In search for tuneable intramolecular intermetallic interactions in polynuclear lanthanide complexes†

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Reaction of unsymmetrical tridentate 2-benzimidazolyl-6-carboxamidopyridine binding units in the ligands L4 and L5 with neutral Ln(NO3)3 (Ln is a trivalent lanthanide) gives mononuclear [Ln(L4)](NO3)(solvent) and binuclear [Ln2(L5)(NO3)3(solvent)] complexes. The crystal structures of L4 and [Eu(L4)](NO3)3(CH3CN) unravel the conformational change of the tridentate binding units required for its coordination to the metal, a process responsible for the change in electronic absorption spectra and in 1H NMR spectra recorded in acetonitrile solution. In the solid state, the bis-tridentate ligand L5 shows variable helical conformations of its central diphenylmethane spacer in its uncoordinated form (amphiverse helix) and in its complexed form in [Eu2(L5)(NO3)3(H2O)] (regular helix), which puts the two metals at a contact distance of 8.564(1) Å. In solution, fast rearrangements yield an average planar extended conformation of the spacer, which increases the intramolecular intermetallic contact distance by 30% in [Ln2(L5)(NO3)3(H2O)]. Surprisingly, the thermodynamic analysis of the complexation processes in solution points to unusual, and to some extent non-predicted triple-stranded helicate [Ln3(L5)]◊◊◊ (Ln · · ·Ln ≈ 9 Å). The origin of this effect and its consequences on programming stable polynuclear complexes is discussed.

Introduction

The undeniable successes brought by supramolecular chemistry in the preparation of heterometallic d–4f (n = 3–5) polynuclear complexes possessing predetermined structures, shapes and intermetallic communications have not yet significantly influenced the parallel design of heterometallic 4f–4f analogues, because of the great similarity of the metallic coordination properties along the lanthanide series. The rational preparation of pure heterometallic 4f–4f assemblies is thus currently limited to stepwise metallation/demetallation processes operating in inertly inert lanthanide complexes including negatively charged ligands such as metalloceptors, macrocyclic phthalocyanins and porphyrins or highly pre-organized polycarboxylates. Beyond the well-documented, but empirical investigations of deviations from statistical distributions resulting from the doping of different lanthanides into solid-state materials, there is some rare, but remarkable and intriguing reports in the literature describing the characteristic in solution and the isolation in the solid state of pure heterometallic 4f–4f polynuclear complexes obtained under apparent thermodynamic control (Fig. S1, ESI). The recurrent qualitative arguments for such fascinating selectivities rely on special size-discriminating or electrostatic effects resulting from the combination of two different types of binding units in the final polynuclear complexes. Whatever the origin of these minor variations, they are systematically assigned to some uncontrolled changes of the microscopic affinities (including desolvation) of the metal along the lanthanide series for each specific i binding site in the ligand (eqn (1) and eqn (2)).

\[ n \text{L} + m \text{Ln}^{3+} \rightleftharpoons [\text{Ln}_m(\text{L})_{3n+}]^{3n+} \]

\[ \beta_{i,j}^{\text{Ln} \times \text{Ln}} = e^{-\Delta G_{i,j}^{\text{Ln} \times \text{Ln}} / RT} \]

A recent quantitative treatment of the competitive binding of different lanthanides in the triangular trinuclear complexes \([\text{Ln}_3^{\text{L}_{1-3}}]^{3+}\) in water with eqn (2) indeed confirms that the microscopic affinity increases by two orders of magnitude in going from Ln = Nd (log(f_{\text{Nd}}^{\text{Nd}})) = 10.56) to Ln = Eu (log(f_{\text{Eu}}^{\text{Eu}})) = 12.64), while no significant variations in intermetallic interactions could be detected (\(\Delta E_{1-2}^{\text{Nd,Eu}} = \Delta E_{1-2}^{\text{Nd,Nd}} = \Delta E_{1-2}^{\text{Eu,Eu}}\), Fig. 1).
Fig. 1 Self-assembly of the trinuclear sandwich complexes $[\text{Ln}_3(\text{L}1-3\text{H})_2]^{3+}$ and its thermodynamic site-binding model ($f^L_{\text{N}2\text{O}4}$) is the microscopic affinity of a lanthanide for the N$_2$O$_4$ binding site and $\Delta E_{1-2}$ represents the free energy of intermetallic interaction. Ln = Nd, Eu.

However, a similar thermodynamic analysis of the distribution of the La/Lu pair in the tetranuclear helicates $[\text{La}_{4-x}\text{Lu}_x(\text{L}2)_3]^{12+}$ in acetonitrile with eqn (2) reaches the opposite conclusion, and the faint changes observed between the microscopic affinity of the central ($\log(f^{L}_{\text{N}6\text{O}3})$) and that of the terminal ($\log(f^{L}_{\text{N}9})$) sites for Ln = La and Lu cannot account for the distribution of the microspecies in solution (Fig. 2). An additional driving force favours the close location of different lanthanides along the helical axis, which is unambiguously assigned to the smaller geminal intramolecular intermetallic repulsion operating between different metals: $\Delta E_{1-2}^{\text{La},\text{Lu}} < (\Delta E_{1-2}^{\text{La},\text{La}} + \Delta E_{1-2}^{\text{Lu},\text{Lu}})/2$. Though this bias is of limited magnitude in these triple-stranded helicates (mixing rule: $\Delta E_{1-2} = (\Delta E_{1-2}^{\text{L},\text{L}} + \Delta E_{1-2}^{\text{L},\text{M}})/2$, $\Delta E_{1-2}^{\text{L},\text{M}} = 2 \text{ kJ mol}^{-1}$), it reveals that both (i) the nature of the binding site (via $f^{L}_{\text{N}L}$) and (ii) the intermetallic interactions (via $\Delta E_{1-2}^{\text{L},\text{L}}$) can be exploited for programming lanthanide complexes under thermodynamic control.

The intimate mechanism controlling the absolute affinity $f^{L}_{\text{L},\text{L}}$ is rather obvious, since it relies on the free energy balance between the bond breaking process required for the desolvation of both metal and binding sites, and the subsequent bond making process leading to the fixation of the metal in site $i$. The physical origin of the intermetallic interaction $\Delta E_{1-2}^{\text{L},\text{L}}$ is more subtle because this parameter reflects the balance between the unfavourable intramolecular electrostatic repulsion produced by the introduction of closely spaced cationic metals in the complex, and the favourable contribution to the global solvation energy brought by the increase of the total charge of the complex. We have therefore launched into a research project, which aims at tuning these non-trivial thermodynamic descriptors by...
using chemically-relevant molecular (i.e. electronic and structural) factors. As a first step toward this goal, we report here on the consequences of the replacement of the charged Ln\textsuperscript{n+} partners obtained from Ln(CF\textsubscript{3}SO\textsubscript{3})\textsubscript{3} or Ln(ClO\textsubscript{4})\textsubscript{3} salts, with neutral Ln(NO\textsubscript{3})\textsubscript{3} metallic units for loading segmental ligands. We indeed reason that the use of the well-established neutral Ln(NO\textsubscript{3})\textsubscript{3} metallic units for loading segmental ligands.

Previous studies have shown that the reaction of the tridentate 2,6-bis(benzimidazolyl-2-yl)pyridine binding unit (N\textsubscript{x}) found in ligands L\textsubscript{3}\textsuperscript{−3} (Scheme 1) with Ln(NO\textsubscript{3})\textsubscript{3}, indeed produces neutral mononuclear complexes [Ln(L\textsubscript{3})(NO\textsubscript{3})\textsubscript{3}] in the solid state.\textsuperscript{19} However, the solution behaviour of these complexes in organic solvent is more complicated with the observation of intricate mixtures containing [Ln(L\textsubscript{3})(NO\textsubscript{3})\textsubscript{n−1}]\textsuperscript{+} (n = 1−2, x = −1, 0, 1) and [Ln\textsubscript{2}(L\textsubscript{3})(NO\textsubscript{3})\textsubscript{6}] (n = 2−3),\textsuperscript{19} in line with similar observations reported for the analogous lanthanide nitrate complexes with 2,2′,6′,2″-terpyridine.\textsuperscript{19} Interestingly, we notice that the closely related, but unsymmetrical tridentate N\textsubscript{2}O ligands L\textsubscript{4}\textsuperscript{−4} (Scheme 2) gave less stable complexes with Ln\textsuperscript{n+} (obtained from its perchlorate salt Ln(ClO\textsubscript{4})\textsubscript{3} in acetonitrile) than those obtained within the L\textsubscript{3} series,\textsuperscript{20,21} a situation that could be turned to an advantage for limiting the number of species in solution upon reaction with Ln(NO\textsubscript{3})\textsubscript{3}. In this contribution, we thus report on the detailed coordination and thermodynamic behaviour of the archetypal ligand L\textsubscript{4}, and of its bis-tridentate segmental derivative L\textsubscript{5} with Ln(NO\textsubscript{3})\textsubscript{3}.

**Results and discussion**

**Preparation, characterization and solid-state structures of the ligands L\textsubscript{4} and L\textsubscript{5}, and of their complexes [Ln(L\textsubscript{4})(NO\textsubscript{3})\textsubscript{3}]-xH\textsubscript{2}O and [Ln\textsubscript{2}(L\textsubscript{5})(NO\textsubscript{3})\textsubscript{6}]-xH\textsubscript{2}O (Ln = La, Eu, Gd, Tb, Lu, Y)**

The ligands L\textsubscript{4}\textsuperscript{20} and L\textsubscript{5}\textsuperscript{22} are prepared following strategies previously developed for the introduction of unsymmetrical 2-benzimidazolyl-6-carboxamidopyridine units into extended segmental receptors (Scheme 2).\textsuperscript{8,15,20,22}

Slow evaporation of an acetonitrile solution of L\textsubscript{4} or diffusion of n-hexane into a concentrated dichloromethane solution of L\textsubscript{5} give colourless prisms whose X-ray crystal structures are shown in Fig. 3. Bond lengths and bond angles are standard (Tables S1 and S2, ESI),\textsuperscript{†} and the tridentate binding units systematically adopt the expected trans–trans conformation, which minimize the global dipole momentum (i.e. the coordinating N-benzimidazole atom is trans to the N-pyridine atom with respect to the interannular C–C bond and the O-amide atom is trans to the N-pyridine atom with respect to the C(py)–C(carbonyl) bond, Fig. 3).\textsuperscript{18,24} The adjacent pyridine and benzimidazole rings are not strictly coplanar (interplane angles: 33.6(1)\textsuperscript{°} in L\textsubscript{4} and 13.58(4)–29.02(5)\textsuperscript{°} in L\textsubscript{5}), while the two benzimidazole rings in L\textsubscript{5} are almost orthogonal (interplane angle 93.97(3)\textsuperscript{°}). However, the latter angle is of very limited interest for characterizing the helicity induced by this famous diphenyl methane spacer.\textsuperscript{22,25} We have therefore resorted to the detailed analysis of crooked lines proposed by Brewster\textsuperscript{26} for the quantitative determination of the helicity index \(H\) (eqn (3)) associated with the specific organization of the five-carbon chain HC\textsubscript{m}−C\textsubscript{n}−CH\textsubscript{j}−C\textsubscript{s}−C\textsubscript{u}H in the spacer and numbered C13−C14−C20−C34−C33 in L\textsubscript{5} (Fig. 3b).

\[
H = \frac{V}{V_{\text{max}}} = 6\sqrt{3}\pi \frac{L \cdot A}{D^3}
\]  

(3)

According to Brewster,\textsuperscript{26} the five atoms are projected onto a plane perpendicular to the helical axis defined by the line passing through the two terminal atoms of the chain. This yields three possible geometrical figures: a line for non-helical organization, a quadrilateral for a regular helical crooked line and two triangles with a common summit for an amphiverse helix (Fig. 4a). The helicity index, computed with eqn (3), corresponds to the ratio of the volume enclosed by the crooked line (\(V\)) with respect to the maximum volume (\(V_{\text{max}}\)) produced when the subtended figure is a

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**Scheme 1** Chemical structures of ligands L\textsubscript{3}–L\textsubscript{5}.  

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Scheme 2  Key synths in the multi-step syntheses of L4 and L5 (numbering for NMR data is given).

circle (L is the end to end distance of the helix, A is the area of the subtended figure in the projection plane and D is the total length of the crooked line, Fig. 4a). For L5, the subtended figure produced by the crooked line of the diphenyl methane spacer is diagnostic for an amphiverse helix with two helical domains possessing opposite helicities (Fig. 4b). The absolute sum of the two helical domains gives an absolute helicity index \( H = 0.21 \), but the difference of the two subtented areas eventually shows a net helicity of only \( H = 0.15 \). In other words, the diphenyl methane spacer in the free ligand L5 possesses a poor global helicity resulting from the successive packing of short helical domains with opposite helicities.

Reaction of 1.0 equivalent of L4 or L5 with stoichiometric amounts (1.0 equiv. for L4 and 2.0 equiv. for L5) of Ln(NO3)\(_3\)·xH\(_2\)O (Ln = La, Eu, Gd, Tb, Lu, Y, x = 2–4) in acetonitrile, followed by precipitation with t-Bu-methyl ether yields 75–85% of microcrystalline powders whose elemental analyses correspond to [Ln(L4)(NO3)\(_3\)]·xH\(_2\)O (Ln = La, x = 2.5; Ln = Eu, x = 2; Ln = Gd, x = 2.5; Ln = Tb, x = 2.5; Ln = Lu, x = 1.5; Ln = Y, x = 1.5) and [Ln(L5)(NO3)\(_3\)]·xH\(_2\)O (Ln = La, x = 3; Ln = Eu, x = 3.5; Ln = Gd, x = 4; Ln = Tb, x = 3.5; Ln = Lu, x = 6; Ln = Y, x = 4; Table S3, ESI).†

Re-dissolution of the Eu complexes in acetonitrile or acetonitrile/propionitrile followed by slow evaporation yielded colourless X-ray quality prisms of [Eu(L4)(NO3)\(_3\)](CH\(_3\)CN)\(_2\) (3) and [Eu\(_2\)(L5)(NO3)\(_6\)](H\(_2\)O)\(_2\)](H\(_2\)O)\(_4\)](CH\(_3\)CH\(_2\)CN)\(_2\) (4). The crystal structure of 3 shows a ten-coordinated [Eu(L4)(NO3)\(_3\)] complex together with two interstitial solvent molecules. In the complex, the ligand L4 adopts the cis–cis conformation required for its meridional tri-coordination to Eu\(_{III}\), together with a slight helical twist of the benzimidazole–pyridine–carboxamide thread (interplane angles: benzimidazole–pyridine 11.3(1)° and pyridine–carboxamide 19.2(1)°, Fig. 5 and Tables S4 and S5, ESI).† The coordination sphere is completed with three bidentate nitrate anions and one solvent molecule as previously noticed for the analogous complexes [Eu(L3)(NO3)\(_3\)](CH\(_3\)OH)\(_2\) and [Eu(L3)(NO3)\(_3\)](CH\(_3\)CN)\(_2\)\(_2\)†.

Except for the slightly shorter Eu–O(carboxamide) bond length in [Eu(L4)(NO3)\(_3\)](CH\(_3\)CN), the coordination spheres in these three mononuclear complexes are almost superimposable (Fig. S2, ESI),† which is further substantiated by the calculation of very
similar ionic radii \( R_{\text{Eu}^{III}}^{CN-10} = 1.18 \text{ Å} \) and bond valence sums \( V_{\text{Eu}} \). Moreover, the agreement found between the ionic radii and valence bond sums calculated in Table 1 and Tables S6–S8, ESI.† Moreover, the agreement found between the ionic radii and valence bond sums calculated in Table 1, with those expected for standard ten-coordinate EuIII (\( R_{\text{Eu}^{III}}^{CN-10} = 1.18 \text{ Å} \) and \( V_{\text{Eu}} = 3.00 \)) points to the lack of significant constraints produced by the coordination of the tridentate N3 (in \( L_3 \)) or N2O (in \( L_4 \)) units in the nitrato complexes. Finally, in the crystal of 3, a single weak intermolecular \( p \)-stacking interaction can be detected between the benzimidazole rings of two adjacent [Eu(\( L_4 \))NO\(_3\)]\_3(CH\(_3\)CN)\] complexes related by a centre of inversion (interplane angle 0°, interplane distance 3.46(1) Å).

Interestingly, the extended binuclear complex [Eu(\( L_5 \))NO\(_3\)\_6(H\(_2\)O)\_2] crystallizes in the \( C2/c \) space group (monoclinic) with the bridging methylene carbon of the diphenyl methane spacer C20 located on a two-fold axis (Fig. 5b). Comparisons with the mononuclear analogue are thus simplified and the metallic coordination sphere of the asymmetrical unit of [Eu(\( L_5 \))NO\(_3\)\_6(H\(_2\)O)\_2] can be almost perfectly superimposed with that of [Eu(\( L_4 \))NO\(_3\)\_3(CH\(_3\)CN), except for the replacement of an acetonitrile solvent molecule with water (Fig. S3, ESI).† The detection of a significant nuclear Overhauser effect (NOE) between H5 and H12 upon reaction of \( L_4 \) with Ln(NO\(_3\))\_3·xH\(_2\)O (Ln = La, Eu, Lu, Y) in acetonitrile

**Structures of the ligands \( L_4 \) and \( L_5 \) and of their complexes**

\[ \text{[Ln(\( L_4 \))NO\(_3\)\_3(\( x \_\)H\(_2\)O)] and [Ln(\( L_5 \))NO\(_3\)\_3(\( x \_\)H\(_2\)O (Ln = La, Eu, Lu, Y) in acetonitrile} \]
Table 1 Ionic radii ($R_{\text{Eu}^{3+}}^{\text{CN}=10}$ Å), average bond valences ($v_{\text{Eu}}$) and bond valence sum ($V_{\text{Eu}}$) in the crystal structures of [Eu(L3)(NO3)3(CH3OH)], [Eu(L3)(NO3)3(CH3-CN)], [Eu(L4)(NO3)3(CH3-CN)] and [Eu2(L5)(NO3)6(H2O)2].

<table>
<thead>
<tr>
<th></th>
<th>[Eu(L3)(NO3)3(CH3OH)]</th>
<th>[Eu(L3)(NO3)3(CH3-CN)]</th>
<th>[Eu(L4)(NO3)3(CH3-CN)]</th>
<th>[Eu2(L5)(NO3)6(H2O)2]</th>
</tr>
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<tbody>
<tr>
<td>$R_{\text{Eu}}$</td>
<td>1.17</td>
<td>1.16</td>
<td>1.17</td>
<td>1.16</td>
</tr>
<tr>
<td>$V_{\text{Eu}-\text{Npy}}$</td>
<td>0.30</td>
<td>0.29</td>
<td>0.28</td>
<td>0.28</td>
</tr>
<tr>
<td>$V_{\text{Eu}-\text{Nbzim}}$</td>
<td>0.39(4)</td>
<td>0.39(3)</td>
<td>0.36</td>
<td>0.39</td>
</tr>
<tr>
<td>$V_{\text{Eu}-\text{ONO2}}$</td>
<td>0.28(5)</td>
<td>0.28(4)</td>
<td>0.27(2)</td>
<td>0.26(3)</td>
</tr>
<tr>
<td>$V_{\text{Eu}-\text{solvent}}$</td>
<td>0.29</td>
<td>0.33</td>
<td>0.31</td>
<td>0.34</td>
</tr>
<tr>
<td>$V_{\text{Eu}}$</td>
<td>3.04</td>
<td>3.06</td>
<td>2.98</td>
<td>2.98</td>
</tr>
</tbody>
</table>

* Ionic radius for ten-coordinate Eu III calculated by using Shannon’s definition with $r(N) = 1.46 \text{ Å}$, $r(O) = 1.35 \text{ Å}$ and $r(\text{O-nitrate}) = 1.31 \text{ Å}$.

 stoichiometric ratio Ln:L4 = 1.0, and resolution is significantly improved when using an excess of metal (Lu:L4 ≥ 1.3 for Ln = Lu, but Ln:L4 ≥ 3.0 for larger lanthanides such as Ln = Eu, La). On the other hand, neither variable-temperature $^1$H NMR data, nor addition of an excess of NBu4NO3 in solution, nor an increase in the total ligand concentration improve resolution, and we conclude that the broadening of the NMR signals can be assigned to slow intermolecular on/off ligand complexation processes on the NMR time scale. In agreement with the expected increase in both stability and kinetic inertness with smaller lanthanides, the broadening is maximum for Ln = LaIII and becomes negligible.
in excess of metal because of the reduced mole fraction of uncomplexed ligand (Fig. S6b and S6c, ESI).† Moreover, even in excess of metal, the NMR signals of the benzimidazole protons H1–H4 in [La(L4)3(ONO)3] remains large (Fig. S6c, ESI),† which further suggests the operation of slow intramolecular partial on/off decomplexation of the benzimidazole side arms with the further suggests the operation of slow intramolecular partial on/off decomplexation of the benzimidazole side arms with the larger lanthanides in solution (i.e. a hemilabile benzimidazole side arms).

Since the reactions of Ln(NO3)3 with tridentate aromatic ligands mainly produce neutral species in acetonitrile,18,19,34 ESI-MS is of limited interest for investigating the speciation of the complexes in solution. We have therefore resorted to diffusion-ordered spectroscopy (DOSY-NMR) for the determination of the translational self-diffusion coefficient D for the ligands and for their complexes in order to unravel the size, the shape and the stoichiometries of the complexes formed in solution. For a hard spherical particle of dimension much larger than the molecules of solvent considered as a continuum, the Stokes–Einstein eqn (4) relates the translational diffusion coefficient with the temperature (T), the viscosity (η = 3.65 × 104 kg m−1 s−1 for acetonitrile at 293 K) and the hydrodynamic radius rH.

\[
D = \frac{kT}{6\pi\eta r_H} \quad (4)
\]

When the size of the particle x approaches that of the solvent molecules, the frictional coefficient (i.e. the denominator of eqn (4)), must be corrected by a factor derived from microfrictional theory,36 and semi-empirically improved by Chen,37 which eventually yields eqn (5), whereby r_{obs} is the hydrodynamic radius of the solvent.

\[
D_x = \left[\frac{kT}{6\pi\eta r_{Hx}}\right] \left(1 + 0.695 \left(\frac{r_{obs}}{r_{Hx}}\right)^{2.241}\right) \quad (5)
\]

In parallel, the spherical equivalent radius of a molecule x can be calculated from its partial specific volume (v_{ps} = (d_x - 1) cm³ g⁻¹) and its molecular weight (Mx in g mol⁻¹) by using eqn (4), in which \( N_A \) is Avogadro's constant.18,38

\[
r_{eq}^x = \sqrt[3]{\frac{3M_x v_{ps}}{4\pi N_A}} = \sqrt[3]{\frac{3V_{mol}}{4\pi}} \quad (6)
\]

It is worth noting that \( M_x v_{ps}/N_A \) simply corresponds to the volume of the molecule \( V_{mol} \) not accessible to the solvent molecules in solution, which can be estimated by using the Connolly volume (i.e. the volume limited by the Connolly surface built around the molecule).39 If the molecule is spherical, we expect \( r_{eq}^x \approx r_{Hx} \), but these two parameters are related by a shape factor (eqn (7)) for non-spherical molecules.40 For the rough treatment proposed here, molecules are considered as ellipsoids characterized by the geometrical factor \( p = a/b \), whereby \( a \) is the semi-major axis and \( b \) is the semi-minor axis of the ellipsoids with \( a > b \). The associated shape factors are then given by eqn (8) for prolate (i.e. cigar-like ellipsoids with two short and one long axes) and by eqn (9) for oblate (i.e. disk-like ellipsoids with two long and one short axes).41

\[
r_{eq}^x = r_{Hx} f\left(p\right) \quad (7)
\]

\[
f\left(p\right) = \frac{p^{1/3}(p^2 - 1)^{1/2}}{\ln[p + (p^2 - 1)^{1/2}]} \quad (8)
\]

\[
f\left(p\right) = \frac{p^{1/3}(p^2 - 1)^{1/2} \arctan[(1 - p^{-1})^{1/2} p^{-1}]}{p^{-1/3}} \quad (9)
\]

The experimental translational diffusion coefficients \( D_x \) obtained by DOSY-NMR for \( L4^+ \) and for its complexes \([Ln(L4)3(NO3)3] \) in acetonitrile (293 K), together with the equivalent spherical radii \( r_{eq} \) calculated with eqn (6) and using the Connolly volume \( V_{mol} \) estimated from the molecular structures found in the crystal structures of \( L4^+ \) and \([Eu(L4)(NO3)3(CH3CN)] \) are collected in Table 2.

<table>
<thead>
<tr>
<th>Compds</th>
<th>( D_x ) ( \text{m}^2 \text{s}^{-1} )</th>
<th>( V_{mol}^{eq} / \AA^1 )</th>
<th>( r_{eq}^x / \AA )</th>
<th>( r_{obs}^x / \AA )</th>
<th>( f\left(p\right) )</th>
<th>( p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( L4^+ )</td>
<td>1.65(6) ( \times 10^{-9} )</td>
<td>298</td>
<td>4.1</td>
<td>3.9(2)</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>([La(L4)3(NO3)3] )</td>
<td>1.28(4) ( \times 10^{-9} )</td>
<td>440</td>
<td>4.7</td>
<td>4.9(2)</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>([Eu(L4)3(NO3)3] )</td>
<td>1.30(5) ( \times 10^{-9} )</td>
<td>440</td>
<td>4.7</td>
<td>4.8(1)</td>
<td>0.96</td>
<td>1.8</td>
</tr>
<tr>
<td>([Lu(L4)3(NO3)3] )</td>
<td>1.30(3) ( \times 10^{-9} )</td>
<td>440</td>
<td>4.7</td>
<td>4.9(1)</td>
<td>0.98</td>
<td>1.5</td>
</tr>
<tr>
<td>( L5 )</td>
<td>1.20(3) ( \times 10^{-9} )</td>
<td>611</td>
<td>5.2</td>
<td>5.1(1)</td>
<td>0.96</td>
<td>1.8</td>
</tr>
<tr>
<td>([La(L5)(NO3)_3(CH_3CN)] )</td>
<td>8.55(9) ( \times 10^{-10} )</td>
<td>972</td>
<td>6.1</td>
<td>7.1(1)</td>
<td>0.86</td>
<td>3.7</td>
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<tr>
<td>([Eu(L5)(NO3)_3(CH_3CN)] )</td>
<td>8.74(9) ( \times 10^{-10} )</td>
<td>972</td>
<td>6.1</td>
<td>6.9(1)</td>
<td>0.88</td>
<td>3.4</td>
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<tr>
<td>([Lu(L5)(NO3)_3(CH_3CN)] )</td>
<td>8.79(4) ( \times 10^{-10} )</td>
<td>972</td>
<td>6.1</td>
<td>6.9(1)</td>
<td>0.88</td>
<td>3.4</td>
</tr>
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</table>

*The Connolly volumes are obtained from the building of the Connolly surface around the molecular structures of ligands and complexes observed in their crystal structure and by using a probe radius of 2.0 Å for modelling acetonitrile solvent molecule \( V_{CDCHCN} = 36.3 \) Å³.

The case of the extended bis-tridentate ligand \( L5 \) is more informative since its \( ^{1}H\) NMR spectrum in solution is diagnostic for an average \( C_{3v} \)-symmetrical conformation (Fig. 6a, two equivalent tridentate units combined with \( A_2 \) spin systems (enantiotopic protons) for the methylene probes H1, H8, H9 and H12) only compatible with a planar arrangement of the diphenyl methane spacer (distal or proximal) with absolute zero helicity on the NMR time scale (Fig. S7, ESI).†
The NOE effects detected between H5–H12 combined with the downfield shift of H6 (Table S12, ESI)† are diagnostic for the meridional tri-coordination of the tridentate benzimidazole-pyridine-carboxamide units to Ln(NO3)3. DOSY-NMR data provide translational diffusion coefficients, from which the calculated hydrodynamic radii ($r_H$) (eqn (5)) now significantly deviate from the equivalent spherical radii estimated from the molecular volume ($r_m$) (eqn (6), Table 2). The resulting shape factors $f(p) = 0.86–0.88$ obtained for [Ln2(L5)(NO3)6(H2O)2] as a starting point (Fig. 5b), we can estimate major $a = 19.3$ Å and minor $b = 8.9$ Å axes yielding $p = a/b = 2.2$ in poor agreement with the solution data (Fig. 7a). The planarization of the diphenylmethane spacer on the NMR time scale, which is required by the $C_{2v}$-symmetry observed for [Ln2(L5)(NO3)6] in solution, is only compatible with a distal arrangement of the spacer for obvious steric constraints (Fig. S7c, ESI)† Consequently, the intramolecular contact Ln···Ln increases (12.3 Å) together with the geometrical factor $p = a/b = 25.4/7.5 = 3.4$, which is now in fair agreement with NMR data (Fig. 7b). More sophisticated shape analysis based on translational diffusion coefficients are available for cylinders and dumbbells, but their application is only justified with rather rigid structures in solution such as cyclodextrins for which one geometrical parameter (diameter or length) is fixed, a condition not met by our flexible single-stranded complex. We can thus safely conclude from the NMR data that the complexes [Ln(L4b)(NO3)3] and [Ln2(L5)(NO3)6] are the only assembled species formed in acetonitrile for Ln:L4b ≥ 1.0 and Ln:L5 ≥ 2.0, respectively. Moreover, the mononuclear complexes retain their pseudo-spherical globular shapes on the NMR time scale for minimizing the effect of the exchange process on the NMR spectra (Fig. 6c). The NOE effects detected between H5–H12 combined with the downfield shift of H6 (Table S12, ESI)† are diagnostic for the meridional tri-coordination of the tridentate benzimidazole-pyridine-carboxamide units to Ln(NO3)3. DOSY-NMR data provide translational diffusion coefficients, from which the calculated hydrodynamic radii ($r_H$) (eqn (5)) now significantly deviate from the equivalent spherical radii estimated from the molecular volume ($r_m$) (eqn (6), Table 2). The resulting shape factors $f(p) = 0.86–0.88$ obtained for [Ln2(L5)(NO3)6] (eqn (7)) indicate a significant deviation from spherical behaviour with $p = 3.4–3.7$. Taking the crystal structure of the single-stranded helical complex [Eu2(L5)(NO3)6(H2O)2] as a starting point (Fig. 5b), we can estimate major $a = 19.3$ Å and minor $b = 8.9$ Å axes yielding $p = a/b = 2.2$ in poor agreement with the solution data (Fig. 7a). The planarization of the diphenylmethane spacer on the NMR time scale, which is required by the $C_{2v}$-symmetry observed for [Ln2(L5)(NO3)6] in solution, is only compatible with a distal arrangement of the spacer for obvious steric constraints (Fig. S7c, ESI)† Consequently, the intramolecular contact Ln···Ln increases (12.3 Å) together with the geometrical factor $p = a/b = 25.4/7.5 = 3.4$, which is now in fair agreement with NMR data (Fig. 7b). More sophisticated shape analysis based on translational diffusion coefficients are available for cylinders and dumbbells, but their application is only justified with rather rigid structures in solution such as cyclodextrins for which one geometrical parameter (diameter or length) is fixed, a condition not met by our flexible single-stranded complex. We can thus safely conclude from the NMR data that the complexes [Ln(L4b)(NO3)3] and [Ln2(L5)(NO3)6] are the only assembled species formed in acetonitrile for Ln:L4b ≥ 1.0 and Ln:L5 ≥ 2.0, respectively. Moreover, the mononuclear complexes retain their pseudo-spherical globular shapes on the NMR time scale for minimizing the effect of the exchange process on the NMR spectra (Fig. 6c).
scale, while the binuclear complexes adopt extended C$_3$-symmetry conformations of the diphenyl spacer with absolute zero helicity.

**Thermodynamics of the complexation of the ligands L4$^b$ and L5 with Ln(NO$_3$)$_3$ (Ln = La, Eu, Lu, Y) in acetonitrile**

The trans–trans toward cis–cis conformational change of the tridentate binding unit accompanying the complexation of the polyaromatic ligands L4$^b$ and L5 to Ln(NO$_3$)$_3$ alters the envelope of the ligand-centred $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions (Fig. S8, ESI)† which allows the quantitative evaluation of the coordination process by using spectrophotometric titrations (Fig. 8). In the process by using spectrophotometric titrations (Fig. 8).

(Fig. 8a) confirms the exclusive formation of [Ln(L4$^b$)(NO$_3$)$_3$] in acetonitrile. For L5, the lack of isosbestic points together with the detection of two smooth end points for Ln.L5 = 1.0 and 2.0 imply the successive formation of [Ln(L5)(NO$_3$)$_3$] and [Ln$_2$(L5)(NO$_3$)$_6$] complexes (Figs. 8b and S8b, ESI)† Factor analyses further support the formation in solution of two absorbing species with L4$^b$, respectively, three absorbing species with L5. The global spectrophotometric data can be then fitted to the three macroscopic equilibria (eqn (10)–(12)) by using non-linear least-squares techniques (Table 3).

![Fig. 8](image)

**Table 3** Experimental and calculated cumulative thermodynamic macroconstants obtained from the spectrophotometric titrations of L4$^b$ and L5 with Ln(NO$_3$)$_3$·xH$_2$O in acetonitrile (293 K, Ln = La, Eu, Lu, Y, x = 2–4)

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Ln$^{III}$</th>
<th>$R^\text{CN-x}^{\bar{y}}$/Å</th>
<th>log(β$_{1,1}^{\text{Lan}}$)</th>
<th>log(β$_{2,1}^{\text{Lan}}$)</th>
<th>log(β$<em>{1,1}^{\text{Lan}}$)$</em>{\text{calcd}}$</th>
<th>log(β$<em>{2,1}^{\text{Lan}}$)$</em>{\text{calcd}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>L4$^b$</td>
<td>La</td>
<td>1.216</td>
<td>5.77(6)</td>
<td>—</td>
<td>5.28</td>
<td>—</td>
</tr>
<tr>
<td>L4$^b$</td>
<td>Eu</td>
<td>1.120</td>
<td>5.27(9)</td>
<td>—</td>
<td>5.23</td>
<td>—</td>
</tr>
<tr>
<td>L4$^b$</td>
<td>Y</td>
<td>1.075</td>
<td>5.99(9)</td>
<td>—</td>
<td>5.69</td>
<td>—</td>
</tr>
<tr>
<td>L4$^b$</td>
<td>Lu</td>
<td>1.032</td>
<td>6.06(9)</td>
<td>—</td>
<td>5.77</td>
<td>—</td>
</tr>
<tr>
<td>L5</td>
<td>La</td>
<td>1.216</td>
<td>5.09(9)</td>
<td>9.20(8)</td>
<td>9.20</td>
<td>9.20</td>
</tr>
<tr>
<td>L5</td>
<td>Eu</td>
<td>1.120</td>
<td>5.49(4)</td>
<td>9.42(6)</td>
<td>9.53</td>
<td>9.42</td>
</tr>
<tr>
<td>L5</td>
<td>Y</td>
<td>1.075</td>
<td>5.69(8)</td>
<td>10.12(9)</td>
<td>10.12</td>
<td>10.12</td>
</tr>
<tr>
<td>L5</td>
<td>Lu</td>
<td>1.032</td>
<td>5.79(9)</td>
<td>10.36(9)</td>
<td>10.36</td>
<td>10.36</td>
</tr>
</tbody>
</table>

*Calculated with eqns (13)–(15) and the microscopic parameters taken from Table S13. *Ionic radii for nine-coordinate lanthanides.**

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parameters \( f_{\text{LNO}^2}^{\text{L,Lb}} \), \( f_{\text{LNO}^2}^{\text{L,Lb}} \) and \( v_{\text{L,Lb}}^{\text{L,Lb}} \) for fitting three experimental stability constants, which obviously yields no uncertainties (Table 4).

We can however globally analyze the trends obtained for these microscopic parameters. Firstly, the absolute affinities increase with decreasing ionic radii, in agreement with the classical electrostatic model developed for polar solvents.\(^{32a}\) The free energies of cation formation of Ln(NO\(_3\))\(_3\) to the tridentate \( \text{N}_2\text{O}_{3}\) binding unit, which reflect the desolvation of the two partners followed by their intermolecular binding, amount to

\[
-32 < \Delta G_{1\text{NO}^2}^{\text{L,Lb}} = -RT \ln f_{\text{LNO}^2}^{\text{L,Lb}} < -27 \text{ kJ mol}^{-1} \quad \text{and} \quad -29 < \Delta G_{1\text{NO}^2}^{\text{L,Lb}} = -RT \ln f_{\text{LNO}^2}^{\text{L,Lb}} < -24 \text{ kJ mol}^{-1}.
\]

These values are comparable to \( \Delta G_{1\text{NO}^2}^{\text{L,Lb}} = -31(1) \text{ kJ mol}^{-1} \) previously estimated for the binding of the same tridentate unit in the same solvent, but to Eu\(^{3+}\) in the triple-stranded helicates [Eu\(_3\)(L5)],\(^{1+}\) (Eu\(^{3+}\) is obtained from Eu(OSCF\(_3\))\(_3\)).\(^{59}\) According to the different effective charge borne by the metal in Ln\(^{3+}\) and in Ln(NO\(_3\))\(_3\), we deduce that solvation processes play a major role in the global stability of these complexes and they probably overcome the decrease in affinity predicted for Ln(NO\(_3\))\(_3\) on simple point charge electrostatic bases. The intermetallic interaction is systematically repulsive with an average value of \( \Delta E_{\text{L,Lb}}^{\text{L,Lb}} = 3.8(1.4) \text{ kJ mol}^{-1} \), which implies the operation of an anti-cooperative process for the successive binding of two Ln(NO\(_3\))\(_3\) to L5.\(^{12}\) Interestingly, its magnitude is also comparable to that obtained in triple-stranded helicates \( \Delta E_{\text{L,Lb}}^{\text{L,Lb}} = 10(4) \text{ kJ mol}^{-1} \),\(^{56}\) despite (i) the increased intermetallic distance (9 Å in [Ln\(_3\)(L5)],\(^{1+}\) and 12.3 Å in [Ln\(_3\)(L5)(NO\(_3\))\(_3\)],\(^{1+}\) and (ii) the charge compensation brought by the bound nitrate anions. Again, this points to the prominent contribution of solvation processes to the assembly process.\(^{18}\) For the neutral complex, the simplistic electrostatic point charge arguments based on Coulomb and Born equations previously used for [Ln\(_3\)(L5)],\(^{14-16}\) cannot be invoked, and more detailed calculations involving neutral polar molecules in a dielectric continuum must be considered.\(^{49}\)

It is however remarkable, and slightly disappointing, that the successive fixation of both neutral Ln(NO\(_3\))\(_3\) and charged Ln\(^{3+}\) metals to L5 produces comparable and weakly repulsive intermetallic interactions. In an attempt to obtain rough, but physically meaningful microscopic parameters, we found eqn (13)-(15) with only two parameters, one average absolute metal–ligand affinity \( f_{\text{LNO}^2}^{\text{L,Lb}} \) and one intermetallic interaction \( \Delta E_{\text{L,Lb}}^{\text{L,Lb}} \) (Table S13, ESI).\(^{51}\) Obviously, the uncertainties are rather large and the experimental data measured for \( \beta_{1\text{NO}^2}^{\text{L,Lb}} \) and \( \beta_{1\text{NO}^2}^{\text{L,Lb}} \) are poorly reproduced (Table 3), but we still notice the operation of a strictly anti-cooperative process along the complete lanthanide series.

### Table 4 Fitted microscopic thermodynamic parameters for [Ln(L4)\(_n\)](NO\(_3\))\(_3\) and [Ln\(_4\)(L5)(NO\(_3\))\(_3\)] \((n = 1, 2)\) in acetonitrile (eqn (13)-(15) using two different affinity parameters \( f_{\text{LNO}^2}^{\text{L,Lb}} \) and \( f_{\text{LNO}^2}^{\text{L,Lb}} \), Ln = La, Eu, Lu, Y, 293 K).

<table>
<thead>
<tr>
<th>Ln(^{3+})</th>
<th>( \log(f_{\text{LNO}^2}^{L,Lb}) )</th>
<th>( \Delta G_{1\text{NO}^2}^{L,Lb}/\text{kJ mol}^{-1} )</th>
<th>( \log(f_{\text{LNO}^2}^{L,Lb}) )</th>
<th>( \Delta G_{1\text{NO}^2}^{L,Lb}/\text{kJ mol}^{-1} )</th>
<th>( \log(v_{\text{L,Lb}}^{L,Lb}) )</th>
<th>( \Delta E_{\text{L,Lb}}^{L,Lb}/\text{kJ mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>5.29</td>
<td>-30.2</td>
<td>4.31</td>
<td>-24.6</td>
<td>-0.38</td>
<td>2.2</td>
</tr>
<tr>
<td>Eu</td>
<td>4.79</td>
<td>-27.3</td>
<td>4.71</td>
<td>-26.9</td>
<td>-0.96</td>
<td>5.5</td>
</tr>
<tr>
<td>Y</td>
<td>5.51</td>
<td>-31.4</td>
<td>4.91</td>
<td>-28.0</td>
<td>-0.66</td>
<td>3.8</td>
</tr>
<tr>
<td>Lu</td>
<td>5.58</td>
<td>-31.8</td>
<td>5.01</td>
<td>-28.6</td>
<td>-0.62</td>
<td>3.5</td>
</tr>
</tbody>
</table>

* Since three parameters are fitted to the three eqn (13)-(15), there are no uncertainties.

### Photophysical properties of the ligands L4\(^{3-}\) and L5, and of their complexes [Ln(L4)\(_n\)](NO\(_3\))\(_3\)-xH\(_2\)O and [Ln\(_4\)(L5)(NO\(_3\))\(_3\)]-xH\(_2\)O (Ln = Eu, Gd, Tb)

The electronic absorption spectra of the ligands in acetonitrile display a broad band centered at 31 200 cm\(^{-1}\) (\( \varepsilon \approx 22 000\, -\, 25 000 \text{ M}^{-1}\text{cm}^{-1} \)) per tridentate binding unit, Table 5, Fig. S8, ESI),\(^{51}\) which can be assigned to the envelope of the \( n \rightarrow \pi^* \) and \( \pi \rightarrow \pi^* \) transitions in analogy with closely related characteristics theoretically established for the tridentate 2,6-bis(benzimidazol-2-yl)pyridine units in L3\(^{3-}\) (31 150 cm\(^{-1}\), \( \varepsilon = 32 000 \text{ M}^{-1}\text{cm}^{-1} \)).\(^{18,45,50}\) The larger molar extinction coefficient in L3\(^{3-}\) results from the more extended aromatic structure. Excitation trough the ligand-centered \( \pi \rightarrow \pi^* \) transitions in L4\(^{3-}\) or in L5 (\( \varepsilon_{\text{ph}} = 32 260 \text{ cm}^{-1} \), solid state, 77K) produces strong and structured fluorescence at ca. 27 000 cm\(^{-1}\) (0–0 phonon), whose short lifetime (\( \tau < 100 \text{ ns} \)) is diagnostic for emission arising from the \( \pi^* \pi^* \) level (Fig. S10a and S11a, ESI).\(^{51}\) Despite the introduction of various delays (0.1–1 ms) in time-resolved spectra, no phosphorescence could be detected for the flexible free ligands. Upon complexation to Ln(NO\(_3\))\(_3\), in the complexes [Ln(L4)\(_n\)](NO\(_3\))\(_3\) and [Ln\(_4\)(L5)(NO\(_3\))\(_3\)] (Ln = Eu, Gd, Tb), we observe a 500–750 cm\(^{-1}\) red-shift of the ligand-centred absorption band, which has been exploited for spectrophotometric titrations (Fig. S8, ESI).\(^{51}\) Since the excited metal-centered levels of Gd\(^{3+}\) lie at too high energy (\( \geq 32 000 \text{ cm}^{-1} \)) for being accessible for efficient intramolecular energy transfer from the ligand-centred \( \pi \rightarrow \pi^* \) levels, the emission spectra of [Gd(L4)](NO\(_3\))\(_3\) and [Gd(L5)](NO\(_3\))\(_3\) indeed probes the energy of the latter levels after complexation, which are indeed located close in energy to those found in the free ligand (Table 5, Fig. S10b and S11b, ESI).\(^{51}\) However, the concomitant operation of spin–orbit coupling and Coulomb interactions between the electrons of the ligands and those of the paramagnetic gadolinium metal mix the ligand-centred singlet and triplet wavefunctions,\(^{32}\) a phenomenon which considerably increases both intersystem crossing (ISC) and the oscillator strength of the spin-forbidden emission originating from the \( \pi \pi^* \) levels. These effects, combined with the rigidification of the aromatic backbone by the complexation to Gd(NO\(_3\))\(_3\)), eventually yield structured emission in time-resolved phosphorescence spectra, which reveals ligand-centred \( \pi \pi^* \) levels located around 20 000 cm\(^{-1}\) (0–0 phonon) in these complexes (Table 5, Fig. S10c and S11c, ESI).\(^{51}\)

In the Eu- and Tb-complexes, the ligand-centered luminescence is almost quantitatively quenched by efficient ligand \( \rightarrow \text{Ln}^{3+} \) energy transfer processes (Fig. S12, ESI).\(^{51}\) Excitation through the \( \pi \pi^* \) levels (\( \varepsilon_{\text{ph}} = 32 260 \text{ cm}^{-1} \)) thus yields the standard red Eu-centered and green Tb-centered luminescence characterized by sharp bands.
Table 5 Absorption (acetonitrile solution, 295K) and emission properties (solid state, 77K) of the ligands L4 and L5 and of their complexes [Ln(L4)(NO3)3] and [Ln(L5)(NO3)3] (Ln = Eu, Gd, Tb)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorption/cm⁻¹ π → π*</th>
<th>Emission/cm⁻¹ ππ*</th>
<th>Emission/cm⁻¹ ππ*</th>
<th>Lifetime/ ms τ (ππ*)</th>
<th>Lifetime/ ms τ (Ln*)</th>
<th>Quantum yield/% ΦL/Eu</th>
</tr>
</thead>
<tbody>
<tr>
<td>L4</td>
<td>31 250</td>
<td>27 200 sh</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>[Gd(L4)(NO3)3]</td>
<td>30 550</td>
<td>26 570 sh</td>
<td>23 810 br</td>
<td>20 600</td>
<td>19 250</td>
<td>17 920</td>
</tr>
<tr>
<td>[Eu(L4)(NO3)3]</td>
<td>30 580</td>
<td>31 570 sh</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>[Tb(L4)(NO3)3]</td>
<td>30 550</td>
<td>26 570 sh</td>
<td>23 810 br</td>
<td>20 600</td>
<td>19 250</td>
<td>17 920</td>
</tr>
<tr>
<td>L5</td>
<td>31 150</td>
<td>26 950 sh</td>
<td>25 500</td>
<td>24 200</td>
<td>26 740</td>
<td>23 810 br</td>
</tr>
<tr>
<td>[Gd(L5)(NO3)3]</td>
<td>29 740</td>
<td>26 740 sh</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>[Eu(L5)(NO3)3]</td>
<td>29 590</td>
<td>25 510</td>
<td>23 640 sh</td>
<td>20 120</td>
<td>18 870</td>
<td>17 400</td>
</tr>
<tr>
<td>[Tb(L5)(NO3)3]</td>
<td>30 050</td>
<td>25 510</td>
<td>23 640 sh</td>
<td>20 120</td>
<td>18 870</td>
<td>17 400</td>
</tr>
</tbody>
</table>

* sh = shoulder, br = broad. * Global quantum yield determined at 10⁻⁴ mol dm⁻³ in acetonitrile. * Ligand-centred luminescence quenched by transfer to Ln ion. * Lifetimes measured for Eu(3D0) excited level. * Lifetimes measured for Tb(3D0) excited level.

easily assigned to Eu(5D0 → 7Fj) (j = 0–6), Eu(5D1 → 7Fj) (j = 0–2), and Tb(5D4 → 7Fj) (j = 6–0) transitions (Fig. S12, ESI). The associated metal-centered lifetimes in the Eu-complexes at 77 K (τEu(3D0) = 1.14(4) ms for [Eu(L4)(NO3)3] and τEu(3D0) = 0.95(2) ms for [Eu(L5)(NO3)3], Table 5), are typical for Eu³⁺ coordinated by three bidentate nitrates, one tridentate aromatic binding unit and one solvent molecule. They can be compared with τEu(3D0) = 0.84 ms measured for [Eu(3L3)(NO3)3(CH3OH)], and with τEu(3D0) = 1.35 ms measured for [Eu(3L3)(NO3)3(CH3CN)] in the same conditions (solid state, 77K). The minor variation of τEu(3D0) observed for [Eu(L4b)(NO3)3] and [Eu(L5b)(NO3)3] in the 77–295 K range points to minor temperature effects on the non-radiative de-excitation processes affecting Eu(3D0), in strong contrast with the 60–80% reduction in lifetime observed for the Tb(5D4) level in the analogous Tb-complexes (Table 5). The latter standard behaviour is usually assigned to thermally-activated back transfer processes resulting from the minor energy gap separating these two levels in the complexes (ΔEpp = E(5D4) – E(ππ*) = 20 600–20 000 = 600 cm⁻¹, Table 5). Interestingly, the global quantum yields measured in acetonitrile are encouraging (ΦL/Eu = 21(4)% for both [Eu(L4)(NO3)3] and [Eu(L5)(NO3)3]), and they compare well with ΦL/Eu = 25(4)% re-determined for [Eu(3L3)(NO3)3] in acetonitrile and using Cs2Eu(dipicolinate), complex as the unique reference in buffered water (see experimental section).

Conclusion

The unsymmetrical tridentate N2O binding unit in L4 reacts with Ln(NO3)3 in acetonitrile to give ten-coordinated complexes [Ln(L4)(NO3)3(CH3CN)] very similar to those previously described with the analogous, but symmetrical N2, binding unit in [Ln(L3)(NO3)3(CH3CN)]. The photophysical properties are also comparable, but [Ln(L4)(NO3)3(CH3CN)] do not show any sign of dimerization in solution, a process which drastically complicates the speciation of [Ln(L3)(NO3)3(CH3CN)] and affects its liquid crystalline properties when amphiphilic derivatives of the latter complexes are used as a building blocks in lanthanidomesogens. The connection of two tridentate N2O units via the diphenyl methane spacer in the ligand L5 slightly reduces the absolute affinity of each binding site for Ln(NO3)3, but the planned saturated complexes [Ln(L5)(NO3)3] complexes are quantitatively formed at millimolar concentrations in acetonitrile. The solid state structure of the binuclear complex [Eu(L5)(NO3)3(H2O)2] confirms the fixation of ten-coordinated metals in the two adjacent tridentate binding sites, but a surprising helical twist of the spacer, comparable to that found in the triple-stranded complexes [Ln(L5)]⁺, results in a shorter intermetallic contact distance in the single-stranded complex (8.72 Å in [Eu(L5)(NO3)3(H2O)2] and 9.06 Å in [Tb2(L5)3(CIO4)6]). The combined analysis of experimental hydrodynamic radii and of NMR data indicates that the binuclear complexes [Ln(L5)(NO3)3] adopt a flat and extended C₃ₙ-symmetrical structure in acetonitrile, in which the Ln⋯Ln contact distance is increased by c.a. 30%. This unsymmetrical N2O tridentate binding unit is thus ideally suited for producing simple and purely intermolecular complexation processes with Ln(NO3)3, which are amenable to reliable thermodynamic modeling. We observe that the successive connection of two neutral Ln(NO3)3 held at 12.3 Å in [Ln(L5)(NO3)3] is anti-cooperative with a repulsive contribution of ΔEpp,= 4 kJ mol⁻¹. The most surprising and striking conclusion of this contribution concerns the free energies of connection of the N2O tridentate binding unit to Ln(NO3)3 (ΔGpp,= N2O) and the intermetallic interactions (ΔEpp,= Ln) in [Ln(L5)(NO3)3], whose magnitudes closely match those found in the triple-stranded helicates [Ln(L5)]⁺ despite (i) the different nature of the entering metallic entity, a triply charged cation [Ln(CH3CN)3]⁺ for the latter complexes and a neutral [Ln(NO3)3(CH3CN)] unit.
for the former complexes, and (ii) the 30% increase of the intramolecular intermetallic contact distance in going from [Ln(L4)]3+ to [Ln(L5)(NO3)3] in solution. For the coordination chemists, this behaviour may be recognized as rather counterintuitive since we are familiar with the interpretation of charge effects based on the exclusive use of point-charge Coulombic interactions, and we consider solution effects mainly for their contribution to translational entropies. However, these results support the current interpretation of intramolecular intermetallic interactions in polymeric complexes as arising from two opposite contributions of comparable and huge magnitudes, one brought by intramolecular electrostatic interactions at the multi polar level and the other associated with macroscopic solvation changes.

Experimental

Solvents and starting materials

These were purchased from Fluka AG or Aldrich and used without further purification unless otherwise stated. The ligands L4 and L5 were prepared following improved strategies, but with specific procedures (Scheme S1, ESI†). Acetonitrile and dichloromethane were distilled over calcium hydride. Thin layer chromatography (TLC) used silica gel plates Merck 60 F254, and dichloromethane was used as reference. The ligands were purified by preparative chromatography (Tidas series) connected to an external computer.

A solution of Ln(NO3)3·6H2O (Ln = La, Eu, Gd, Tb, Lu, Y; x = 2–4) was prepared from the corresponding oxides (Rhodia, 99.99%) and dried according to published procedures. The Ln content of solid salts was determined by complexometric titrations with Titirplex III (Merck) in the presence of urotropine and xylene orange.

Preparation of the complexes [Ln(L4)(NO3)3]·xH2O (Ln = La, x = 2.5; Ln = Eu, x = 2; Ln = Gd, x = 2.5; Ln = Tb, x = 2.5; Ln = Y, x = 1.5) and [Ln(L5)(NO3)3]·xH2O (Ln = La, x = 3; Ln = Eu, x = 3.5; Ln = Gd, x = 4; Ln = Tb, x = 3.5; Ln = Lu, x = 6; Ln = Y, x = 4)

A solution of Ln(NO3)3·xH2O (Ln = La, Eu, Gd, Tb, Lu; Y, 0.06 mmol) in acetonitrile (5 cm3) was added to a solution of either L4 (19.3 mg, 0.06 mmol, 1 equiv.) or L5 (19.7 mg, 0.03 mmol, 1.5 equiv.) in acetonitrile (5 cm3). After stirring for 1 h at rt, the solution was concentrated to 5 cm3 and further purification unless otherwise stated. The ligands 1–4 were prepared following previous strategies, but with improved specific procedures (Scheme S1, ESI†). Acetonitrile and dichloromethane were distilled over calcium hydride. Thin layer chromatography (TLC) used silica gel plates Merck 60 F254, and dichloromethane was used as reference. The ligands were purified by preparative chromatography (Tidas series) connected to an external computer.

Spectroscopic and analytical measurements

Electronic spectra in the UV-vis were recorded at 293 K from solutions in MeCN with a Perkin-Elmer Lambda 900 spectrometer using quartz cells of 0.1 and 1 mm path length. Spectrophotometric titrations were performed with a J & M diode array spectrometer (Tidas series) connected to an external computer. In a typical experiment, 50 cm3 of ligand in acetonitrile (10−4 mol dm−3) were titrated at 293 K with a solution of Ln(NO3)3·xH2O (10−3 mol dm−3) in acetonitrile under an inert atmosphere. After each addition of 0.20 mL, the absorbance was recorded using Hellma optodes (optical path length 0.1 cm) immersed in the thermostated titration vessel and connected to the spectrometer. Mathematical treatment of the spectrophotometric titrations was performed with factor analysis and with the SPECFIT program. IR spectra were obtained from KBr pellets with a FT-IR Perkin-Elmer Spectrum One. 1H NMR spectra were recorded at 25 °C on Bruker Avance 400 MHz spectrometer. Chemical shifts are given in ppm with respect to TMS. Diffusion ordered spectroscopy (DOSY) was carried out at 400 MHz Larmor frequency (293 K, 10−2 mol dm−3, CD3CN). The pulse sequence used was the Bruker pulse program ledppp25 which employs stimulated echo, bipolar gradients and longitudinal eddy current delay as the filter. The four 2 ms gradient pulses have sine-bell shapes and amplitudes ranging linearly from 2.5 to 50 G cm−1 in 32 steps. The diffusion delay was in the range 60–140 ms depending on the analyte diffusion coefficient, and the no. of scans was 32. The processing was done using a line broadening of 5 Hz and the diffusion coefficients were calculated with the Bruker processing package. Pneumatically-assisted electrospray (ESI-MS) mass spectra were recorded from 10−4 mol dm−3 solutions on a Finnigan SSQ7000 instrument. Elemental analyses were performed by Dr H. Eder from the Microchemical Laboratory of the University of Geneva. Linear least-square fits were performed with Excel. Emission spectra, phosphorescence spectra and global quantum yields were determined using a Perkin Elmer LS50B fluorimeter. The quantum yields were calculated using the equation ϕx = (1 − 0.45,νx) · Ix (νx) · ϕx · Dx

where x refers to the sample and r to the reference; A is the absorbance, ν the excitation wavenumber used, I the intensity of the excitation light at this energy, n the refractive index (n = 1.341 for acetonitrile solution and n = 1.330 for 0.1 mol dm−3 aqueous tris-buffer solution) and D the integrated emitted intensity. When (A, νx) − (A, νr) ≤ 0.05 , the original exponential law was used

ϕx = (1 − 0.45,νx) · Ix (νx) · Dx

The four 2 ms gradient pulses have sine-bell shapes and amplitudes ranging linearly from 2.5 to 50 G cm−1 in 32 steps. The diffusion delay was in the range 60–140 ms depending on the analyte diffusion coefficient, and the no. of scans was 32. The processing was done using a line broadening of 5 Hz and the diffusion coefficients were calculated with the Bruker processing package. Pneumatically-assisted electrospray (ESI-MS) mass spectra were recorded from 10−4 mol dm−3 solutions on a Finnigan SSQ7000 instrument. Elemental analyses were performed by Dr H. Eder from the Microchemical Laboratory of the University of Geneva.

Single-crystal structure determinations of L4, L5,

Summary of crystal data, intensity measurements and structure refinements are collected in Table S14 (ESI†). All crystals were mounted on quartz fibers with protection oil. Cell dimensions and intensities were measured at 150 K on a Stoe IPDS diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Data were corrected for Lorentz and polarization effects and for absorption. The structures were solved by direct methods (SIR97), all other calculation were performed with XTAL42 and ORTEP43 programs.
Comments on the crystal structure of $L_4^b$. All non hydrogen atoms (49) were refined with anisotropic atomic displacement parameters. The hydrogen atoms were calculated and refined with $U_{iso}$ = 0.04 Å² except for the terminal methyl groups, for which the atomic positions of the hydrogen atoms were refined with constraints on bond angles and on bond distances. Among the three water molecules in the asymmetric unit, only O3w was slightly disordered and the propionitrile solvent molecule showed large displacement parameters. The complex was located onto a crystallographic twofold axis with C20 on special position (4e).

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References


