Strong intramolecular π–π interactions favor the formation of 2 : 1 (L : M) lanthanide complexes of tris(2-benzimidazolylmethyl)amine

Raphaël Wietzke,[a] Marinella Mazzanti,*[a] Jean-Marc Latour[b] and Jacques Pécaut[b]

[a] Laboratoire de Reconnaissance Ionique and [b] Laboratoire de Chimie de Coordination Service de Chimie Inorganique et Biologique, Département de Recherche Fondamentale sur la Matière Condensée, CEA-Grenoble, 38054 Grenoble, Cedex 09, France. E-mail: mazzanti@drfmc.ceng.cea.fr

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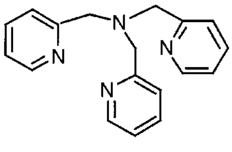
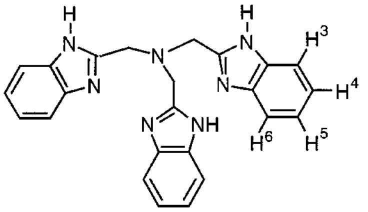
Reaction of the tripodal ligand tris(2-benzimidazolylmethyl)amine with lanthanides(III) in the presence of counterions ClO_4^-, OTf^- or Cl^- results, even for ligand to metal ratios lower than 2, in the formation of bisligand complexes showing strong p–p interactions between the benzimidazole rings both in solution and in the solid state.

The search for strongly luminescent lanthanide complexes has motivated the synthesis of lanthanide(III) complexes containing only neutral aromatic N-donor ligands.[1] So far, such complexes have been reported only for the tridentate ligand terpyridine (terpy) and for terpy analogues containing benzimidazole side arms.[2,3] These tris(ligand) complexes are formed in a non-aqueous solvent, in absence of coordinating anions and at ligand to metal ratios L/M ⩾ 3. The high stability against ligand dissociation shown by the benzimidazole derivative has been attributed to the presence of intramolecular π stacking interactions.[4] We have recently synthesized, and characterized by crystallographic and NMR studies, some 1 : 1 lanthanide(III) complexes of the tripodal neutral N-donor ligands tris[(2-pyridyl)methyl]amine (tpa) and tris[(2-pyrazinyl)methyl]-amine.[5] Attempts to add a second ligand to these complexes in the presence of coordinating counterions failed. On the other hand, in the presence of non-coordinating anions, addition of an excess of tripodal ligand to the mono(ligand) complexes resulted in the formation of hydroxo-derivatives.[6] In order to investigate whether π–π interactions could stabilize the 2 : 1 complexes, we studied lanthanide(III) complexation by the tripodal N-donor ligand tris(2-benzimidazolylmethyl)amine (ntb), and analogue of tpa in which the pyridine arms are replaced by a benzimidazole. Indeed, ntb demonstrates a strong stabilization of the 2 : 1 complexes in solution as well as in the solid state.



tpa



ntb

Reaction of $Ln(ClO_4)_3 \cdot 6H_2O$ (Ln = La, Nd, Eu) with 2 equiv. of ntb in acetonitrile yields complexes $[Ln(ntb)_2]$-$[ClO_4]_3 \cdot 2MeCN \cdot 3Et_2O$ (**1**, Ln = La; **2**, Ln = Nd; **3**, Ln = Eu) in which the two tripodal ligands encapsulate the lanthanide ion and shield it entirely from solvent molecules (see below).† Reaction of $LuCl_3 \cdot 6H_2O$ with ntb in a 2 : 1 (ntb/Lu) ratio in methanol yields also the bis(ligand) complex $[Lu(ntb)_2]$-$Cl_3 \cdot 7H_2O \cdot 0.5MeOH$ **4**. This is the first example, to our knowledge, in which a neutral N-donor ligand displaces all the strongly coordinating chloride ions. An X-ray diffraction study‡ allowed the determination of the crystal structures of the complexes **1–4**, which all present the same structural arrangement for the cation $[Ln(ntb)_2]^{3+}$. The crystal structure of the cation $[Eu(ntb)_2]^{3+}$ is shown in Fig. 1. The coordination geometry is best described as a distorted bicapped trigonal antiprism, in which the lanthanide ion is eight-coordinated by two tetradentate ligands with a pseudo-C_3 symmetric arrangement. The most important feature of these structures is the presence of strong π–π interactions[7] between the benzimidazole rings as shown by the interplanar distances and angles reported in Table 1. Very recently preliminary results on the crystal structures of supramolecular networks using $[Ln(ntb)_2][ClO_4]_3$ as building blocks have been reported.[8] In these structures the stacking interactions between the benzimidazole units are completely lost probably due to the hydrogen-bonding interaction with the 4,4′-bipyridyl space present in the assembly.

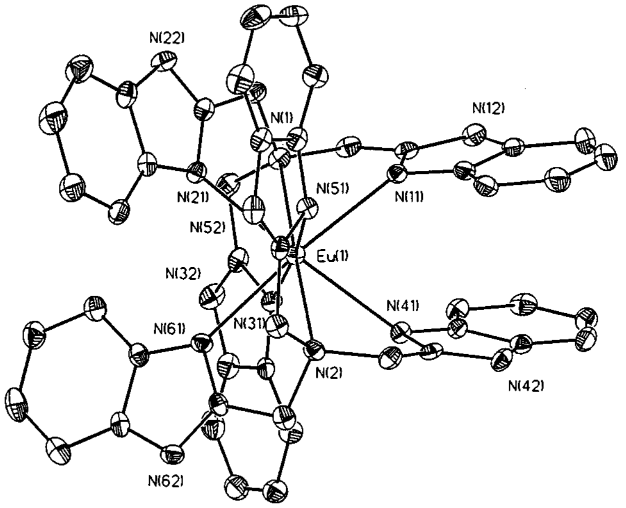


Fig. 1 Crystal structure of the cation of $[Eu(ntb)_2]^{3+}$ **3** with thermal ellipsoids at 30% probability. Selected bond lengths (Å): Eu–N(1) 2.713(4), Eu–N(2) 2.725(4), Eu–N(31) 2.507(4), Eu–N(11) 2.504(4), Eu–N(51) 2.503(4), Eu–N(641) 2.500(4), Eu/N(21) 2.496(4), Eu–N(61) 2.479(4).

The titration of $Ln(OTf)_3$ (Ln = La, Eu, Lu) with ntb in anhydrous acetonitrile was followed by ^1H NMR spectroscopy under a dry argon atmosphere. For a metal to ligand ratio of 1 : 1 two sets of signals were observed (Fig. 2) which were assigned to the 1 : 1 and 2 : 1 ntb complexes. The presence of the two complexes in solution was confirmed by electrospray mass spectrometry. Comparison of the chemical shift of the benzimidazole ring protons in the 1 : 1 and 2 : 1 complexes of lanthanum

Table 1 Interplane distances and angles between the planes of the benzimidazole rings

	$\alpha_1/°$	$d_1/Å$	$\alpha_2/°$	$d_2/Å$	$\alpha_3/°$	$d_3/Å$
$[La(ntb)_2][ClO_4]_3$	13.3	3.55	12.2	3.50	34.0	3.48
$[Nd(ntb)_2][ClO_4]_3$	13.9	3.38	14.5	3.53	34.3	3.40
$[Eu(ntb)_2[ClO_4]_3$	15.3	3.30	15.4	3.38	34.6	3.47
$[Lu(ntb)_2]Cl_3$	16.7	3.15	19.9	3.18	2.31	3.20

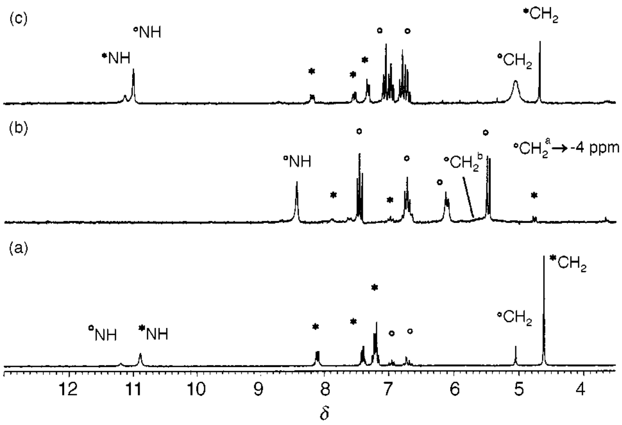


Fig. 2 ^{1}H NMR spectra at 298 K of: (a) a 1 : 1 mixture of La(OTf)$_3$ and ntb in anhydrous acetonitrile; (b) a 1 : 1 mixture of Eu(OTf)$_3$ and ntb in acetonitrile; (c) a 1 : 1 mixture of Lu(OTf)$_3$ and ntb in acetonitrile [(*) indicates the 1 : 1 complex and (○) indicates the 2 : 1 complex].

reveals an upfield shift of 0.4–1.00 ppm for the bis(ntb) complex in agreement with the presence of intramolecular π-stacking interactions in solution.[9] Integration of the NMR signals of the two species gave an approximate value of the ratio (K_2/K_1) of the stepwise formation constants of the 2 : 1 and 1 : 1 complexes. This ratio varies along the series: 0.03 for La, 14 for Eu, 3 for Lu. While for La, $K_1 > K_2$, the value of the ratio K_2/K_1 indicates, in the case of Eu and Lu, a strong preference of the ntb ligand for the formation of the 2 : 1 complexes. This is a rare behavior in coordination chemistry which has only previously been observed twice for lanthanides in presence of tripodal amines with phenolato or phosphinato donors.[10,11] As expected, this ratio is dependent on the counter anion, with the coordinating anions opposing the formation of the 2 : 1 complex. In this respect, it is striking that the bis(ntb) complex already exists in methanol solution of LuCl$_3$·6H$_2$O and ntb in a 1 : 1 ratio, as shown by ^{1}H NMR and ESMS.

The high formation constant in water solution of the 2 : 1 complex of the tripodal aminophenol ligand reported by Orvig and coworkers[10,11] was attributed to an entropic effect associated with the release of water molecules. On the other hand, the entropy changes associated with the complexation of strongly basic polydentate amines with lanthanide perchlorate in anhydrous acetonitrile are large and negative and the complexes are enthalpy stabilized.[10] In the Ln–ntb system it is unlikely that an entropy effect related to a change in coordination number is responsible for the observed anomaly ($K_2 > K_1$). The preference for the bis(ntb) complexes might be rather of enthalpic origin and related to the strong π–π interactions found in solution as well as in the solid state.

As a consequence of this π–π stacking of the ligands the metal is completely shielded from the solvent since no water molecule is coordinated to the lanthanide ions in the solid state. This is also true in solution, since comparison of the luminescence lifetimes of [Tb(ntb)$_2$](OTf)$_3$ in MeOH and MeOD gave a value for the number of coordinated methanol molecules close to zero (q = 0.35 ± 0.5).[12]

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Notes and references

† Elemental analyses for complexes **1**–**4**: Calc. for [La(ntb)$_2$][ClO$_4$]$_3$·3H$_2$O, C$_{48}$H$_{48}$Cl$_3$N$_{14}$O$_{15}$La: C, 44.15; H, 3.70; N, 15.01. Found: C, 43.86; H, 3.80; N, 14.99. Calc. for [Nd(ntb)$_2$][ClO$_4$]$_3$, C$_{48}$H$_{42}$Cl$_3$N$_{14}$O$_{12}$Nd: C, 45.71; H, 3.69; N, 15.88. Found: C, 45.84; H, 3.37; N, 15.59. Calc. for [Eu(ntb)$_2$][ClO$_4$]$_3$·2H$_2$O, C$_{48}$H$_{46}$Cl$_3$N$_{14}$O$_{14}$Eu: C, 44.41; H, 3.74; N, 14.90. Found: C, 44.31; H, 3.56; N, 15.07. Calc. for [Lu(ntb)$_2$]Cl$_3$·6H$_2$O, C$_{48}$H$_{54}$Cl$_3$N$_{14}$O$_6$Lu: C, 47.87; H, 4.52; N, 16.28. Found: C, 47.66; H, 4.46; N, 15.91%.

‡ *Crystal data*: **1**: [La(ntb)$_2$][ClO$_4$]$_3$·2MeCN·3Et$_2$O, C$_{64}$H$_{78}$N$_{16}$O$_{15}$Cl$_3$La, M = 1556.68, monoclinic, $P2_1/c$, a = 18.4451(4), b = 25.0336(6), c = 16.9564(4) Å, β = 111.7940(10)°, V = 3903.0(13) Å^3, Z = 4, D_c = 1.422 g cm^{-3}, μ = 0.771 mm^{-1}, 9937 independent reflections ($2\theta_{\max}$ = 26) were collected at 173 K. Refinement using the SHELXTL 5.05 package on all data converged at $R_1[F > 4\sigma(F)]$ = 0.0767, wR_2 = 0.1827.

2: [Nd(ntb)$_2$][ClO$_4$]$_3$·2MeCN·3Et$_2$O, C$_{64}$H$_{78}$N$_{16}$O$_{15}$Cl$_3$Nd, M = 1562.01, monoclinic, $P2_1/c$, a = 18.2235(7), b = 24.8434(10), c = 16.8575(7) Å, β = 111.79(1), V = 7086.5(5) Å^3, Z = 4, D_c = 1.464 g cm^{-3}, μ = 0.921 mm^{-1}. 12398 independent refelections ($2\theta_{\max}$ = 26) were collected at 293 K. Refinement using the SHELXTL 5.05 package on all data converged at $R_1[F > 4\sigma(F)]$ = 0.0618, wR_2 = 0.1250.

3 [Eu(ntb)$_2$][ClO$_4$]$_3$·2MeCN·3Et$_2$O, C$_{64}$H$_{78}$N$_{16}$O$_{15}$Cl$_3$Eu, M = 1569.73, monoclinic, $P2_1/c$, a = 18.1861(4), b = 24.8563(6), c = 16.9481(4) Å, β = 111.93(1), V = 7106.9(3) Å^3, Z = 4, D_c = 1.467 g cm^{-3}, μ = 1.070 mm^{-1}. 12490 independent reflections ($2\theta_{\max}$ = 26) were collected at 173 K. Refinement using the SHELXTL 5.05 package on all data converged at $R_1[F > 4\sigma(F)]$ = 0.0481, wR_2 = 0.0865.

4 [Lu(ntb)$_2$]Cl$_3$·7H$_2$O·0.5MeOH, C$_{48.5}$H$_{58}$N$_{14}$Cl$_3$O$_{7.5}$Lu, M = 1238.41, orthorhombic, *Pbcn*, a = 28.03400(10), b = 14.87580(10), c = 27.7355(3) Å, V = 11566.5(2) Å^3, Z = 8, D_c = 1.422 g cm^{-3}, μ = 1.905 mm^{-1}. 10926 independent reflections ($2\theta_{\max}$ = 26) were collected at 293 K. Refinement using the SHELXTL 5.05 package on all data converged at $R_1[F > 4\sigma(F)]$ = 0.0867, wR_2 = 0.2266.

To prevent loss of solvent, all the crystals were coated with a light hydrocarbon oil and quickly transferred to a stream of cold nitrogen on the diffractometer.

All data sets were collected using a Siemens SMART CCD area detector three-circle diffractometer (Mo-Kα radiation, graphite monochromator, λ = 0.71073 Å). Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in calculated positions. For complex **4**, one water molecule was refined isotropically due to a disorder problem. CCDC 182/1127. See http://www.rsc.org/suppdata/cc/1999/209/ for crystallographic files in .cif format.

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