

# C<sub>3</sub>-Symmetrical lanthanide podates organized by intramolecular trifurcated hydrogen bonds

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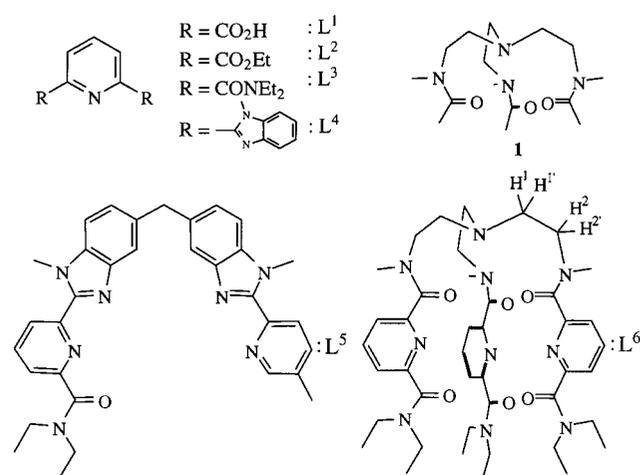
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The protonated tripodal podand [L<sup>6</sup> + H]<sup>+</sup> forms stable and organized monometallic podates [Ln(L<sup>6</sup> + H)]<sup>4+</sup> where Ln<sup>III</sup> is facially nine-coordinated by three wrapped unsymmetrical tridentate binding units. An unusual trifurcated hydrogen bond assists the organisation of the covalent tripod.

Symmetrical tridentate binding units containing a central pyridine ring L<sup>1-4</sup> are promising receptors for the design of triple helical nine-coordinate lanthanide(III) building blocks [Ln(L<sup>1</sup> - 2H)<sub>3</sub>]<sup>3+</sup> and [Ln(L<sup>i</sup>)<sub>3</sub>]<sup>3+</sup> (i = 2-4) with pre-

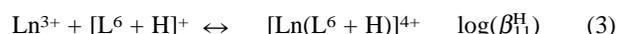
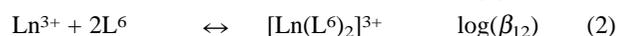
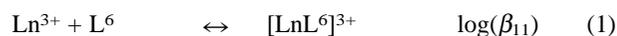


determined physico-chemical properties.<sup>1</sup> Good structural and electronic control has also been demonstrated for unsymmetrical tridentate ligands whose facial orientation in the final C<sub>3</sub>-symmetrical complexes is provided by a non-covalent tripod in the heterobimetallic d-f triple-stranded helicates (HHH)-[LnM(L<sup>5</sup>)<sub>3</sub>]<sup>5+</sup> (M = Fe<sup>II</sup>, Co<sup>II</sup>, Zn<sup>II</sup>).<sup>1,2</sup> Surprisingly, covalent tripods which are systematically used for organizing unsymmetrical bidentate binding units around octahedral d-block metal ions in monometallic<sup>3</sup> and polymetallic<sup>4</sup> podates have rarely been involved in the related arrangement of tridentate binding units around tricapped trigonal prismatic f-block ions.<sup>5-7</sup> Here, we report the preparation and complexation properties of the new podand L<sup>6</sup> which is designed to encapsulate nine-coordinate lanthanide ions into a tricapped trigonal prismatic geometry.

The podand L<sup>6</sup> is obtained in one step (yield 84%) from the condensation of tris[2-(N-methylaminoethyl)amine (Me-tren)]<sup>8</sup> with an excess of 6-(N,N-diethylcarbamoyl)pyridine-2-carboxylic acylchloride.<sup>2</sup> Potentiometric titration of L<sup>6</sup> with trifluoromethanesulfonic acid in water-acetonitrile (95:5) in the pH range 7.0-2.0 (0.1 M NaClO<sub>4</sub>) reveals a single pK<sub>a</sub> = 4.66(1) which is attributed to the protonation of the apical nitrogen atom of the Me-tren tripod by comparison with pK<sub>a</sub> =

5.19(2) found for the model compound **1** in the same conditions. When this titration is monitored by <sup>1</sup>H NMR in (CD<sub>3</sub>)<sub>2</sub>SO, the methylene protons H<sup>1,1'</sup> and H<sup>2,2'</sup> undergo the expected downfield shifts [Δδ(H<sup>1,1'</sup>) = 0.9 ppm, Δδ(H<sup>2,2'</sup>) = 0.3 ppm] resulting from the protonation of the apical nitrogen atom.<sup>9</sup> However, pK<sub>a</sub>([L<sup>6</sup> + H]<sup>+</sup>) and pK<sub>a</sub>([**1** + H]<sup>+</sup>) are six orders of magnitude lower than that of the triethylammonium cation (pK<sub>a</sub> = 11.01) which strongly suggests that the protonated apical nitrogen adopts an *endo* conformation stabilized by an intramolecular trifurcated hydrogen bond with the surrounding oxygen atoms of the side arms as previously described for protonated cryptands<sup>10</sup> and tris(2-hydroxyethyl)amine podands.<sup>11</sup> The severely reduced hydrophilicity of the resulting clipped conformation accounts for the drastic destabilization of the protonated form in polar media.<sup>10,11</sup>

ESMS titrations of L<sup>6</sup> in acetonitrile with Ln(ClO<sub>4</sub>)<sub>3</sub>·xH<sub>2</sub>O (Ln = Sm-Lu; x = 6-9) show the exclusive formation of the 1:1 complexes [LnL<sup>6</sup>]<sup>3+</sup> while signals corresponding to [LnL<sup>6</sup>]<sup>3+</sup> and [Ln(L<sup>6</sup>)<sub>2</sub>]<sup>3+</sup> are detected for large Ln<sup>III</sup> ions (Ln = La-Pr). This qualitative speciation is confirmed by spectrophotometric data obtained in the same conditions and fitted to eqn. (1) for Ln = Sm-Lu and eqns. (1) and (2) for Ln = La-Nd (Table 1). The formation of 1:2 complexes [Ln(L<sup>6</sup>)<sub>2</sub>]<sup>3+</sup> in acetonitrile is limited to light Ln<sup>III</sup> (Ln = La-Pr) as a result of their larger ionic radii which make them more accessible in [LnL<sup>6</sup>]<sup>3+</sup> for further complexation, as previously reported for hexadentate podands with twelve-coordinated Ln<sup>III</sup>.<sup>12</sup>

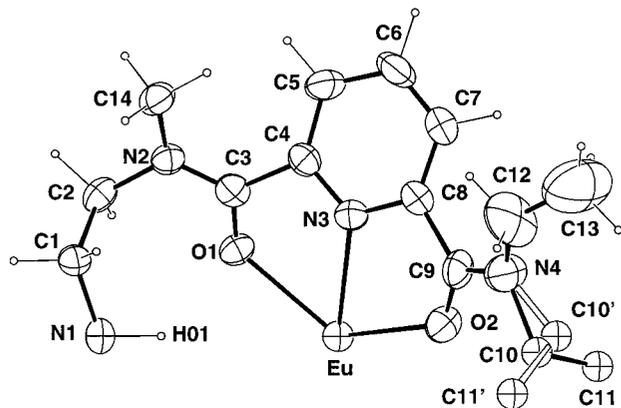


No clear size-discriminating effect is observed for log(β<sub>11</sub>), but the stability constants are large enough to ensure the quantitative formation of [LnL<sup>6</sup>]<sup>3+</sup> in solution for ligand concentrations > 1 mM and a stoichiometric ratio Ln:L<sup>6</sup> = 1. This is confirmed by <sup>1</sup>H and <sup>13</sup>C NMR spectra (0.05 M in CD<sub>3</sub>CN at 298 K) which indicate that [LnL<sup>6</sup>]<sup>3+</sup> (Ln = Ce-Lu) exist as inert and compact C<sub>3</sub>-symmetrical complexes. Spectrophotometric titrations of [L<sup>6</sup> + H]<sup>+</sup> by Ln(ClO<sub>4</sub>)<sub>3</sub> in acetonitrile can be fitted to eqn. (3) and give log(β<sub>11</sub><sup>H</sup>) = 6.7(2), 6.4(2) and 6.4(5) for Ln = Sm, Y and Lu, respectively. The only marginal decrease of log(β<sub>11</sub><sup>H</sup>) compared to log(β<sub>11</sub>) points to a remarkable preorganization of the protonated podand in [L<sup>6</sup> + H]<sup>+</sup> which essentially overcomes the increased electrostatic

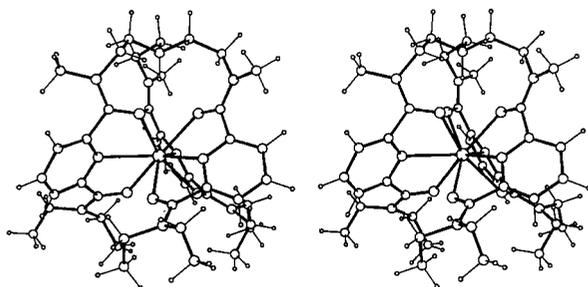
**Table 1** Selected thermodynamic formation constants of [Ln(L<sup>6</sup>)<sub>i</sub>]<sup>3+</sup> (i = 1,2) in acetonitrile at 298 K

Ln	log(β <sub>11</sub> )	log(β <sub>12</sub> )	Ln	log(β <sub>11</sub> )
La	8.3(2)	13.6(2)	Sm	7.0(4)
Ce	8.5(7)	13.3(9)	Dy	7.4(3)
Pr	8.0(7)	12.9(9)	Lu	8.0(6)

repulsion occurring upon complexation to  $\text{Ln}^{3+}$ . X-Ray quality prisms of  $[\text{Eu}(\text{L}^6 + \text{H})](\text{CF}_3\text{SO}_3)_3(\text{PF}_6) \cdot 0.5\text{MeCN}$  **2** can be grown from a solution containing a mixture of triflate and hexafluorophosphate anions. The crystal structure of **2** confirms the presence of a protonated cationic podate  $[\text{Eu}(\text{L}^6 + \text{H})]^{4+}$  located on a crystallographic threefold axis passing through N1, H01 and Eu.<sup>†</sup>



**Fig. 1** Atomic numbering scheme of the cation  $[\text{Eu}(\text{L}^6 + \text{H})]^{4+}$  in **2**. Ellipsoids are represented at 40% probability level. The disordered ethyl group [C(10), C(11)] is represented with arbitrary fixed  $U_{\text{iso}}$  ( $0.04 \text{ \AA}^2$ ) for clarity. Selected bond and contact distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) in **2**: Eu–O(1) 2.404(8), Eu–N(3) 2.568(7), Eu–O(2) 2.395(7), N(1)⋯H(01) 1.10(1), N(1)⋯O(1) 3.02(1), O(1)⋯H(01) 2.167(8), O(1)–Eu–N(3) 63.5(3), O(1)–Eu–O(2) 125.5(2), N(3)–Eu–O(2) 62.4(4), N(1)–H(01)⋯O(1) 131.8(4).



**Fig. 2** ORTEP stereoview of the cation  $[\text{Eu}(\text{L}^6 + \text{H})]^{4+}$  perpendicular to the threefold axis.

The three tridentate binding units of the podand are tricoordinated to  $\text{Eu}^{\text{III}}$  whose coordination sphere is best described as a slightly distorted tricapped trigonal prismatic site in which the six oxygen atoms of the carboxamide units occupy the vertices of the prism and the three pyridine nitrogen atoms cap the rectangular faces. The Eu atom lies almost in the equatorial plane defined by the threefold symmetry related nitrogen atoms N(1), N(1'), N(1'') [deviation  $0.0281(1) \text{ \AA}$ ], but is significantly closer to the lower oxygen tripod [ $1.649(1) \text{ \AA}$  from {O(2), O(2'), O(2'')} and  $1.780(1) \text{ \AA}$  from {O(1), O(1'), O(1'')}]. The Eu–N and Eu–O distances are standard<sup>7</sup> and the triple-helical podate adopts a conical shape which is exemplified by the larger non-bonded O⋯O distances observed between the oxygen atoms of the lower tripod {O(2), O(2'), O(2'')} [O(2)⋯O(2')  $3.01 \text{ \AA}$ , O(1)⋯O(1')  $2.80 \text{ \AA}$ ] and which strongly contrasts with the cylindrical arrangement of the helical strands found in  $[\text{Eu}(\text{L}^3)_3]^{3+}$ .<sup>7</sup> The remarkable trifurcated hydrogen bond observed between atom N(1) (*endo* conformation) and atoms O(1), O(1') and O(1'')<sup>13</sup> provides three fused and helically twisted seven-membered rings [N(1)–C(1)–C(2)–N(2)–C(3)–O(1)–H(01)] which contribute to the rigidity and the compact arrangement of the tripod. The podate  $[\text{Eu}(\text{L}^6 + \text{H})]^{4+}$  can be thus described as two helical fractions (*i.e.* the covalent tripod and the coordinated strands) which are put on top of each other. The two helical domains display opposite helicity leading to an irregular conical amphiverse *PM* (or *MP*) helix.<sup>14</sup>

Protonation of the apical *endo* nitrogen atoms associated with intramolecular hydrogen bonds is thought to play a crucial role

in the stability, rigidity and organization of the final podate as similarly suggested by Shanzer and coworkers for lateral interstrand hydrogen bonding in related podates with d-block metal ions.<sup>4</sup> Preliminary photophysical studies in the solid state and in solution confirm that the  $C_3$ -symmetrical structure of the cation  $[\text{Eu}(\text{L}^6 + \text{H})]^{4+}$  is maintained in acetonitrile in agreement with paramagnetic NMR data. The high-resolution emission spectra of  $[\text{Eu}(\text{L}^6 + \text{H})]^{4+}$  display only two components for the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  transition<sup>2,7</sup> and three components for the transition  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  which are diagnostic for a  $C_3$ -symmetrical arrangement of the donor atoms around  $\text{Eu}^{\text{III}}$ . The luminescence quantum yield of  $[\text{Eu}(\text{L}^6 + \text{H})]^{4+}$  in acetonitrile is small ( $\Phi_{\text{abs}} = 1.5 \times 10^{-4}$ ) as a result of inefficient ligand-centered  ${}^1\pi\pi^* \rightarrow {}^3\pi\pi^*$  intersystem crossing, but the edifice displays a good resistance toward hydrolysis: addition of 10 M water in acetonitrile has only a minor effect on the emission spectrum of  $[\text{Eu}(\text{L}^6 + \text{H})]^{4+}$  and its associated  $\text{Eu}({}^5\text{D}_0)$  lifetime [1.96(3) ms in absence of water and 1.29(5) ms with 10 M water], while a drastic quenching of the luminescence was observed for  $[\text{Eu}(\text{L}^3)_3]^{3+}$  after the addition of 1 M water.<sup>7</sup> A comparison between the quenching efficiencies of  $\text{H}_2\text{O}$  vs.  $\text{D}_2\text{O}$  using the empirical Horrocks' equation<sup>15</sup> allows one to estimate  $q = 0.2 \pm 0.5$  water molecule coordinated to  $\text{Eu}^{\text{III}}$  in acetonitrile containing 10 M of water. Such a small number can be accounted for by second sphere interactions. We conclude that a combination of the podand effect with secondary weak intramolecular interactions allows a precise control of facial nine-coordinate trigonal prismatic site around  $\text{Ln}^{\text{III}}$ , thus offering promising possibilities for the development of pre-organized anchors in heteropolymetallic lanthanide-containing supramolecular complexes.

## Notes and references

<sup>†</sup> *Crystal data*:  $\text{C}_{45}\text{H}_{61}\text{N}_{10}\text{O}_{15}\text{F}_{15}\text{P}_3\text{S}_3\text{Eu} \cdot 0.5\text{CH}_3\text{CN}$ ,  $M = 1566.6$ ; trigonal, space group  $R\bar{3}$ ,  $Z = 6$ ,  $a = 13.2949(5)$ ,  $c = 61.020(3) \text{ \AA}$ ,  $V = 9340.6(8) \text{ \AA}^3$ ,  $\mu = 9.43 \text{ mm}^{-1}$ ,  $F(000) = 4758$ ,  $D_c = 1.67 \text{ g cm}^{-3}$ , 5097 measured reflections, 2552 unique reflections of which 2179 were observables [ $|F_o| > 4\sigma(F_o)$ ];  $R_{\text{int}}$  for equivalent reflections 0.049. Full-matrix least-squares refinement based on  $F$  using weight of  $1/[\sigma^2(F_o) + 0.0001(F_o)^2]$  gave final values  $R = 0.065$ ,  $wR = 0.062$ , and  $S = 2.33(4)$  for 285 variables and 2179 contributing reflections. CCDC 182/1150.

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