_2O$: C, 48.23; H, 4.88; N, 12.98; Cl, 10.95. Found: C, 48.02; H, 4.91; N, 12.83; Cl, 10.62.

$[Gd_2(\mathbf{1})]Cl_6{\cdot}6H_2O$: FAB^+ (*m*-NBA) *m/z* 1759.2 (M – Cl), 1724.3 (M – 2Cl), 1589.2 (M – Cl – CH_2bpy + H), 1554.2 (M – 2Cl – CH_2bpy), 861.2 (M – 2Cl2, doubly charged). Anal. Calcd for $C_{78}H_{78}N_{18}Gd_2Cl_6{\cdot}6H_2O$: C, 49.23; H, 4.77; N, 13.25; Cl, 11.18. Found: C, 48.99; H, 4.52; N, 13.09; Cl, 10.92.

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

The absorption spectra were recorded with a Perkin-Elmer Lambda 6 spectrophotometer. The luminescence spectra were measured with the spectrofluorometers Perkin-Elmer LS50 and Perkin-Elmer 650-40, both equipped with a Hamamatsu R 928 phototube. Luminescence decays, which were measured with a Perkin-Elmer LS50 spectrofluorometer, could be fitted by a single exponential. Luminescence quantum yields were obtained with a Perkin-Elmer 650-40 spectrofluorometer following the method described by Haas and Stein[25] using as standards $Ru(bpy)_3^{2+}$ (Φ = 0.028 in aerated water)[26] for the Eu^{3+} complex and quinine sulfate (Φ = 0.546 in 1 N H_2SO_4)[27] for the Tb^{3+} complex. High-resolution emission spectra were obtained by a Jasco R300 Raman spectrophotometer using a filtered (260–350-nm band pass filter) Xenon lamp as an excitation source.

Results

1 is only slightly soluble in water, but it can be easily dissolved in alcohol (EtOH/MeOH, 5:1 v:v) and CH_3CN. In all these solvents at room temperature the absorption spectrum of **1** shows a maximum at 285 nm, (ϵ = 83 000 M^{-1} cm^{-1}) (Table I); in H_2O, this absorption band shows a pronounced red tail. The emission spectrum shows a very weak and broad band in the 350–500-nm region. At 77 K, in alcohol and CH_3CN the emission spectrum is intense and structured, with the highest energy feature at 435 nm (τ = 1 s). In H_2O, the spectrum at 77 K is very weak and similar to that shown at room temperature.

$[Gd_2(\mathbf{1})]Cl_6$, $[Tb_2(\mathbf{1})]Cl_6$, and $[Eu_2(\mathbf{1})]Cl_6$ can be dissolved in H_2O, alcohol, and CH_3CN. The solutions are stable in the dark, at least over 1 week.

FAB^+ mass spectroscopy carried out with the $[Eu_2(\mathbf{1})]^{6+}$ complex in CH_3OH solution showed the absence of the characteristic molecular peaks at *m/z* 1746.8 and at 1711.8 (for $[Eu_2(\mathbf{1})Cl_5]$ and $[Eu_2(\mathbf{1})Cl_4]$), but the presence of some mononuclear species at *m/z* 1453.2 (for $[Eu(\mathbf{1})Cl]$) and a huge amount of the free ligand at *m/z* 1267.6 (for [**1** + H]). Free ligand (ca. 20%) was isolated from $[Eu_2(\mathbf{1})]^{6+}$ solution in H_2O/CH_3OH by extraction with CH_2Cl_2 followed by silica gel chromatography and characterized by its ^{1}H-NMR and UV absorption spectra. No free ligand could be detected and extracted by dissolution of the dinuclear europium complex in a CH_3CN solution.

The absorption spectra of the three complexes in CH_3CN display a band at 306 nm. In H_2O and alcohol the band maximum is at 285 nm (Table I). In alcohol, a shoulder is also present at ~315 nm ($\epsilon \simeq$ 10 000 M^{-1} cm^{-1}). For illustration purposes, the absorption spectra of $[Gd_2(\mathbf{1})]Cl_6$ in alcohol and CH_3CN are displayed in Figure 1a, and the absorption spectra of **1** and $[Eu_2(\mathbf{1})]Cl_6$ in alcohol are shown in Figure 2.

At room temperature the Gd^{3+} compound exhibits a very weak luminescence in H_2O, alcohol, and CH_3CN, with a maximum around 350 nm. In rigid matrix at 77 K a structured luminescence band can be observed in H_2O and CH_3CN with the highest energy feature at 455 nm (τ = 2.4 and 1.8 ms, respectively). In ethanol/methanol mixture, besides the band with its highest energy feature at 455 nm (τ = 3.9 ms), a long-lived (τ = 1.2 s) emission with

---

(24) Lauffer, R. B. *Chem. Rev.* **1987**, *87*, 901.

(25) Haas, Y.; Stein, G. *J. Phys. Chem.* **1971**, *75*, 3668.

(26) Nakamaru, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2697.

(27) Meech, S. R.; Philips, D. *J. Photochem.* **1983**, *23*, 193.

Table I. Ligand-Centered Absorption and Emission Data

	absorption λ_{max} nm (ϵ, M^{-1} cm^{-1})			77 K emission λ_{max}, nm[a] (τ, ms)		
	H_2O	alcohol[b]	CH_3CN	H_2O	alcohol[b]	CH_3CN
1	285	285 (83 000)	285 (83 000)	*c*	435 (1.0 × 10^3)	435 (1.0 × 10^3)
	237	236 (59 000)	238 (59 000)			
[Gd_2(**1**)]Cl_6	285 (51 000)	286[d] (51 000)	306 (52 000)		435 (1.2 × 10^3)	
	237 (40 900)	236 (40 900)	244 (50 500)	455 (2.4)	455 (3.9)	455 (1.8)
[Tb_2(**1**)]Cl_6	285 (59 200)	285[d] (57 000)	306 (60 400)	*e*	*e*	*e*
	238 (47 600)	240 (63 500)	242 (57 900)			
[Eu_2(**1**)]Cl_6	285 (54 000)	285[d] (48 000)	306 (49 000)	*e*	*e*	*e*
	237 (39 000)	238 (39 300)	245 (40 700)			

[a] Highest energy feature. [b] Ethanol/methanol, 5:1 v/v. [c] Weak and broad band in the 350–500-nm region. [d] A shoulder is present at ≃315 nm. [e] Only the metal-centered luminescence (Table II) can be observed.

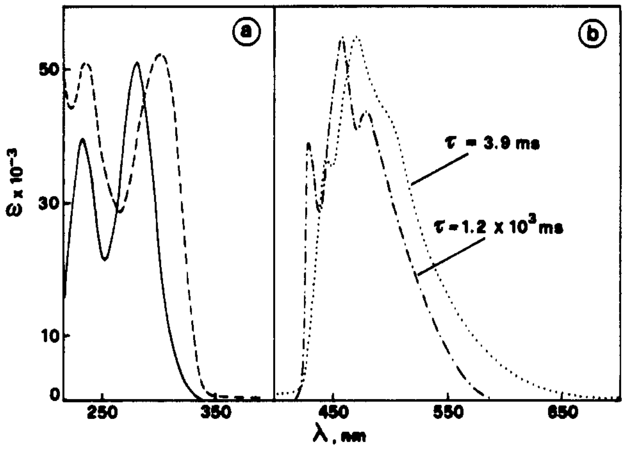


Figure 1. (a) Room-temperature absorption spectra of [Gd_2(**1**)]Cl_6 in alcohol (—) and acetonitrile (- - -) solution. (b) Time-resolved luminescence spectra at 77 K of [Gd_2(**1**)]Cl_6 in alcohol. The curves are labeled with their decay lifetimes.

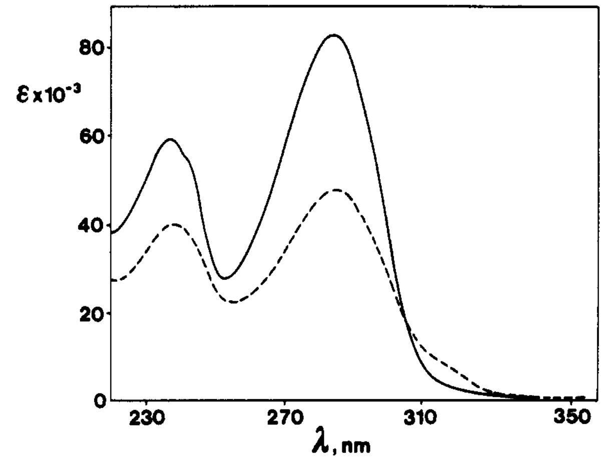


Figure 2. Absorption spectra of **1** (—) and [Eu_2(**1**)]Cl_6 (- - -) in alcohol at room temperature.

its high-energy feature at 435 nm can also be time-resolved (Figure 1b). The excitation spectra of the short-lived and long-lived emissions show maxima at 306 and 285 nm, respectively.

[Tb_2(**1**)]Cl_6 and [Eu_2(**1**)]Cl_6 in CH_3CN solution at room temperature show an intense and structured luminescence in the visible region, characteristic of the Tb^{3+} and Eu^{3+} metal ions, with the highest energy feature at 488 and 578 nm, respectively. Under such conditions the excitation spectra (λ_{max} ≃ 305 nm for both complexes) are similar to the absorption spectra, but slightly less intense in the 270–290-nm region. Figure 3 shows the absorption, emission, and excitation spectra of [Tb_2(**1**)]Cl_6 in CH_3CN solution at room temperature. In H_2O and alcohol the excitation spectra continue to exhibit a maximum at 306 nm, which strongly contrasts with the maximum of the absorption spectrum (285 nm) in these solvents. High-resolution spectra carried out on [Eu_2(**1**)]Cl_6 in the region of the $^5D_0 \rightarrow {}^7F_0$ transition have evidenced the presence of one band in aqueous solution (17 258 cm^{-1}) and three well-resolved bands in CH_3CN (17 229, 17 240, and 17251 cm^{-1}).

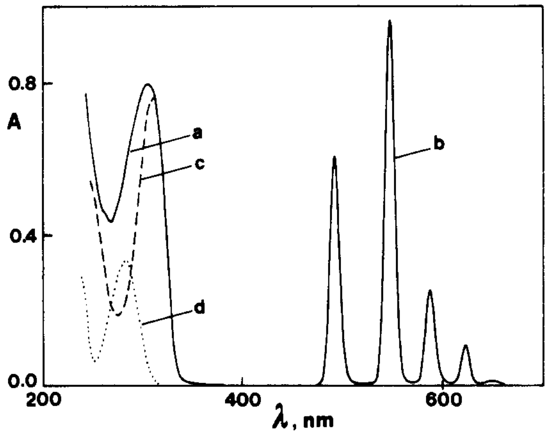


Figure 3. Absorption (**a**, —), emission (**b**, —), excitation (**c**, - - -), and differential (see text) (**d**, ···) spectra of [Tb_2(**1**)]Cl_6 in CH_3CN solution at room temperature.

The Tb^{3+} and Eu^{3+} complexes in rigid CH_3CN matrix at 77 K display only the structured metal-centered luminescence. In alcohol solution, however, a band is also present with its highest energy feature at 435 nm, very similar to that exhibited by the free ligand in alcohol and CH_3CN and by the Gd^{3+} complex in alcohol. Data concerning the absorption and emission spectra and the luminescence decays at room temperature and at 77 K are gathered in Tables I and II.

Discussion

The characterization of the [M_2(**1**)]Cl_6 (M = Gd^{3+}, Tb^{3+}, Eu^{3+}) complexes by FAB^+ mass spectrometry and microanalysis unambiguously shows complexation of two cations per molecule of **1**, without free **1** molecules (see e.g. Figure 4). Looking at a space-filling model of **1**, one can see that two metal ions can be lodged on opposite sides of the plane defined by the hexaazacyclooctadecane macrocyclic ring, each one being surrounded by three bpy units. This coordination arrangement is schematized in Figure 5a. The space-filling model of this geometrical arrangement shows that the coordination sphere offered by three (alternating) N-atoms of the ring and three (alternating) bpy units is larger than that required for coordination of a metal ion of the size of Gd^{3+}, Tb^{3+}, and Eu^{3+}. A much more suitable coordination sphere is offered by the previously investigated triazacyclononane-based ligand **2**. From space-filling models it can also be seen that an alternative geometrical arrangement for the dinuclear complexes of **1**, which utilizes three contiguous bpy units on each side of the plane (Figure 5b), would also be not ideal for metal ion coordination. These simple considerations suggest that the dinuclear complexes can be less stable than the complexes of **2** or of other cage-type ligands.[11,16] The results

Table II. Metal-Centered Luminescence[a]

	77 K (τ, ms)			300 K (τ, ms)			300 K (Φ)	
	$\tau(H_2O)$	$\tau(D_2O)$	$\tau(CH_3CN)$	$\tau(H_2O)$	$\tau(D_2O)$	$\tau(CH_3CN)$	$\Phi(H_2O)$	$\Phi(CH_3CN)$
$[Tb_2(\mathbf{1})]Cl_6$	0.71	2.12	1.74	0.70	1.56	1.36	0.003	0.015
$[Tb(\mathbf{2})]Cl_3$	1.4	1.5		1.5	1.5		0.37	
$[Eu_2(\mathbf{1})]Cl_6$	0.30	1.78	1.02	0.23	1.89	0.73	0.002	0.020
$[Eu(\mathbf{2})]Cl_3$	0.87	1.1		0.50	0.57		0.05	

[a] λ_{exc} = 306 nm.

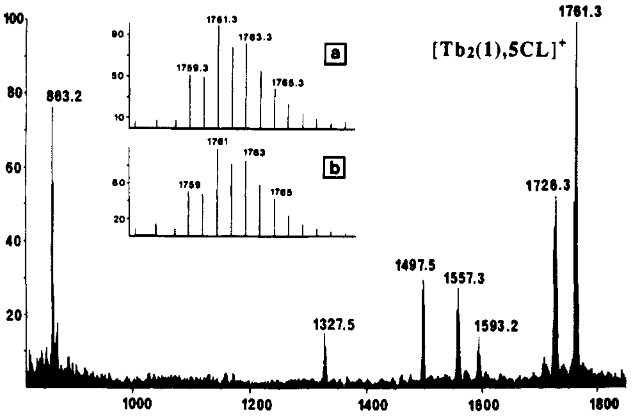


Figure 4. FAB$^+$ mass spectrum of $[Tb_2(\mathbf{1})]Cl_6{\cdot}8H_2O$ in *m*-NBA. Doubly charged ions are observed at *m*/*Z* 863.2. Inserts: (a) Isotopic profile of the molecular peak at *m*/*Z* 1761.3; (b) computerized isotopic profile for $C_{78}H_{78}N_{18}Cl_5Tb_2$.

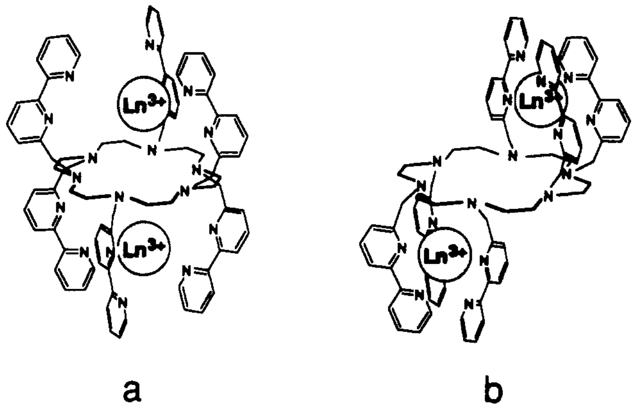


Figure 5. Schematic representation of possible coordination arrangements in the dinuclear complexes.

obtained show that this is indeed the case, especially in solution of strongly coordinating solvents.

Coordination of the bpy Units. Besides solvent extraction and FAB$^+$ mass spectra, we have performed three types of measurements that can throw light on the extent of metal–bpy coordination in solution: (i) absorption spectra; (ii) emission spectra; (iii) excitation spectra. In the following discussion, we will make the reasonable assumption that each bpy unit exhibits its own characteristic absorption, emission, and energy-transfer properties regardless of the other bpy units. Such properties, of course, depend on whether the bpy unit is free or coordinated to the metal ion.

Previous investigations have shown that the 285-nm absorption band of uncoordinated bpy ligands is displaced to longer wavelength upon coordination to a lanthanide ion (from 299 to 311 nm, depending on the degree of ligand–metal interaction).[4,5,9-12] In CH_3CN solution the $[M_2(\mathbf{1})]Cl_6$ complexes ($M = Gd^{3+}, Eu^{3+}$, and Tb^{3+}) display a band at 306 nm. Therefore, under such conditions most of tbe bpy units (four out of five; vide infra) are coordinated to the two metal centers, as confirmed by FAB$^+$ mass spectrometry in CH_3CN solution for the europium complex. The reverse is true for H_2O and alcohol solutions, where the complexes display an absorption band at 285 nm (Figure 1), as does the free ligand **1** (Figure 2), with a shoulder around 315 nm in alcohol. In these solvents, therefore, most of the bpy units are not coordinated. As one can see from Figure 2, the molar absorption coefficient of the free ligand **1** is small at 306 nm, where the bpy-coordinated units show their absorption maximum. For $[Eu_2(\mathbf{1})]^{6+}$, assuming that only the bpy-coordinated units absorb at 306 nm and taking a value of 61 300 M^{-1} cm^{-1} (vide infra) at 306 nm for the fully coordinated **1**, from the spectrum of the complexes in alcohol one can estimate that about $^1/_6$ of the bpy units are coordinated. This is in agreement with the results of FAB$^+$ mass spectrometry and solvent extraction which showed the presence of some mononuclear species and free ligand. In H_2O, the fraction of coordinated bpy units is likely smaller, but it cannot be evaluated because the absorption spectrum of **1** in H_2O shows a pronounced red tail, presumably due to a stacking interaction between bpy units.[28]

The luminescence results are fully consistent with the above conclusions. Luminescence, in fact, can give important pieces of information on the occurrence and extent of bpy–metal coordination. In the Gd^{3+}-bpy complexes, the lowest excited state is a luminescent $^3\pi\pi^*$ bpy-centered level, which is perturbed by the metal when coordination takes place. On the other hand, in the Eu^{3+} and Tb^{3+} complexes the metal centered luminescence is "pumped" by light absorption by the *coordinated* bpy units; as a consequence, the excitation spectrum in the bpy absorption region of the metal-centered emission can also give information on the occurrence and extent of metal–ligand coordination.

As we have seen above, the free ligand **1** at 77 K exhibits a structured luminescence spectrum in alcohol and CH_3CN, with the highest energy feature at 435 nm and τ = 1 s. This is the characteristic phosphorescence emission of the lowest $^3\pi\pi^*$ bpy level.[29] For CH_3CN solutions of $[Gd_2(\mathbf{1})]Cl_6$ at 77 K, only a perturbed ligand-centered phosphorescence band (λ = 455 nn, τ = 1.8 ms) can be observed, indicating that most of the bpy units are affected by (i.e., coordinated to) the metal ion. In alcohol solution, however, both the perturbed and the unperturbed ligand-centered emissions can be observed (Figure 1), which indicates that some bpy units are coordinated and some are not coordinated. The reason why in water only the perturbed phosphorescence can be seen is not due to the absence of uncoordinated bpy units (which, in fact, are predominant) but to the intrinsic lack of phosphorescence of free bpy in this solvent (see Results). Further evidence of bpy–metal coordination is given by the presence of bpy-centered fluorescence at 350 nm in the room-temperature solutions of $[Gd_2(\mathbf{1})]Cl_6$, in contrast with the broad and weak luminescence band of the free ligand (presumably due to stacking interaction, absent in the coordinated ligands).

In the Eu^{3+} and Tb^{3+} complexes, the excitation spectrum of the metal-centered luminescence shows a maximum at 306 nm in all the solvents used, which coincides with the absorption maximum in CH_3CN solution but not with the absorption maximum (285 nm) in water or alcohol. This result shows that (i) only the coordinated bpy units can transfer energy to the luminescent metal ions and (ii) most of the bpy units are

---

(28) 2,2′-Bypiridine is known to give rise to aggregates in several experimental conditions; see, e.g.: Dhanya, S.; Bhattacharyya, P. K. *J. Photochem. Photobiol. A: Chem.* **1992**, *63*, 179.

(29) De Armond, M. K.; Hillis, J. E. *J. Chem. Phys.* **1971**, *54*, 2247.

coordinated in CH_3CN solution and uncoordinated in water and alcohol. Comparison between the absorption and excitation spectra in CH_3CN solution (Figure 3 for the case of $[Tb_2(\mathbf{1})]Cl_6$) shows that the matching is excellent above 310 nm, where the absorption of uncoordinated bpy units is negligible (Figure 2), but not so good below 300 nm, where the uncoordinated bpy units exhibit their absorption maximum. On the reasonable assumption that the efficiency of ligand-to-metal energy transfer does not depend on the excitation wavelength for the bpy-coordinated units, the excitation spectrum can be used as a model of the absorption spectrum of coordinated bpy. Subtraction of the normalized excitation spectrum from the absorption spectrum (Figure 3) yields a spectrum with maximum at 285 nm, indicating that a fraction of uncoordinated bpy units is in fact present. By using the molar absorption coefficient of free **1** in CH_3CN, the fraction of uncoordinated bpy units for $[Tb_2(\mathbf{1})]Cl_6$ in CH_3CN solution results to be $^1/_5$. A similar value is obtained for $[Eu_2(\mathbf{1})]Cl_6$. Since for the latter compound the high-resolution luminescence spectrum shows that at least three species are present, the above result reflects the *average* number (4 out of 5) of bpy units of each ligand **1** that are coordinated to the metal ions in the various species present in CH_3CN solution. The result concerning the fraction of coordinated bpy units allows us to conclude that the molar absorption coefficient for fully coordinated **1** is $^5/_4$ times that observed for the $[Tb_2(\mathbf{1})]Cl_6$ and $[Eu_2(\mathbf{1})]Cl_6$ complexes in CH_3CN, i.e. 75 500 and 61 300 $M^{-1}\ cm^{-1}$, respectively. This is the value used above to estimate the fraction of coordinated bpy units in alcohol solution.

Metal-Centered Luminescence. It is well-known that Eu^{3+} (or Tb^{3+}) species with different coordination environment display different luminescence spectra and luminescence lifetimes. In view of the presence of several species in the $[Eu_2(\mathbf{1})]Cl_6$ and $[Tb_2(\mathbf{1})]Cl_6$ solutions, a multiexponential decay for the metal-centered luminescence could be expected. This, however, does not seem to be the case. Rather than to an equilibration of the various species within the excited-state lifetime (which would not be possible at least in rigid matrix), we believe that the monoexponential decay originates for the following reasons. In CH_3CN solution the excited-state lifetime should not be much influenced by replacing bpy ligands with solvent molecules since the frequency of the C–N vibration in the CH_3CN "ligand" is only ca. 2200 cm^{-1}, practically uneffective for the deactivation of the MC excited states.

For aqueous solutions the absorption spectra of $[Eu_2(\mathbf{1})]Cl_6$ and $[Tb_2(\mathbf{1})]Cl_6$ show that, as we have seen above, the average number of coordinated bpy units per ligand is lower than 1. It follows that the by far predominant bpy-containing species must have a 1:1 bpy-unit/metal-ion ratio. Thus, excitation at 306 nm concerns practically only this species. The observed monoexponential decay in aqueous solution is also in agreement with the presence of only one $^5D_0 \rightarrow {}^7F_0$ band in the high-resolution spectrum of $[Eu_2(\mathbf{1})]Cl_6$.

As far as the MC luminescence of $[Eu_2(\mathbf{1})]Cl_6$ and $[Tb_2(\mathbf{1})]Cl_6$ is concerned, a comparison with the data previously obtained[11] for the complexes of **2** (Table II) is instructive. For the complexes of **2**, the luminescence lifetimes in H_2O and D_2O are practically the same, indicating that **2** shields the metal ion almost completely from interaction with the solvent molecules. For the complexes of **1**, however, the lifetime values are very different and application of the Horrocks relationship[18] shows that three or four water molecules belong to the first coordination sphere in the luminescent species (which, as we have seen above, contains only one coordinated bpy unit per metal ion).

Comparison between the lifetime values at 77 and 300 K (in D_2O and CH_3CN) shows that for $[Eu_2(\mathbf{1})]Cl_6$ the thermally activated radiationless decay path ($k_{nr}(T) \simeq 400\ s^{-1}$) is less important than for $[Eu(\mathbf{2})]Cl_3$($k_{nr}(T) = 840\ s^{-1}$).[11] This indicates that in the Eu^{3+} complex of **2** a LMCT level (involving the nitrogen atoms of the aliphatic ring) lies at lower energy than in the Eu^{3+} complex of **1**.

For $[Tb(\mathbf{2})]Cl_3$, the luminescence lifetime in D_2O at 77 and 300 K are identical, showing that no temperature-dependent contribution to the excited-state decay is present. This result is in agreement with the large energy gap (2200 cm^{-1}) between the luminescent $^5D_4$ Tb^{3+} level and the higher lying $^3\pi\pi^*$ LC level.[11] For $[Tb_2(\mathbf{1})]Cl_6$, a small temperature dependence of the excited-state lifetime is observed (Table II), which is consistent with the smaller energy gap (1500 cm^{-1}) between the $^5D_4$ and the $^3\pi\pi^*$ level (and the consequent occurrence of back energy transfer).

The luminescence quantum yields for $[Eu_2(\mathbf{1})]Cl_6$ and $[Tb_2(\mathbf{1})]Cl_6$ in water are very low (Table II). This is not surprising because most of the exciting light at 306 nm is absorbed by uncoordinated bpy units. The values observed in CH_3CN are in fact much larger because in this solvent most of the bpy units, which are responsible for the 306 nm absorption, are coordinated.

Acknowledgment. We thank Prof. G. Fini for the high-resolution spectra, V. Cacciari, G. Gubellini, and F. Minghetti for technical assistance, and R. Hueber for helpful discussion. This work was supported by the Ministero della Università e della Ricerca Scientifica e Tecnologica, the Progetto Finalizzato Chimica Fine II del CNR, and the Centre National de la Recherche Scientifique.