

# Isolation and characterization of the first circular single-stranded polymetallic lanthanide-containing helicate†

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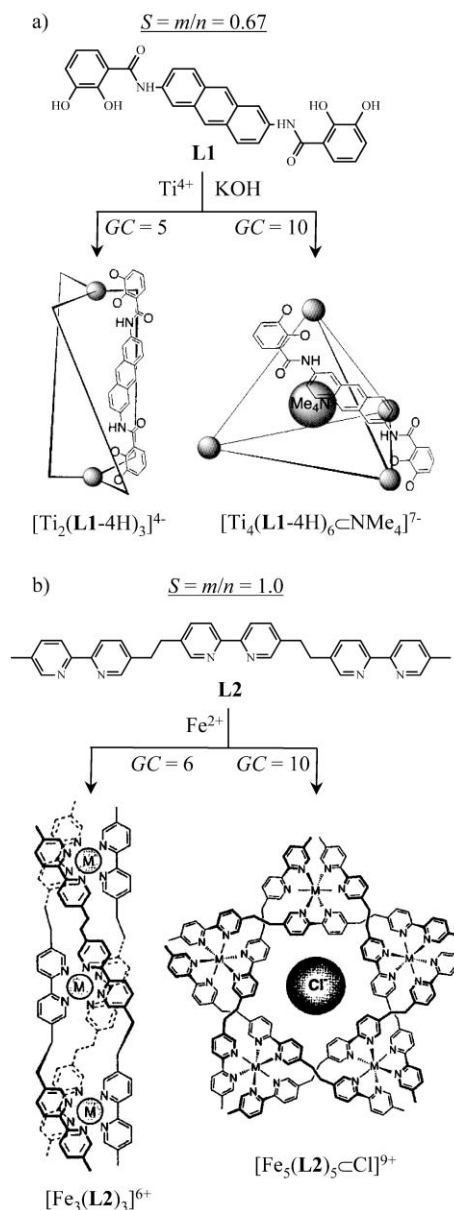
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A thorough examination of the disassembly of bimetallic triple-stranded lanthanide helicates  $[\text{Ln}_2(\text{L}i)_3]^{6+}$  (stoichiometry  $S = m/n = 2/3 = 0.67$ , global complexity  $GC = m + n = 2 + 3 = 5$ ) in excess of metals shows the competitive formation of standard linear bimetallic complexes  $[\text{Ln}_2(\text{L}i)_2]^{6+}$  ( $S = 1.0$ ,  $GC = 4$ ), and circular trimetallic single-stranded helicates  $[\text{Ln}_3(\text{L}i)_3]^{9+}$  ( $S = 1.0$ ,  $GC = 6$ ).

Although the decisive influence of the stoichiometric ratio  $S = m/n$  on the final structure adopted by metallosupramolecular complexes  $[\text{M}_m\text{L}_n]$ , and its eventual control, have been the subject of continual interest during the past 15 years,<sup>1</sup> the factors affecting the global complexity  $GC \ddagger = m + n$  remain elusive despite their crucial consequences on the issue of the assembly processes.<sup>2</sup> The alternative formation of a bimetallic triple-stranded helicate  $[\text{Ti}_2(\text{L}1)_3]^{4+}$  ( $S = m/n = 0.67$ ,  $GC = m + n = 5$ ) versus a tetrametallic tetrahedral cluster  $[\text{Ti}_4(\text{L}1)_6\text{C}(\text{NMe}_4)]^{7-}$  ( $S = 0.67$ ,  $GC = 10$ , Fig. 1a),<sup>3</sup> or of a trimetallic triple-stranded helicate  $[\text{Fe}_3(\text{L}2)_3]^{6+}$  ( $S = 1.0$ ,  $GC = 6$ ) versus a pentametallic circular double-stranded helicate  $[\text{Fe}_5(\text{L}2)_5\text{C}(\text{Cl})]^{9+}$  ( $S = 1.0$ ,  $GC = 10$ , Fig. 1b)<sup>4</sup> illustrates this challenge, while the thermodynamic preference for the complexes displaying the maximum global complexity in these systems has been assigned to counter-ion templating effects.<sup>3–5</sup>

Inspired by the cyclic structures found for DNA in some organisms (*i.e.* plasmid DNA),<sup>2</sup> polymetallic d-block complexes have been designed for exploring the much simpler interconversion between bimetallic double-stranded helicates  $[\text{M}_2(\text{L}i)_2]^{2+}$  ( $S = 1.0$ ,  $GC = 4$ ) and circular single-stranded helicates  $[\text{M}_n(\text{L}i)_n]^{2+}$  ( $S = 1.0$ ,  $GC = 2n$ ,  $n > 2$ ).<sup>6</sup> The small internal cavities found in these two-dimensional circular helicates are not compatible with templating processes, and a plethora of debatable intramolecular interstrand interactions have been thus invoked for rationalizing the ultimate thermodynamic preference for the cyclic structures.<sup>6</sup> In this context, intensive efforts are currently focused on the modelling of sophisticated self-assembly processes with a minimum set of reliable thermodynamic arguments.<sup>7</sup> The design of new segmental ligands programmed for the selective formation of multicomponent metallosupramolecular architectures is thus becoming a crucial issue for the validations of these predictive theories,<sup>8</sup> and the ligands **L3–L6** (Scheme 1) have been synthesized for

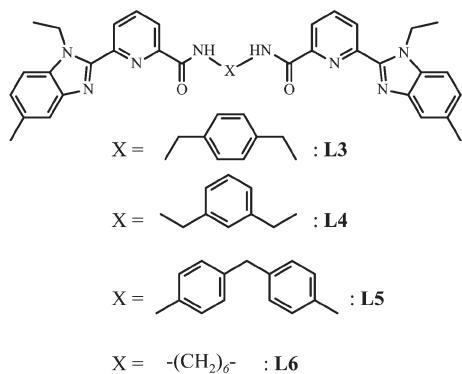
systematically exploring the structures and stabilities of the polymetallic lanthanide complexes obtained with bis-tridentate receptors connected by simple semi-flexible secondary amide linkers.§



**Fig. 1** Influence of the global complexity ( $GC$ ) on the final structures of  $[\text{M}_m\text{L}_n]$  supramolecular complexes. a) Linear triple-stranded helicate vs. tetrahedral cluster (adapted from ref. 3) and b) linear triple-stranded helicate vs. circular double-stranded helicate (adapted from ref. 4).

† Electronic supplementary information (ESI) available: experimental part for the synthesis of **L3–L6** and of their complexes. Tables of bond distances and interplanar angles in **1**. Figures reporting detailed numbering schemes, molecular structures and NMR data. See <http://www.rsc.org/suppdata/cc/b5/b501399b/>

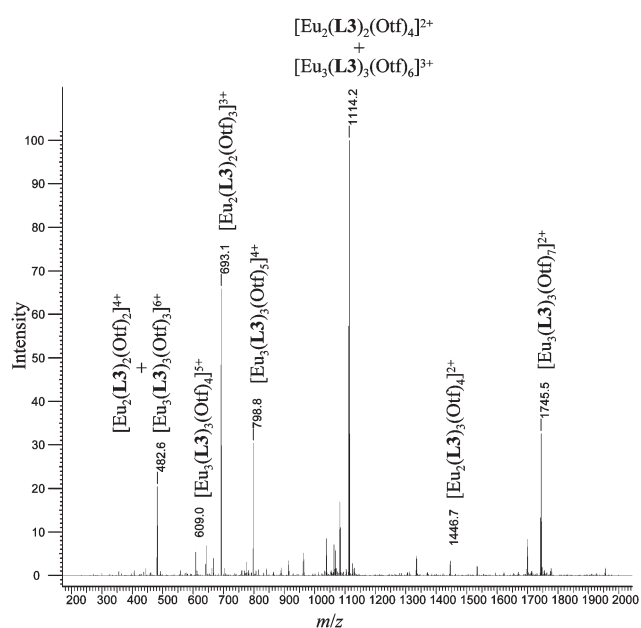
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**Scheme 1** Chemical structures of the ligands **L3**–**L6**.

Except for **L5**, for which the planned triple-stranded helicate  $[\text{Ln}_2(\text{L5})_3]^{6+}$  is formed quantitatively for a ratio  $\text{Ln} : \text{L5} = 0.67$ , we systematically detect intricate mixtures of slowly interconverting complexes by using  $^1\text{H}$  NMR in acetonitrile/chloroform (1 : 1). Parallel ESI-MS titrations recorded under the same conditions (solvent and concentration) for  $\text{Ln} : \text{Li}$  ( $i = 3$ – $6$ ) in the range 0.5–1.0 strongly suggest the co-existence of three complexes,  $[\text{Ln}_2(\text{Li})_3]^{6+}$  ( $S = 0.67$ ,  $GC = 5$ ),  $[\text{Ln}_2(\text{Li})_2]^{6+}$  ( $S = 1.0$ ,  $GC = 4$ ), and  $[\text{Ln}_3(\text{Li})_3]^{9+}$  ( $S = 1.0$ ,  $GC = 6$ , Fig. 2). Although solid-state and solution structures for the first two complexes, respectively bimetallic triple-stranded helicates<sup>9</sup> and bimetallic side-by-side solvated complexes,<sup>10</sup> have been firmly established for closely related analogues, we are not aware of any structural information reported for the latter complexes  $[\text{Ln}_3(\text{Li})_3]^{9+}$ .<sup>11</sup>

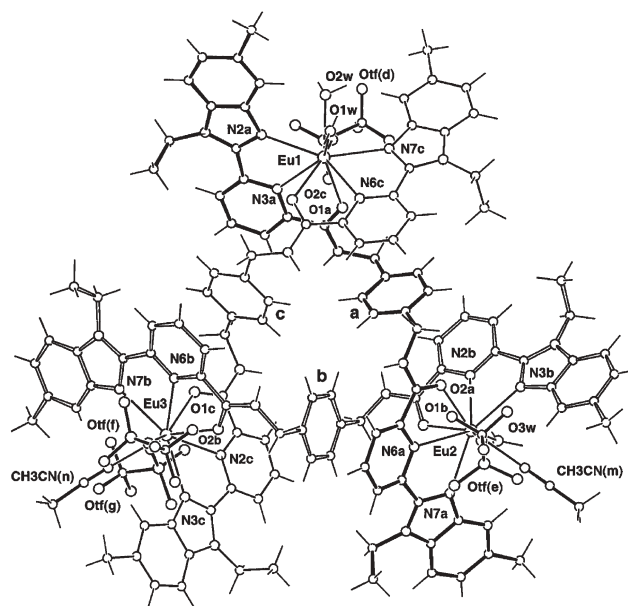
In order to maximize the formation of the oligomer with the highest global complexity in solution, we have used an exact ratio  $\text{Ln} : \text{Li} = 1$  combined with a high concentration of the components. Crystallisation of the most charged cations is then induced thanks to a stepwise decrease of the dielectric constant resulting from the slow diffusion of volatile non-polar ether. In this



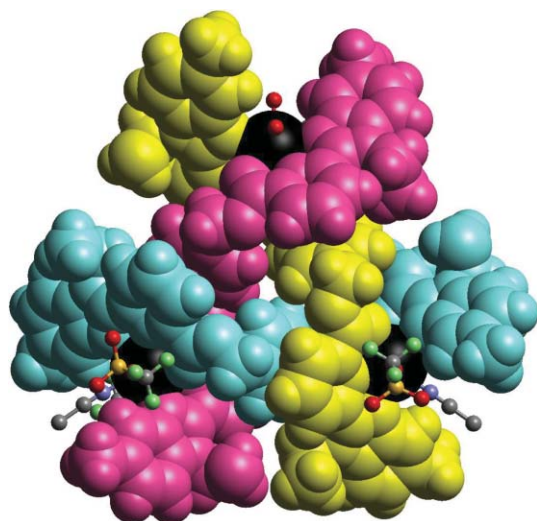
**Fig. 2** ESI-MS spectrum recorded for a stoichiometric 1 : 1 mixture of **L3** and  $\text{Eu}(\text{CF}_3\text{SO}_3)_3 \cdot 5\text{H}_2\text{O}$  in  $\text{CD}_3\text{CN}/\text{CDCl}_3$  (1 : 1).  $\text{Otf} = \text{CF}_3\text{SO}_3^-$ .

communication, we focus on the mixing of stoichiometric amounts of **L3** (1 equiv.) and  $\text{Eu}(\text{CF}_3\text{SO}_3)_3 \cdot 5\text{H}_2\text{O}$  (1 equiv.) in acetonitrile/chloroform, which provided 84% of microcrystalline  $[\text{Eu}_3(\text{L3})_3(\text{CF}_3\text{SO}_3)_9](\text{H}_2\text{O})_4$  after slow diffusion of diethyl ether.<sup>§</sup> Recrystallization from acetonitrile/di-isopropyl ether gave very fragile X-ray quality prisms of  $[\text{Eu}_3(\text{L3})_3(\text{CF}_3\text{SO}_3)_4(\text{CH}_3\text{CN})_2(\text{H}_2\text{O})_3](\text{CF}_3\text{SO}_3)_5(\text{CH}_3\text{CN})_9(\text{H}_2\text{O})_2$  (**1**).<sup>¶</sup> The associated crystal structure confirms the existence of  $[\text{Eu}_3(\text{L3})_3(\text{CF}_3\text{SO}_3)_4(\text{CH}_3\text{CN})_2(\text{H}_2\text{O})_3]^{5+}$  cations with  $GC = 6$ , together with partially disordered ionic triflates and non-coordinated solvent molecules. The three europium atoms lie at the corners of an approximate equilateral triangle (length  $\approx 12.0$  Å), whose sides are defined by the three helically wrapped ligand strands (Fig. 3).

Each europium atom is nine-coordinated in strongly distorted mono-capped square antiprismatic sites, the six donor atoms of the two bound tridentate segments of the ligands **L3** forming the basal rectangular face (carboxamide oxygen and pyridine nitrogen atoms) and one half of the upper capped face (benzimidazole nitrogen atoms). Two monodentate triflate anions around Eu2 and Eu3, and one triflate and one water molecule around Eu1 complete the upper rectangular faces, while one additional bound solvent molecule (water for Eu1 and acetonitrile for Eu2 and Eu3) eventually caps these faces (Fig. 3). Neglecting the replacement of the acetonitrile molecule bound to Eu2 or Eu3, with the water molecule in Eu1 leads to an approximate  $D_3$  symmetry for the circular single-stranded cation  $[\text{Eu}_3(\text{L3})_3(\text{CF}_3\text{SO}_3)_4(\text{CH}_3\text{CN})_2(\text{H}_2\text{O})_3]^{5+}$  (Fig. 4). Interestingly, we do not detect significant intramolecular interstrand interactions, or strong templating effect, which could rationalize the formation of the circular helicate. However, the cyclic arrangement of the three helically wrapped strands produces two half bowl-shaped cavities located at the center of the cation, which are capped by the ionic triflates  $j$  and  $l$  (Fig. S1, ESI).<sup>†</sup> Only three weak intermolecular



**Fig. 3** Perspective view along the pseudo-threefold axis, and partial numbering scheme for the cation  $[\text{Eu}_3(\text{L3})_3(\text{CF}_3\text{SO}_3)_4(\text{CH}_3\text{CN})_2(\text{H}_2\text{O})_3]^{5+}$  in the crystal structure of **1** ( $\text{Eu1} \cdots \text{Eu2} = 11.9977(7)$  Å,  $\text{Eu2} \cdots \text{Eu3} = 11.7933(8)$  Å and  $\text{Eu1} \cdots \text{Eu3} = 12.3217(8)$  Å;  $\text{Otf} = \text{CF}_3\text{SO}_3^-$ ).



**Fig. 4** View of the circular single-stranded cation  $[\text{Eu}_3(\text{L}3)_3(\text{CF}_3\text{SO}_3)_4(\text{CH}_3\text{CN})_2(\text{H}_2\text{O})_3]^{3+}$  with the three helically wrapped strands represented with CPK spheres of different colors.

(pyridine)CH $\cdot$ O(triflate) interactions are detected, but we cannot definitively rule out their possible contribution to the stabilization of the final pseudo- $D_3$ -symmetrical complex.

Dissolution of **1** in  $\text{CD}_3\text{CN}$  provides a clean paramagnetically-shifted  $^1\text{H}$  NMR spectrum diagnostic for the existence of a single highly symmetrical species in solution on the NMR timescale, which is compatible with the solvated  $D_3$ -symmetrical cation  $[\text{Eu}_3(\text{L}3)_3]^{9+}$  (13 signals are observed for the protons, together with diastereomeric methylenes, Fig. S2a, ESI). $\ddagger$  However, slow thermodynamic re-equilibration leads to complicated mixtures of  $[\text{Eu}_3(\text{L}3)_3]^{9+}$  and  $[\text{Eu}_2(\text{L}3)_2]^{6+}$  after a few hours (Fig. S2b, ESI). $\ddagger$

In conclusion, the assembly of the bimetallic triple-stranded helicates  $[\text{Ln}_2(\text{L}i)_3]^{6+}$  ( $i = 3-6$ ,  $S = 0.67$ ) competes with the formation of complexes with 1 : 1 stoichiometry and variable global complexities  $[\text{Ln}_n(\text{L}i)_n]^{3n+}$  ( $n = 2$ ,  $GC = 4$  and  $n = 3$ ,  $GC = 6$ ). The use of the exact stoichiometry  $S = 1$  combined with high concentration favors the formation of the oligomer displaying the maximum global complexity. Crystallisation of the resulting mixture allows the isolation of the first circular single-stranded lanthanide helicate. Particular attention is currently focused on the factors controlling the interconversion process  $3[\text{Ln}_2(\text{L}i)_2]^{6+} \rightleftharpoons 2[\text{Ln}_3(\text{L}i)_3]^{9+}$  in solution, because no obvious templating effects or intramolecular interactions have been evidenced in the cyclic complex.

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## Notes and references

$\ddagger$  The global complexity of a system strictly refers to the multiplying factor, which correlates the final oligomer with its basic monomeric building block. We thus exclude extra templating agents, specifically included within the oligomeric form and absent in the monomer, for calculating  $GC$ .

$\S$  The syntheses and characterizations of the ligands **L3-L6** and of the complex  $[\text{Eu}_3(\text{L}3)_3(\text{CF}_3\text{SO}_3)_9](\text{H}_2\text{O})_4$  are given in the ESI.

$\P$  Crystal data:  $[\text{Eu}_3(\text{C}_{40}\text{H}_{38}\text{N}_8\text{O}_2)_3(\text{CF}_3\text{SO}_3)_4(\text{CH}_3\text{CN})_2(\text{H}_2\text{O})_3](\text{CF}_3\text{SO}_3)_5(\text{CH}_3\text{CN})_9(\text{H}_2\text{O})_2$ ,  $fw = 4327.0$ ,  $T = 200$  K, monoclinic,  $P1$ ,  $Z = 2$ ,  $a = 14.7345(11)$ ,  $b = 21.8136(12)$ ,  $c = 31.790(2)$  Å,  $\alpha = 100.262(7)$ ,  $\beta = 100.850(8)$ ,  $\gamma = 103.813(8)^\circ$ ,  $V = 9475(1)$  Å $^3$ . 100621 measured reflections, 34501 unique reflections ( $R_{\text{int}} = 0.060$ ),  $R = 0.063$ ,  $\omega R = 0.065$  for 2228 variables and 19896 contributing reflections ( $|F_o| > 4 \sigma(F_o)$ ). Hydrogen atoms of the disordered water molecules O5w and O6w (with population parameters of 0.50) were not observed nor calculated. CCDC 261626. See <http://www.rsc.org/suppdata/cc/b5/b501399b/> for crystallographic data in CIF or other electronic format.

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