

# Construction of two- and three-dimensional supramolecular networks with an encapsulated lanthanide(III) complex as building block and hydrogen-bonded 4,4'-bipyridyl as spacer

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Reaction of the tripodal ligand tris(2-benzimidazolyl-methyl)amine (ntb) with hydrated lanthanide(III) perchlorates in methanol affords the complexes  $[\text{Ln}(\text{ntb})_2]^{3+}$  (Ln = Pr, Eu and Tb) in which the central  $\text{Ln}^{3+}$  ion is well encapsulated in a cubic coordination environment; *in situ* co-crystallization of the complexes in the presence of 4,4'-bipyridyl produces either a double salt containing the bipyridinium(1+) cation or adducts with two to three bipyridyl molecules, the latter adducts forming doubly interpenetrating two- or three-dimensional cationic networks.

The control of molecular assembly using supramolecular interactions represents a new area of considerable general and topical interest.<sup>1</sup> In particular, strong, selective and directional hydrogen bonding has been exploited for molecular recognition associated with biological activity, and for crystal engineering of molecular solids.<sup>2</sup> Much progress has been made in the construction of organic building blocks into one-, two- or three-dimensional hydrogen-bonded architectures;<sup>2,3</sup> however, the use of metal complexes for assembly or self-assembly by hydrogen bonding has attracted little attention until recently,<sup>4</sup> although the resulting products are often expected to exhibit certain desirable electronic, magnetic, or inclusion behavior.<sup>1b</sup>

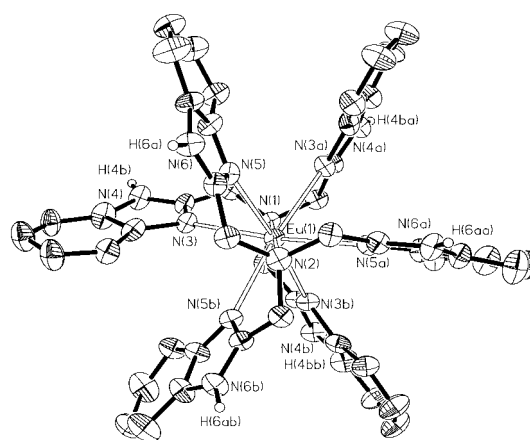
The specific spectroscopic and magnetic properties of lanthanide(III) ions have made them essential components in the preparation of new materials and ideal probes in studies of biological systems.<sup>5</sup> The incorporation of trivalent lanthanide ions into supramolecular complexes that act as molecular photonic devices is currently of great interest in supramolecular chemistry.<sup>6</sup> Probes based on  $\text{Eu}^{\text{III}}$  and  $\text{Tb}^{\text{III}}$  are of special relevance because of their long-lived  $^5\text{D}_0$  and  $^5\text{D}_4$  excited states and their large Stokes' shift. However, the design of a good lanthanide luminescent probe has to overcome difficulties arising from the low oscillator strengths of the f-f transitions and from the easy de-excitation of the  $\text{Ln}^{\text{III}}$  excited state.<sup>6a,c</sup>

Current research has mainly focused on the encapsulation of the  $\text{Ln}^{\text{III}}$  ions using pre-organized ligands such as coronands, cryptands, podands, calixarenes or Schiff bases.<sup>5c,6d</sup> We now report the syntheses and crystal structures of new lanthanide complexes with the tripodal ligand tris(2-benzimidazolyl-methyl)amine (ntb), in which the central  $\text{Ln}^{\text{III}}$  ion displays a rarely found cubic coordination environment and is well encapsulated from interaction with its surroundings by the rigid heterocyclic rings of ntb. Employing the linear difunctional H-bond acceptor 4,4'-bipyridyl as a spacer, the bipyridinium(1+) double salt  $[\text{Eu}(\text{ntb})_2](\text{ClO}_4)_3 \cdot (\text{bipyH})\text{ClO}_4 \cdot 3\text{H}_2\text{O}$  **1** and two types of bipyridyl adducts bearing different lanthanide/bipy molar ratios, namely  $[\text{Pr}(\text{ntb})_2](\text{ClO}_4)_3 \cdot 2\text{bipy} \cdot 1.5\text{H}_2\text{O}$  **2** and  $[\text{Ln}(\text{ntb})_2](\text{ClO}_4)_3 \cdot 3\text{bipy} \cdot n\text{H}_2\text{O}$  (**3**, Ln = Eu,  $n = 2$ ; **4**, Ln = Tb,  $n = 1$ ) were obtained. Doubly interpenetrating two- or three-dimensional extended networks are formed in complexes **2–4**.

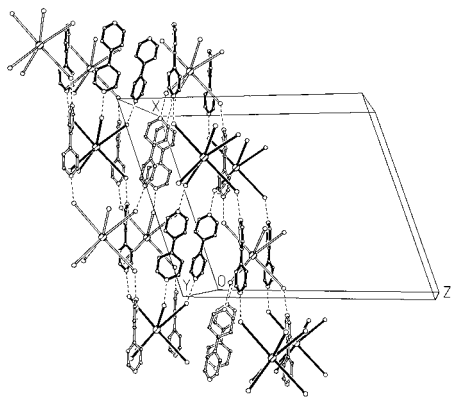
In the presence of 4,4'-bipyridyl, reaction of ntb with hydrated lanthanide(III) perchlorates afforded complexes **1–4**.<sup>‡</sup> The nature of the products isolated is evidently sensitive to the presence of a trace amount of acid<sup>8</sup> and different equivalents of 4,4'-bipyridyl. Single crystals suitable for X-ray analyses were obtained by slow diffusion of diethyl ether into a dilute reaction mixture.<sup>§</sup>

The main structural feature common to all four complexes is the presence of the  $[\text{Ln}(\text{ntb})_2]^{3+}$  motif, in which the  $\text{Ln}^{\text{III}}$  ion is coordinated by eight nitrogen atoms from the two ntb ligands to give a slightly distorted cubic environment (Fig. 1). Both ntb ligands display a tripod-type tetradentate coordination mode in wrapping around the central lanthanide ion. This kind of coordination geometry is seldom found for eight-coordinated  $\text{Ln}^{\text{III}}$  ions, although Wood *et al.*<sup>9</sup> suggested long ago that the cube should not be energetically unfavorable relative to either the square antiprism ( $D_{4d}$ ) or the triangular dodecahedron ( $D_{2d}$ ). The ability of two ntb tripods to shield completely a  $\text{Ln}^{\text{III}}$  ion with N-donor sites without additional bound solvent molecules, especially water or alcohol, is important for the design of lanthanide(III) supramolecular photonic devices since such coordinated solvent molecules are frequently efficient quenchers of  $\text{Ln}^{\text{III}}$  luminescence.<sup>6d</sup>

Since each ntb ligand possesses three NH groups that are potential hydrogen-bond donors (see Fig. 1), the possibility of controlling the assembly of  $[\text{Ln}(\text{ntb})_2]^{3+}$  moieties by employing the linear difunctional hydrogen-bond acceptor 4,4'-bipyridyl as a spacer component was explored. X-Ray crystal structure analysis showed that in complex **1**, one nitrogen atom of (bipyH<sup>+</sup>) forms an acceptor hydrogen bond to  $[\text{Eu}(\text{ntb})_2]^{3+}$  (N...N, 2.900 Å) while the protonated nitrogen atom is connected to one oxygen atom of a perchlorate anion (N...O,

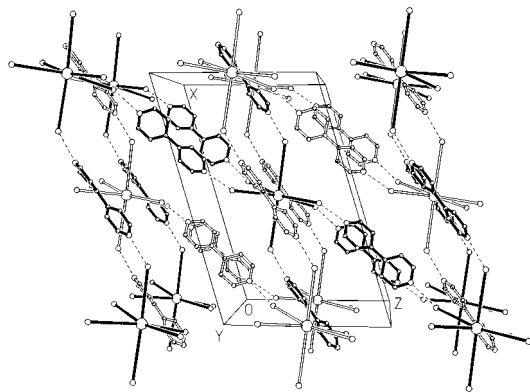


**Fig. 1** Perspective view of the  $[\text{Eu}(\text{ntb})_2]^{3+}$  cation in **3** showing atoms as thermal ellipsoids at the 30% probability level. All H atoms have been omitted, except those of the NH groups that are shown as small spheres.



**Fig. 2** Interlocking two-dimensional cationic frameworks constituting a layer matching the (001) plane in the crystal structure of **2**. For clarity, each 2-benzimidazolymethyl arm of the ntb ligand is represented by a long rod joining each NH group to the lanthanide atom, so that each  $[\text{Pr}(\text{ntb})_2]^{3+}$  cation takes the appearance of an octahedron. All hydrogen atoms, water molecules and perchlorate ions have been omitted. The independent interlocking frameworks are differentiated by solid and open shading.

2.942 Å), thus precluding the formation of the linear chain  $\dots[\text{Eu}(\text{ntb})_2]^{3+}\dots\text{bipy}\dots[\text{Eu}(\text{ntb})_2]^{3+}\dots\text{bipy}\dots$ . In complex **2**, each bipy forms a pair of acceptor hydrogen bonds with two different  $[\text{Pr}(\text{ntb})_2]^{3+}$  cations (N $\cdots$ N distances lie in the range 2.783–2.852 Å), thereby generating an open, two-dimensional cationic framework with each  $[\text{Pr}(\text{ntb})_2]^{3+}$  cation alternately connected to one and three bipy molecules in the *a* direction. Moreover, two independent frameworks of this type interpenetrate each other to form an extended layer corresponding to the (001) plane (Fig. 2), with the perchlorate ions and water molecules located in the inter-layer region. In complex **4** the NH groups of both independent ntb ligands in the  $[\text{Tb}(\text{ntb})_2]^{3+}$  ion and the bipy molecule are involved in the supramolecular hydrogen-bonding scheme (N $\cdots$ N range 2.818–2.871 Å). Linkage between each  $[\text{Tb}(\text{ntb})_2]^{3+}$  cation and six neighbouring bipy units leads to an open, three-dimensional cationic network, leaving large voids to be filled by another identical, interlocking network (Fig. 3), and the perchlorate ions and water molecules are located in the residual interstices. Compound **3**, in which the  $[\text{Eu}(\text{ntb})_2]^{3+}$  ion lies on a three-fold symmetry axis (Fig. 1), exhibits the same type of supramolecular structure as **4**, although the two adducts crystallize in different space groups.



**Fig. 3** Three-dimensional doubly interpenetrating networks in the crystal structure of **4**. Representation of the supramolecular structure is simplified in the same manner as in Fig. 2.

In summary, the present study has demonstrated that the intrinsic steric constraints of the tripodal ligand ntb facilitate complete encapsulation of a lanthanide(III) ion in a rare cubic coordination geometry. Assembly of  $[\text{Ln}(\text{ntb})_2]^{3+}$  building blocks with bipy spacers using supramolecular NH $\cdots$ bipy $\cdots$ HN hydrogen bonds results in two- or three-dimensional two-fold

interpenetrating networks, which may be profoundly influenced by the presence of acid and different equivalents of the spacer component.

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## Notes and References

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‡ All complexes were prepared using a similar procedure: 0.2 mmol of tris(2-benzimidazolymethyl)amine<sup>7</sup> (ntb) and 0.1 mmol of  $\text{Ln}(\text{ClO}_4)_3 \cdot n\text{H}_2\text{O}$  (prepared by dissolving the corresponding lanthanide oxides (99.99%) in 50% perchloric acid) were dissolved in 5 ml methanol. To this solution was added 5 ml of a methanolic solution of 4,4'-bipyridyl (0.1 mmol for **1**, 0.2 mmol for **2** and 0.3 mmol for **3** or **4**, respectively). The resulting mixture was left standing for several hours to give microcrystals. Complex **1**: Found: C, 44.07; H, 3.61; N, 13.93. Calc. for  $\text{C}_{38}\text{H}_{57}\text{N}_{16}\text{O}_{19}\text{Cl}_4\text{Eu}$ : C, 44.20; H, 3.65; N, 14.22%; **2**: Found: C, 50.23; H, 3.71; N, 15.55. Calc. for  $\text{C}_{68}\text{H}_{61}\text{N}_{18}\text{O}_{13.5}\text{Cl}_3\text{Pr}$ : C, 51.25; H, 3.86; N, 15.82%; **3**: Found: C, 52.62; H, 3.71; N, 15.55. Calc. for  $\text{C}_{78}\text{H}_{70}\text{N}_{20}\text{O}_{14}\text{Cl}_3\text{Eu}$ : C, 52.93; H, 3.99; N, 15.84%; **4**: Found: C, 52.46; H, 3.67; N, 15.53. Calc. for  $\text{C}_{78}\text{H}_{68}\text{N}_{20}\text{O}_{13}\text{Cl}_3\text{Tb}$ : C, 53.27; H, 3.90; N, 15.93%. For **1–4**: IR (KBr,  $\text{cm}^{-1}$ ), 4200 [broad,  $\nu(\text{O–H})$ ], 1623–1625, 1596 [ $\nu(\text{C=N})$ ], 1085–1091, 626 [ $\nu(\text{Cl–O})$ ]; UV–VIS ( $\text{CH}_3\text{CN}$ ),  $\lambda/\text{nm}$ : 280, 273 and 198–201. Emission spectra (excited at 280 nm, 77 K) for complexes **1** and **3** are nearly identical,  $\lambda/\text{nm}$ : 598 ( $^5\text{D}_0\text{--}^7\text{F}_1$ ) and 615 ( $^5\text{D}_0\text{--}^7\text{F}_2$ ).

§ *Crystal data*: **1**: *M* = 1593.6, orthorhombic, space group *Pca*2<sub>1</sub>, *a* = 26.109(3), *b* = 12.7780(10), *c* = 20.755(3) Å, *Z* = 4, yellowish crystal  $0.6 \times 0.7 \times 0.8$  mm, 7772 reflections measured, final *R*1 = 0.071 and *wR*2 = 0.149 for 4656 observed [*I* > 2 $\sigma$ (*I*)] reflections. **2**: *M* = 1593.6, monoclinic, *C*2, *a* = 20.562(2), *b* = 16.303(1), *c* = 24.079(2) Å,  $\beta$  = 109.04(1)°, *Z* = 4, colorless crystal  $0.2 \times 0.2 \times 0.15$  mm, 9088 reflections measured, final *R*1 = 0.078 and *wR*2 = 0.208 for 7779 observed reflections. **3**: *M* = 1769.9, trigonal, *R*3, *a* = 16.449(2), *c* = 27.354(4) Å, *Z* = 3, yellowish crystal  $0.4 \times 0.55 \times 0.6$  mm, 4906 reflections measured, final *R*1 = 0.078 and *wR*2 = 0.199 for 3305 observed reflections. **4**: *M* = 1758.8, monoclinic, *C*2, *a* = 20.503(2), *b* = 16.323(1), *c* = 13.083(1) Å,  $\beta$  = 106.61(1)°, *Z* = 2, colorless crystal  $0.3 \times 0.2 \times 0.2$  mm, 4982 reflections measured, final *R*1 = 0.068 and *wR*2 = 0.179 for 4780 observed reflections. CCDC 182/896.

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