The First Self-Assembled Trimetallic Lanthanide Helicates Driven by Positive Cooperativity


Abstract: The segmental tris-tridentate ligand L7 reacts with stoichiometric quantities of LnIII (Ln = La–Lu) in acetonitrile to give the complexes [Ln2(L7)]n+ and [Ln3(L7)]n+. Formation constants point to negligible size-discriminating effects along the lanthanide series, but Scatchard plots suggest that the self-assembly of the trimetallic triple-stranded helicates [Ln3(L7)]n+ is driven to completion by positive cooperativity, despite strong intermetallic electrostatic repulsions. Crystallization provides quantitatively [Ln3(L7)](CF3SO3)9 (Ln = La, Eu, Gd, Tb, Lu) and the X-ray crystal structure of [Eu3(L7)9](CF3SO3)9. Photophysical data confirm that the three coordination sites possess comparable pseudo-trigonal symmetries in the solid state and in solution. High-resolution luminescence analyses evidence a low-lying LMCT state affecting the central EuN9 site, so that multi-metal-centered luminescence is essentially dominated by the emission from the two terminal EuN6O3 sites in [Eu3(L7)]9+. New multicenter equations have been developed for investigating the solution structure of [Ln3(L7)]n+ by paramagnetic NMR spectroscopy and linear correlations for Ln = Ce–Tb imply isosctructurality for these larger lanthanides. NMR spectra point to the triple helical structure being maintained in solution, but an inversion of the magnitude of the second-rank crystal-field parameters, obtained by LIS analysis, for the LnN6O3 and LnN9 sites with respect to the parameters extracted for EuIII from luminescence data, suggests that the geometry of the central LnN9 site is somewhat relaxed in solution.

Keywords: cooperative effects • crystal-field parameters • helical structures • lanthanides • self-assembly

Introduction

Although interelectronic repulsions in open-shell configurations induce rich and varied optical and magnetic properties for d-block metal ions, the strong mixing between metal- and ligand-centered orbitals in their complexes drastically limits the programming of electronic properties in molecular or supramolecular devices.[1] For the lanthanide ions (LnIII), the

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Supporting information for this article is available on the WWW under http://www.chemeurj.org or from the author. Table S1 lists the ESI-MS peaks observed during titrations and Table S2 lists elemental analyses for complexes 5–9. Tables S3 and S4 list selected least-square plane coordinates for the aromatic protons factors for the aromatic protons of 10, and Tables S5–S7 give the structural data for the europium coordination spheres. Geometrical G‡ factors for the aromatic protons of 10 are given in Table S8, the integrated luminescence intensities of the Eu(II) energy levels of [Eu(L7)(CF3SO3)9].(H2O)3 (6) are listed in Table S9, the energy of the D0–F0 transitions in Table S10, the Eu(D0) lifetimes in Table S11, while Table S12 lists the Tb(D2) lifetimes measured for [Tb(L7)(CF3SO3)9.(H2O)3] (8). Figure S1 shows ESI-MS spectra obtained during the titration of L7 with EuIII; Figure S2 shows the calculated ligand speciation during the titration L7 with LaIII. Figure S3 displays a view of the unit cell in 10. Figures S4–S6 show emission spectra of [Ln3(L7)]n+, Ln = La (5), Eu (6), Gd (7), Tb (8), and Lu (9).
4f orbitals are screened from external perturbations by outer filled 5s² and 5p⁶ shells,[23] and the electronic properties of their complexes can be rationally tuned by weak crystal-field effects resulting from the precise control of the coordination sphere:[20] a crucial point for the implementation of specific functions.[4] Sophisticated mononuclear lanthanide complexes have been thus designed for operating as 1) efficient catalysts for asymmetric organic transformations,[3] 2) contrast agents that possess two vacant coordination sites for magnetic resonance imaging (MRI),[6, 9] 3) luminescent probes for sensing base-pairing in oligonucleotides,[7] and 4) magnetically addressable metallomesogens.[8] An increased density of magnetic or optical probes in polymeric f–f complexes offers new perspectives for programming molecular devices in that several lanthanide ions can be selectively introduced into the final architectures.[6–12] For instance, the intermolecular energy transfers evidenced in the heterobimetallic helicates [LnLn′(L7)]ⁿ⁺ (n = 1, 2)[13, 14] and [LnLn′(L2-2H₃)] (n = 3, 4)[15, 16] have no counterpart in monometallic analogues, but the intrinsic equivalence of the metallic sites prevents the isolation of pure heterobimetallic complexes exhibiting directional magnetic[17] and optical[18] properties. The connection of functional magnetic[19] and optical[20] properties in the final complexes. A partial description of the metallic sites for controlling the magnetic and photophysical crystal-field parameters generated by the nonequivalent metallic sites for controlling the magnetic and photophysical properties in the final complexes. A partial description of the crystal structure of [Eu₃(L7)₃]²⁺ has been reported in a preliminary communication.[21]

Results and Discussion

Synthesis of ligands L7 and L8: The C₅₆-symmetrical heterotopic ligand 2,6-bis[1-ethyl-5-[1-ethyl-2-[6-(N,N-diethylcarbamoyl)pyridin-2-yl]benzimidazol-5-yl]benzimidazole-2-yl]pyridine (L7) consists of two terminal carboxamide–pyridine–benzimidazole (ONN) segments connected through methylene spacers to a central tridentate bis(benzimidazole)–pyridine unit. Ligand L7·H₂O is obtained in three steps from the synthsins 1 and 2 according to a strategy based on the preparation of four benzimidazole rings from the tetra[N-(2-nitroarene)carboxamide] precursor 4 (Scheme 1).[22] Harsh basic conditions are required to hydrolyse the terminal carboxamide units to give the poorly soluble dicarboxylic ligand L8 isolated as its salt K[L8-H]·5.6H₂O. The lack of nuclear Overhauser effects (NOEs, ¹H NMR) between the ethyl group of the benzimidazole and the proton of the adjacent pyridine rings (H2 or H9) for L7 and L8 in solution points to transoid arrangements of the benzimidazole–pyridine units, as found for L2 and L3.[14, 15] Ligand L7 is soluble enough in acetonitrile to allow complexation studies, but the ambivalent lipophilic/hydrophilic nature of L8 prevents significant solubility in common solvents except hot DMSO, and no complexation study could be performed with this ligand.

Thermodynamic self-assembly processes of L7 with LnIII: ESI-MS titrations of L7 (2 × 10⁻⁴ m in acetonitrile) with Ln(CF₃SO₃)x·x H₂O (Ln = La, Eu, Gd, Tb, Lu; x = 1–4), for an Ln:L7 ratio in the range 0.1–1.2, show the successive formation of two cationic complexes [Ln₂(L7)]ⁿ⁺ and [Ln₃(L7)]ⁿ⁺ together with their adduct ions [Ln₂(L7)x·(CF₃SO₃)x]ⁿ⁻ (n = 1–3) and [Ln₃(L7)x(CF₃SO₃)x]ⁿ⁻ (n = 1–7) (Table S1, Figure S1a and S1b in the Supporting Information). In the presence of excess metal (Ln:L7 > 2.0), the peaks corresponding to [Ln₃(L7)]ⁿ⁺ are replaced with new signals assigned to [Ln₃(L7)ₓ(CH₃CN)]ₓ(H₂O)ₓ-
(CF₃SO₃)ₙ⁻ (n = 3, 5, 7), which involve the formation of the "unsaturated" species [Ln₃(L₇)₃]⁺⁺ (Table S1 and Figure S1c in the Supporting Information).

Batch spectrophotometric titrations of L₇ (2 × 10⁻⁴ M) with Ln(CF₃SO₃)₃·xH₂O (Ln = La, Nd, Eu, Tb, Ho, Tm, Lu; x = 1–4) in acetonitrile display complicated variations of the absorption spectra with end points for Ln:L₇ = 1.0 and 1.5 and a smooth inflexion around Ln:L₇ = 0.5–0.7 (Figure 1). Factor analysis⁵ points to the existence of four absorbing species (L₇, [Ln₂(L₇)₃]⁺⁺, [Ln₃(L₇)₃]⁺⁺, and [Ln₃(L₇)₂]⁺⁺) in agreement with the ESI-MS results, and the spectrophotometric data can be fitted with nonlinear least-squares techniques⁶ to the equilibria given in Equations (1)–(3), which characterize the assembly process (the formation constants log(βᵢᵢ) are collected in Table 1).

\[2\text{Ln}^{3+} + 3\text{L₇} \rightleftharpoons [\text{Ln₃(L₇)₃}]^{++} \quad \log(β_{1}) \]  
\[3\text{Ln}^{3+} + 3\text{L₇} \rightleftharpoons [\text{Ln₃(L₇)₃}]^{++} \quad \log(β_{2}) \]  
\[3\text{Ln}^{3+} + 2\text{L₇} \rightleftharpoons [\text{Ln₃(L₇)₂}]^{++} \quad \log(β_{3}) \]

The variables β₁, β₂, and β₃ do not vary significantly from their average values (log(β₁) = 25.7 and log(β₃) = 34.6) within experimental error along the lanthanide series. The stability constants for the formation of the bimetallic complexes [Ln₃(L₇)₃]⁺⁺ is close to log(β₁) = 25.3–24.0, obtained for [Ln₃(L₂)₃]⁺⁺ in the same conditions and for which the lanthanides are nine-coordinate by three wrapped NNO binding units.⁵ Complexation of three NNN binding units to LnIII in [Ln₃(L₇)₃]⁺⁺ produces less stable complexes (log(β₃) = 17.5–20.0) suggesting that the two Ln³⁺ ions occupy the terminal nine-coordinate N₆O₃ sites in [Ln₃(L₇)₃]⁺⁺, while the central N₉ site remains unoccupied. The variable β₃ reflects the stability of the trimetallic triple-stranded helicates [Ln₃(L₇)₃]⁺⁺ in which the three nine-coordinate sites (one central N₉ and two terminal N₆O₃ sites) are occupied by metals. In contrast to the triple-helical complexes [Ln₃(L₇)₃]⁺⁺, which display a marked

![Scheme 1. Reagents: i) SOCl₂/DMF; ii) NEt₃; iii) 2,6-bis(chlorocarboxy)pyridine, NEt₃; iv) Fe, HCl, EtOH/H₂O; v) KOH, EtOH/H₂O.](image_url)
The distribution curves computed by using the formation constants reported in Table 1 show that the trimetallic complexes \([\text{Ln}_3(\text{L7})_3]^{9+}\) in the presence of excess metal is statistical (i.e., no cooperativity occurs), while concave downward or convex upward curves characterize positive or negative cooperativity, respectively.[26] The Scatchard plots obtained for [\(\text{Ln}_3(\text{L7})_3]^{9+}\) (\(\text{Ln} = \text{La, Eu, Lu}\)) are similar and concave; this implies that the self-assembly processes are driven to completion by positive cooperativity as previously reported for trimetallic Ag[27] and Cu[28] double-stranded helicates (Figure 3). Since \(\beta_{13}\) is not accessible, the cooperativity process refers to the fixation of the third lanthanide ion with respect to the average binding of the metal ions in [\(\text{Ln}_3(\text{L7})_3]^{9+}\), and we conclude that electrostatic repulsion associated with the complexion of the third \(\text{Ln}^{III}\) is more than compensated by the preorganization of the receptor brought about by the first two metal ions. Related Scatchard plots for the bimetallic helicates [\(\text{Ln}_2(\text{L1})_3]^{8+}\) (\(\text{Ln} = \text{La, Eu, Lu}\)) display convex curves and negative cooperativity,[29] this highlights the crucial role played by 1) the ligand design (i.e., the replacement of terminal benzimidazole groups in L1 or L6[20] with carboxamide groups in L7) and 2) the overall nuclearity of the assembly processes.

1H NMR titrations of L7 \((5 \times 10^{-3}\text{M})\) with \(\text{Ln}^{III}\)·\(\text{xH}_2\text{O} (\text{Ln} = \text{La, Eu, Lu} ; x = 1 \sim 4)\) in CD$_3$CN qualitatively confirm the successive formation of the three complexes with \(\text{Ln(ClO}_4)_3\)·\(\text{xH}_2\text{O}\) in acetonitrile give \(\log(\beta_{ij})\), which are identical within experimental errors to those reported in Table 1. This rules out some specific coordinating behavior of \(\text{CF}_3\text{SO}_3^-\) that could be responsible for the formation of the “unsaturated” complexes [\(\text{Ln}_3(\text{L7})_3]^{9+}\) in the presence of excess metal.

The two formation constants \(\beta_{13}\) and \(\beta_{13}\) allow an estimate of the cooperativity of the assembly process leading to the trimetallic triple-stranded helicates \([\text{Ln}_3(\text{L7})_3]^{9+}\).[26-28] According to the speciation reported on Figure 2, the formation of \([\text{Ln}_3(\text{L7})_3]^{9+}\) can be neglected for \(\text{Ln}:\text{L7}\) ratios in the range 0.1 – 1.0, and the occupancy factor \(r\) corresponding to the average number of sites occupied by the metal in the triple-helix is thus given by Equation (5):[26]

\[
r = \frac{[\text{Ln}^{III}_{bound}]}{[\text{L7}_{total}]} = \frac{3[Ln^{III}_{bound} - [L_n]_i]}{[L_7]_{total}} = \frac{3 \sum L_i^{\beta_j} [\text{Ln}^{III}_{bound}] [\text{L7}]^j}{1 + 3 \sum L_i^{\beta_j} [\text{Ln}^{III}_{bound}]} \quad (5)
\]

Plots of \(r\) vs. \([\text{Ln}]\) as a function of \(r\) (Scatchard plots)[26][28] correspond to reliable tests for cooperativity, because a straight line is expected when the successive binding of the metal ions is statistical (i.e., no cooperativity occurs), while concave downward or convex upward curves characterize positive or negative cooperativity, respectively.[28] The Scatchard plots obtained for [\(\text{Ln}_3(\text{L7})_3]^{9+}\) (\(\text{Ln} = \text{La, Eu, Lu}\)) are similar and concave; this implies that the self-assembly processes are driven to completion by positive cooperativity as previously reported for trimetallic Ag[27] and Cu[29] double-stranded helicates (Figure 3). Since \(\beta_{13}\) is not accessible, the

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**Table 1.** Formation constants \(\log(\beta_{ij})\) for the complexes \([\text{Ln}_3(\text{L7})_3]^{9+}\) in acetonitrile at 298 K.

<table>
<thead>
<tr>
<th>(\text{Ln}^{III})</th>
<th>(\log(\beta_{12}))</th>
<th>(\log(\beta_{23}))</th>
<th>(\log(\beta_{13}))</th>
<th>(\log(K_i))</th>
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<tr>
<td>(\text{La}^{III})</td>
<td>25.0 ± 1.1</td>
<td>34.3 ± 1.2</td>
<td>25.8 ± 1.1</td>
<td>8.8 ± 1.5</td>
</tr>
<tr>
<td>(\text{Nd}^{III})</td>
<td>26.0 ± 1.0</td>
<td>35.0 ± 1.1</td>
<td>26.4 ± 1.0</td>
<td>9.2 ± 1.1</td>
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<tr>
<td>(\text{Eu}^{III})</td>
<td>25.9 ± 1.4</td>
<td>34.8 ± 1.6</td>
<td>26.0 ± 1.4</td>
<td>8.4 ± 1.5</td>
</tr>
<tr>
<td>(\text{ Tb}^{III})</td>
<td>25.8 ± 0.2</td>
<td>35.0 ± 1.2</td>
<td>27.2 ± 0.1</td>
<td>11.6 ± 0.9</td>
</tr>
<tr>
<td>(\text{ Ho}^{III})</td>
<td>26.0 ± 1.0</td>
<td>35.0 ± 1.2</td>
<td>26.5 ± 1.0</td>
<td>9.5 ± 1.1</td>
</tr>
<tr>
<td>(\text{ Tm}^{III})</td>
<td>26.0 ± 1.6</td>
<td>34.5 ± 1.8</td>
<td>26.9 ± 0.9</td>
<td>11.7 ± 1.4</td>
</tr>
<tr>
<td>(\text{ Lu}^{III})</td>
<td>25.5 ± 1.1</td>
<td>33.9 ± 0.3</td>
<td>27.4 ± 0.5</td>
<td>14.4 ± 0.4</td>
</tr>
</tbody>
</table>

[a] \(\log(K_i) = 3\log(\beta_{ij}) - 2\log(\beta_{ij})\) calculated by using the centroid values of the formation constants.
are given in the section dedicated to the solution structure of $[\text{Ln}_2(\text{L}_7)_3]^{5+}$.[21] In the presence of excess ligand ($\text{Ln}:\text{L}_7 < 1.0$), we observe the formation of a new species ascribed to $[\text{Ln}_2(\text{L}_7)_3]^{5+}$, which does not interconvert rapidly with $[\text{Ln}_2(\text{L}_7)_3]^{5+}$ on the NMR timescale, and whose $^1\text{H}$ NMR signals strongly overlap with those of $[\text{Ln}_3(\text{L}_7)_3]^{9+}$ (Figure 4b). Although a detailed assignment of the point group of symmetry and of the solution structure is complicated by the limited set of individual signals detected for this complex ($[\text{Ln}_2(\text{L}_7)_3]^{5+}$ corresponds to a maximum of 50% of the ligand speciation in a mixture of $\text{L}_7$, $[\text{Ln}_2(\text{L}_7)_3]^{6+}$ and $[\text{Ln}_2(\text{L}_7)_3]^{5+}$), Figure S2 in the Supporting Information), the observation of anomalously shielded aromatic signals around $\delta = 5.9$–6.4 ppm for the diamagnetic complexes $[\text{Ln}_2(\text{L}_7)_3]^{5+}$ ($\text{Ln} = \text{La, Lu}$, Figure 4b) is characteristic for the helication of the strands, which puts H5 and H6 in the shielding region of the wrapped benzimidazole rings.[21, 22] We tentatively conclude that the triple-helical arrangement is maintained in solution for $[\text{Ln}_2(\text{L}_7)_3]^{5+}$, which may exist as a mixture of structural isomers in which either one terminal or the central metallic site remains unoccupied. In the presence of excess metal ($\text{Ln}:\text{L}_7 > 1.0$), the signals of H5 and H6 that occur at $\delta = 5.88$ and 5.76 ppm, respectively, in the triple-helix $[\text{Ln}_2(\text{L}_7)_3]^{5+}$ (Table 4 below) are shifted toward the "regular" aromatic range ($\delta = 7.0$–8.5 ppm), because the wrapping of the strands is relaxed in $[\text{La}_3(\text{L}_7)_2]^{9+}$ (Figure 4c). The broadening of the peaks together with the systematic observation of enantiotopic signals for the methylene probes H12–H14, H15–H15', H15–H15', and H16–H16' point to fast dynamic equilibria compatible with an average $C_3$ symmetry of the ligand strands, as found for the free ligand. Significant paramagnetic shifts in $[\text{Eu}_3(\text{L}_7)_2]^{9+}$ confirm that the ligands remain coordinated to the metal ions, and these results are compatible with $[\text{Ln}_2(\text{L}_7)_3]^{5+}$ adopting a flexible double-helical structure in which PPP $\rightarrow$ MMM helical interconversion is fast on the NMR timescale. ESI-MS data strongly suggest that solvent molecules and/or triflate counterions complete the coordination sphere. $^1\text{H}$ NMR spectra of $[\text{Lu}_2(\text{L}_7)_3]^{5+}$ and $[\text{Lu}_3(\text{L}_7)_2]^{9+}$ in CD$_3$CN at 298 K show one singlet corresponding to ionic triflate anions ($\delta_t = -79.68$ ppm with respect to CFCl$_3$), but low-temperature spectra for $[\text{Lu}_3(\text{L}_7)_2]^{9+}$ display signals for both ionic and coordinated triflates, which are involved in partial complexation in the first coordination sphere. In conclusion, NMR data support ESI-MS and spectrophotometric data obtained at lower concentrations and points to the formation of three complexes in solutions: one bimetallic triple-helical complex $[\text{Ln}_2(\text{L}_7)_3]^{5+}$ existing as a mixture of isomers, one rigid and well-defined trimetallic triple-stranded helicate $[\text{Ln}_3(\text{L}_7)_2]^{9+}$, and one dynamically flexible trimetallic double-stranded helicate $[\text{Lu}_3(\text{L}_7)_2]^{9+}$. Since the ultimate goal of our approach is concerned with the design of saturated lanthanide complexes with predetermined properties, only the trimetallic triple-stranded helicates $[\text{Ln}_3(\text{L}_7)_2]^{9+}$ have been further characterized.

**Isolation of the complexes:** Stoichiometric mixing of L7 with Ln(CF$_3$SO$_3$)$_3$·xH$_2$O ($\text{Ln} = \text{La, Eu, Gd, Tb, Lu}; x = 1–4$) in acetonitrile followed by slow diffusion of diethyl ether provide microcrystalline powders of $[\text{Ln}_n(\text{L}_7)_3]^{2n+}$ ($\text{Ln} = \text{La, Eu, Gd, Tb, Lu}; n = 2$; 7; $\text{Ln} = \text{Th}$; x = 12; 8; $\text{Ln} = \text{Lu}, x = 6$; 9) in 77–89% yield. Elemental analyses support the proposed formulations (Table S2 in the Supporting Information) together with the IR spectra, which display the bands characteristics of the ligand strands. Complexation to Ln$^{3+}$ in 5–9 induces a splitting and a red shift (20 cm$^{-1}$) of the ν$_{C=O}$ stretching frequency, while new strong absorptions at 1250 (ν$_{v} + ν_{as}(\text{CF})$), 1160 (ν$_{as}(\text{SO}_3)$), 1050 (ν$_{s}(\text{SO}_3)$), and 640 cm$^{-1}$ (ν$_{s}(\text{SO}_3)$) are typical for ionic triflate counterions.[29] Re-dissolution of 5–9 in acetonitrile
gives $^1$H NMR and ESI-MS spectra identical to those obtained from direct titrations after thermodynamic equilibration. X-ray quality prisms of [Eu$_3$(L7)$_3$](CF$_3$SO$_3$)$_9$·(CH$_3$CN)$_9$·(H$_2$O)$_2$ (10) were obtained by slow diffusion of diethyl ether into a concentrated acetonitrile solution of 6.

Crystal and molecular structure of [Eu$_3$(L7)$_3$](CF$_3$SO$_3$)$_9$·(CH$_3$CN)$_9$·(H$_2$O)$_2$ (10): The crystal structure of 10 consists of discrete triple-helical [Eu$_3$(L7)$_3$]$_{135}^{3+}$ ions, uncoordinated triflate anions, and solvent molecules. The anions and solvent molecules are partially disordered (see CCDC data and Experimental Section). Figure 5 shows the atom-numbering scheme, Figure 6 displays a view of the cation perpendicular to the pseudo-threefold axis, and selected geometrical parameters are collected in Table 2.

![Figure 5. Perspective view of one strand in the cation [Eu$_3$(L7)$_3$]$_{135}^{3+}$ with the atomic numbering scheme.](image)

![Figure 6. View of the cation [Eu$_3$(L7)$_3$]$_{135}^{3+}$ perpendicular to the pseudo-$C_3$ axis with a different representation for each strand.](image)

The molecular structure of [Eu$_3$(L7)$_3$]$_{135}^{3+}$ confirms the formation of a triple-stranded helicate, with its pseudo-threefold axis passing through the three europium atoms. The helical twist of the ligands results from successive torsions about the interannular C–C bonds within each tridentate segments (12–41°, Table S3 in the Supporting Information) combined with approximate orthogonal arrangements (60–87°, average 76°) of the benzimidazole rings connected to the same methylene spacer (Figure 6). The total length of a helical strand in [Eu$_3$(L7)$_3$]$_{135}^{3+}$ amounts to 21.6 Å [as measured by the distance between the facial planes (F1 and F9) defined by the

Table 2. Selected bond lengths [Å] and angles [°] for [Eu$_3$(L7)$_3$](CF$_3$SO$_3$)$_9$·(CH$_3$CN)$_9$·(H$_2$O)$_2$ (10).

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<th>ligand a</th>
<th>ligand b</th>
<th>ligand c</th>
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terminal oxygen atoms F₁: O₂a, O₂b, O₂c and F₉: O₁a, O₁b, O₁c, Scheme 2) for 1.58 turns, thus leading to an average pitch of 13.6 Å. A detailed analysis of each helical portion defined by the nine almost parallel facial planes F₁–F₉ (Scheme 2, Table 3). Helical pitches within the terminal EuN₆O₃ sites is irregular with tight the ligands occur along the helical axis. Firstly, the helicity parameters. Significant variations of the wrapping mode of the nine- coordinate metallic sites, the helical twist is severely relaxed in the intermetallic portions of the triple helix (F₃/F₄ and F₆/ F₇), while a tighter rotation is associated with the complexation of the central bis(benzimidazole)pyridine segments to Eu₁ (F₄/F₅ and F₅/F₆).

Table 3. Helical pitches Pᵢj linear distances d(Fᵢ–Fⱼ) and average twist angles ωᵢj along the pseudo-C₃ axis in the crystal structure of [Eu₁-(L₇)]₉(CH₃CN)₉·(H₂O)₉ (10).

<table>
<thead>
<tr>
<th>Fᵢ – Fⱼ</th>
<th>d(Fᵢ–Fⱼ) [Å]</th>
<th>ωᵢj [°]</th>
<th>Pᵢj [Å]</th>
</tr>
</thead>
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<tr>
<td>F₁ – F₂</td>
<td>1.42</td>
<td>56.6</td>
<td>9.03</td>
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<tr>
<td>F₂ – F₃</td>
<td>1.86</td>
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<tr>
<td>F₃ – F₄</td>
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<tr>
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<td>10.45</td>
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<tr>
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<td>11.35</td>
</tr>
<tr>
<td>F₆ – F₇</td>
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<td>122.4</td>
<td>17.97</td>
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<tr>
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<td>51.7</td>
<td>11.84</td>
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<tr>
<td>F₈ – F₉</td>
<td>1.47</td>
<td>56.4</td>
<td>9.38</td>
</tr>
</tbody>
</table>

[a] ωᵢj are given as C₃-average values (see Tables S5–S7 for the definition of ωᵢj in the Supporting Information). [b] F₁: O₂a, O₂b, O₂c; F₂: N₁a, N₁b, N₁c; F₃: N₁₀a, N₁₀b, N₁₀c; F₄: N₆a, N₆b, N₆c; F₅: N₁₇a, N₁₇b, N₁₇c; F₆: N₂a, N₂b, N₂c; F₇: N₄a, N₄b, N₄c; F₈: N₆a, N₆b, N₆c; F₉: O₁a, O₁b, O₁c (see Scheme 2).

No significant interstrand stacking interaction is detected in [Eu₃(L₇)]₉⁺ and the stability of the final helicate relies on the formation of 27 dative bonds (21 Eu–N and 6 Eu–O bonds) that overcome the electrostatic repulsion associated with three Eu³⁺ held at approximately 9.0 Å (Table 2). In contrast to the molecular structure of the monometallic model compound [Eu(L₉)]₉⁺, in which strong interstrand π–π stacking interactions between the imidazole rings prevent complexation of small Ln³⁺ [25, 32] stericchemical constraints induced by the terminal metallic sites in [Eu₃(L₇)]₉⁺ affect the wrapping of the strands around Eu₁. Interstrand interactions are removed in [Eu₃(L₉)]₉⁺ and this may explain the lack of size-discriminating effects affecting β₉₁₅ along the lanthanide series (Table 1). The three metals are nine-coordinate surrounded by three wrapped tridentate segments leading to slightly distorted triapped trigonal prisms in which the three nitrogen atoms of the pyridine rings occupy the capping positions. Detailed geometrical analyses based on the φ, β, and α₉ angles (Tables S5 – S7 in the Supporting Information) [31, 12] show only minor deformations from perfect trigonal prisms, except for small twists of the trigonal faces (ω₉₁ = 9–15°) that closely match those reported for the model compounds [Eu(L₉)]₉⁺ (ω₉₁ = 10°) [32] and [Eu(L₁₀)]₉⁺ (ω₉₁ = 15–17°) [33]. The only significant differences between the geometry of the terminal and the central metallic sites are the slight shifts of Eu₂ and Eu₃ out of the facial planes F₈ (0.148(1) Å) and F₇ (0.191(1) Å) toward the oxygen tripods, while Eu₁ lies in the facial plane F₅ (deviation 0.0023(1) Å). The Eu–N(benzimidazole), Eu–N(pyridine), and Eu–O–(amide) bond lengths are standard (Table 2) [13, 14], although considerable bending of the pyridine and benzimidazole rings preclude ideal alignments of the nitrogen lone pairs with the coordinated Eu³⁺ ion (Figure 6). We conclude that the replacement of heterocyclic nitrogen atoms in NNN segments with oxygen atoms in NNO segments has minor effects on the geometrical arrangement of the nine-coordinate pseudo-tricapped trigonal prismatic metallic sites, but the stronger (and shorter) Eu–O bonds reinforce the nonequivalence of the coordination sites along the helix.
In the crystals, the triple helical cations are closely packed parallel with the bc plane with their pseudo-threefold axis almost aligned (4.6°) with the [0 1 2] direction (Figure S3 in the Supporting Information).

**Multicenter paramagnetic NMR spectra and solution structure of** \([\text{Ln}_3(L_7)_3]^{9+}\) \((\text{Ln} = \text{La} – \text{ Tb}, \text{Y}, \text{Lu})\): The \(^1H\) NMR spectra of \([\text{Ln}_3(L_7)_3]^{9+}\) for the diamagnetic metals \(\text{Ln} = \text{La}, \text{Y}, \text{Lu}\) display 25 well-resolved signals assigned to eleven aromatic protons (H1–H11), ten methylene protons (H12–H21), and four methyl groups (Me17–Me20) characteristic of a half ligand strand and pointing to average \(D_h\), \(D_{3h}\), or \(C_{3v}\) symmetry for the complexes in solution (Figure 4a). The systematic diasterocticity of all methylene protons (H12–H16) (observed as pseudo-sexets because \(J \approx 2 \text{Hz} \)) excludes a \(D_{3h}\) symmetrical arrangement of the three strands (i.e., a nonhelical arrangement or a fast helical interconversion), but it is compatible with a non-interconverting racemic mixture of 1), helicates \(\text{PPP}[\text{Ln}_3(L_7)_3]^{9+}\) and \(\text{MMM-}\)[\(\text{Ln}_3(L_7)_3]^{9+}\) or 2) side-by-side complexes \(\text{PPM}[\text{Ln}_3(L_7)_3]^{9+}\) and \(\text{MMP-}[\text{Ln}_3(L_7)_3]^{9+}\) belonging to the \(D_3\) point group.\(^{34}\)

The large upfield complexation shifts of the protons bound to the 4-position of the benzimidazole rings (H5, H6) in \([\text{La}_3(L_7)_3]^{9+}\) (\(\Delta \delta = 1.83 – 1.93 \text{ ppm}\), \([\text{Y}_3(L_7)_3]^{9+}\) (\(\Delta \delta = 2.21 – 2.37 \text{ ppm}\), and \([\text{Lu}_3(L_7)_3]^{9+}\) (\(\Delta \delta = 2.32 – 2.50 \text{ ppm}\), Table 4) are diagnostic for a regular helixation that puts these protons in the shielded region of the connected benzimidazole ring\(^\text{[22]}\) in agreement with the crystal structure of \([\text{Eu}_3(L_7)_3]^{9+}\) (Figure 6), but in complete contradiction with amphiphilic \(\text{PPM}\) (or \(\text{MMP}\)) conformers. The observation of weak but significant interstrand NOE effects involving protons of the terminal and central binding units (for instance H4–H18) points to three strands tightly wrapped about the helical axis\(^\text{[22]}\) this rules out complexes that possess a central lanthanide with no helicity such as the racemic mixture of \(\text{PPP}[\text{Ln}_3(L_7)_3]^{9+}\) and \(\text{MM-}[\text{Ln}_3(L_7)_3]^{9+}\) (\(D_3\) symmetry) or the side-by-side complex \(\text{PPM}[\text{Ln}_3(L_7)_3]^{9+}\) (\(C_{3v}\) symmetry). These NMR data unambiguously establish that the triple-helical structure observed in the solid state is maintained in solution along the complete lanthanide series and that relaxation of intermolecular constraints provides a racemic mixture of inert triple-stranded helicates \(\text{PPP}[\text{Ln}_3(L_7)_3]^{9+}\) and \(\text{MMM-}[\text{Ln}_3(L_7)_3]^{9+}\) with average \(D_h\) symmetry on the NMR timescale.

Further geometrical and electronic information can be gained from the separation of contact (through-bond, \(\delta_{\text{h}}\)) and pseudo-contact (through-space, \(\delta_{\text{ps}}\)) contributions to the isotropic paramagnetic shifts (\(\delta_{\text{iso}}\)) produced by fast-relaxing \(\text{Ln}^{3+}\).\(^{35,36}\) For any nucleus \(i\) in a complex of a lanthanide \(j\), the paramagnetic shifts are obtained from the experimental chemical shifts \(\delta_{\text{exp}}\) by using Equation (6) if the residual signal of the solvent is taken as an internal reference.\(^{35,36}\) The diamagnetic contribution \(\delta_{\text{d}}\) in the paramagnetic complexes \([\text{Ln}_3(L_7)_3]^{9+}\) is obtained from the NMR spectra of the isosstructural diamagnetic complexes \([\text{La}_3(L_7)_3]^{9+}\) (\(\text{Ln} = \text{Ce–Nd}\)), \([\text{Y}_3(L_7)_3]^{9+}\) (\(\text{Ln} = \text{Sm–Ho}\)) and \([\text{Lu}_3(L_7)_3]^{9+}\) (\(\text{Ln} = \text{Er–Yb}\)).

\[
\delta_{\text{iso}} = \delta_{\text{h}} + \delta_{\text{ps}} = \delta_{\text{exp}} - \delta_{\text{d}}
\]

(6)

The contact contribution results from spin delocalization according to the Fermi mechanism [Eq. (7)] in which \(F_i\) is the contact term (proportional to the hyperfine Fermi constant \(A_i\)) and \((S_i)\) is the spin expectation value of the \(i\)th operator tabulated by Golding and Halton for the free lanthanide ions at 300 K.\(^{37}\)

\[
\delta_{\text{h}} = \frac{A_i}{h \gamma_i I_i} (S_i) = F_i (S_i)
\]

(7)

For axial complexes possessing at least a threefold axis, the development of the paramagnetic anisotropy of lanthanide complexes in a power series of \(T^{-1}\) limited to \(n = 2\) proposed by Bleaney\(^{38}\) leads to Equation (8) for the pseudo-contact contribution, in which \(B_j\) is the second-rank crystal-field parameter of the complex, \(C_j\) is the Bleaney’s factor tabulated for each lanthanide \(j\) at 300 K and scaled to \(C_{ Db} = -100\)\(^{35,38}\) and \(G_i = (3 \cos^2(\theta_j) - 1) / r_j^2\) is the structural factor of the nucleus \(i\) containing its internal axial coordinates \(\theta_j\) and \(r_j\).

\[
\delta_{\text{ps}} = \frac{J_i}{(1 + p_j) C_j} B_j \left( \frac{3 \cos^2(\theta_j) - 1}{r_j^2} \right) = C_j B_j G_i
\]

(8)

Substituting Equation (7) and (8) into Equation (6) gives Equation (9), which is well suited for extracting contact \((F_i)\) and pseudo-contact \((B_i^G)\) terms for any nucleus by a multilinear least-squares fit of \(\delta^{para}_{ij}\) versus \(\langle S_i \rangle\) and \(S_j\) along a series of isostructural monometallic lanthanide complexes\(^{30}\) for which the hyperfine constants and the crystal-field parameter do not vary.\(^{17}\)

\[
\delta^{para}_{ij} = F_i\langle S_i \rangle + C_i B_i^G \tag{9}
\]

The existence of three paramagnetic centers in the homotrimetallic helicates \([\text{Ln}_n(\text{L7})_3]^{9+}\) requires some modifications of the classical Equation (9) derived for monometallic complexes; Equation (10) holds for an axial multicenter homopolymetallic lanthanide complex containing \(n\) paramagnetic centers.

\[
\delta^{para}_{ij} = \left(\sum_{k=1}^{n} B_{ki}^G S_k \right) + \left(\sum_{k=1}^{n} B_{ki}^G G_k \right) S_j \tag{10}
\]

Since 1) no magnetic coupling occurs at room temperature between the \(\text{Ln}^{III}\) ions lying at distances larger than 4 Å\(^{40}\) and 2) the tridentate binding units are separated by methylene bridges in \(\text{L7}\) that are poor electronic relays, we assume that the contact contributions \(\delta^{para}_{ij}\) result from through-bond Fermi interactions with a single metallic center as previously demonstrated for \([\text{Ln}_2(\text{L3-2H})_3]^{9+}\).\(^{15}\) On the other hand, the pseudo-contact contribution \(\delta^{pc}_{ij}\) in the \(D_3\)-symmetrical helicates \([\text{Ln}_n(\text{L7})_3]^{9+}\) results from the sum of the effect induced by each metal ion according to Scheme 3. Different crystal-field parameters for the central \(\text{LnN}_6\) \((B_{ii}^{\text{central}})\) and the two terminal \(\text{LnN}_6\) \((B_{iii}^{\text{term}})\) metallic sites are required and Equation (10) reduces to Equation (11) for \([\text{Ln}_3(\text{L7})_3]^{9+}\) with \(S_i\) defined as \([B_{ii}^{\text{central}} G_1^{\text{central}} + B_{iii}^{\text{term}} (G_1^{\text{central}} + G_2^{\text{central}})]\).

\[
\delta^{para}_{ij} = F_i\langle S_i \rangle + C_i S_j \tag{11}
\]

The associated linear forms [Eqs. (12) and (13)] can be used for testing isostucturality, since plots of \(\delta^{para}_{ij}/\langle S_i \rangle\) versus \(C_i/\langle S_j \rangle\) [Eq. (12)] and \(\delta^{para}_{ij}/C_i\) versus \(\langle S_i \rangle/C_j\) [Eq. (13)] are expected to give linear correlations as long as the structural factors \(G_i^{m}\) \((m = 1-3)\), the contact term \(F_i\), and the crystal-field parameters do not change along the lanthanide series.\(^{17, 39}\)

\[
\frac{\delta^{para}_{ij}}{\langle S_i \rangle} = F_i + \frac{\langle S_i \rangle}{C_j} S_j \tag{12}
\]

\[
\frac{\delta^{para}_{ij}}{C_i} = S_i + \frac{\langle S_i \rangle}{C_j} \tag{13}
\]

For paramagnetic \([\text{Ln}_n(\text{L7})_3]^{9+}\) helicates, a reliable assignment of the \(25^1\text{H}\) NMR signals depends on the detection of \(1^1\text{H}–1^1\text{H}\) scalar (from COSY spectra) and dipolar couplings (from NOESY or ROESY spectra).\(^{35}\) Since lanthanide-induced paramagnetic nuclear relaxation increases with the effective magnetic moments of the complexes,\(^{35}\) useful COSY and NOESY spectra for fast-relaxing lanthanides can be recorded only for weakly paramagnetic complexes (\(\text{Ln} = \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{and Eu, Table 4}\). For the diastereotopic methylene protons \((\text{H12}–\text{H16})\), the multiplets cannot be assigned unambiguously to one specific proton of the pair along the lanthanide series, and these signals are not considered in the structural analysis.\(^{36}\) Plots of \(\delta^{para}_{ij}/\langle S_i \rangle\) versus \(C_i/\langle S_j \rangle\) [Eq. (12)] and \(\delta^{para}_{ij}/C_i\) versus \(\langle S_i \rangle/C_j\) [Eq. (13)] are linear for all aromatic protons \((\text{H1}–\text{H11})\) and for the methyl groups \((\text{Me17}–\text{Me20})\) along the series \(\text{Ln} = \text{Ce}–\text{Eu}\), in agreement with the existence of an isostructural series (Figure 7). A first set of \(F_i\) and \(S_i\) factors obtained with Equation (11) have been used for the prediction of the \(1^1\text{H}\) NMR spectra of \([\text{Ln}_3(\text{L7})_3]^{9+}\) with the strongly paramagnetic lanthanides \((\text{Ln} = \text{Tb}–\text{Yb})\).\(^{43}\) Comparison between predictions and experimental data is only satisfying for \([\text{Tb}(\text{L7})]^{9+}\), thus allowing a complete assignment for this complex (Table 4) and its consideration for the calculations of
the final set of \(F_i\) and \(S_i\) factors collected in Table 5. For \(Ln = Dy - Yb\), the experimental \(1^H\) NMR spectra do not fit those predicted with Equation (11), but we cannot ascribe this deviation to an abrupt structural change, since variations of the crystal-field parameters near the middle of the lanthanide series, sometimes referred to as the gadolinium break effect,[41] are likely to occur in \([Ln(L7)_3]^9_+\), as previously observed for related homo- and heteropolynuclear triple-stranded helicates.[17, 41] More sophisticated mathematical analyses using novel crystal-field independent techniques[36, 42] extended to trimetallic complexes with different crystal-field parameters will be discussed elsewhere,[43] but they eventually confirm isostructurality along the complete lanthanide series for \([Ln(L7)_3]^9_+\) (\(Ln = Ce - Yb\)), together with an abrupt variation of the crystal-field parameters between Tb and Dy.

For the \(Ln = Ce - Tb\) series, the Wilcox agreement factors[43] are acceptable for all aromatic protons (0.02 < \(AF_i\) < 0.23, Table 5), and they can be compared to similar mathematical treatments applied to the monometallic model complexes \([Ln(L9)]^9_+\) (0.04 < \(AF_i\) < 0.25)[31] and \([Ln(L10)]^9_+\) (0.01 < \(AF_i\) < 0.33).[39] The large \(AF_i\) values observed for Me18 and Me19 result from minor paramagnetic shifts associated with negligible spin delocalization (\(F_i\)) and dipolar effects (\(S_i\)).

The \(F_i\) values are negligible for protons separated from the paramagnetic center by more than five bonds, thus justifying that the contact contribution can be limited to a single magnetic center in \([Ln(L7)]^9_+\). Interestingly, the absolute values \(|F_i|\) for the central pyridine protons H1 and H2 are larger than those found for the related protons of the terminal pyridine groups H9–H11; this strongly suggests larger spin delocalization onto the bis(benzimidazole)pyridine units. These results closely parallel the \(|F_i|\) values obtained for \([Ln(L9)]^9_+\) (\(|F_{H1}| = 0.26, |F_{H2}| = 0.42|\)[25] a model for the central LnN6O3 metallic site, and which are larger than those found in \([Ln(L10)]^9_+\) (\(|F_{H1}| = 0.11, |F_{H2}| = 0.13|\)[31] a model for the terminal LnN6O3 metallic sites. The unsymmetrical delocalization \(|F_{H1}| > |F_{H2}|\) is characteristic for NNO tridentate binding units, as previously established for heterobimetallic LnCoIII helicates in which LnIII lies in a similar LnN6O3 site.[38] The structural factor \(S_i\) is difficult to interpret because it combines two crystal-field and three geometrical parameters. The maximum values found for H5 and H6 confirm the tight helical wrapping of the strands that forces them to point inside the triple helix, close to the metal ions (i.e., \((r^2)^n\) are large). The larger values of \(S_i\) observed for H9–H11 relative to those obtained for the central pyridine (H1, H2) are responsible for the strong paramagnetic shift experienced by the terminal pyridine ring; however, its eventual assignment to specific geometrical parameters requires the evaluation of the crystal-field parameters. Taking the crystal structure of \([Eu(L7)]^9_+\) as a structural model for the solution structure, the geometrical factors \(G^\mu\) (\(\mu = 1 - 3\)) can be calculated (Table S8 in the Supporting Information) and a multilinear least-squares fit of \(S_i\) versus \(G_i\) (Eq. (12)).

The quality of the linear correlation is satisfying and leads to an agreement factor \(AF_i = 0.06\) between calculated and experimental \(S_i\) factors; this strongly suggests that only minor structural changes occur between the solid-state and the solution structures in these rigid polynuclear helicates, as previously established for bimetallic \(d^9[36] f^1[39]\) helicates. We can now rationalize the origin of the larger values observed for \(S_{H9-H11}\) relative to \(S_{H1-H2}\); these result from a combination of 1) the larger crystal-field effects associated with the terminal sites (\(|B^\alpha_{H9-H11}^{(\uparrow)}| > |B^\alpha_{H1-H2}^{(\uparrow)}|\)) and 2) the larger compensation effect resulting from opposite paramagnetic contributions in the central metallic site [i.e., \(G^1_1\) and \(G^2_2 + G^3_3\)] display opposite signs for all pyridine protons (Table S8 in the Supporting Information), but the absolute value of the ratios \(|B^\alpha_{H1-H2}^{(\uparrow)}|/|B^\alpha_{H9-H11}^{(\uparrow)}| = 1.7 – 1.8\) are smaller for H1 and H2 than \(|B^\alpha_{H9-H11}^{(\uparrow)}|/|B^\alpha_{H1-H2}^{(\uparrow)}| = 5.8 – 6.9\) for H9–H11]. Finally, the only significant discrepancies evidenced between experimental and calculated paramagnetic shifts occur for H1, H2, H5, and H6 in \([Eu(L7)]^9_+\) (Table 4), because these protons possess large \(F_i\) constants (Table 5). The non-magnetic \(T_0\) ground state of EuIII prevents a reliable definition of the Landé factor (g), and we have used the standard spin expectation values \(S_i\) of 10.68[32, 33] associated with \(g(T_0) = 2S_i[37]\) for our calculations of \(F_i\) and \(S_i\), given in Table S5. However, a systematic survey of paramagnetic data led Pinkerton et al. to propose that the non-magnetic EuIII ground-state is better modeled with \(g(T_0) = 4.4\) and \(S_i\) of 7.5.[40] Re-calculations with Equation (11) and the latter values do not improve the quality of the separation of contact and pseudo-contact shifts for \([Ln(L7)]^9_+\), and the resulting values of \(F_i\) and \(S_i\) only marginally differ from those reported in Table S5. However, slightly better predictions can be made for H1, H2, H5, and H6 in \([Eu(L7)]^9_+\) (Table 4). We conclude from the analysis of NMR data that the triple-stranded helical

Table 5. Computed values for contact (\(F_i\)) and pseudo-contact \(S_i = [B^{\alpha}_{H1-H2}^{(\uparrow)} G^\mu_i + B^{\alpha}_{H1-H2}^{(\uparrow)} G^\mu_j]/G^\mu\) terms and agreement factors (\(AF_i\)) for aromatic and methyl protons in complexes \([Ln(L7)]^9_+\) (\(Ln = \text{Ce}-\text{Tb}\), CD, CN, 298 K).[31]

| \(H\) | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
| \(F_i\) | 0.18(3) | 0.42(6) | 0.10(1) | 0.04(34) | 0.45(7) | 0.61(1) | 0.031(3) | 0.26(3) | 0.28(5) | 0.07(4) | 0.16(3) | 0.01(2) | 0.01(4) | 0.02(1) | 0.11(2) |
| \(S_i\) | 0.08(1) | 0.03(2) | 0.02(52) | 0.09(51) | 1.20(2) | 1.20(3) | 0.06(81) | 0.05(1) | 0.27(1) | 0.23(1) | 0.17(1) | 0.15(84) | 0.06(01) | 0.02(54) | 0.47(05) |
| \(AF_i\) | 0.23 | 0.12 | 0.07 | 0.02 | 0.04 | 0.05 | 0.02 | 0.05 | 0.18 | 0.04 | 0.04 | 0.05 | 0.29 | 0.33 | 0.01 |

[a] \(F_i\) and \(S_i\) are obtained by linear least-squares fits of \(\frac{\Delta F_{i,j}}{\Delta Si,j}\) versus \(C_i/S_i\) (Eq. (12)). [b] Calculated according to \(AF_i = \sum \left(\frac{\Delta F_{i,j}}{\Delta Si,j}\right)^2\) \(\sum \left(\frac{\Delta Si,j}{\Delta F_{i,j}}\right)^2\).
Ligand-centered luminescence: The absorption spectrum of L7 in acetonitrile displays a broad band centered at 30680 cm\(^{-1}\) (\(\tau = 78000 \text{ s} \cdot \text{cm}^{-1}\)) and assigned to the envelope of the \(\pi \rightarrow \pi^*\) transitions. This band is slightly red-shifted by approximately 300 cm\(^{-1}\) upon complexation toLn\(^{10+}\) in 5–9 (Figure 1a), and a broad shoulder appears on the low-energy side (25600 cm\(^{-1}\)). A phenomenon also seen in the reflectance spectra of solid-state samples for which the shoulder becomes more pronounced.

The emission spectrum of [Eu\(_3\)(L7)\(_3\)]\(_{9}\)(CF\(_3\)SO\(_3\))\(_9\)(H\(_2\)O)\(_4\) recorded under various conditions: a) solid state, 10 K, excitation via the ligand-centered \(\pi \rightarrow \pi^*\) levels, b) solid state, 10 K, selective excitation of site I (\(\tau_{\text{exc}} = 17211 \text{ ms}\)), c) selective excitation of site II (\(\tau_{\text{exc}} = 17234 \text{ cm}^{-1}\)), d) solid state, 295 K, excitation via the ligand-centered \(\pi \rightarrow \pi^*\) levels (\(\tau_{\text{exc}} = 2778 cm^{-1}\)), and e) solution (acetonitrile 10 \(^{-3}\) M), 295 K, excitation via the ligand-centered \(\pi \rightarrow \pi^*\) levels (\(\tau_{\text{exc}} = 27397 cm^{-1}\)).

Multi-metal-centered luminescence: The ligand-centered luminescence in [Eu\(_3\)(L7)\(_3\)]\(_{9}\)(CF\(_3\)SO\(_3\))\(_9\)(H\(_2\)O)\(_4\) is quenched by efficient L7 \(\rightarrow\) Eu\(^{11+}\) energy-transfer processes, and excitation through the \(\pi \rightarrow \pi^*\) transitions produces only the Eu-centered red luminescence, characterized by sharp bands associated with \(\tilde{D}_0 \rightarrow \tilde{F}_j\) (\(j = 0–6\)) transitions (Figure 8, relative corrected and integrated intensities are collected in Figure S4 in the Supporting Information).

Table S9 in the Supporting Information). Emission spectra in the solid state show a very weak, broad, and slightly asymmetric \(\tilde{D}_0 \rightarrow \tilde{F}_0\) transition (10 K, 17219 cm\(^{-1}\), fwhh = 24.3 cm\(^{-1}\); 295 K, 17225 cm\(^{-1}\), fwhh = 274 cm\(^{-1}\) compatible with the luminescence emitted by a single metal ion center, termed site I.\(^{[33]}\) At 10 K, the crystal field splitting of site I can be interpreted in terms of a pseudo-\(D_4\) symmetry around the Dy\(^{3+}\) ion.

Table 6. Ligand-centered absorption at 295 K and emission properties at 77 K for the ligand L7 and its complexes [Ln\(_3\)(L7)\(_3\)]\(_{9}\)(CF\(_3\)SO\(_3\))\(_9\)(H\(_2\)O) (Ln = La, x = 4 (5); Ln = Eu, x = 4 (6); Ln = Gd, x = 2 (7); Ln = Tb, x = 1 (8); Ln = Lu, x = 6 (9)) in the solid state.

<table>
<thead>
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<th>Complex</th>
<th>(E(\pi \rightarrow \pi^*)) in cm(^{-1})</th>
<th>(E(\pi \rightarrow \pi^*)) in cm(^{-1})</th>
<th>(E(\pi \rightarrow \pi^*)) in cm(^{-1})</th>
<th>(E(\pi \rightarrow \pi^*)) in cm(^{-1})</th>
<th>(r(\pi \rightarrow \pi^*)) in ms</th>
</tr>
</thead>
<tbody>
<tr>
<td>[La(_3)(L7)(<em>3)](</em>{9})</td>
<td>30680</td>
<td>28490</td>
<td>24970</td>
<td>19920oh</td>
<td>18770</td>
</tr>
<tr>
<td>[Eu(_3)(L7)(<em>3)](</em>{9})</td>
<td>30320</td>
<td>25870 (sh)</td>
<td>25125</td>
<td>22780</td>
<td>20040</td>
</tr>
<tr>
<td>[Gd(_3)(L7)(<em>3)](</em>{9})</td>
<td>30390</td>
<td>25770 (sh)</td>
<td>24940</td>
<td>[d]</td>
<td>[d]</td>
</tr>
<tr>
<td>[Tb(_3)(L7)(<em>3)](</em>{9})</td>
<td>30120</td>
<td>25640 (sh)</td>
<td>24940</td>
<td>23030</td>
<td>20260</td>
</tr>
<tr>
<td>[Lu(_3)(L7)(<em>3)](</em>{9})</td>
<td>29900</td>
<td>25380 (sh)</td>
<td>24875</td>
<td>23420</td>
<td>20103</td>
</tr>
</tbody>
</table>

[a] \(10^{-3}\) M in acetonitrile, sh = shoulder. [b] Reflectance spectra in the solid state. [c] Data obtained from the emission spectra. [d] \(\pi \rightarrow \pi^*\) and \(\pi \rightarrow \pi^*\) luminescence quenched by transfer to Ln\(^{10+}\) ion.
Eu III ion (Table 7). The faint ¹D₉ → ¹F₉ transition (1 % of the intensity of the magnetic dipole ¹D₉ → ¹F₁ transition) is consistent with the fact that it is symmetry forbidden in the D₃ point group.[35] The three observed transitions to the ¹F₁ level can be labeled A₁ → A₂ (A₂ at 327 cm⁻¹ with respect to ¹F₀) and A₁ → split E sublevel (barycenter: 402 cm⁻¹). The splitting of the E sublevel is connected to the distortion from the idealized D₃ symmetry and amounts to ∆E₂/E = 42 cm⁻¹. A theoretical approach from the point-charge electrostatic model (PCEM) allows approximate correlations between the magnitude and signs of the second-rank crystal-field parameters B₂ and B₄ and the amount of the A and E levels in distorted trigonal tricapped prismatic sites.[3, 46] Moreover, the absolute magnitude of B₁ is proportional to the difference in energy between the ¹F₁(A₂) and ¹F₁(E) sublevels (ΔE₁, E), which increases in the order [Eu(L10)₃]³⁺ (53 cm⁻¹)[35] < site I in [Eu(L7)₃]³⁺ (75 cm⁻¹) < [LaEu(L5)₃]³⁺ (104 cm⁻¹)[19] < [Eu(L9)₃]³⁺ (114 cm⁻¹)[12] < anhydrous [Eu₂(L1)₃]³⁺ (127 cm⁻¹).[33] Secondly, the magnitude of B₁ is proportional to the difference in energy between the split components of the ¹F₁(E) sublevel.[3, 46] Examination of the reported splittings ΔE₂/E for [Eu(L9)₃]³⁺ (17 cm⁻¹),[32] anhydrous [Eu₂(L1)₃]³⁺ (18 cm⁻¹),[13] [LaEu(L5)₃]³⁺ (46 cm⁻¹),[19] and [Eu(L10)₃]³⁺ (57 cm⁻¹)[33] points to a relatively large distortion around the Eu III ions for site I (ΔE₂/E = 42 cm⁻¹) in the trimetallic helicate. The ¹D₉ → ¹F₁ transition displays two main bands assigned to the allowed electric dipole transitions A₁ → E in D₃ symmetry, the latter being further split into two components separated by 20 cm⁻¹. The analysis of the ¹D₉ → ¹F₁ transition shows six components, also consistent with a distorted trigonal symmetry.[32, 33] All these data are compatible with site I being composed of a set of very similar slightly distorted pseudo-trigonal Eu III sites associated with a microcrystalline sample containing some minor structural defects.

However, the crystal structure of [Eu₃(L₇)₃](CF₃SO₃)₉ involves two different pseudo-tricapped trigonal prismatic sites: a central EuN₉ and two terminal EuN₆O₃ sites; these are expected to produce specific metal-centered emission in a 1:2 ratio. The observation of single site upon ligand irradiation in [Eu₃ (L₇)₃](CF₃SO₃)₉ results from the quantum yield associated with the central EuN₉ site; this is expected to be of orders of magnitude smaller than that of EuN₆O₃, because low-lying LMCT states quench the ³ππ* energy transfer.[32] The 50-fold increase in the quantum yield observed when going from [Eu₂(L1)₃]³⁺ (which contains two EuN₆ sites)[35] to [Eu(L2)₃]³⁺ (which contains two EuN₆O₃ sites)[14] strongly supports this hypothesis, and we have resorted to high-resolution laser-excitation spectra of the ¹D₉ → ¹F₁ transition for evidencing the existence of a second site. Figure 9 shows the excitation profiles obtained for 6 at 10 K upon monitoring different Eu(¹D₉ → ¹F₁) (j = 1, 2, 4) transitions (Table S10 in the Supporting Information). The three closely spaced sites Ia, Ib, and Ic (17210–17220 cm⁻¹, Figure S5 in the Supporting Information) correspond to a single site affected by small defects in the microcrystalline sample, while site II (17238 cm⁻¹) unambiguously corresponds to a different environment. Selective excitation of sites Ia, Ib, and Ic produces similar intense emission spectra (Figure 8b) reminiscent of that obtained upon irradiation of the ligand-centered ³ππ* state (Figure 8a) and assigned to the terminal EuN₆O₃ sites (site I). Selective excitation of site II provides a weak emission spectrum with a splitting pattern of the ¹F₁ manifolds typical of distorted D₃ symmetry (Figure 8c). Detailed analysis of the ¹D₉ → ¹F₁ transition at 10 K leads to the two magnetic dipole allowed components A₁ → A₂ (A₂ at 1871

Table 7. Energy [cm⁻¹] of the identified crystal-field sub-levels of the Eu(¹F)j manifold (j = 1–4) in [Eu₃(L₇)₃](CF₃SO₃)₉ • (H₂O)₄ (6) as determined from excitation and emission spectra in the solid state at 10 and 295 K (¹F₀ is taken as the origin).

<table>
<thead>
<tr>
<th>j</th>
<th>E(¹F₁)</th>
<th>E(¹F₂)</th>
<th>E(¹F₃)</th>
<th>E(¹F₄)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 K</td>
<td>24016</td>
<td>17238</td>
<td>27778</td>
<td>17239</td>
</tr>
<tr>
<td>295 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Site I</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Site II</td>
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<td>1</td>
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<td>394</td>
<td>408</td>
</tr>
<tr>
<td>Site I</td>
<td>423</td>
<td>448</td>
<td>427</td>
<td>446</td>
</tr>
<tr>
<td>Site II</td>
<td>997</td>
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<td>1003</td>
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</tr>
<tr>
<td>Site II</td>
<td>17219</td>
<td>17238</td>
<td>17225</td>
<td>17239</td>
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</table>

295 cm$^{-1}$ with respect to $^7F_0$) and A$_1 \rightarrow$ E level (barycenter: 429 cm$^{-1}$), the latter being split by $\Delta E_{A,E} = 38$ cm$^{-1}$ (Table 7). The value of $B^1_0$ is still negative for site II,[3, 46] but the separation between the A$_2$ and E (barycenter) sublevels ($\Delta E_{A_2,E}$ = 134 cm$^{-1}$) is significantly larger than that observed for site I (75 cm$^{-1}$); this implies a larger $B^2_0$ parameter for site II. Although the nephelauxetic effects produced by the EuN$_6$ and EuN$_6$O$_3$ environments are very similar[22, 33, 53] and cannot be used for unambiguously assigning site I and site II (we calculate energies of 17 236 and 17 233 cm$^{-1}$ for the $^3D_0 \rightarrow ^3F_{2}$ transitions of EuN$_6$ and EuN$_6$O$_3$, respectively, at 295 K)[22, 33] the faint emission intensity of site II matches the one previously reported for [Eu$_3$(L$_7$)$_3$]$^9^{2-}$[32] hence, we can safely ascribe it to the central EuN$_6$O$_3$ site. The negative signs of $B^2_0$ in the solid state and compares well with lifetimes measured in the solid state, eventually confirming the lack of interaction between the solvent and the Eu$_{III}$ sites.

Finally, efficient sensitization of Tb$^{III}$ in 8 only occurs at low temperature in the solid state, because thermally activated $^3I_{5/2} \leftrightarrow$ Tb$^{III}$ energy back-transfer processes quench the luminescence at room temperature.[13-15] The emission spectrum is dominated by the $^4G_{5/2} \rightarrow ^4F_7$ transition (Figure S6 in the Supporting Information), while the Tb$^{III}$ lifetime drops from 2.23–2.30 ms at 10 K to 40–96 µs at 295 K (Table S12 in the Supporting Information). Residual emission originating from the ligand-centered $^3I_{5/2}$ state (20 000 cm$^{-1}$) is detected at 295 K in agreement with the existence of a $^3I_{5/2} \rightarrow$ Tb$^{III}$ energy back transfer that populates Tb$^{III}$.

**Conclusion**

Although the concept of positive cooperativity has been demonstrated in the early 1990’s for trimetallic d-block helicates,[27, 28, 54] its planned application for the stabilization of highly charged polymetallic helicates remains scarce.[16, 34, 55] In this context, the formation of the triple-stranded trimetallic helicates [Ln$_3$(L)$_3$]$^{13+}$ represents the first well-characterized self-assembly process in which the fixation of three 4f-block ions is driven by positive cooperativity. The considerable electrostatic repulsion associated with the fixation of the third Ln$^{III}$ ion is overcome by the preorganization of the receptor, a phenomenon that has deep roots in biological processes for which the overall free energy gains result from multisite interactions (protein zipper, recombinatation of DNA).[56] The crystal structure and the photophysical properties of [Eu$_3$(L)$_3$]$^{13+}$ evidence the formation of a “regular” triple helix in the solid state, roughly corresponding to the packing of three monometallic triple-helical lanthanide complexes along the threefold axis. The nonequivalence of the terminal (EuN$_6$O$_3$) and central (EuN$_6$) metallic sites is clearly evidenced by high-resolution luminescence data and could be useful in the programming of directional intramolecular energy transfers required in the rational design of multicenter luminescent probes.[18, 57] Moreover, the significant difference between the crystal-field parameters of the two lanthanide sites in [Ln$_3$(L)$_3$]$^{13+}$ induces large, variable, and tunable paramagnetic anisotropies along the strand, a crucial point for (1) the preparation of magnetically-addressable liquid crystals,[58, 59] and (2) related lifetimes obtained for nine-coordinate Eu$^{III}$ sites in the bimetallic helicates [Eu$_3$(L)$_3$]$^{13+}$ (1.78(8) ms at 4 K)[33] and [Eu$_3$(L)$_2$]$^{11+}$ (2.28(2) ms at 10 K).[14] Above 200 K, the lifetimes of both sites in [Eu$_3$(L)$_3$]$^{13+}$ sharply decrease to reach 1.7(1) ms at 295 K, because of thermally activated vibrational-quenching processes. Interestingly, the lifetime of the central EuN$_6$ sites is less affected at 295 K than that reported for the bimetallic model complex [Eu$_2$(L)$_3$]$^{13+}$ ($\tau$ = 0.29(1) ms at 295 K).[13] this suggests that the slide of the strands around the central EuN$_6$ site shifts the LMCT state toward slightly higher energies. In solution, the Eu$^{III}$ lifetime only reflects the emission of the terminal EuN$_6$O$_3$ sites ($\tau \approx$ 2.4 ms, Table S11 in the Supporting Information) and compares well with lifetimes measured in the solid state, eventually confirming the lack of interaction between the solvent and the Eu$^{III}$ sites.
in paramagnetic matrices for structural investigation by multidimensional NMR spectroscopy,[39] and 3) the elucidation of the abrupt change affecting the crystal-field parameters near the middle of the lanthanide series (i.e., the “gadolinium break” effect).[40, 41] Finally, our paramagnetic NMR study of \([\text{Ln} \cdot \text{L7}]\)\(^{[9]}\) (\(\text{Ln} = \text{Ce} - \text{Tb}\)) combined with luminescence data indicate that the triple-helical structure is essentially maintained in solution and that the terminal \(\text{Eu} \cdot \text{NH}_3\) sites do not evidence significant distortions. However, the decrease of the crystal field parameter of the central coordination unit \(\text{Ln}\text{N}_9\) (\(B_{\text{eff}}\)) in solution with respect to its solid-state value implies that some geometrical relaxation of the central \(\text{Eu} \cdot \text{NH}_3\) site takes place, and this has considerable effects on the magnetic anisotropy.

**Experimental Section**

**Solvents and starting materials:** These were purchased from Fluka AG (Buchs, Switzerland) and used without further purification unless otherwise stated. Thionyl chloride was distilled from elemental sulfur, acetonitrile, dichloromethane, and triethylamine were distilled from CaH\(_2\), Silicagel (Acros, 0.035 – 0.07 mm) was used for preparative column chromatography, 3,3'-Dimino-4,4'-bis(\(N\)-ethylamino)diethylenephosphine (1)\[^{[2]}\] and 6-(\(N\)-diethylcarbamoyl)pyridine-2-carboxylic acid (2)\[^{[2]}\] were prepared according to literature procedures. The triflate salts \(\text{Ln(CF}_3\text{SO}_3)\_2\cdot \text{H}_2\text{O (Ln = La - Lu)}\) were prepared from the corresponding oxides (Rhodia, 99.99%). The \(\text{Ln}\) content of solid salts was determined by complexometric titrations with Titriplex III (Merck) in the presence of urotropine and xylene orange.

**Preparation of 6-(\(N\)-diethylcarbamoyl)-N-methyl-\(N\)-\(\{4\.ToUpper\([\text{ethylami}-\text{no}-\text{\text{-3-nitrophenyl}]-2\text{-nitrophosphoryl}-2\text{-carboxamide (3): A mixture of compound 2 (814 mg, 3.66 mmol), thionyl chloride (2.50 mL, 33.5 mmol), and DMF (0.2 mL) was refluxed for 90 min in dry dichloromethane (40 mL). The mixture was evaporated and dried under vacuum. The solid residue was dissolved in dichloromethane (40 mL) and added dropwise to a solution of 1 (1.147 g, 3.33 mmol) and triethylamine (1.4 mL, 9.3 mmol) in dichloromethane (40 mL). The solution was refluxed for 12 h under an inert atmosphere and evacuated. The residue was partitioned between dichloromethane (150 mL) and half-saturated aqueous \(\text{NH}_4\text{Cl}\) solution (150 mL). The aqueous phase was extracted with dichloromethane (2 × 150 mL), and the combined organic phases were dried (\(\text{Na}_2\text{SO}_4\)) and evaporated. The crude product was purified by column chromatography (silicagel, CH\(_2\)\(_2\)Cl\(_2\)/MeOH 97:3) to give 855 mg (0.38 mmol, yield 84%) as an oil which was further purified by column chromatography (silicagel, CH\(_2\)\(_2\)Cl\(_2)/\text{MeOH} 97:3\), yield 84%; \(R_s = 0.8 \pm 0.1\) in acetone)) and then dried under vacuum.\]}

**Preparation of 6-(\(N\)-diethylcarbamoyl)pyridin-2-yl)benzimidazol-5-methylene[benzimidazole-2-yl]pyridine (\(\text{L7}\): Ligated \(\text{L7} \cdot \text{H}_2\text{O} (50 mg, 0.048 mmol) and potassium hydroxide (86%, 1.58 g, 24.2 mmol) were refluxed in ethanol/water (10 mL/2.5 mL) for 15 h. The ethanol was distilled under vacuum, water (25 mL) was added, and the aqueous phase extracted with dichloromethane (3 × 25 mL). The combined organic phases were evaporated and dried under vacuum.\]**

**Preparation of the complexes \([\text{Ln} \cdot \text{L7}]\)\(^{[21]}\): \([\text{Eu} \cdot \text{L7}]\)\(^{[21]}\): A solution of \(\text{Ln} \cdot \text{CF}_3\text{SO}_3\) (3.57 mmol) in ethanol/water (112 mL/28 mL). The mixture was refluxed for 15 h. After cooling to room temperature, the resulting precipitate was filtered, washed with water (5 mL), and dried to give 32 mg (0.03 mmol, yield 62%) of \(\text{K(L8-H)}\cdot \text{H}_2\text{O as a white powder. M.p. > 200 °C.} \)**

was performed with factor analysis[23] and with the SPECFIT program.[24] Full-matrix least-squares refinement based on F using weight of U

energy (\(E_i\)) gave final values \(R = 0.055\), \(aR = 0.055\), and \(S = 1.814(9)\) for 3024 variables and 24081 contributing reflections. The full difference electron density map showed a maximum of 1.62 e Å\(^{-3}\). The hydrogen atoms were placed in calculated positions and contributed to \(F_i\) calculations. The methyl group C33a was disordered and refined with two distinct atomic sites and population

298 K. The absorption spectrum of each sample was transferred to the spectrometer. \(1H\) NMR spectra were recorded at 25

1 mm path length. Spectrophotometric titrations were performed in batch by using the Equation (14), in which \(x\) refers to the sample and \(r\) to the intensity of the excitation light at this energy,

\[
\Phi = \frac{A(\Phi)}{A(r)} \frac{I(\Phi)}{I(r)} \frac{R_D}{R_r},
\]

(14)

\[
\Phi^* = \frac{A(\Phi^*)}{A(r)} \frac{I(\Phi^*)}{I(r)} \frac{R_D}{R_r},
\]

fiber with protection oil. Cell dimensions and intensities were measured at 200 K on a Stoe IPDS diffractometer with graphite-monochromated MoK\(_\alpha\) radiation (\(\lambda = 0.71073\) Å). 13172 measured reflections \(2\theta_{max} = 51.9^\circ\), 42673 unique reflections of which 22616 were observed \([\bar{F}_o] = 4\sigma(\bar{F}_o);\) \(R_{free}\) for 89046 equivalent reflections 0.071. Data were corrected for Lorentz and polarization effects and for absorption (min/max transmission = 0.7552/0.8963). The structure was solved by direct methods (SIR97)[5] all other calculations were performed with XTAL system[5] and ORTEP[6] programs. Full-matrix least-squares refinement on \(F\) with weight of \(U^{1/2}\) for low-temperature measurements. The quantum yields

Acknowledgement

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[3] a) W. T. Carnall, in Handbook on the Physics and Chemistry of Rare Earths (Eds.: K.A. Gschneidner, Jr., L. Eyring), North-Holland, Amsterdam, 1979, pp. 171–208; b) C. Görler-Walrand, K. Binne-


Lanthanide Helicates 1860–1875

New York, Chichester, 1980.


[a] £ is usually expressed in cm$^{-1}[3]$ but only relative values (formally in ppm$^{-1}$) are obtained from paramagnetic NMR data because the Bleaney’s factors are arbitrary scaled to $C_{00} = -100$ and are given without units.[30]


[a] £ is usually expressed in cm$^{-1}[3]$ but only relative values (formally in ppm$^{-1}$) are obtained from paramagnetic NMR data because the Bleaney’s factors are arbitrary scaled to $C_{00} = -100$ and are given without units.[30]