Tunable Intramolecular Intermetallic Interactions as a New Tool for Programming Linear Heterometallic 4f–4f Complexes

Natalia Dalla-Favera,‡ Josef Hamacek,‡ Michal Borkovec,‡ Damien Jeannerat,‡ Gianfranco Ercolani,§ and Claude Piguet*†

Department of Inorganic, Analytical and Applied Chemistry, and Department of Organic Chemistry, University of Geneva, 30 quai E. Ansermet, CH-1211 Geneva 4, Switzerland. Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Via della Ricerca Scientifica, 00133 Roma, Italy

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Statistical mechanics predicts that the design of pure organized heteropolymetallic chains of metal ions bound to linear receptors depends on controlled deviations from the mixing rule $\Delta E^{\text{MMM}} = \frac{1}{2}(\Delta E^{\text{M}i\text{M}j} + \Delta E^{\text{M}j\text{M}i})$, whereby $\Delta E^{\text{MMM}}$ is the intramolecular intermetallic interaction between neighboring metal $i$ and metal $j$ along the receptor. A thorough investigation of linear polymeric trivalent lanthanide triple-stranded helicates shows that such deviations are amplified by an increase in the nuclearity of the final complexes and are thus easily evidenced in the tetranuclear heterobimetallic helicates $[\text{La}^{3+}_4\text{Lu}(\text{L}6)^3]^{2+}$ ($\gamma = 0–4$). The chemical and physical origins of this unprecedented behavior are discussed together with its practical consequences for programming pure heteropolymetallic 4f–4f complexes.

Introduction and Theory

Since the magnetic communication between trivalent lanthanides, Ln(III), is particularly inefficient,† homopolymetallic 4f–4f complexes have been mainly exploited for the confinement of charged,‡ noncoupled magnetically active,§ and optically active探 probes within a small (supra)molecular volume. The rational preparation of organized heteropolymetallic lanthanide complexes is more attractive because of the novel properties emerging from the asymmetry of the intermetallic communication processes.¶ Obvious applications can be found in homogeneous fluorimunoassays, in the combination of luminescent stains with magnetic probes for the double sensing of protein domains, in the design of efficient catalysts for cleaving phosphodiester bonds, and in the synthesis of materials for directional light conversion, photographic amplification, and nonlinear optical up-conversion.¶¶ Because of the similar coordination behavior


* To whom correspondence should be addressed. E-mail: Claude.Piguet@chiam.unige.ch (C.P.), Josef.Hamacek@chiam.unige.ch (J.H.)
† Department of Inorganic Chemistry, University of Geneva.
‡ Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma.
§ Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma.
of the trivalent lanthanides along the 4f series, thermodynamic segregation between different metals was limited for a long period to empirical, but remarkable, deviations from pure statistical doping in solid-state materials. However, the contribution of the noncontrolled crystallization processes to the latter deviations remained obscure, which limited the thermodynamic recognition of different lanthanides may result from a judicious combination of different binding sites within a semiflexible ligand. With this idea in mind, Bünzli and co-workers designed several neutral heteroleptic bis-tridentate ligands derived from \(L_2\) (part d of Figure 1), which react with stoichiometric amounts of Ln\(^A\) and Ln\(^B\) to give thermodynamic mixtures of homometallic (([(Ln\(^A\))^2(L\(^B\))]\(^{6+}\)) and [(Ln\(^B\))^2(L\(^A\))]\(^{6+}\)) and heterobimetallic ([((Ln\(^A\)))(Ln\(^B\))]\(^{6+}\)) binuclear triple-stranded helicates (eq 1, for the sake of simplicity, the lanthanides Ln\(^A\) and Ln\(^B\) are abbreviated with A and B in the thermodynamic models).}

\[
\frac{([L(n)^A]_2(L_k))^{6+} + ([L(n)^B]_2(L_k))^{6+}}{2([L(n)^A]_2(L(n)^B)k)^{6+}} = K_{eq}^{A,B,L_k} \text{exch} \tag{1}
\]

Interestingly, exchange equilibrium 1 is significantly shifted to the right when the difference in size between the two nine-coordinate cations \(\Delta \rho_{LnA,LnB} = |\rho_{LnA} - \rho_{LnB}|\) increases \(K_{eq}^{A,B,L_k} = 4\) for \(\Delta \rho_{LnA,LnB} = 0.025\) Å and it reaches \(K_{eq}^{A,B,L_k} \text{exch} = 263\) for \(\Delta \rho_{LnA,LnB} = 0.184\) Å.\(^{17}\) but the rationalization of this behavior suffers from the low symmetry of the ligand \(L_2\) (C\(^3\) symmetry), which leads to \(HHH \neq HHT\).
isomerism (HHH = head-to-head-to-head, HHT = head-to-head-to-tail). Upon reaction of the closely related, but C$_2$-symmetrical homotopic bis-tridentate ligands L$_3$ and L$_4$, with a pair of lanthanides Ln$^\text{III}$/Ln$^\text{III}$, the binuclear complexes [(Ln$_2$(L$_3$)$_3$)$_6$$]^{2+}$, [(Ln$_2$(L$_4$)$_3$)$_6$$]^{2+}$, (c) [(Ln$_3$(L$_5$)$_3$)$_9$$]^{3+}$, and the associated site-binding model for their formation constants ($f_{N_9}^A$ and $f_{N_{603}}^B$) are the microscopic affinities of Ln(III) for the N$_9$ and N$_6$O$_3$ sites, respectively, and $\Delta E_{1-2}^{Ln,Ln} = -RT\ln(u_{1-2}^{Ln,Ln})$ represents the intramolecular intermetallic interaction between two nearest neighbors. The final helicates correspond to X-ray crystal structures.
The study of 21 different lanthanide pairs with L₄ systematically gives $K_{\text{exch}}^{\text{mix},L_4} = 4.0(3)$, thus demonstrating that the mixing rule is obeyed for binuclear lanthanide helicates (i.e., $\Delta E_{\text{mix}}^{1-2} = 0$). For the longer trinuclear helicates $[(\text{Ln})_3(\text{L})_3]^{9+}$ (y = 0–3), the existence of two different binding sites along the strands ($\text{N}_9$)–($\text{N}_9$)–$\text{N}_9$, in part c of Figure 2) leads to six microspecies (eqs 8–13, in part c of Figure 2), which can be combined to give the four macroconstants required for computing the relevant exchange equilibrium $K_{\text{exch}}^{\text{mix},L_5}$ (eqs 15 and 16).\(^{22}\)

\[
[(\text{Ln})_3(\text{L})_3]^{9+} \rightleftharpoons [(\text{Ln})_2(\text{L})_2(\text{L})_2]^{9+} \quad \quad \text{K}_{\text{exch}}^{\text{mix},L_5} = (\beta_{a,a,a,b,b,b})^2/(\beta_{b,b,b})^2 = 4(u_{1-2}^{(A,B,B,B)}u_{1-2}^{(A,B,B,B)})^{-1} \quad (14)
\]


cal mechanics, was used to predict the partition function of infinite 1D chains of charged metals bound to a single receptor. The associated binding isotherm characterizing the metal loading of the receptor strongly depends on the

Figure 4. Self-assembly of the tetranuclear homo- and heterobimetallic triple-stranded helicates $[\text{La}_{4-y}\text{Lu}_y(L6)_3]^{12+}$ showing the possible micro- and macrospecies.

Programming Linear Heterometallic 4f–4f Complexes

Figure 5. Experimental $^1$H NMR spectra of H$_3$, H$_9$, and H$_{12}$ in [La$_4$–2La$_3$(L6)$_3$]$_{12}^{12+}$ recorded for the titration of L6 with La(III) and Lu(III) ($y = 0$–4), total ligand concentration = 10$^{-2}$ M, total metal concentration = 1.33 × 10$^{-2}$ M, lanthane mole fractions $x_{La} = [La]/[La] + [Lu] = 0$–1, CD$_3$CN/CD$_2$Cl$_2$ = 95:5.

nearest-neighbor pairs interaction $\Delta E_{1-2}^{Ln,Ln}$ (part a of Figure 3). Interestingly, a strict analogy exists between the latter loading process and the competition of two different metal ions A and B for saturating the linear receptor, assuming that $\Delta E_{1-2}^{Ln,Ln}$ is replaced with $\Delta E_{1-2}^{mix} = (\Delta E_{1-2}^{A,A} + \Delta E_{1-2}^{B,B})/2 - \Delta E_{1-2}^{A,B}$ (Figure 3). When $\Delta E_{1-2}^{Ln,Ln} = 0$ or $\Delta E_{1-2}^{mix} = 0$, the binding sites are statistically occupied by the metals, which corresponds to non-cooperative behaviors. For the homometallic loading process (part a of Figure 3), this situation refers to a random occupancy of the metals among the binding site, whereas the related competition process produces a random distribution of the different metal ions among the coordination sites (part b of Figure 3). $\Delta E_{1-2}^{Ln,Ln} > 0$ or $\Delta E_{1-2}^{mix} > 0$ characterize anti-cooperative processes for which the repulsive interactions between the metals produce a plateau in the binding isotherm corresponding to (i) the half occupancy of the sites with strict succession of empty and occupied sites for the homometallic loading (part a of Figure 3) and (ii) a strict alternance of different metals for the heterobimetallcal competition (part b of Figure 3). Finally, the (positively) cooperative processes $\Delta E_{1-2}^{Ln,Ln} < 0$ or $\Delta E_{1-2}^{mix} < 0$ result in the clustering of identical metal along the strands in both situations.

We however note that these well-defined organizations form only if $|\Delta E_{1-2}^{Ln,Ln}| \gg RT$ or $|\Delta E_{1-2}^{mix}| \gg RT$, whereby $RT \approx 2.5$ kJ·mol$^{-1}$ at room temperature. When $|\Delta E_{1-2}^{Ln,Ln}| \ll RT$ or $|\Delta E_{1-2}^{mix}| \ll RT$, the situation is similar to a non-cooperative process, whereas $|\Delta E_{1-2}^{Ln,Ln}| \approx RT$ or $|\Delta E_{1-2}^{mix}| \approx RT$ corresponds to a transition region for which deviations from random organizations can be detected. Although such predictable programming of organized heteropolymetallic lanthanide chains is attractive for the engineering of novel materials with unusual photophysical and electronic properties, only little attention has been focused on the tuning of intramolecular intermetallic interactions for improving complexation selectivities.21 In this contribution, we push forward the bottom-up approach with the goal of inducing deviations from the statistics for the competition between La(III) and Lu(III) in the tetraneuclear helicates [Ln$_6$(L6)$_3$]$_{12}^{24+}$ (Figure 4). Unprecedented selectivity is indeed observed, and its assignment to a combination of solvation effects, mechanical couplings, and intermetallic electrostatic interactions amplified by the nuclearity of the final (supra)molecular complexes represents a novel approach for the preparation of pure heteropolymetallic complexes and polymers.

Results and Discussion

Theoretical Model for the Metal-Exchange Process Occurring in the Tetraneuclear Bimetallic Helicates [La$_4$–Lu$_3$(L6)$_3$]$_{12}^{24+}$ ($y = 0$–4). Previous spectroscopic and thermodynamic investigations established that L6 reacts with Ln(III) along the complete lanthanide series in acetonitrile (Ln = La–Lu, Figure 4) to give very stable tetraneuclear...
When the total ligand concentration is large enough (≥ 10−2 M) to ensure the quantitative formation of [Ln−L6]12+ under stoichiometric conditions (i.e., Lntot/L6 = 4:3), the competition between the two metal ions, such as La(III) and Lu(III), simply corresponds to the intermolecular metal exchange between the saturated trigonal helicates [La4−, Lu4(L6)3]12+ (y = 0−4, Figure 4).

Investigation of the Experimental Metal-Exchange Process Occurring in the Tetranuclear Bimetallic Helicates [La4−, Lu4(L6)3]12+ (y = 0−4). The detailed 1H NMR analysis (COSY, NOESY, ROESY) of the homometallic tetranuclear complexes [La4(L6)3]12+ (part a of Figure S1, Supporting Information) and [Lu4(L6)3]12+ (part b of Figure S1, Supporting Information)23 allows the complete assignment of the 39 signals (numbering in Figure 4). Let us now focus on the unusually shielded aromatic protons H3, H9, and H12, which are put in the diamagnetic shielding region of a neighboring strand by the wrapping of the ligands (δH = 5.0−6.0 ppm, Figure 5 and Figure S2, Supporting Information).23 If all 10 [La4−, Lu4(L6)3]12+ microspecies provided a specific set of chemical environments for the protons H3, H9, and H12, we would expect the detection of 48 different 1H NMR signals. However, the stepwise transformation of [Lu4(L6)3]12+ into [La4(L6)3]12+ displays only 12 resolved 1H NMR signals arising from H3, H9, and H12 (Figure 5), whose evolution during the titration of L6 with La(III) and Lu(III) is shown in part a of Figure 6.

The spectral overlap can be rationalized by using a simple structural model, in which the chemical shift of each aromatic proton H3, H9, H12 (i = 3, 9, 12) depends only on (1) the lanthanide coordinated to the incriminated benzimidazole rings (LnL) and (2) the lanthanide bound to the closest

Figure 7. Individual 1H NMR spectra of the 10 microspecies [La4−, Lu4(L6)3]12+ in the 5−6 ppm range (y = 0−4).
neighboring site (Ln2). In these conditions, we indeed expect only 12 different $^1$H NMR chemical environments (Table S2, Supporting Information), whose unambiguous assignment to H$_{x}$, H$_{y}$, and H$_{z}$ in the different microspecies relies on simulated intensities assuming that the mixing rule $\Delta E_{\text{mix}} = (\Delta E_{\text{L-A}} + \Delta E_{\text{B-B}})/2 - \Delta E_{\text{A-B}} = 0$ is obeyed.

We thus first calculate the distribution of the saturated bimetallic tetranuclear complexes $[\text{La}_4 - _{_{-1}}\text{Lu}(\text{L6})]^{12+}$ using the formation constants of eqs 17–26 with $\Delta E_{\text{mix}} = 0$ ($y = 0–4$, Table S3, Supporting Information). Second, the resulting predicted ligand distribution (part b of Figure 6) is combined with the intensity of each proton in each microspecies (Table S2) to give the simulated evolution of the 12 $^1$H NMR signals for the titration of L6 with La(III) and Lu(III) in part c of Figure 6. Comparison between the integrated experimental (part a of Figure 6) and simulated (part c of Figure 6) $^1$H NMR signals for H$_{x}$, H$_{y}$, and H$_{z}$ shows strong correlations, and factor analysis$^{25}$ indicates that only 5 spectra are mathematically independent.

**Quantitative Analysis of the Experimental Metal-Exchange Process Occurring in the Tetrancular Bimetallic Helicates $[\text{La}_4 - _{_{-1}}\text{Lu}(\text{L6})]^{12+}$ ($y = 0–4$).** Taking into account the correlation between the experimental $^1$H NMR spectra of the microspecies (Figure 7), we limited the eventual estimation of the experimental concentrations of the bimetallic complexes in the mixtures to the five macrospecies $[\text{La}_4 - _{_{-1}}\text{Lu}(\text{L6})]^{12+}$ ($y = 0–4$) for each different La/Lu ratio. The associated mole fractions of each macrospecies $y$, given as $z_y$, with respect to the total concentration of tetrancular helicates are given in eqs 27–31, assuming that the relative contributions of the different microspecies within a given macrospecies is a priori fixed by the ratio of the microconstants calculated with $\Delta E_{\text{mix}} = 0$ (Table S3).

\[
\begin{align*}
    z_0 &= [\text{La}_4] = [\text{LaLaLaLa}] \quad (27) \\
    z_1 &= [\text{La}_3\text{Lu}] = 0.33[\text{LaLaLaLu}] + 0.67[\text{LaLaLuLa}] \quad (28) \\
    z_2 &= [\text{La}_2\text{Lu}_2] = 0.31[\text{LaLaLaLu}] + 0.30[\text{LaLaLuLa}] + 0.31[\text{LaLuLuLa}] + 0.08[\text{LaLuLuLu}] \quad (29) \\
    z_3 &= [\text{La}_3\text{Lu}] = 0.67[\text{LuLuLuLa}] + 0.33[\text{LuLuLuLu}] \quad (30) \\
    z_4 &= [\text{Lu}_4] = [\text{LuLuLuLu}] \quad (31)
\end{align*}
\]

The total intensity of the protons can be then easily modeled by combining the individual spectra of Figure 7 with the mole fractions expressed in eqs 27–31 to give a set of 12 equations summarized in Table S5 (eqs S2–S13, Supporting Information). Multilinear least-squares fits of these equations to the experimental intensities for each La/Lu ratio (Table S4, Supporting Information) provides an estimate of the experimental concentrations $z_y$ of the five $[\text{La}_4 - _{_{-1}}\text{Lu}(\text{L6})]^{12+}$ ($y = 0–4$) macrospecies (part a of Figure 8). Comparison of the latter experimental distribution of the macrospecies (part a of Figure 8), with the one predicted with $\Delta E_{\text{mix}} = 0$ (part b of Figure 8), shows systematic deviations favoring the formation of the heterobimetallic complexes. Because the absolute affinities of the N6O3 and N6 sites for La(III) and Lu(III) are very similar ($f_{\text{La}}^{\text{N6O3}} \approx f_{\text{Lu}}^{\text{N6O3}}$ and $f_{\text{La}}^{\text{N6}} \approx f_{\text{Lu}}^{\text{N6}}$ Table 1), we can rule out a selective distribution of the lanthanides in the different sites based on specific metal–ligand recognition events. We can safely conclude that the mixing rule is not obeyed and $\Delta E_{\text{mix}} = (\Delta E_{\text{LaLa}} + \Delta E_{\text{LuLu}})/2 - \Delta E_{\text{LaLu}} > 0$, which is diagnostic for an anticooperative process (part b of Figure 3).$^{20}$ Consequently, the intermetallic repulsion between identical neighbors is larger than that operating between different metals. This thermodynamic deviation from statistics is in line with the experimental strong preference exhibited by the heterotopic bis-tridentate ligand L2 for producing heterometallic $[\text{LaLu(L2)}]^{6+}$ complexes,$^{13}$ but we cannot invoke here any subtle driving forces resulting from specific interligand interactions varying with the relative orientations of the ligand strands because L6 (C$_{2v}$ point group) is homotopic, whereas L2 (C$_{5v}$ point group) is heterotopic.

Two possible origins can be considered for rationalizing this deviation. First, the mechanical coupling between adjacent coordination sites may favor the formation of heterometallic neighboring pairs for steric (i.e., enthalpic) reasons. However, the observation that deviations from the mixing rule increase stepwise when going from the binuclear $[\text{La}_2(\text{Lk})]^{6+}$ ($k = 3, 4$, the mixing rule is obeyed)$^{18,19}$ to

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Table 2. Experimental (log (β_{La(Lu,L6)}^{La(Lu,L6)}) and Calculated (log (β_{La(Lu,L6)}^{La(Lu,L6)}) Formation Constants for the Macrospecies [La₄ – Lu(L6)]^{12+} (Acetonitrile/dichloromethane = 95.5, 298 K)

<table>
<thead>
<tr>
<th>Macrospecies</th>
<th>log(β_{La(Lu,L6)}^{La(Lu,L6)})</th>
<th>log(β_{La(Lu,L6)}^{La(Lu,L6)})</th>
<th>log(β_{La(Lu,L6)}^{La(Lu,L6)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>La₄</td>
<td>39.4</td>
<td>39.4</td>
<td>39.3</td>
</tr>
<tr>
<td>La₃Lu</td>
<td>41.0</td>
<td>40.3</td>
<td>41.1</td>
</tr>
<tr>
<td>La₂Lu₂</td>
<td>41.8</td>
<td>40.9</td>
<td>41.8</td>
</tr>
<tr>
<td>La₄Lu</td>
<td>41.5</td>
<td>41.0</td>
<td>41.4</td>
</tr>
<tr>
<td>Lu₃</td>
<td>40.6</td>
<td>40.7</td>
<td>40.6</td>
</tr>
</tbody>
</table>

Log(K_{exch})

| Log(K_{exch}) | 8.5 | 4.3 | 8.7 |

the trinuclear [La₃(L₅)]^{3+} (slight deviations from the mixing rule, often difficult to address),²² to the tetranuclear [La₄(L₆)]^{12+} helicates (significant deviations from the mixing rule) is difficult to correlate with a simple short-range mechanical coupling. The second possible explanation involves the formation of irregular helices when metal ions of different sizes are incorporated. Because we have shown that solvation effects are crucial in controlling apparent intermetallic interactions in solution,²¹ a slight change in the total solvation energy of one complex in equilibrium 32 is expected to have drastic effect on the associated exchange constant K_{exch,La,Lu,L₆} (eq 33). This effect is expected to increase with the nuclearity of the complex, that is, with the total charge q borne by the helicate because the solvation energies Δω,G ≈ q² according to the Born equation.²¹

3[La₄(L₆)]^{12+} + 3[Lu₃(L₅)]^{12+} = 2[La₃Lu(L₆)]^{12+} + 2[La₄Lu₂(L₅)]^{12+} (32)

K_{exch} = \left(\frac{β_{La₄Lu₂L₆}^{La₄Lu₂L₆} β_{La₄Lu₃L₆}^{La₄Lu₃L₆} β_{La₄Lu₃L₆}^{La₄Lu₃L₆}}{β_{La₄Lu₃L₆}^{La₄Lu₃L₆} β_{La₄Lu₃L₆}^{La₄Lu₃L₆} β_{La₄Lu₃L₆}^{La₄Lu₃L₆}}\right)^{2/3} \left(\frac{β_{La₄Lu₃L₆}^{La₄Lu₃L₆} β_{La₄Lu₃L₆}^{La₄Lu₃L₆}}{β_{La₄Lu₃L₆}^{La₄Lu₃L₆} β_{La₄Lu₃L₆}^{La₄Lu₃L₆}}\right)^{3/2} (33)

For the pure statistical situation, f_{La,N₆O₃}^{La,N₆O₃} = f_{Lu,N₆O₃}^{Lu,N₆O₃} = f_{La}^{La} = f_{Lu}^{Lu} and ΔE_{La,Lu} = ΔE_{La,Lu} = ΔE_{La,Lu} = ΔE_{La,Lu} = 25119, computed with eq 33 (Table 2, column 3) and by using the formation constants obeying the mixing rule ΔE_{min} = (ΔE_{La,Lu} + ΔE_{La,Lu} + ΔE_{La,Lu})/2 = 0 (Table S3, Supporting Information). The latter value indicates that the slight differences in the absolute affinities of La(III) and Lu(III) for the terminal (N₆O₃) and central (N₆) binding sites in the tetranuclear helicates [La₄ – Lu(L₆)]^{12+} is responsible for a limited increase of K_{exch,La,Lu,L₆} by a factor of 25119:9216 = 2.8. Despite the significant uncertainties affecting the experimental concentrations of the heterobimetallic macrospecies due to the limited accuracy of the integration of original correlation ¹H NMR signals, we have performed a nonlinear least-square fit of these concentrations (part a of Figure 8) by using the macroscopic equilibria eqs 34–38, and we obtain a set of experimental macroconstants β_{La₄,L₆}^{La₄,L₆} (Table 2, column 2), which satisfyingly reproduces the experimental data (Figure S3, Supporting Information, Agreement factor AF = √\sum((Conc_{exp} – Conc_{calc})^2)/\sum((Conc_{exp})^2) = 0.24, Conc = concentration).

4 La₃³⁺ + 3 L₆ ⇌ [La₄(L₆)]^{12+} β_{La₄,L₆}^{La₄,L₆} (34)

3 La₃⁺ + Lu₃⁺ + 3 L₆ ⇌ [La₃Lu₃(L₆)]^{12+} β_{La₃,L₆}^{La₃,L₆} (35)

2 La₃⁺ + 2 Lu₃⁺ + 3 L₆ ⇌ [La₃Lu₂(L₆)]^{12+} β_{La₃,L₆}^{La₃,L₆} (36)

La₃³⁺ + 3 Lu⁺ + 3 L₆ ⇌ [La₃Lu₃(L₆)]^{12+} β_{La₃,L₆}^{La₃,L₆} (37)

4 Lu₃⁺ + 3 L₆ ⇌ [Lu₄(L₆)]^{12+} β_{Lu₄,L₆}^{Lu₄,L₆} (38)

The introduction of β_{La₄,L₆}^{La₄,L₆} in eq 33 gives K_{exch,La,Lu,L₆} = 10^8.5, which indeed corresponds to a further increase by more than 4 orders of magnitude (Table 2, column 2) of the exchange constant in favor of the heterometallic helicates. The latter effect can be thus unambiguously assigned to a deviation of the mixing rule. Nonlinear least-square fits of the five constants β_{La₄,L₆}^{La₄,L₆} to the site binding model (eqs 17–26), for which f_{La,L₆}^{La,L₆} f_{Lu,L₆}^{Lu,L₆} f_{La,L₆}^{La,L₆} f_{Lu,L₆}^{Lu,L₆} ΔE_{La,Lu} = 25119, and ΔE_{La,Lu} = 25119, were fixed (Table 1), eventually gives ΔE_{La,Lu} = 45.4 kJ mol⁻¹ as the single fitted parameter, in agreement with an anti-cooperative mixing factor of ΔE_{La,Lu} = (ΔE_{La,Lu} + ΔE_{La,Lu} + ΔE_{La,Lu})/2 = ΔE_{La,Lu} = 0.2 kJ mol⁻¹ (Table 2). The agreement of the recalculated formation constants (Table 2, column 4) with the experimental data (Table 2, column 2) is excellent, and we conclude that a minor deviation from the mixing rule induces a drastic effect in the polynuclear linear chain of metal ions because of the increasing amount of intermetallic interactions accompanying the increase in nuclearity of the (supra)molecular objects. The calculation of partial occupancy factors f_{La,L₆}^{La,L₆} introduced by Hamacheck et al.,²⁶ for the fixation of either La(III) or Lu(III) to the virtually preorganized receptor (L₆)₁ (eqs 39–40) provides globally upward convex Scatchard-like plots,²⁶ which are diagnostic for anti-cooperative mechanisms accompanying the successive introduction of similar metal ions within the tetranuclear helicates [La₄ – Lu(L₆)]^{12+} (part a of Figure 9). We can thus predict that [La₄Lu₂] is the thermodynamically favored heterobimetallic macrospecies, in agreement with the computed experimental distribution curves (part b of Figure 9).

A close scrutiny of these Scatchard-like plots indicates that
the successive introduction of La(III) is less anti-cooperative (even slightly positively cooperative for 0 ≤ $r_{\text{La}}$ ≤ 2) than the same process with Lu(III), and therefore the [La3+ Lu(L6)]12+ macrospecies dominates the related [LaLu3- (L6)]12+ macrospecies during the titration. This unsymmetrical situation drastically differs from the non-cooperative case characterized by $\Delta E_{1-2}^{\text{mix}} = 0$, for which the Scatchard-like plots are linear (part a of Figure S4, Supporting Information), and the distribution curves do not show preferences for a specific heterobimetallic macrospecies (part b of Figure S4).

Introduction of the microscopic parameters of Table 1 for $L_n = \text{La}, \text{Lu}$ and $\Delta E_{1-2}^{\text{La, Lu}} = 45.4 \text{ kJ mol}^{-1}$ into eqs 17–26 provides the target experimental set of 10 microconstants (part a of Figure 10), which allows the calculation of the experimental distribution curves for the 10 microspecies (part b of Figure 10). The relative contributions of the different microspecies to a given macrospecies do not deviate significantly from those originally calculated in eqs 27–31 with $\Delta E_{1-2}^{\text{mix}} = 0$, which does not require further iterative fitting processes, according to the limited accuracy of the integration of the $^1$H NMR signals. It is, however, worth noting that, when the number of La(III) metals is larger than the number of Lu(III) in a macrospecies, that is, in [La3Lu], the dominant microspecies maximizes the amount of alternance between different metals, whereas the reverse situation holds when the macrospecies contains a larger number of Lu(III), that is, in [Lu2La] (Figure 10).

Experimental Section

Chemicals were purchased from Fluka AG and Aldrich and used without further purification, unless otherwise stated. Ligand L6 was prepared according to a literature procedure.23 Ln(CF₃SO$_3$)$_3$·9H₂O (Ln = La, Lu)$_{27}$ were prepared from the corresponding oxides (Aldrich, 99.99%). The lanthanide content of solid salts was determined by complexometric titrations with Titriplex III (Merck) in the presence of urotropine and xylene orange.28 Acetonitrile and dichloromethane were distilled over calcium hydride.

Spectroscopic and Analytical Measurements. $^1$H NMR spectra were recorded at 25 °C on Bruker Avance 400 MHz and Bruker DRX-500 MHz spectrometers. Chemical shifts are given in ppm with respect to TMS. The samples for $^1$H NMR spectroscopy were prepared by the stoichiometric 3:4 mixing of L6 and Ln(CF₃SO$_3$)$_3$·9H₂O (Ln = La, Lu) in 700 μL of CD$_2$CN/CDCl$_3$ (95:5). The total concentration of the ligand was maintained at 10 mM in each sample and 48 h equilibration was required before measurements. Because of partial overlap in the proton spectrum, signal amplitudes were determined by line-shape analysis followed by spectral reconstruction using the Bruker’s WinNmr deconvolution tool. Computations of the concentrations were performed with the HySS2 computer program.


Conclusion

Better understanding of the thermodynamic driving forces controlling multicomponent self-assembly processes opens novel perspectives for addressing the unsolved chemical challenge of selectively introducing different lanthanides possessing very similar coordination properties, but slightly different sizes, into organized linear polymetallic chains. According to the present results, the stepwise increasing length of the ligand strands, and consequently of the number of successive binding sites, produces an anti-cooperative process, which favors the alternance of lanthanides of different sizes along the helical axis (part b of Figure 3). For the investigated La(III)/Lu(III) pair, the minor deviation from the mixing rule \( \Delta E_{1-2}^{\text{mix}} = (\Delta E_{1-2}^{\text{La,Lu}} + \Delta E_{1-2}^{\text{La,La}})/2 - \Delta E_{1-2}^{\text{La,Lu}} \approx 2 \text{kJ/mol}^{-1} \) indeed agrees with the minor changes occurring between La(III) and Lu(III), but it becomes significant for the tetranuclear helicates \([\text{La}_4(\text{L}_6)]^{12+}\) because of its amplification by the repetition of this specific effect in polynuclear complexes. Because mechanical coupling is limited to short-range interactions, we can conclude that solvation effects and electrostatic interactions, which operate on large nanometric scales, are mainly responsible for this unprecedented segregation. Although we are still not in a position to chemically control this effect, we have succeeded to find a case where \( \Delta E_{1-2}^{\text{mix}} \neq 0 \) for which we predict a particularly attractive application in the prospection of bifunctional sensors\(^7\) and directional energy transfer processes\(^4,5\) and the development of four-level molecular lasers.\(^29\)

With this novel tool at hand, the next step for addressing the heterometallic \(4f-4f\) challenge involves the design of novel systems displaying \(\Delta E_{1-2}^{\text{mix}} \gg RT\) and for which a robust thermodynamic organization of the metals occurs along the ligand strands.

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Supporting Information Available: Tables (S1–S5) and Figures (S1–S4) corresponding to thermodynamic and structural modeling, spectroscopic analyses, and fitting processes. This material is available free of charge via the Internet at http://pubs.acs.org. IC701308H