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Luminescent Lanthanide Complexes with Encapsulating Polybenzimidazole Tripodal Ligands

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The design and synthesis of luminescent lanthanide complexes have attracted considerable current attention due to their potential uses as supramolecular devices,[1] as fluorescent sensors, or as luminescent probes.[2] Much effort has been devoted to the investigation of synthetic strategies for the design of suitable encapsulating ligands which can efficiently optimize the luminescent properties of lanthanide ions by facilitating the well-known light conversion process, i.e. ligand absorption, ligand-to-metal energy transfer, and metal emission.[1a] It has been demonstrated that, to achieve strong luminescence, some important features such as inclusion, protection, energy transfer from the ligand, etc. should be incorporated.[3] In other words, it is essential to design a suitable ligand capable of encapsulating lanthanide ions while preserving or enhancing their luminescent properties. 2.2′-Bipyridine, 3,3′-bis[isoquinoline], and their *N*-oxide derivatives have previously been proved to be suitable species to the design of macrocyclic, macrobicyclic, and branched-macrocyclic ligands capable of forming highly stable and strongly luminescent Eu(III) and Tb(III) complexes.[4] Recently, calixarenes[5] and terpyridine-like ligands[3b,6] have attracted much attention mainly because they are cheap and easy to synthesize. The latter cases are of particular interest since the benzimidazole (BIm) ring in a terpyridine-like ligand allows easy derivation and incorporation in segmental di- and trileptic ligands used as building blocks in self-assembling processes. Interesting triple-stranded helices have been obtained as mononuclear,[7] homodinuclear,[8] and heterodinuclear[9] complexes.

The tripodal ligands derived from the Schiff-base condensation with tris(2-aminoethyl)amine have been vigorously studied recently as contrast agents for magnetic resonance imaging (MRI).[10] Such ligands have been demonstrated to provide hosts for the lanthanide ions and the three arms of a suitably designed tripodal ligand can encapsulate the central ions. This suggests that the tripodal ligands could be used for the development of luminescent lanthanide complexes providing proper multiple absorption groups suitable for energy transfer. Therefore, we have engaged in the investigation of lanthanide complexes with tripodal ligands incorporating the BIm ring.[11] In this paper, the substituted tris(*N*-alkylbenzimidazol-2-ylmethyl)amines Rntb (R = ^{n}propyl (^{n}Pr), methyl (Me)) have been chosen for the purpose.

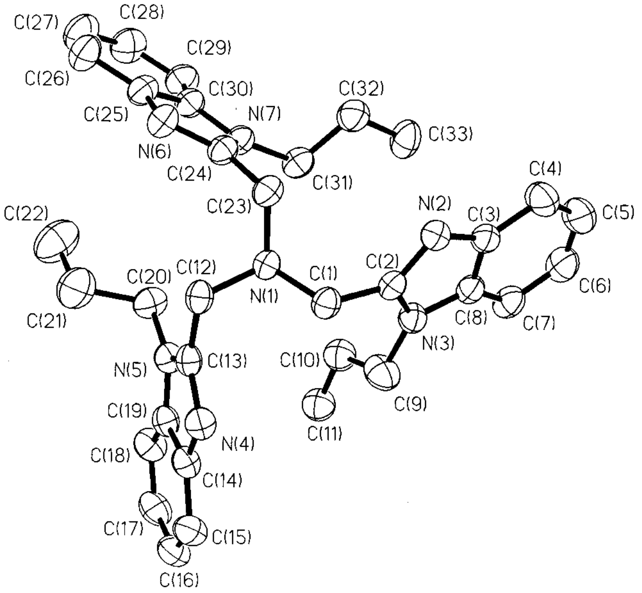

Figure 1. ORTEP drawing of ^{n}Prntb with thermal ellipsoids at the 30% probability level.

The ligand ^{n}Prntb was prepared by a method similar to that for Mentb[12] using ^{n}propyl iodide and was structurally characterized by X-ray crystallography (Figure 1).[13] Complexes **1** and **2** can be obtained by a similar procedure: $Eu(ClO_4)_3 \cdot nH_2O$ in 2 mL of acetonitrile was added to the hot methanol solution of Rntb (R

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(13) Crystallographic data for ^{n}Pr-ntb: $C_{33}H_{39}N_7$, colorless crystal, monoclinic, space group $P2_1/c$, $a = 16.627(3)$ Å, $b = 13.161(2)$ Å, $c = 14.045(2)$ Å, $\beta = 95.82(1)°$, $V = 3057.6(8)$ Å^3, $Z = 4$, $D_c = 1.159$ g cm^{-3}, μ(Mo Kα) = 0.071 mm^{-1}, R_1 (wR_2) = 0.0836 (0.2482).

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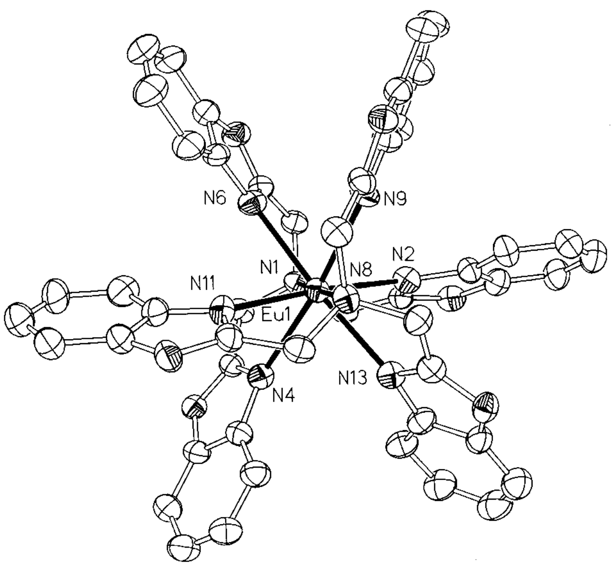

Figure 2. Perspective view of the cation $[Eu(^nPrntb)_2]^{3+}$ in complex **1** showing atoms as thermal ellipsoids at the 30% probability level. All the H atoms and the ^{n}propyl groups have been omitted for clarity.

= Me or ^{n}Pr, 0.2 mmol, 5 mL) at room temperature. The resulting mixture was left standing for several days to give crystalline complex in 70−75% yield. The solid products were formulated as $[Eu(^nPrntb)_2](ClO_4)_3\cdot 2CH_3CN\cdot 0.5H_2O$ (**1**) and $[Eu(Mentb)_2](ClO_4)_3\cdot CH_3CN\cdot 0.5H_2O$ (**2**) by elemental microanalyses[14] and have been structurally characterized.[15]

The crystal structure of the free ligand ^{n}Prntb shows that the three BIm arms form a cone-shaped cavity with the tertiary amine-N atom lying at the bottom as shown in Figure 1. The imine-N atoms of the BIm rings point outside. On coordination, they rotate inside to ligate the central lanthanide ion to form the chelate rings. Thus, the ligand displays a tripod-type tetradentate coordination mode with the central metal ion settling in the cavity. The main structural feature common to the two complexes is the presence of the $[Eu(Rntb)_2]^{3+}$ motif, in which the Eu(III) ion is coordinated by the eight nitrogen atoms from the two ligands (Figure 2 shows the structure of **1** with the alkyl groups omitted for clarity). The six BIm arms wrap around the metal ion alternately to give a *pseudo*-C_3 symmetry with the axis passing through the two apical tertiary nitrogen atoms and the central Eu^{3+} atom. When viewed down this axis, each chelate twists about the $N_{amine}-C$ bond leading to a helical structure. In each cation $[Eu(Rntb)_2]^{3+}$ the two ligands show the same right- or left-handed screw resulting in a chiral enantiomer. It is interesting to note that compound **1** crystallizes with pairs of enantiomeric cations to form racemic complex, while only one enantiomer exists for compound **2**, leading to a chiral space group $P2_12_12_1$. The intrinsic reason that causes this stereochemical difference is not yet clear, but marked difference can be found for the arrangement of the BIm rings in the two complexes. The individual BIm ring is planar within experimental error, and nearly coplanar with the Eu^{3+} in $[Eu(^nPrntb)_2]^{3+}$ (mean deviation 0.485 Å) but significantly deviated in $[Eu(Mentb)_2]^{3+}$ (mean deviation 1.175 Å). The six interplanar angles formed between two adjacent BIm rings fall into two groups: 42.1−49.4 and 59.5− 71.1° in the former, but 15.0−15.8 and 90.8−93.5° in the latter, which suggests that each pair of closely adjacent rings from different ligands has a certain amount of intramolecular stacking interaction.[7] The larger difference of the two types of interplanar angles in the latter implies that such stacking is more marked in compound **2**, with average distance between the three pairs of stacked BIm rings being 3.35 Å. Such small interplanar distances and angles (15.0−15.8°) further illustrate that ring overlapping[17] exists in compound **2**. The average $Eu-N_{imine}$ distances do not differ much for $[Eu(^nPrntb)_2]^{3+}$ (average 2.501 Å) and $[Eu(Mentb)_2]^{3+}$ (average 2.488 Å), although that of the former is slightly longer than the latter, which might be related to the different substituents R. The long $Eu-N_{amine}$ bond distances (average 2.715 Å for $[Eu(^nPrntb)_2]^{3+}$; 2.660 Å for $[Eu(Mentb)_2]^{3+}$) may be related to the steric requirement and to the relatively weak coordination capability of the apical tertiary nitrogen atoms. The coordination sphere around the Eu(III) ion may best be described as a slightly distorted cube in which the eight ligating nitrogen atoms occupy the corners. Although eight-coordinate complexes of lanthanides are fairly common, highly symmetrical polyhedral geometry is observed only of two types: dodecahedron (D_{2d}) and square antiprism (D_{4d}). The cubic geometry is rare in discrete metal complexes,[18] and cubic lanthanide complexes are mainly found for monodentate or bidentate chelating ligands.[19]

The ability of the two tripods to shield an Ln(III) ion completely with N-donors without additional bound solvent molecules, especially water or alcohol, is important for the design of Ln(III) supramolecular photonic devices since coordinated solvent molecules are frequently efficient quenchers of Ln(III) luminescence.[2] The two Eu complexes are highly luminescent, and ligand-centered excitation produces exclusively metal-centered luminescence. The emission spectra show $^5D_0 \rightarrow {}^7F_j$ transitions which are dominated by the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition. The broad emission band around 467 nm observed for the free ligands is significantly reduced, indicating an efficient ligand-to-metal energy-transfer process (antenna effect).[6−9] Detailed luminescence studies are in progress.

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Supporting Information Available: A file, in CIF format, is available on the Internet only. Information on data collection and reduction and structure solution and refinement, tables of crystallographic parameters, atomic coordinates and equivalent isotropic temperature factors, bond distances and bond angles, and anisotropic temperature factors for **1** and **2** are also available. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Anal. Calcd for $C_{70}H_{85}N_{16}Cl_3O_{12.5}Eu$ (**1**): C, 52.26; H, 5.32; N, 13.93. Found: C, 52.36; H, 5.32; N, 13.75. For $C_{56}H_{58}N_{15}Cl_3O_{12.5}Eu$ (**2**): C, 48.06; H, 4.17; N, 15.01. Found: C, 47.59; H, 4.13; N, 15.00. IR (KBr, cm^{-1}): 3200 [broad, ν_{O-H}], 1623−1625, 1596 [$\nu_{C=N}$], 1085−1091, 626 [ν_{O-Cl}].

(15) Crystallographic data for complex **1**: yellow crystal, 0.35 × 0.4 × 0.4 mm, monoclinic, space group $P2_1/n$, $a = 13.412(1)$ Å, $b = 24.019(2)$ Å, $c = 23.685(2)$ Å, $\beta = 93.20(1)°$, $V = 7618.1(11)$ Å^3, $Z = 4$, $D_c = 1.403$ g cm^{-3}, $F(000) = 3324$, μ(Mo Kα) = 0.998 mm^{-1}, final R_1 and wR_2 are 0.0600 and 0.1693, respectively. Complex **2**: yellowish crystal, 0.2 × 0.2 × 0.5 mm, orthorhombic, space group $P2_12_12_1$, $a = 12.819(1)$ Å, $b = 21.056(2)$ Å, $c = 22.638(2)$ Å, $V = 6110.4(9)$ Å^3, $Z = 4$, $D_c = 1.511$ g cm^{-3}, $F(000) = 2852$, μ(Mo Kα) = 1.232 mm^{-1}, final R_1 and wR_2 0.0884 and 0.2340, respectively. Intensities were collected on Rigaku AFC7R (**1**) and Rigaku RAXIS IIC image-plate (**2**) diffractometer with graphite monochromator at 294 K. The structures were solved by direct methods and refined by full-matrix least-squares using the SHELXLTL-PC program package.[16] All the non-hydrogen atoms except some disordered carbon atoms of ^{n}Pr substituents, the perchlorate anions and the water molecules, were refined anisotropically, while the hydrogen atoms were included at the calculated positions isotropically but not refined. The largest peaks (ca. 1.6 e/Å^3) were found near the Eu position in the final difference Fourier map of complex **2**.

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