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Structural and Photophysical Properties of Lanthanide Complexes with Planar Aromatic Tridentate Nitrogen Ligands as Luminescent Building Blocks for Triple-Helical Structures

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The ligand 2,6-bis(1-methylbenzimidazol-2-yl)pyridine (mbzimpy, **1**) reacts with lanthanide perchlorate in acetonitrile to give the successive complexes $[\mathrm{Ln(mbzimpy)}_n]^{3+}$ (n = 1–3). Tris complexes were isolated for La, Eu, Gd, and Tb, while a bis complex only could be crystallized for Lu. The crystal structure of $[\mathrm{Lu(mbzimpy)_2(H_2O)(CH_3OH)}](\mathrm{ClO_4})_3\cdot 3\mathrm{CH_3OH}$ (**12**, $\mathrm{LuC_{46}H_{52}N_{10}O_{17}Cl_3}$, a = 13.140(3) Å, b = 22.007(4) Å, c = 18.927(7) Å, β = 107.53(1)°, monoclinic, $P2_1/c$, Z = 4) shows three uncoordinated $\mathrm{ClO_4^-}$ anions and a $[\mathrm{Lu(mbzimpy)_2(H_2O)(CH_3OH)}]^{3+}$ cation where Lu(III) is eight-coordinated by two meridional tridentate mbzimpy ligands, one methanol molecule, and one water molecule, leading to a low-symmetry coordination sphere around the metal ion. The crystal structure of $[\mathrm{Eu(mbzimpy)_3}](\mathrm{ClO_4})_3$ [**6**, $\mathrm{EuC_{63}H_{51}N_{15}O_{12}Cl_3}$, a = 24.703(2) Å, c = 16.982(2) Å, trigonal, $R\bar{3}$, Z = 6) shows a mononuclear cation $[\mathrm{Eu(mbzimpy)_3}]^{3+}$ with C_3 symmetry where Eu(III) is nine-coordinated by three tridentate mbzimpy (**1**) which are wrapped around the metal ion to give an approximate trigonal tricapped prismatic arrangement of the nine nitrogen donor atoms leading to a pseudo-D_3 symmetry. Luminescence studies of crystalline $[\mathrm{Eu(mbzimpy)_3}](\mathrm{ClO_4})_3$ (**6**) confirm the high symmetry for the Eu(III) sites while ^{1}H-NMR and luminescence measurements in solution indicate that the triple-helical structure of $[\mathrm{Eu(mbzimpy)_3}]^{3+}$ is maintained in acetonitrile. Spectrophotometric titrations show that the three expected successive complexes $[\mathrm{Ln(mbzimpy)}]^{3+}$, $[\mathrm{Ln(mbzimpy)_2}]^{3+}$, and $[\mathrm{Ln(mbzimpy)_3}]^{3+}$ are formed in solution for all the lanthanide ions studied (Ln = La, Nd, Eu, Gd, Tb, Ho, Yb, Lu), but that $[\mathrm{Ln(mbzimpy)_3}]^{3+}$ complexes are significantly less stable for the heavier lanthanides (Ln = Ho, Yb, Lu) and for the tridentate ligands 2,6-bis(1-X-benzimidazol-2-yl)pyridine (X = propyl, pbzimpy, **2**; X = 3,5-dimethoxybenzyl, dmbbzimpy, **3**] which have bulky groups bound to the aromatic benzimidazole rings. The origin of these effects is discussed together with the use of these complexes as luminescent building blocks for the formation of triple-helical structures.

Introduction

The development of new luminescent and fluorescent probes based on the spectroscopic properties of Eu(III) has been the subject of intensive research during the last few years.[1] Particular interest has been focused on the incorporation of heterocyclic aromatic donor groups[2] into macrocyclic,[3] macrobicyclic,[4] or podand-type[4] ligands capable of giving stable and strongly luminescent Eu(III) and Tb(III) complexes.[5] Although supramolecular photochemistry is developing rapidly,[3–6] only a few reports have dealt with the self-assembly[7] of well-defined polynuclear lanthanide complexes[8] and, more specifically, of helical structures where the lanthanide ions lie on the helical axis.[9] However, such polynuclear structures would allow the detailed study of the mechanisms involved in energy transfer between the lanthanide ions[10] which are directly correlated to the transfer of photonic information along the helical axis. The stereochemical preference of lanthanide ions for high coordination numbers[1] requires the design of helical building blocks containing tridentate units[11] which are synthetically more difficult to introduce into oligo-multidentate ligands than bidentate moieties[12] and this probably explains their limited use in supramolecular chemistry.[13] However, the pseudo-D_3 symmetry reported for the cation $[\mathrm{Eu(terpy)_3}]^{3+}$ [14](terpy = 2,2′:6′,2″-terpyridine) strongly suggests that this type of chromophore could be used for the development of a luminescent triple-helical structure. We

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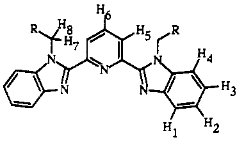
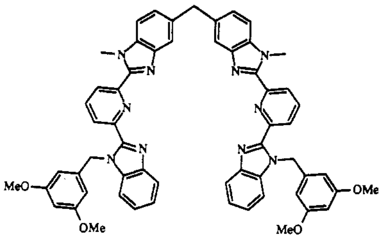
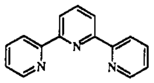
previously used the ligand 2,6-bis(1-methyl-benzimidazol-2-yl)-pyridine (mbzimpy, **1**), a structural and chemical analogue of terpy,[15] as a building block for self-assembly of helical copper(I) complexes.[16] In contrast to terpy, the ligand mbzimpy (**1**) may easily be derivatized[16,17] as exemplified by the binding of two mbzimpy units to give a bis-tridentate ligand (bismbzimpy) which forms a dinuclear triple-stranded helicate with Eu(III).[18] A recent detailed structural and photophysical study of the highly luminescent lanthanide nitrate 1:1 complexes [Ln(mbzimpy)-$(NO_3)_3(CH_3OH)$] (Ln = Eu, Tb)[19] established very similar photophysical properties for terpy and mbzimpy (**1**) and showed a good fit between the ligand coordination cavity and the size of midrange Ln(III) ions, suggesting the possible formation of complexes containing two or three mbzimpy ligands per lanthanide ions as observed for the mononuclear complex $[Eu(terpy)_3]$-$(ClO_4)_3$[14] and the dinuclear $[Eu_2(bismbzimpy)_3](ClO_4)_6$,[18] where each Eu(III) is coordinated by three tridentate ligands. In this paper, we report further chemistry of the ligand mbzimpy (**1**) with lanthanide ions together with the structure and the photophysical properties of $[Lu(mbzimpy)_2]^{3+}$ and triple-helical $[Ln(mbzimpy)_3]^{3+}$ (Ln = La, Nd, Eu, Gd, Tb, Ho, Yb, Lu) complexes. Data are presented to show that the high symmetry found for the helical 1:3 complex is maintained in solution, and particular attention is paid to the luminescent properties and to the stability of these species in solution, since these points are crucial to the planned synthesis of luminescent dinuclear triple-helical complexes with lanthanide ions.



R=H: mbzimpy (**1**)
R=CH_2CH_3: pbzimpy (**2**)
R=$(CH_3O)_2C_6H_3$: dmbbzimpy (**3**)
R=$(CH_2)_6CH_3$: obzimpy (**4**)



Bismbzimpy



Terpy

Experimental Section

Solvents and starting materials were purchased from Fluka AG (Buchs, Switzerland) and used without further purification, unless otherwise stated. Aluminum oxide (Merck activity II-III, 0.063–0.200 mm) was used for preparative column chromatography.

Preparation of the Ligands. The ligands 2,6-bis(1-methylbenzimidazol-2-yl)pyridine (mbzimpy, **1**)[15] and 2,6-bis(1-(3,5-dimethoxybenzyl)-benzimidazol-2-yl)pyridine (dmbbzimpy, **3**)[16] were prepared according to literature procedures. 2,6-bis(1-propylbenzimidazol-2-yl)pyridine (pbzimpy, **2**) was obtained according to the same method[15,16] but using 1-propyl iodide as alkylating agent. The crude product was purified by column chromatography (Al_2O_3, CH_2Cl_2/MeOH 99:1) and then crystallized from acetonitrile (yield = 73%). Mp: 126–128 °C. ^1H-NMR in $CDCl_3$: 0.71 (6H, t, J^3 = 7.3 Hz), 1.77 (4H, sext, J^3 = 7.3 Hz), 4.71 (4H, t, J^3 = 7.3 Hz), 7.4 (6H, m), 7.8 (2H, m), 8.04 (1H, t, J^3 = 7.5 Hz), 8.33 (2H, d, J^3 = 7.5 Hz). EI-MS: 395 (M^+).

Table I. Summary of Crystal Data, Intensity Measurements and Structure Refinement for $[Eu(mbzimpy)_3](ClO_4)_3$ (**6**) and $[Lu(mbzimpy)_2(CH_3OH)(H_2O)](ClO_4)_3 \cdot 3CH_3OH$ (**12**)

	6	**12**
formula	$Eu(C_{21}H_{17}N_5)_3(ClO_4)_3$	$Lu(C_{21}H_{17}N_5)_2(ClO_4)_3$-$(CH_3OH)_4(H_2O)$
mol wt	1468.5	1298.3
cryst syst	trigonal	monoclinic
space group	$R\bar{3}$	$P2_1/c$
a, Å	24.703(2)	13.140(3)
b, Å		22.007(4)
c, Å	16.982(2)	18.927(7)
β, deg		107.53(1)
V, Å^3	8975(1)	5219(2)
Z	6	4
D_{calc}, g cm^{-3}	1.63	1.65
μ, mm^{-1}	1.260	2.126
R_w (=R)[a]	0.055	0.064

[a] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{0.5}$; w = 1.

Preparation of Lanthanide Complexes. The perchlorate salts Ln-$(ClO_4)_3 \cdot nH_2O$ (n = 6–8) were prepared from the corresponding oxide (Glucydur, 99.99%) according to a literature method.[20]

Preparation of $[Ln(mbzimpy)_3](ClO_4)_3 \cdot H_2O$ (Ln = La, 5; Ln = Eu, 6; Ln = Gd, 7; Ln = Tb, 8]. $Ln(ClO_4)_3 \cdot nH_2O$ (n = 6–8) (0.0393 mmol) in ethanol (5 mL) was slowly added to a solution of mbzimpy (**1**) (0.4 g, 0.118 mmol) in ethanol (30 ml) at 80 °C. The mixture was maintained at this temperature for 1 h and then cooled to −20 °C, the resulting crude precipitate was filtered and dissolved in acetonitrile, and methanol was allowed to diffuse into the solution for 10 days. The resulting white (Ln = La, Gd, Tb) or yellow (Ln = Eu) X-ray quality hexagonal prisms were separated by filtration to give 65–90% yield of $[Ln(mbzimpy)_3]$-$(ClO_4)_3 \cdot H_2O$ (Ln = La, **5**; Ln = Eu, **6**; Ln = Gd, **7**; Ln = Tb, **8**]. Eu-doped (2%) and Tb-doped (2%) compounds of Gd or La were prepared according to the same procedure using stoichiometric mixtures of lanthanide perchlorate salts.

Preparation of $[Ln(pbzimpy)_3](ClO_4)_3 \cdot H_2O$ (Ln = La, 9; Ln = Eu, 10) and $[(Eu(dmbbzimpy)_3](ClO_4)_3 \cdot 5H_2O$ (11). $Ln(ClO_4)_3 \cdot nH_2O$ (n = 6–8) (0.295 mmol) in acetonitrile (10 mL) were slowly added to a solution of pbzimpy (**2**) (0.35 g, 0.885 mmol) in dichloromethane (30 mL). The resulting solution was evaporated to dryness and the solid residue dissolved in acetonitrile and ether was slowly diffused into the solution for 24 h to give white (Ln = La) or yellow (Ln = Eu) needles of $[Ln(pbzimpy)_3]$-$(ClO_4)_3 \cdot H_2O$ (Ln = La, **9**; Ln = Eu, **10**) in 78–81% yield. The same procedure was used to prepare yellow needles of $[Eu(dmbbzimpy)_3]$-$(ClO_4)_3 \cdot 5H_2O$ (**11**) in 74% yield.

Preparation of $[Lu(mbzimpy)_2(CH_3OH)(H_2O)](ClO_4)_3 \cdot 3CH_3OH$ (12). $Lu(ClO_4)_3 \cdot 7H_2O$ (0.266 g, 0.44 mmol) in methanol (5 mL) were added to a solution of mbzimpy (**1**) (0.3 g, 0.88 mmol) in methanol (10 mL) at 70 °C. After cooling, the crude precipitate was filtered and dissolved in acetonitrile, and methanol was allowed to diffuse for 8 days to give transparent X-ray quality prisms of $[Lu(mbzimpy)_2(CH_3OH)(H_2O)]$-$(ClO_4)_3 \cdot 3CH_3OH$ (**12**) (0.46 g, 0.354 mmol, yield = 81%).

Complexes **5–12** were all characterized by their IR spectra and gave satisfactory elemental analyses.

Caution! Perchlorate salts with organic ligands are potentially explosive and should be handled with the necessary precaution.[21]

Crystal Structure Determination of $[Eu(mbzimpy)_3](ClO_4)_3$ (6) and $[Lu(mbzimpy)_2(CH_3OH)(H_2O)](ClO_4)_3 \cdot 3CH_3OH$ (12). Crystal data and details of intensity measurements and structure refinements are given in Table I. Cell dimensions and intensities were measured at room temperature on a Philips PW1100 diffractometer. Data were corrected for Lorentz, polarization, and absorption[22] effects. The structures were solved by direct methods using MULTAN 87;[23] all other calculations

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used XTAL[24] system and ORTEP II[25] programs. Atomic scattering factors and anomalous dispersion terms were taken from ref 26. All coordinates of hydrogen atoms were calculated. The structure of the complex $[Lu(mbzimpy)_2(CH_3OH)(H_2O)](ClO_4)_3{\cdot}3CH_3OH$ (**12**) shows a slight disorder of the three perchlorate anions and of the three uncoordinated methanol molecules which were refined with isotropic atomic displacement parameters for C and O atoms. This disorder has been partially resolved for two perchlorate anions where a total of six atomic sites have been observed for three oxygen atoms (site occupancy factors of 0.5, Table SII, supplementary material). All other non-hydrogen atoms were refined with anisotropic atomic displacement parameters.

Spectroscopic and Analytical Measurements. Electronic spectra in the UV–visible range were recorded in solution with Perkin-Elmer Lambda 5 and Lambda 2 spectrophotometers at 20 °C using quartz cells of 1, 0.1, and 0.01 cm path length. Spectrophotometric titrations were performed with a Perkin-Elmer Lambda 5 spectrophotometer connected to an external computer. In a typical experiment, 50 mL of ligand mbzimpy (**1**) in acetonitrile (2×10^{-4} M) were titrated with a 1.67×10^{-3} M solution of the perchlorate salt of the appropriate metal ion (La(III), Nd(III), Eu(III), Gd(III), Tb(III), Ho(III), Yb(III), Lu(III)) in acetonitrile. After each addition of 0.25 mL, the absorbances at 10 different wavelengths were recorded using a 0.1 cm quartz cell and transfered to the computer. Plots of extinction as a function of the metal/ligand ratio gave a first indication of the number and stoichiometry of the complexes formed: factor analysis[27] was then applied to the data to confirm the number of different absorbing species. Finally, a model for the distribution of species (in all cases four absorbing species—mbzimpy, $[Ln(mbzimpy)]^{3+}$, $[Ln(mbzimpy)_2]^{3+}$, and $[Ln(mbzimpy)_3]^{3+}$) was fitted with a nonlinear least-squares algorithm to give stability constants as previously described.[11] IR spectra were obtained from KBr pellets with a Perkin-Elmer IR 597 spectrophotometer. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on Varian XL 200 and Bruker AMX 400 spectrometers. Chemical shifts are given in ppm with respect to TMS; abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, sext, sextet. EI-MS (70 eV) were recorded with VG 7000E and Finnigan 4000 instruments. IS-MS (ion spray–mass spectra) were recorded at the Laboratory of Mass Spectroscopy of Prof. Henion (Cornell University). The experimental procedures for high-resolution, laser-excited luminescence experiments have been previously published.[28] Solid-state excitation and emission spectra were recorded on microcrystalline powders. The emission spectra were corrected for the instrumental function, but not the excitation spectra. Elemental analyses were performed by Dr. H. Eder of the Microchemical Laboratory of the University of Geneva. Metal contents were determined by ICP (Perkin-Elmer Plasma 1000) after acidic oxidative mineralization of the complexes.

Results

Preparation of the Complexes. The 1:3 complexes $[Ln(mbzimpy)_3](ClO_4)_3{\cdot}H_2O$ (**5–8**), $[Ln(pbzimpy)_3](ClO_4)_3{\cdot}H_2O$ (**9, 10**), and $[Ln(dmbbzimpy)_3](ClO_4)_3{\cdot}5H_2O$ (**11**) are prepared by mixing 2,6-bis(1-methylbenzimidazol-2-yl)pyridine (mbzimpy, **1**), 2,6-bis(1-propylbenzimidazol-2-yl)pyridine (pbzimpy, **2**) or 2,6-bis(1-(3,5-dimethoxybenzyl)benzimidazol-2-yl)pyridine (dmbbzimpy, **3**) with stoichiometric amounts of $Ln(ClO_4)_3{\cdot}nH_2O$ ($n = 6$–8)[20] in ethanol or dichloromethane/acetonitrile. With ligand **1**, the initial precipitates may be recrystallized in good yield by slow diffusion of methanol into an acetonitrile solution to give X-ray quality hexagonal prisms (white for Ln = La, Gd, Tb and yellow for Ln = Eu). No solvent molecule could be found in the crystal structure of $[Eu(mbzimpy)_3](ClO_4)_3$ (vide infra), but the prisms are slowly transformed into thin needles when separated from the mother liquor and elemental analyses of the isolated products are compatible with the formulations $[Ln(mbzimpy)_3](ClO_4)_3{\cdot}H_2O$ (Ln = La, **5**; Ln = Eu, **6**, Ln = Gd, **7**, Ln = Tb, **8**) where the additional water molecule is probably responsible for the modification of the crystal shape. The use of the lipophilic ligands **2** and **3** requires the slow diffusion of ether instead of methanol into an acetonitrile solution to give white (Ln = La) or yellow (Ln = Eu) needles whose elemental analyses correspond to $[Ln(pbzimpy)_3](ClO_4)_3{\cdot}H_2O$ (Ln = La, **9**; Ln = Eu, **10**) and $[Eu(dmbbzimpy)_3](ClO_4)_3{\cdot}5H_2O$ (**11**). The IS-MS spectrum of complex **6** exhibits only one strong peak centered at m/z = 389.9 whose isotopic distribution corresponds to the triply charged $[Eu(mbzimpy)_3]^{3+}$ species. The IR spectra show that the characteristic ligand vibrations at 1590 and 1570 cm^{-1} (C=C, C=N stretching) are slightly shifted toward high energy (1605, 1575 cm^{-1}) upon complexation in **5–11** as previously observed for the complexes $[Eu(mbzimpy)(NO_3)_3(CH_3OH)]$ and $[Eu(obzimpy)(NO_3)_3]$.[19] The ClO_4^- anions all show the two expected symmetrical vibrations (1095, 625 cm^{-1}) typical of ionic perchlorate.[29] We were unable to isolate $[Lu(mbzimpy)_3](ClO_4)_3$ even from stoichiometric 1:3 mixtures of $Lu(ClO_4)_3{\cdot}7H_2O$ and ligand **1**. A 1:2 complex crystallizes instead in good yield when methanol is allowed to diffuse into an acetonitrile solution to give transparent prisms whose elemental analysis corresponds to $[Lu(mbzimpy)_2](ClO_4)_3{\cdot}4CH_3OH{\cdot}H_2O$ (**12**). The IR spectrum of **12** is very similar to those obtained for **5–11**, but some typical vibrations associated with methanol (3400, 2960, 2840 cm^{-1})[30] are significantly more intense, confirming the presence of solvent molecules in the isolated compound. The ClO_4^- moieties still

Table II. Fractional Atomic Coordinates with Esd's in Parentheses for $[Eu(mbzimpy)_3](ClO_4)_3$ (**6**)

	x/a	y/b	z/c	U_{eq},[a] Å^2
Eu	$^2/_3$	$^1/_3$	0.57960(5)	0.0320(2)
N(1)	0.6659(3)	0.2514(3)	0.6758(4)	0.040(3)
N(2)	0.6468(4)	0.1530(3)	0.6753(5)	0.052(4)
N(3)	0.5677(3)	0.2244(3)	0.5785(4)	0.036(3)
N(4)	0.5769(3)	0.3175(3)	0.4843(4)	0.042(3)
N(5)	0.4740(3)	0.2825(4)	0.4902(5)	0.054(4)
C(1)	0.6257(4)	0.1926(4)	0.6544(5)	0.046(4)
C(2)	0.7134(4)	0.2482(4)	0.7154(5)	0.046(4)
C(3)	0.7655(4)	0.2957(4)	0.7549(6)	0.051(4)
C(4)	0.8068(5)	0.2788(5)	0.7856(7)	0.070(6)
C(5)	0.7964(6)	0.2186(6)	0.7803(8)	0.083(7)
C(6)	0.7445(5)	0.1712(5)	0.7440(7)	0.075(6)
C(7)	0.7034(4)	0.1879(4)	0.7127(6)	0.054(5)
C(8)	0.5668(4)	0.1756(4)	0.6156(5)	0.045(4)
C(9)	0.5138(4)	0.1167(4)	0.6184(6)	0.061(5)
C(10)	0.4608(4)	0.1078(4)	0.5804(7)	0.063(5)
C(11)	0.4605(4)	0.1566(4)	0.5417(6)	0.057(4)
C(12)	0.5146(4)	0.2154(4)	0.5455(5)	0.046(4)
C(13)	0.5214(4)	0.2710(4)	0.5066(5)	0.045(4)
C(14)	0.5657(4)	0.3606(4)	0.4470(5)	0.047(4)
C(15)	0.6047(4)	0.4162(4)	0.4081(6)	0.054(5)
C(16)	0.5792(5)	0.4505(5)	0.3803(7)	0.067(5)
C(17)	0.5147(6)	0.4298(6)	0.3876(7)	0.077(7)
C(18)	0.4741(5)	0.3733(5)	0.4218(7)	0.071(6)
C(19)	0.5002(4)	0.3394(4)	0.4525(6)	0.053(5)
C(20)	0.6187(5)	0.0858(4)	0.6565(7)	0.075(6)
C(21)	0.4076(4)	0.2451(5)	0.5089(7)	0.071(5)
Cl	0.3563(1)	0.3618(1)	0.2361(2)	0.060(1)
O(1)	0.4112(3)	0.4212(4)	0.2446(5)	0.094(4)
O(2)	0.3695(4)	0.3137(4)	0.2520(6)	0.108(5)
O(3)	0.3086(4)	0.3567(4)	0.2860(6)	0.098(5)
O(4)	0.3344(4)	0.3558(4)	0.1576(5)	0.109(6)

[a] U_{eq} is the average of eigenvalues of U.

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Table III. Selected Bond Distances (Å) and Angles (deg) and Least-Squares Plane Data for $[Eu(mbzimpy)_3](ClO_4)_3$ (**6**)[a]

Distances

Eu–N(1)	2.592(8)	Eu–N(3)	2.576(5)	Eu–N(4)	2.613(7)

Angles

N(1)–Eu–N(3)	63.8(2)	N(3)–Eu–N(4′)	70.2(2)
N(1)–Eu–N(4)	126.9(2)	N(3)–Eu–N(1″)	71.2(2)
N(1)–Eu–N(1′)	84.6(3)	N(3)–Eu–N(4″)	141.1(2)
N(1)–Eu–N(3′)	71.3(3)	N(4)–Eu–N(1′)	141.3(4)
N(1)–Eu–N(4′)	77.9(3)	N(4)–Eu–N(4′)	85.7(3)
N(1)–Eu–N(3″)	141.1(2)	N(4)–Eu–N(1″)	77.8(3)
N(1)–Eu–N(4″)	141.4(4)	N(4)–Eu–N(3″)	70.1(3)
N(3)–Eu–N(4)	63.1(2)	N(4)–Eu–N(4″)	85.7(3)

Least-Squares Planes

		deviations, Å	
	description	max	atom
1	benzimidazole, N(1), N(2)	0.05	C(3)
2	pyridine, N(3)	0.04	C(12)
3	benzimidazole, N(4), N(5)	0.05	C(15)
4	benzimidazole N(4′), N(5′)	0.05	C(15′)

Interplane Angles

	2	3	4
1	25.1(3)	44.7(2)	9.1(2)
2		25.4(3)	33.0(2)
3			49.3(2)

[a] The primed and double-primed atomic sites are respectively obtained by the following symmetry operations: $1 - y, x - y, z$ and $1 - x + y, 1 - x, z$.

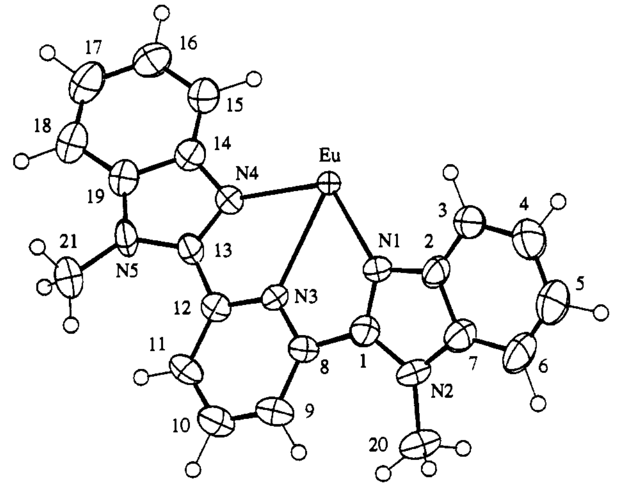

Figure 1. Atomic numbering scheme for the asymmetric unit of $[Eu(mbzimpy)_3]^{3+}$. Ellipsoids are represented with 50% probability.

display the two expected symmetrical vibrations typical of ionic perchlorate.[29]

X-ray Crystal Structure of $[Eu(mbzimpy)_3](ClO_4)_3$ (6). Atomic coordinates are given in Table II, and selected bond lengths and angles and least-squares plane data, in Table III. Figure 1 shows the atomic numbering scheme. Figure 2 gives ORTEP[25] stereoscopic views of the complex respectively perpendicular to and along the C_3 axis.

In agreement with IS-MS and IR results, the crystal structure of **6** shows it to be composed of a cation, $[Eu(mbzimpy)_3]^{3+}$, and three uncoordinated perchlorate anions. The anions have relatively high atomic displacement parameters but otherwise show no feature of interest. The $[Eu(mbzimpy)_3]^{3+}$ cation lies on a C_3 crystallographic axis leading to the observation of three equivalent mbzimpy (**1**) wrapped around the metal ion. Each ligand adopts a cis–cis conformation[16,19] leading to a tridentate meridional coordination to the europium atom which lies approximately in the plane defined by the three coordinating nitrogen atoms of each ligand (deviation: 0.05(1) Å). The individual aromatic rings are planar within experimental error and the main torsion of the mbzimpy ligand is achieved by twisting about the interannular C–C bonds between the pyridine and the benzimidazole rings (25.1(3), 25.4(3)°), leading to a helical twist[16] of the tridentate ligand as found in the structures of $[Eu(terpy)_3]^{3+}$ (12°, 26°)[14] and $[Eu_2(bismbzimpy)_3]^{6+}$ (average value: 23.3°).[18] The Eu(III) atom in $[Eu(mbzimpy)_3]^{3+}$ is coordinated by nine heterocyclic nitrogen atoms giving a slightly distorted tricapped trigonal prismatic coordination around the metal ion with six benzimidazole nitrogen atoms occupying the vertices of the prism and the three pyridine nitrogen atoms occupying the capping positions and forming an equatorial plane containing the Eu(III) (deviation from the plane: 0.019(2) Å (Figure 2)). The effective ionic radius of the Eu(III) ion can be calculated using Shannon's definition[31] and $r(O) = 1.31$ Å and $r(N) = 1.46$ Å[28] and amounts to 1.13 Å for **6** which is in agreement with the reported value for nine-coordinate Eu(III) complexes (1.12 Å)[1] and confirms the good fit between the ligand coordination cavity and Eu(III).[19] As a result of the symmetric coordination of the tridentate ligands to Eu(III), we observe three noncrystallographic pseudo-C_2 axes along the Eu–N(pyridine) directions leading to a pseudo-D_3 symmetry for the cation $[Eu(mbzimpy)_3]^{3+}$ as previously proposed for $[Eu(terpy)_3]^{3+}$ which also displays some distortions from pure D_3-symmetry.[14] The helical wrapping of the three mbzimpy ligands around the C_3 axis in $[Eu(mbzimpy)_3]^{3+}$ leads to the observation of three strong intramolecular stacking interactions between almost parallel aromatic benzimidazole rings (9.1(2)°) belonging to different threads (contact distance: 3.1–3.3 Å (Figure 2)) which give some rigidity to the structure and stabilize the complex.[32]

In complex **6**, the cylindrical pseudo-D_3 $[Eu(mbzimpy)_3]^{3+}$ cations are packed in columns of closely spaced cations along the *c* direction (Figure 3); the resulting interstitial channels being occupied by ClO_4^- lying close to a 3-fold screw axis along the *c* direction. The intermolecular Eu–Eu distances within one column of $[Eu(mbzimpy)_3]^{3+}$ are rather short (8.364(2), 8.618(2) Å) and can be compared to the intramolecular Eu–Eu distance in the dinuclear triple-helical complex $[Eu_2(bismbzimpy)_3]^{6+}$ (8.876(3) Å),[18] where the europium atoms also lie on the helical axis.

X-ray Crystal Structure of $[Lu(mbzimpy)_2(CH_3OH)(H_2O)](ClO_4)_3 \cdot 3CH_3OH$ (12). Atomic coordinates are given in Table IV; selected bond lengths and angles and least-squares plane data are given in Table V. Figure 4 shows the atomic numbering scheme. Figure 5 gives ORTEP[25] stereoscopic views of the complex.

The structure of **12** shows it to be composed of a cation, $[Lu(mbzimpy)_2(CH_3OH)(H_2O)]^{3+}$, three uncoordinated perchlorate anions and three molecules of methanol. The anions and the uncoordinated methanol molecules are slightly disordered (see Experimental Section) but show no other feature of interest. The lutetium atom in the cation $[Lu(mbzimpy)_2(CH_3OH)(H_2O)]^{3+}$ is eight-coordinated by two meridional tridentate mbzimpy ligands, one molecule of water, and one molecule of methanol, leading to a low-symmetry coordination site around the metal ion. The Lu–N distances are significantly shorter than the Eu–N distances for $[Eu(mbzimpy)_3]^{3+}$ as a result of the smaller ionic radius of Lu(III).[1] The calculation of the effective ionic radius

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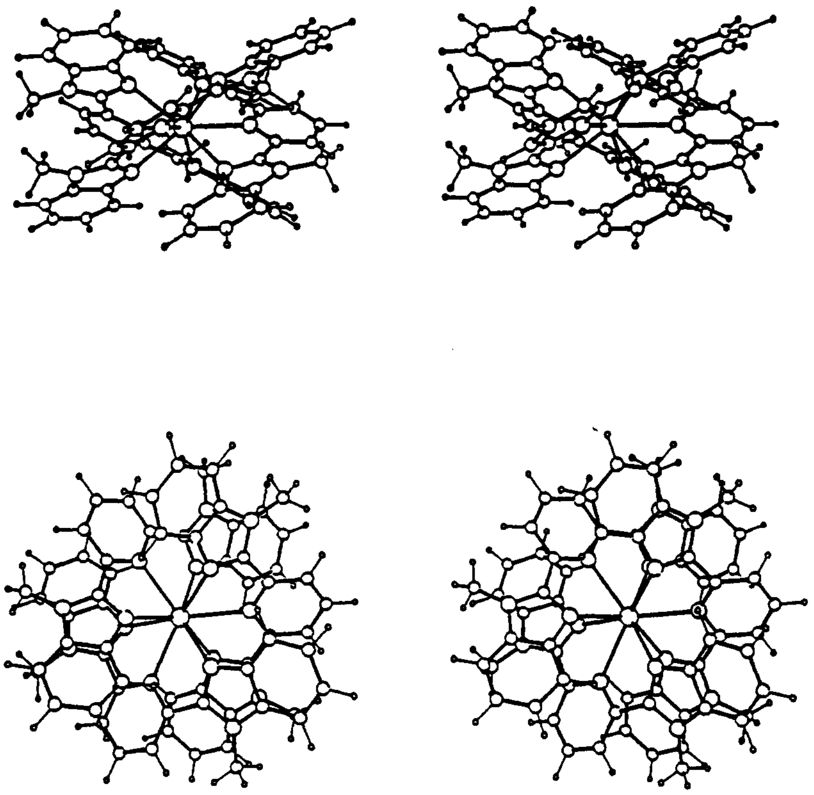

Figure 2. ORTEP[25] stereoscopic views of $[Eu(mbzimpy)_3]^{3+}$ perpendicular to the C_3 axis and along it showing the intramolecular stacking interactions.

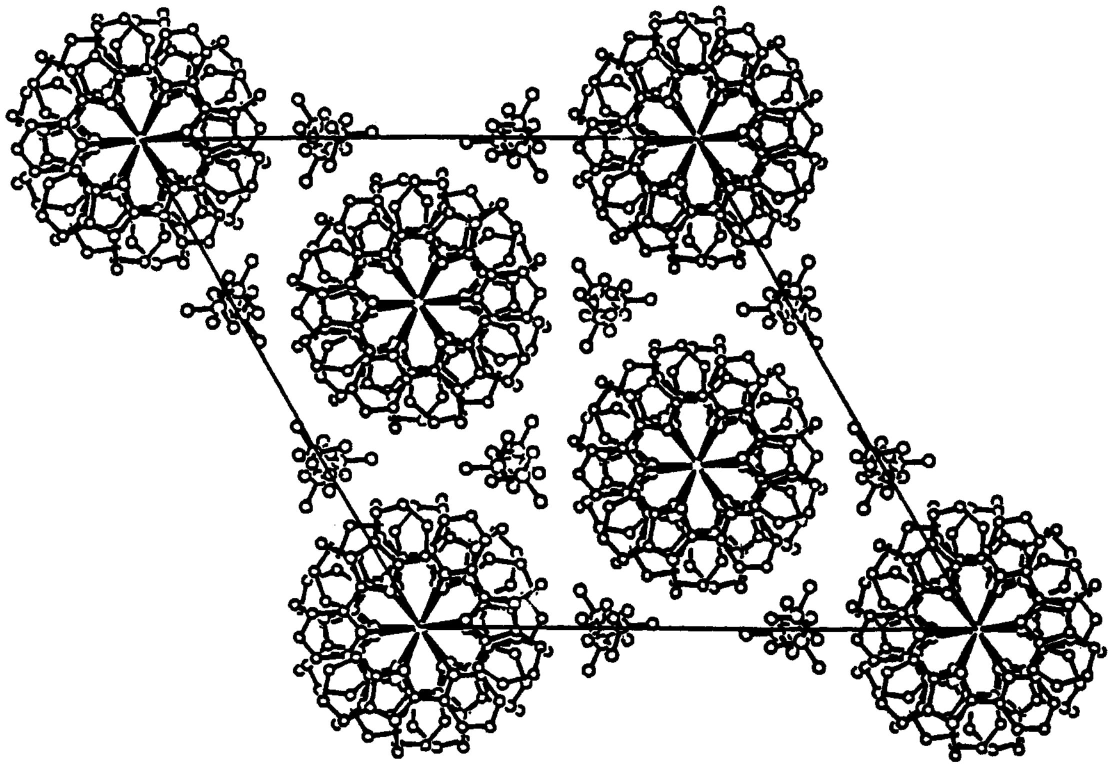

Figure 3. View of the unit cell along the *c* axis for the complex **6**.

of Lu(III) in complex **12** using Shannon's definition[26,31] gives a value of 0.97 Å in good agreement with the reported value of 0.977 Å for eight-coordinate Lu(III).[1] As for **6**, the mbzimpy ligands in $[Lu(mbzimpy)_2(CH_3OH)(H_2O)]^{3+}$ are not planar, and the main torsions result from significant dihedral angles (3.4(5)–28.8(6)°, Table V) between the central pyridine ring and the aromatic benzimidazole side arms, leading to a similar twist for both tridentate ligands in **12**. If we neglect the nature of the metal ion, the structure of $[Lu(mbzimpy)_2(CH_3OH)(H_2O)]^{3+}$ may be roughly derived from the structure of $[Eu(mbzimpy)_3]^{3+}$ by removing one tridentate mbzimpy ligand and replacing it by two molecules of solvent near the corners of the trigonal prism.

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(32) Constable, E. C.; Ward, M. D. *J. Am. Chem. Soc.* **1990**, *112*, 1256. Constable, E. C.; Ward, M. D.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.* **1991**, 1675. Barley, M.; Constable, E. C.; Corr, S. A.; McQueen, R. S.; Nutkins, J. C.; Ward, M. D.; Drew, M. G. B. *J. Chem. Soc., Dalton Trans.* **1988**, 2655.

Table IV. Fractional Atomic Coordinates with Esd's in Parentheses and Population Parameters for $[Lu(mbzimpy)_2(CH_3OH)(H_2O)](ClO_4)_3 \cdot 3CH_3OH$ (**12**)

	x/a	y/b	z/c	U_{eq}[a] Å^2	PP (if ≠ 1)
Lu	0.64586(5)	0.20030(3)	0.23152(4)	0.0327(3)	
N(1)	0.764(1)	0.1265(6)	0.3038(8)	0.043(6)	
N(2)	0.923(1)	0.0816(7)	0.3497(8)	0.054(6)	
N(3)	0.8317(9)	0.2218(6)	0.2444(7)	0.031(5)	
N(4)	0.668(1)	0.2798(6)	0.1473(7)	0.037(5)	
N(5)	0.767(1)	0.3608(7)	0.1380(8)	0.048(6)	
C(1)	0.871(1)	0.1308(8)	0.3131(9)	0.039(7)	
C(2)	0.752(1)	0.0728(7)	0.3400(9)	0.037(7)	
C(3)	0.662(1)	0.0437(9)	0.348(1)	0.055(8)	
C(4)	0.675(2)	−0.0101(8)	0.389(1)	0.053(8)	
C(5)	0.776(2)	−0.0344(8)	0.419(1)	0.055(8)	
C(6)	0.864(1)	−0.0100(8)	0.407(1)	0.058(8)	
C(7)	0.853(1)	0.0449(7)	0.3690(9)	0.039(7)	
C(8)	0.909(1)	0.1838(7)	0.2825(9)	0.036(6)	
C(9)	1.015(1)	0.1938(9)	0.290(1)	0.062(8)	
C(10)	1.040(1)	0.246(1)	0.256(1)	0.068(9)	
C(11)	0.963(1)	0.2837(8)	0.216(1)	0.055(8)	
C(12)	0.859(1)	0.2690(8)	0.2124(9)	0.043(7)	
C(13)	0.765(1)	0.3059(8)	0.1669(8)	0.040(7)	
C(14)	0.603(1)	0.3220(8)	0.1013(9)	0.045(7)	
C(15)	0.497(1)	0.3179(8)	0.0607(9)	0.044(7)	
C(16)	0.452(2)	0.366(1)	0.016(1)	0.058(8)	
C(17)	0.512(2)	0.417(1)	0.010(1)	0.066(9)	
C(18)	0.618(2)	0.4217(9)	0.049(1)	0.063(9)	
C(19)	0.662(2)	0.3729(9)	0.093(1)	0.056(8)	
C(20)	1.035(1)	0.0690(9)	0.369(1)	0.067(9)	
C(21)	0.853(2)	0.4058(8)	0.152(1)	0.067(9)	
N(01)	0.674(1)	0.2953(6)	0.3033(7)	0.041(5)	
N(02)	0.635(1)	0.3939(7)	0.2801(7)	0.046(6)	
N(03)	0.482(1)	0.2597(6)	0.2082(7)	0.037(6)	
N(04)	0.490(1)	0.1449(7)	0.1698(8)	0.045(6)	
N(05)	0.316(1)	0.1394(8)	0.1057(9)	0.065(7)	
C(01)	0.599(1)	0.3353(9)	0.2727(9)	0.045(8)	
C(02)	0.763(1)	0.3299(9)	0.336(1)	0.052(8)	
C(03)	0.865(2)	0.3119(9)	0.378(1)	0.061(9)	
C(04)	0.942(2)	0.357(1)	0.399(1)	0.08(1)	
C(05)	0.919(2)	0.417(1)	0.383(1)	0.08(1)	
C(06)	0.819(2)	0.438(1)	0.344(1)	0.08(1)	
C(07)	0.741(1)	0.3909(9)	0.3201(9)	0.052(8)	
C(08)	0.490(1)	0.3174(8)	0.236(1)	0.045(7)	
C(09)	0.397(2)	0.3499(8)	0.230(1)	0.054(8)	
C(010)	0.302(1)	0.327(1)	0.197(1)	0.066(9)	
C(011)	0.294(1)	0.267(1)	0.168(1)	0.056(8)	
C(012)	0.389(1)	0.2354(8)	0.1770(9)	0.039(7)	
C(013)	0.395(1)	0.1720(7)	0.1510(8)	0.036(7)	
C(014)	0.467(1)	0.0879(8)	0.138(1)	0.045(7)	
C(015)	0.542(2)	0.0395(8)	0.140(1)	0.053(8)	
C(016)	0.497(2)	−0.0123(9)	0.098(1)	0.064(9)	
C(017)	0.388(2)	−0.013(1)	0.056(1)	0.09(1)	
C(018)	0.320(2)	0.033(1)	0.056(1)	0.09(1)	
C(019)	0.362(1)	0.084(1)	0.098(1)	0.056(8)	
C(020)	0.583(2)	0.4477(9)	0.244(1)	0.07(1)	
C(021)	0.204(1)	0.154(1)	0.074(1)	0.09(1)	
O(100)	0.6831(9)	0.1487(5)	0.1372(7)	0.054(5)	
O(200)	0.5755(9)	0.1786(5)	0.3288(6)	0.046(5)	
C(200)	0.638(2)	0.185(1)	0.409(2)	0.107(9)	
O(300)	0.862(2)	0.097(1)	0.136(1)	0.164(9)	
C(300)	0.927(3)	0.111(2)	0.094(2)	0.16(1)	
O(400)	0.339(3)	0.165(2)	0.943(2)	0.27(2)	
C(400)	0.290(4)	0.218(3)	0.909(3)	0.24(2)	
O(500)	0.538(2)	0.156(1)	0.008(2)	0.19(1)	
C(500)	0.584(6)	0.181(4)	−0.051(4)	0.37(4)	
Cl(1)	0.1658(5)	0.0601(3)	0.8108(3)	0.074(3)	
O(01)	0.118(2)	0.112(1)	0.777(2)	0.19(1)	
O(02)	0.257(2)	0.050(1)	0.791(1)	0.148(8)	
O(03)	0.089(2)	0.017(1)	0.781(2)	0.20(1)	
O(04)	0.180(2)	0.061(1)	0.883(2)	0.167(9)	
Cl(2)	0.2955(3)	0.1042(3)	0.3055(3)	0.061(2)	
O(05)	0.399(1)	0.0974(9)	0.306(1)	0.114(6)	
O(06)	0.226(2)	0.087(1)	0.238(1)	0.142(7)	
O(07)	0.279(2)	0.064(1)	0.359(1)	0.148(8)	
O(08)	0.271(3)	0.166(2)	0.298(2)	0.12(1)	0.5
O(09)	0.260(3)	0.147(2)	0.346(2)	0.11(1)	0.5
Cl(3)	1.0065(6)	0.1915(3)	0.5256(3)	0.089(3)	
O(010)	1.054(1)	0.1530(9)	0.582(1)	0.116(6)	
O(011)	1.020(2)	0.249(1)	0.560(1)	0.163(9)	
O(012)	1.096(4)	0.191(2)	0.488(3)	0.15(2)	0.5
O(013)	0.925(3)	0.172(2)	0.474(2)	0.12(1)	0.5
O(014)	1.022(4)	0.202(2)	0.461(2)	0.13(1)	0.5
O(015)	0.883(3)	0.200(2)	0.519(2)	0.14(1)	0.5

[a] U_{eq} is the average of eigenvalues of U.

We therefore expect only one intramolecular stacking interaction to remain as indeed observed in **12** between two aromatic benzimidazole rings belonging to each mbzimpy (interplane angle = 20.9(7)°; contact distance = 2.8–3.6 Å (Figure 5)) in a similar way as described for $[Eu(mbzimpy)_3]^{3+}$. Examination of the crystal packing in **12** shows that the packing arrangement produces some cavities between the cations which are occupied by uncoordinated methanol molecules and perchlorate anions.

Photophysical Properties of $[Ln(mbzimpy)_3](ClO_4)_3 \cdot H_2O$ (5–8) in the Solid State. The broad and intense $\pi_1 \rightarrow \pi^*$ transition of free mbzimpy which occurs at 27 800 cm^{-1} [19] is split and shifted upon complexation, giving rise to two minima in the reflectance spectra (Figure F1, supplementary material): $\pi_1{}^a \rightarrow \pi^*$ ranges from 29 410 (La, Eu, Gd) to 28 730 cm^{-1} (Tb), and $\pi_1{}^b \rightarrow \pi^*$, from 26 320 (La, Eu) to 26 180 (Tb) and 25 380 cm^{-1} (Gd). Excitation of the La (**5**) and Gd (**7**) complexes through this $\pi_1 \rightarrow \pi^*$ transition at 77 K results in emission spectra containing two broad bands (Figures F2 and F3, supplementary material). One is weak, centered at 22 220 cm^{-1}, and its lifetime is short; we assign it as arising from the $^1\pi\pi^*$ state. The second band extends from 470 to 650 nm. It is structured, with a maximum at 18 520 cm^{-1} and a lifetime of 87 ± 2 (La) or <3 ms (Gd), and therefore originates from the $^3\pi\pi^*$ state. In comparison, the lifetimes of the $^3\pi\pi^*$ state of the free ligand and of the 1:1 complexes are 323, 7 (Gd), and 157 (Lu) ms.[19] Similar results are obtained with the 1:2 Lu complex **12** (lifetime of the $^3\pi\pi^*$ state: 37 ± 1 ms). The addition of 2% Tb to the Gd 1:3 complex leads to a noticeable quenching of the ligand luminescence and to energy transfer to the Tb(III) ion *via* the ligand triplet (Figure F4, supplementary material). The ligand luminescence vanishes in the pure Eu (**6**) and Tb (**8**) complexes, resulting in spectra displaying almost exclusively the metal ion luminescence.

For the europium complex (**6**), the corresponding luminescence spectra are similar to those obtained by direct laser excitation through the $^5D_{0,1} \leftarrow {}^7F_0$ transitions. Measurements have been performed both at 4 and 77 K and on a pure Eu complex and a Eu-doped Gd complex. Negligible differences were noticed between these spectra. A close scrutiny of both the emission spectra (Figure 6) and the excitation spectrum in the region of the $^5D_0 \rightarrow {}^7F_0$ transition (Figure 7) reveals the presence of two slightly different chemical environments for the Eu(III) ion, labelled sites I and II (bands at 17 223 and 17 236 cm^{-1}). The crystal field splittings reported in Table VI are calculated from spectra measured after direct laser excitation to the $^5D_0$ and $^5D_1$ levels followed by luminescence from the $^5D_0$ level exclusively. They may be interpreted in terms of either pseudo-D_3 or C_3 symmetry around the Eu ion. The $^5D_0 \rightarrow {}^7F_0$ transition, which is symmetry forbidden in D_3 but allowed in C_3, is extremely weak (*cf.* Table VII). There are two main transitions to the $^7F_1$ level, $A_1 \rightarrow A_2$ and $A_1 \rightarrow E$ (both are allowed in D_3 and C_3), the latter being further broken up into two closely spaced components, 15–18 cm^{-1} for site I and 8–9 cm^{-1} for site II. Such an additional splitting is often observed and may arise either from a slight deviation from the ideal trigonal symmetry (*cf.* the crystal structure discussed above) or from a distortion induced by the excitation to the $^5D_0$ level: luminescence spectra reflect the

Table V. Selected Bond Distances (Å) and Angles (deg) and Least-Squares Plane Data for $[Lu(mbzimpy)_2(CH_3OH)(H_2O)](ClO_4)_3 \cdot 3CH_3OH$ (**12**)

Distances

Lu–N(1)	2.37(1)	Lu–N(3)	2.43(1)	Lu–N(4)	2.44(1)
Lu–N(01)	2.46(1)	Lu–N(03)	2.45(1)	Lu–N(04)	2.37(1)
Lu–O(100)	2.29(1)	Lu–O(200)	2.35(1)		

Angles

N(1)–Lu–N(3)	67.3(4)	N(4)–Lu–N(03)	76.7(5)
N(1)–Lu–N(4)	133.1(5)	N(4)–Lu–N(04)	107.5(4)
N(1)–Lu–N(01)	107.4(4)	N(4)–Lu–O(100)	75.7(4)
N(1)–Lu–N(03)	148.9(5)	N(4)–Lu–O(200)	144.1(4)
N(1)–Lu–N(04)	104.5(5)	N(01)–Lu–N(03)	67.9(4)
N(1)–Lu–O(100)	81.6(5)	N(01)–Lu–N(04)	132.3(5)
N(1)–Lu–O(200)	75.6(5)	N(01)–Lu–O(100)	145.2(5)
N(3)–Lu–N(4)	67.3(4)	N(01)–Lu–O(200)	76.6(4)
N(3)–Lu–N(01)	78.4(4)	N(03)–Lu–N(04)	66.4(5)
N(3)–Lu–N(03)	136.1(4)	N(03)–Lu–O(100)	120.6(4)
N(3)–Lu–N(04)	147.7(5)	N(03)–Lu–O(200)	73.5(4)
N(3)–Lu–O(100)	74.4(4)	N(04)–Lu–O(100)	73.6(5)
N(3)–Lu–O(200)	125.7(4)	N(04)–Lu–O(200)	78.1(4)
N(4)–Lu–N(01)	74.0(5)	O(100)–Lu–O(200)	137.6(4)

Least-Squares Planes

		deviations, Å	
	description	max	atom
1	benzimidazole, N(1), N(2)	0.045	C(5)
2	pyridine, N(3)	0.015	C(10)
3	benzimidazole, N(4), N(5)	0.042	C(14)
4	benzimidazole, N(01), N(02)	0.043	C(03)
5	pyridine, N(03)	0.018	C(011)
6	benzimidazole, N(04), N(05)	0.043	C(016)

Interplane Angles

	2	3	4	5	6
1	3.4(5)	21.1(4)	33.7(4)	52.6(5)	56.7(4)
2		18.8(5)	33.3(5)	54.0(6)	57.4(5)
3			20.4(5)	48.0(5)	47.5(4)
4				28.8(6)	27.1(4)
5					10.2(6)

properties of the excited state and not of the ground state. The transition to the $^7F_2$ level of site I comprises two main bands which are further split into two components each (separation 10–20 cm^{-1}) we assign to $A_1 \rightarrow E$ (D_3 symmetry). The emission spectrum of site II is somewhat different, with a broad and weak component corresponding to one of the $A_1 \rightarrow E$ transitions of site I and a triplet that we assign to two transitions: $A \rightarrow E$ (split into two components) and $A \rightarrow A$. Therefore, the symmetry of site II is close to C_3 whereas the symmetry of site I is closer to D_3. This finding is corroborated by the examination of the transition to $^7F_4$. The emission spectrum of site I consists of four bands split into eight identified components (C_3 symmetry: six transitions allowed, three $A \rightarrow A$ and three $A \rightarrow E$). For site II, six components only could be distinguished. The more intense band at 691.1 nm is assigned to the $A_1 \rightarrow A_2$ transition, while the three other, broad and weak, bands are assigned to the three allowed $A_1 \rightarrow E$ transitions (D_3 symmetry). The luminescence spectra of the Tb complex (**8**) are dominated by the $^5D_4 \rightarrow {}^7F_5$ transition, as is usually the case for terbium complexes [Table VII).

The decays of the Eu($^5D_0$) and Tb($^5D_4$) luminescence are monoexponential and yield the lifetimes listed in Table VIII. At low temperatures, they are much longer than those observed for the 1:1 complexes $[Ln(mbzimpy)(NO_3)_3(MeOH)]$ (4–77 K; Eu, 0.85 ms; Tb, 1.2 ms) and $(Eu(obzimpy)(NO_3)_3]$ (4–77 K; 1.13 ms)[19] which may be explained by the absence of nitrate and methanol in the inner coordination sphere. This also proves that the water molecule of the Eu and Tb complexes **6** and **8** is interstitial and not bonded into the coordination sphere of the metal ions. For the Eu complex, no variation is observed between 4 and 77 K, but the lifetime at room temperature is much shorter, indicating a luminescence quenching by several ligand vibrational modes and, possibly, by a metal to ligand charge-transfer state.

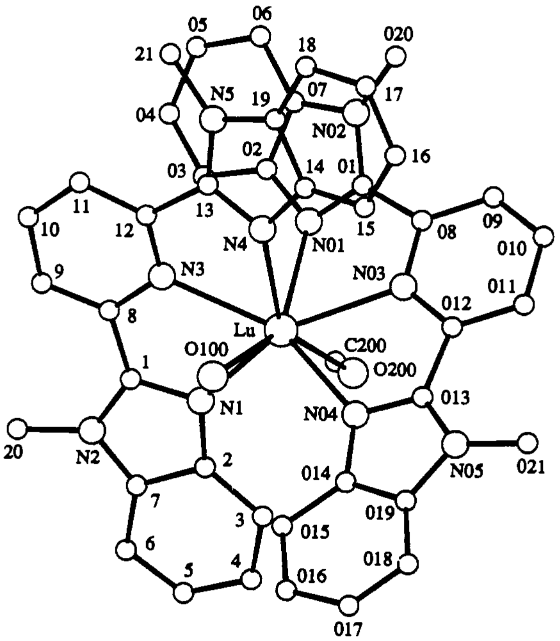

Figure 4. Atomic numbering scheme for $[Lu(mbzimpy)_2(CH_3OH)(H_2O)]^{3+}$.

Structure in Solution. The X-ray crystal structure and the luminescence measurements show the formation of nine-coordinate pseudo-D_3 $[Ln(mbzimpy)_3]^{3+}$ in the solid state for Ln = La, Eu, Gd, and Tb, but if these complexes are to be considered as building blocks for the self-assembly of more complicated structures, it remains essential to show that they are stable in solution and that the axial symmetry is maintained.

Spectrophotometric titrations of ligand mbzimpy (**1**) with $Ln(ClO_4)_3$ (Ln = La, Nd, Eu, Gd, Tb, Ho, Yb, Lu) in acetonitrile (Ln:ligand ratio in the range 0.1–1.8) show a complicated variation of the UV spectra with a rather sharp first end point for a Ln:ligand ratio around 0.35 and an end point at 1.0. For Ln = La, Nd, Eu, Gd, and Tb, an isosbestic point is observed in the range 330–360 nm for a Ln:ligand ratio in the range 0–0.33, which implies only two absorbing species (mbzimpy and $[Ln(mbzimpy)_3]^{3+}$) under these conditions. With Ln = Ho, Yb, and Lu, no isosbestic points are observed. In all cases, factor analysis[27] implies the existence of four different absorbing species and the spectrophotometric data can be satisfactorily fitted with the following equilibria:

$$Ln^{3+} + n\text{mbzimpy} \leftrightarrow [Ln(mbzimpy)_n]^{3+} \quad (n = 1\text{–}3)$$

In all cases, convergence was obtained with a root-mean-square difference between observed and calculated absorbance of 0.006 absorbance units or less. The similarity of the calculated spectra for the three complexes (1:1, 1:2, 1:3) gives very strong correlations between the values and prevents a precise determination of the stability constants (log (β_i)). However, least-squares fits of the data clearly indicate a lower stability for the complexes $[Ln(mbzimpy)_3]^{3+}$ with the heavier lanthanides (Ln = Ho, Yb, Lu), which is in agreement with the absence of isosbestic points during the titration of mbzimpy (**1**) with these metal ions and may explain our failure to isolate $[Lu(mbzimpy)_3](ClO_4)_3$ and the reported unavoidable contamination of $[Lu(terpy)_3](ClO_4)_3$ with a bis(terpyridine) complex.[14] A similar decrease in stability is observed when the methyl groups bound to the benzimidazole side arms in mbzimpy (**1**) are replaced by more bulky and lipophilic groups like 3,5-dimethoxybenzyl in dmbbzimpy (**3**) as exemplified by the almost complete disappearance of the $\pi_1^{a,b} \rightarrow \pi^*$ splitting[15]

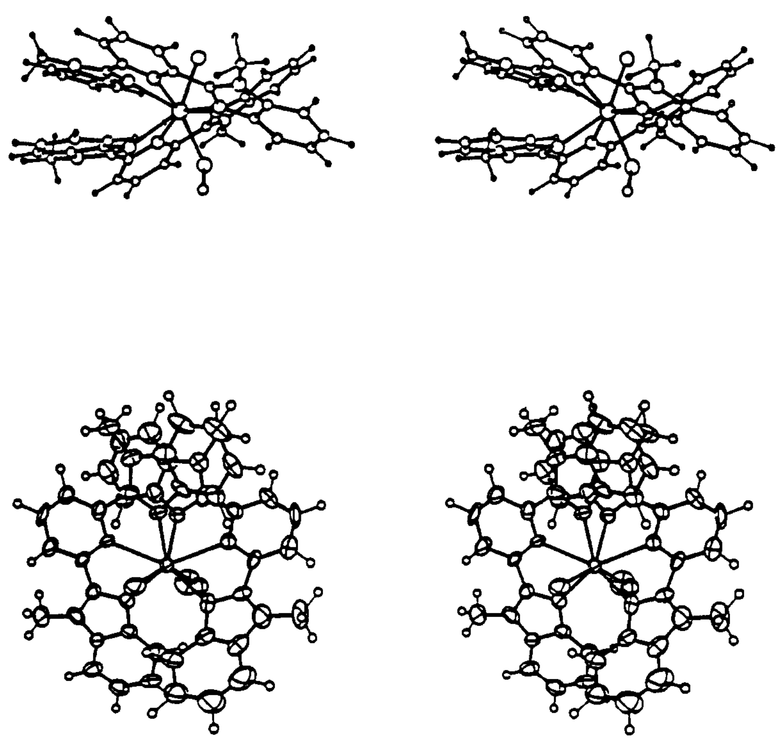

Figure 5. Stereoscopic views of $[Lu(mbzimpy)_2(CH_3OH)(H_2O)]^{3+}$ showing the intramolecular stacking interaction (ORTEP[25]).

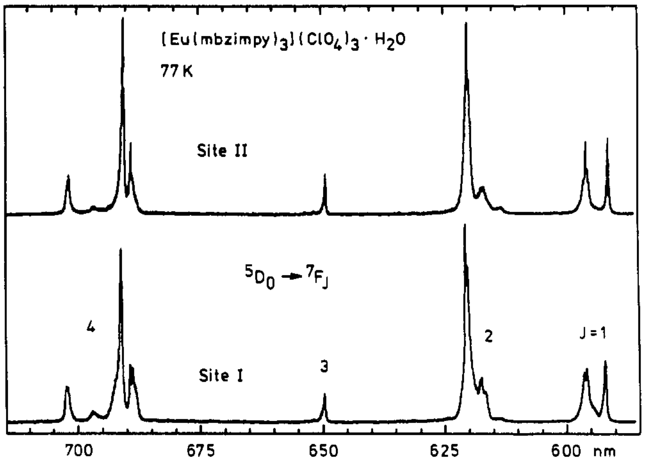

Figure 6. Part of the emission spectrum of a microcrystalline sample of $[Eu(mbzimpy)_3](ClO_4)_3$ at 77 K: (top) site II (λ_{exc} = 580.18 nm); (bottom) site I (λ_{exc} = 580.61 nm).

for 2 × 10^{-4} M acetonitrile solution of $[La(pbzimpy)_3]^{3+}$ (**9**) while both transitions are still well resolved for $[La(mbzimpy)_3]^{3+}$ (**5**) in the same conditions (Figure 8).

Upon complexation to Lu(III) in complex **12**, the pyridine protons H_5, H_6 of mbzimpy (**1**) are significantly shifted to lower field (0.26 ppm for H5 and 0.68 ppm for H_6, Table IX) which is typical for N-coordination of the pyridine ring[33] as similarly observed when mbzimpy (**1**) is meridionally coordinated to Zn(II),[15] Fe(II)[17] and Lu(III).[19] Both ligands are equivalent on the NMR time scale, implying a symmetry element in $[Lu(mzimpy)_2]^{3+}$ which does not exist in the crystal structure of **12**. These observations suggest that the molecules of solvent bound to the Lu(III) in the solid state undergo rapid exchange in acetonitrile solution as confirmed by the sharp singlet (3.25 ppm) corresponding to the methanol in the spectrum of complex **12**.

For $[La(mbzimpy)_3]^{3+}$ (**5**), we observe one singlet for the methyl groups at 3.76 ppm and six aromatic signals at lower field. These features correspond to three equivalent mbzimpy ligands coordinated to La(III) implying a C_3 axis together with an other symmetry element (plane or C_2 axis) connecting the benzimidazole side arms and reflecting a high symmetry (*e.g.* D_3) for the cation $[La(mbzimpy)_3]^{3+}$. To establish definitely the symmetry of the cation in solution, we used the analogous ligand pbzimpy (**2**), which possesses a RCH_2 probe covalently bound to its backbone.[16] The methylene protons H_7 and H_8 in $[La(pbzimpy)_3]^{3+}$ (**9**) clearly

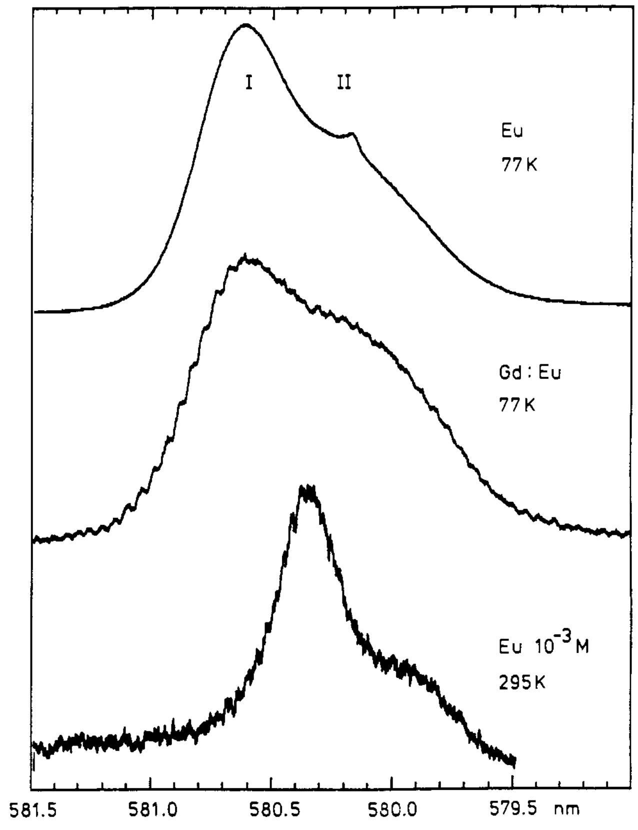

Figure 7. $^5D_{0,1} \leftarrow {}^7F_0$ excitation spectra of microcrystalline samples of $[Ln(mbzimpy)_3](ClO_4)_3$ (Ln = Eu and $Gd_{0.98}$:$Eu_{0.02}$) and of a solution in CH_3CN (λ_{an} = 590.3 nm).

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Table VI. Eu(^7F_J) Energy Levels (cm^{-1}, $J = 1–4$) in $[Eu(mbzimpy)_3](ClO_4)_3$ (**6**) As Calculated from Luminescence Spectra at 77 K: Site I, $\lambda_{exc} = 580.61$ and 527.32 nm; Site II, $\lambda_{exc} = 580.18$ and 527.17 nm[a]

level	site I	site II
$^7F_0(A)$	0	0
$^7F_1(A)$	300	292
$^7F_1(E)$	410	417
	427	425
$^7F_2(E)$	986	1002
	1009	1016
$^7F_2(E)$	1077	1083
	1089	1090
$^7F_2(A)$[b]	*c*	
$^7F_3$	1819	1821
	1871	1877
$^7F_4$	2693	
	2705	2713
	2715	2721
	2754[d]	2754[d]
	2785	
	2876	
	2981	2885[e]
	2988	2990[e]
		2995[e]

[a] Symmetry labels refer to C_3 symmetry. The correspondence $D_3 \rightarrow C_3$ is $A_1,A_2 \rightarrow A$ and $E \rightarrow E$ (see text). [b] For C_3 symmetry only. [c] Unidentified. [d] Assigned to the A → A transition. [e] Assigned to one of the A → E transitions.

show an intramolecular diastereotopic effect[11,16,34] resulting from a complicated $ABMNX_3$ spin system for the propyl residue (Figure 9), which implies that the cation is helical on the NMR time scale in agreement with the X-ray crystal structure of **6**. Although $[La(mbzimpy)_3]^{3+}$ is the only significant species in acetonitrile at 5×10^{-3} M, the spectrum of $[La(pbzimpy)_3]^{3+}$, under the same conditions, clearly shows the presence of other minor species (*ca* 12%, Figure 9) probably arising from partial decomplexation of the aromatic rings as previously reported[35] for $[Eu(terpy)_3]^{3+}$. We have recorded the NMR spectra of the paramagnetic[36] complex $[Eu(mbzimpy)_3]^{3+}$ [**6**] under the same conditions as those reported for $[Eu(terpy)_3]^{3+}$.[35] In our case, the pseudo-D_3 cation $[Eu(mbzimpy)_3]^{3+}$ is the only species in acetonitrile solution which implies a greater stability compared to the analogous complex $[Eu(terpy)_3]^{3+}$ where significant decomplexation was observed.[35] However, when mbzimpy (**1**) is replaced by pbzimpy (**2**), we observe in the ^1H-NMR spectrum the appearance of approximately 8–10% of minor paramagnetic Eu(III) complexes, and with dmbbzimpy (**3**), where bulky 3,5-dimethoxybenzyl groups are bound to the tridentate ligand, $[Eu(dmbbzimpy)_3]^{3+}$ represents only 70% of the total species. These results parallel the spectrophotometric titrations and confirm the stability decrease of the triple-helical cation (D_3 symmetry) when going from mbzimpy (**1**) to dmbbzimpy (**3**). Finally, the ^1H-NMR spectrum of $[Tb(mbzimpy)_3]^{3+}$ (**8**), although more affected by paramagnetic effects,[36] also confirms the existence of only one stable species on the NMR time scale corresponding to the triple-helical cation.

The absorption spectra of the free ligands **1**, **2** in acetonitrile display a strong $\pi_1 \rightarrow \pi^*$ transition[17,37] centered at 31 150 cm^{-1} which is split into two components ($\pi_1{}^a \rightarrow \pi^*$ and $\pi_1{}^b \rightarrow \pi^*$, Table X, Figure 8) upon complexation to Ln(III) in complexes **5**–**12** as previously described.[15,17,19,38] However, careful examination of the electronic spectra show that the absorbance for $[Eu(mbzimpy)_3]^{3+}$ (**6**) and $[Eu(pbzimpy)_3]^{3+}$ (**10**) tails off into the visible, whereas all the other complexes display a sharp cut off near 25 000 cm^{-1}. The origin of this tail is probably a LMCT (N → Eu(III)) transition which is expected at lower energy for Eu(III)[39] and is responsible for the pale yellow color of the Eu(III) complexes **6**, **10**, and **11**.

The luminescence intensity of 10^{-3} M solutions in acetonitrile is very weak for Eu and Tb, preventing a detailed analysis. In view of the short Eu($^5D_0$) lifetime (0.48 ms), some quenching by the water molecule is conceivable. As far as $[Ln(mbzimpy)_3]^{3+}$ cations are concerned, we note that the emission spectrum of the Tb complex **8** is almost identical to the solid-state spectrum (Figure F5, supplementary material, and Table VII), pointing to very similar geometries around the Tb(III) ion. The situation is somewhat different for the Eu complex **6**. The $^5D_0 \leftarrow {}^7F_0$ excitation spectrum still displays two components whose separation is 12–13 cm^{-1}, but they are red-shifted by 7–8 cm^{-1} with respect to the solid-state spectrum at 77 K. The relative intensities of the $^5D_0 \rightarrow {}^7F_J$ transitions differ substantially from their values at 77 K, but the overall crystal field splitting remains similar to the one observed for the solid state. Therefore, despite interaction with the solvent and/or water in the first coordination sphere of the ion, the geometry of the complex cations remains close to a trigonal arrangement.

Discussion

The results show that mbzimpy (**1**), in the absence of coordinating anions, reacts with all the studied lanthanide ions (Ln = La, Nd, Eu, Gd, Tb, Ho, Yb, Lu) to give $[Ln(mbzimpy)_n]^{3+}$ ($n = 1–3$) in acetonitrile solution where respectively three, six, and nine heterocyclic nitrogen atoms are coordinated to the metal ion. The successive formation of 1:1 $[Ln(mbzimpy)]^{3+}$ and 1:2 $[Ln(mbzimpy)_2]^{3+}$ complexes show the considerable affinity of mbzimpy (**1**) for all the lanthanide ions studied, which is strongly supported by the good fit between the coordination cavity of the ligand and the Ln(III) ions observed in the X-ray crystal structures of $[Eu(mbzimpy)(NO_3)_3(CH_3OH)]$[19] and $[Lu(mbzimpy)_2(CH_3OH)(H_2O)](ClO_4)_3\cdot 3CH_3OH$ (**12**). However, the presence of three tridentate mbzimpy ligands around the metal ion in the cations $[Ln(mbzimpy)_3]^{3+}$ leads to new steric constraints. The X-ray crystal structure of $[Eu(mbzimpy)_3](ClO_4)_3$ (**6**) shows that the mbzimpy ligands are twisted about the interannular C-C bonds leading to a distortion of the aromatic system. However, this twist allows the wrapping of the tridentate ligands around the C_3 axis producing a compact pseudo-D_3 cation $[Eu(mbzimpy)_3]^{3+}$ which exhibits three strong intramolecular stacking interactions, as measured by the short contact distance between the aromatic benzimidazole rings from different strands. These observations indicate that this structure is well-fitted to the midrange Ln(III) ions. While adjustment of the cavity to hold larger ions may be forseen, a contraction of the structure to produce a smaller cavity, required for the efficient coordination of heavier lanthanide ions, is certainly limited by the steric constraints. These statements are strongly supported by the NMR and luminescence results which clearly establish that the triple-helical structures (pseudo-D_3 symmetry) of $[Ln(mbzimpy)_3]^{3+}$ (Ln = La, Eu, Tb) are stable in solution and by spectrophotometric titrations which show a significant stability decrease for the cations $[Ln(mbzimpy)_3]^{3+}$ with the heavier lanthanide ions (Ln = Ho, Yb, Lu) eventually leading to the isolation of $[Lu(mbzimpy)_2(CH_3-$

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Table VII. Corrected Relative Intensities of the Transitions Eu($^5D_0 \rightarrow {}^7F_J$) (Average of Sites I and II) and Tb($^5D_4 \rightarrow {}^7F_J$) in [Ln(mbzimpy)$_3$](ClO$_4$)$_3$ Complexes at Various Temperatures

Eu					Tb				
J	4 K	77 K	295 K	sol[a]	*J*	4 K	77 K	295 K	sol[a]
0	0.004	0.004	0.04	0.07	6	1.0	1.0	1.0	1.0
1	1.0	1.0	1.0	1.0	5	2.7	2.9	3.4	2.8
2	2.6	2.4	7.0	6.1	4	0.9	0.9	1.6	0.8
3	0.2	0.2	0.2	b	3	0.5	0.4	0.5	0.4
4	2.1	2.3	2.3	1.8	2.1	0.1	0.1	b	b

[a] Solution 10^{-3} M in CH$_3$CN, at 295 K. [b] Too weak to be measured.

Table VIII. Lifetimes (ms) of the Eu($^5D_0$) and Tb($^5D_4$) Levels in [Ln(mbzimpy)$_3$](ClO$_4$)$_3$ Complexes as a Function of Temperature

		lifetimes	
T/K	compd	Eu	Tb
4	100%	1.87 ± 0.04	1.80 ± 0.04
77	100%	1.85 ± 0.04	1.46 ± 0.04
	2% in Gd	1.86 ± 0.02	1.23 ± 0.06
295	100%	0.26 ± 0.02	*a*
295	solution[b]	0.48 ± 0.09	*a*

[a] Intensity too weak to be measured. [b] 10^{-3} M in CH$_3$CN.

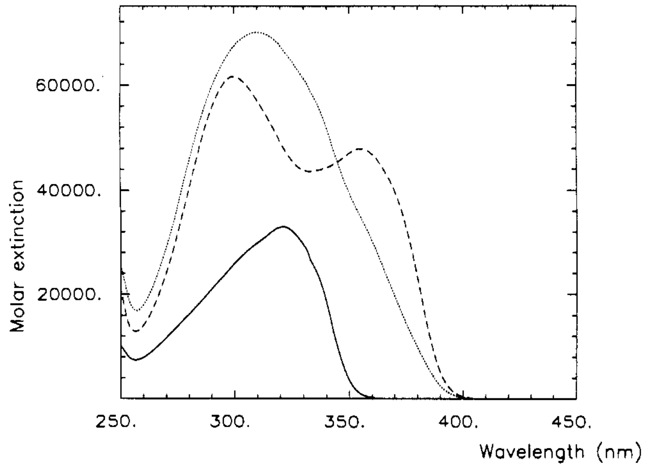

Figure 8. Absorption spectra of mbzimpy (**1**, full line), [La(mbzimpy)$_3$]$^{3+}$ (**5**, dashed line) and [La(pbzimpy)$_3$]$^{3+}$ (**9**, dotted line) in acetonitrile (2 × 10^{-4} M).

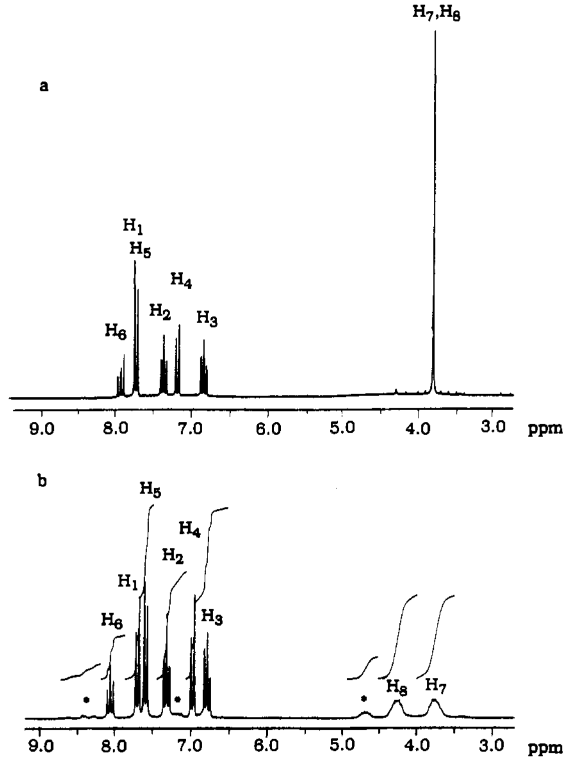

Figure 9. 200-MHz ^{1}H-NMR spectra of (a) [La(mbzimpy)$_3$]$^{3+}$ (**5**) and (b) [La(pbzimpy)$_3$]$^{3+}$ (**9**) 5 × 10^{-3} M in CD$_3$CN [an asterisk denotes minor species).

Table IX. ^{1}H NMR Shifts (with respect to TMS) for Ligands **1–3** in CDCl$_3$ and Complexes **5**, **6**, and **8–12** in CD$_3$CN

compd	H$_1$	H$_2$	H$_3$	H$_4$	H$_5$	H$_6$	H$_{7,8}$
1	7.85		7.20–7.40		8.42	8.05	4.25
2	7.85		7.3–7.40		8.33	8.04	4.71
3	7.82		7.22–7.38		8.39	8.02	5.54
12	7.02	7.10	7.37	7.60	8.68	8.73	4.17
5	7.70	7.33	6.79	7.15	7.70	7.90	3.76
9	7.70	7.32	6.80	7.00	7.60	8.06	3.80 4.25
6	13.43	7.53	7.29	5.67	2.80	4.85	1.81
10	11.34	7.24	7.30	5.75	3.77	6.00	2.20 2.50
11	11.32	7.37	7.29	5.74	3.52	5.68	3.50 3.60
8	−53.08	0.54	9.22	11.95	18.82	17.40	20.5

OH)(H$_2$O)](ClO$_4$)$_3$ even from 1:3 stoichiometric mixtures of Lu^{3+} and mbzimpy. The fact that bulky substituents bound to the stacked aromatic benzimidazole rings in [Eu(pbzimpy)$_3$]$^{3+}$ and [Eu(dmbbzimpy)$_3$]$^{3+}$ reduce the stability of the pseudo-D_3 cations also indicates that intramolecular stacking interactions play a prominant part in the stabilization of the mononuclear triple-helical complexes **5–11**. A direct comparison with the analogous cation [Eu(terpy)$_3$]$^{3+}$ is of interest because it displays similar pseudo-D_3 symmetry in the solid state,[14] and the replacement of the aromatic benzimidazole rings in mbzimpy (**1**) by pyridine rings in terpyridine should lead to different stacking possibilities. Unfortunately, the reported X-ray crystal structure[14] of [Eu(terpy)$_3$](ClO$_4$)$_3$ is not accurate enough to allow a detailed comparison, but a detailed luminescence and NMR study in acetonitrile solution[35] have firmly established that [Eu(terpy)$_3$]$^{3+}$ exhibits on–off equilibria of the pyridine rings, giving a predominantly eight-coordinate solution structure. In the same conditions, such decomplexation processes are not observed for [Eu(mbzimpy)$_3$]$^{3+}$, which is the only species in solution. This increase in stability on going from [Eu(terpy)$_3$]$^{3+}$ to [Eu(mbzimpy)$_3$]$^{3+}$ we assign to the intramolecular stacking interactions in the cations, which we expect to be significantly increased when pyridines are replaced by more extended aromatic benzimidazoles.

The luminescent properties of the complexes **5–8** are consistent with the above description. They show the Ln(III) ions well protected by the ligands, except in solution where some solvent interaction seems to occur. The solid state and solution spectra reflect the pseudotrigonal symmetry of the [Ln(mbzimpy)$_3$]$^{3+}$ complexes. The ligand to lanthanide energy transfer is efficient and the antenna effect significant. However, at room temperature, the luminescence undergoes a marked quenching. For both the Eu and Tb complexes **6** and **8**, it mainly arises from the fluxionality of the ligands resulting in a substantial mixing of vibrational functions with the 4f states. In addition, it is conceivable that the additional quenching observed for the Eu complex **6** arises from a low-lying ligand to metal charge-transfer state.

Table X. Electronic Spectral Data for Ligands **1** and **2** and Complexes **5–12** in CH_3CN at 293 K

compd	$\pi_1{}^a \rightarrow \pi^*$	$\pi_1 \rightarrow \pi^*$	$\pi_1{}^b \rightarrow \pi^*$
mbzimpy (**1**)		31 150 (32 000)[a]	
pbzimpy (**2**)		31 150 (30 800)	
$[Lu(mbzimpy)_2]^{3+}$ (**12**)	32 360 (44 960)		28 010 (31 460)
$[La(mbzimpy)_3]^{3+}$ (**5**)	33 450 (61 590)		28 170 (47 915)
$[Eu(mbzimpy)_3]^{3+}$ (**6**)	33 450 (59 400)		27 700 (48 500)
$[Gd(mbzimpy)_3]^{3+}$ (**7**)	33 445 (59 950)		27 780 (48 500)
$[Tb(mbzimpy)_3]^{3+}$ (**8**)	33 445 (59 440)		27 625 (48 400)
$[La(pbzimpy)_3]^{3+}$ (**9**)	32 050 (61 200)		27 400 (40 000)
$[Eu(pbzimpy)_3]^{3+}$ (**10**)	32 360 (56 600)		27 320 (44 300)

[a] Energies are given for the maximum of the band envelope in cm^{-1}, and the molar absorption coefficient (ϵ) is given in parentheses in M^{-1} cm^{-1}.

In conclusion these complexes $[Ln(mbzimpy)_3]^{3+}$ are ideally suited to act as building blocks for the formation of triple-helical structures containing lanthanide ions and we have recently used them for the successful self-assembly of a dinuclear triple-helical coordination compound $[Eu_2(bismbzimpy)_3](ClO_4)_6$ where each metal ion is nine-coordinate by three tridentate donor units wrapped around the helical axis.[18] The stability decrease observed for $[Ln(mbzimpy)_3]^{3+}$ with the heavier lanthanide ions (Ln = Ho, Yb, Lu) indicates a very interesting size discrimination effect along the lanthanide series which offers new possibilities for the synthesis of heterodinuclear lanthanide complexes with two ion binding sites of different dimensions.

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Supplementary Material Available: Tables giving crystal data and details of the structure determination, bond lengths, bond angles, dihedral angles, least-squares planes, anisotropic thermal parameters and hydrogen atom locations and figures showing reflectance, excitation, and emission spectra of complexes **5–8** and **12** (Figures F1–F5) (19 pages). Ordering information is given on any current masthead page.