Planned Failures from the Principle of Maximum Site Occupancy in Lanthanide Helicates

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Despite the recent emergence of a toolbox fitted with microscopic thermodynamic descriptors for predicting the stabilities and speciations of polynuclear complexes in solution, the discovery of novel or unusual type of metal–ligand assemblies in metallosupramolecular chemistry still often relies on serendipity. In order to highlight the novel perspectives offered by a rational exploitation of these thermodynamic parameters, the segmental bis-tridendate ligands L7 and L8 have been designed for providing effective molarities upon reaction with trivalent lanthanides, LnIII, so small that the saturated binuclear triple-stranded helicates [Ln2(Lk)13]6+, which obey the well-respected principle of maximum site occupancy, cannot be detected in solution because of their deliberately planned instabilities. The hierarchical evolution of the effective molarities with an increasing number of ligand strands in these complexes indeed favors the formation of the alternative unsaturated single-stranded [Ln2(Lk)12]6+ and double-stranded [Ln2(Lk)13]6+ complexes, whose relative speciations in solution depend on the nature of the binding sites introduced into the segmental ligand.

Introduction

It is now well-established that the cumulative stability constant of any self-assembly process involving metals and ligands (equilibrium 1) can be modeled with the simple free energy additive strategy shown in eq 2.1

\[ m\text{M}^{2+} + nL \rightleftharpoons [M_{m-L}^{n-}]^{z+} \cdot f_{m,n}^{M,L} \]  

\[ \beta_{m,n}^{M,L} = \omega_{chir}^{M,L} \cdot \omega_{unord}^{M,L} \cdot \Pi_{i=1}^{m} (f_{i}^{M,L}) \cdot \Pi_{i=1}^{m+n} (f_{i}^{L,L}) \]  

\[ c^{eff} \cdot \Pi_{i=1}^{m} (u_{i}^{M,M}) \cdot \Pi_{i=1}^{m+n} (u_{i}^{L,L}) \]  

\[ \omega_{chir}^{M,L}, \omega_{unord}^{M,L} \] is the statistical factor of the assembly, \( f_{i}^{M,L} \) is the hetero-component intermolecular microscopic affinity characterizing the connection of a metal M to the binding site i of a ligand L (including desolvation), \( c^{eff} \) is the effective concentration correcting \( f_{i}^{M,L} \) for intramolecular macrocyclization.

References


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selection of the most stable coordination complex under thermodynamic control, obviously requires (i) a maximum number of these favorable microscopic metal-binding site contributions (this simple deduction is known as the principle of maximum site occupancy)\(^6\) and (ii) the chemical optimization of each metal-binding site interaction (this second deduction is often referred to as the principle of stereochemical matching).\(^1\) In this context, the three additional thermodynamic microscopic descriptors \(c_{\text{eff}}, \Delta E_{\text{MM}}, \text{and } \Delta E_{\text{LL}}\) offer attractive opportunities for putting into perspective these two well-respected “ukazes” in coordination and metallo-supramolecular chemistry, which often discourage the rational design of a wealth of unexpected nanoscopic polymeric structures, thus leaving an empty space for serendipity.\(^5\) We note, however, that the opposite contributions of similar magnitudes brought by Coulombic and solvation effects within the homo-component interactions \(\Delta E_{\text{MM}}, \text{and } \Delta E_{\text{LL}}\) usually produce negligible cooperative effects (slightly positive or negative). Consequently, these parameters do not significantly influence the formation of the target saturated complexes in solution (\(\Delta E_{\text{MM}} \approx \Delta E_{\text{LL}}\)).\(^1\) In contrast, the experimental values found for the effective molarity EM (i.e., the experimental term for the concept of effective concentration, \(c_{\text{eff}}\)) often refer to (i) in metal-mediated porphyrin arrays,\(^11\) (ii) in multisite ligand-proteins aggregates\(^12\) or (iii) in sophisticated electrostatic adducts\(^13\) cover a large domain (10\(^{-4}\) < EM < 10\(^{3}\) M). Assuming a pure entropic origin for the effective concentration, the theory predicts \(c_{\text{eff}} \approx \Delta \mu^n\) with \(n = \frac{1}{2}\) for free joint chains and \(n = 3\) for an optimized spacer, whereby \(d\) is the separation between the two connected binding sites responsible for the intramolecular macrocyclization.\(^3,12,14\) Therefore, only closely spaced donor atoms joined by a short linker may give EM \(\approx 1\) M, a particular situation often referred to as the chelate effect, in which the intramolecular connection is energetically preferred over its intermolecular counterpart (\(\Delta G_{\text{intra}}^{\text{MM}} - \Delta G_{\text{inter}}^{\text{MM}}\)).\(^1\)

It is thus not so surprising that triple-stranded polynuclear helicates \([\text{Lu}_{3}(\text{L}1)]^{30+} (k = 1–3)\), in which two tridentate adjacent binding sites are separated by 9 Å and connected by semiflexible twisted diphenylmethane spacers, display (i) very limited preorganization for intramolecular macrocyclization and (ii) small effective molarities (EM = 10\(^{-4}\) M) for the macrocyclization between two adjacent sites, Figure 1a).\(^9\)

Interestingly, this parameter is extremely sensitive to minor enthalpic structural constraints, as illustrated by the removal of two degrees of rotational freedom in the terminal tridentate binding units in the ligand \(\text{L}4\), which indeed reduces EM by 5 orders of magnitude (Figure 1b), while an obvious increase of EM is expected if we solely consider the entropic contribution.\(^16\) Although not unambiguously assigned to the sole variation of EM, the recent report of a decrease in magnitude on an order of 3 for the stability constants of

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(10) Mulder, A.; Huskens, J.; Reinhardt, D. N. Org. Biomol. Chem. 2004, 2, 3409–3424. As recommended by Mulder et al., the term of effective molarity EM will be used for the experimental values, while the effective concentration, \(c_{\text{eff}}\), will be used for the concept expressed in the mathematical equations. Please keep in mind that EM \(\equiv c_{\text{eff}}\) for numerical values.


mononuclear lanthanide complexes, in which the ethylene spacer has been replaced with peptides of variable lengths, suggests that the effective molarity is also amenable to significant modulation when the spacer is systematically varied.8,20 Since $\Delta G_{\text{intra}} - \Delta G_{\text{inter}} = -RT \ln (EM)$, this parameter indeed represents a considerable contribution to the global free energy change accompanying the assembly process. In this context, the unexpected isolation of the trinuclear circular single-stranded helicates $[\text{Ln}_3(L5)_3]^{3+}$ or the formation of bridged binuclear side-by-side complexes $[\text{Ln}_2(L6)_2(\mu-\text{CH}_3\text{CO}_2)(\text{H}_2\text{O})_3]^{5+}$ instead of the planned saturated bicyclic trinuclear triple-stranded helicates $[\text{Ln}_3(L8)_3]^{5+}$ upon reaction of the constrained ligands L5 and L6 with trivalent lanthanides, Ln(III), in a Ln:L = 2:3 stoichiometric ratio could be the result of systems minimizing some unfavorable intramolecular connections (Scheme 1 and Figure S1, Supporting Information). However, the last two observations entirely rely on solid-state structures obtained by serendipity with no direct access to the thermodynamic parameters controlling the chemical assembly occurring in solution. The question thus arises about a possible rational programming of polynuclear complexes, for which the speciation obtained under thermodynamic control deliberately deviates from the two classical principles of (i) maximum site occupancy and (ii) stereochemical matching, without resorting to the formation of ternary complexes with highly competitive solvent molecules or counteranions.8,20

In this contribution, we build on this reasoning with the design of the bis-tridentate ligands L7 and L8 (Scheme 1), in which (i) the rotational degrees of freedoms are restricted to

![Scheme 1. Chemical Structures of Ligands L5–L8](image1)

interannular rotations about $C_{\text{aromatic}}$-$C_{\text{aromatic}}$ bonds and (ii) the flexibility of the spacer is limited by the central rigid phenyl ring. We thus expect effective molarities upon complexation to trivalent lanthanides so small that the saturated triple-stranded helicates $[\text{Ln}_3(L8)_3]^{5+}$ ($k = 7, 8$), obeying both principles of maximum site occupancy and of stereochemical matching, cannot be formed in solution under accessible concentrations at Ln:Ln = 2:3 stoichiometric ratio.

### Results and Discussion

#### Syntheses and Structures of the Constrained Ligands L7 and L8

In comparison with L5 and L6, the removal of some rotational degrees of freedom in the phenyl spacer used in L7 and L8 requires the formation of $C_{\text{aromatic}}$-$C_{\text{aromatic}}$ bonds via a Miyaura–Suzuki strategy.21 Among the various criteria of reactivity favoring this coupling reaction, the optimum situation requires the use of a polar solvent.22 an electron-poor aromatic ring bearing the $C$-$X$ bond (X = halogen, pseudohalogen), an electrondonating aromatic boronic acid,23 and the addition of a poorly hydrolyzing base, such as carbonate or fluoride.24

For synthetic reasons,25 the Suzuki coupling reactions connecting two peripheral benzimidazole rings to the

![Scheme 2. Synthetic Strategy for the Preparation of Ligands L7 and L8 with Numbering Scheme for $^1H$ NMR](image2)

para positions of the central phenyl ring in L7 and L8 (Scheme 2) deal with the unfavorable combination of electron-rich triflate acceptors (3 and 4) with the electron-deficient bis-boronic acid 5. We were thus forced to develop a smooth methodology for the selective transfer of a triflate group onto the hydroxybenzimidazole rings 1 and 2 without producing either ring opening or N- versus O-alkylation. For this purpose, we first optimized the reaction of N-phenyl-bistriflimide (O-N-(Ts)2, Scheme 2) with the easily accessible hydroxybenzimidazole scaffold S6 (Scheme S1, Figure S2, and Table S1 in the Supporting Information). Once 3 or 4 could be obtained from 1 and 2 with this technique (Scheme 2), their Suzuki coupling with 5 then simply used a Pd(0) catalyst in dioxane/ethanol with CsF as a source of fluoride. The 1H NMR spectra of L7 and L8 (Figure 3a and Figure S9a and Tables S3 and S4 in the Supporting Information) indicate 2-fold symmetries in solution (i.e., two equivalent tridentate binding units) combined with mirror planes responsible for the systematic observation of enantiotopic methylene protons (H9,9', H10,10', and H11,11' in L7; H9,9' and H10,10' in L8). None of the four blocked conformations of the bis-benzimidazole-phenyl spacer, compatible with C2h or C2v symmetry in solution (Scheme S2, Supporting Information), indeed correspond to the crystal structure of L8·3CHCl3 (Figure 2), which displays an intermediate situation with interplanar benzimidazole—phenyl angles of 26.0(2) and 34.2(2)° (Table S2, Supporting Information). This arrangement corresponds to the best compromise for minimizing steric hindrance produced by the four hydrogen atoms occupying the ortho positions around the Cbzim–Cphenyl bond, while retaining some favorable π overlap between the three conjugated aromatic rings of the spacer. Moreover, the pyridine and benzimidazole rings of L8 take part in intermolecular aromatic stacking interactions in the crystal lattice, which further produce distortions in the solid state (Figure S3, Supporting Information). We conclude that the apparent C2h or C2v symmetries observed in solution result from fast rotations about the Cbzim–Cphenyl bonds in L7 and L8 on the NMR time scale. We also note that the approximately planar tridentate bis-benzimidazole pyridine binding units in L8 (interplanar benzimidazole—pyridine angles: 5.2–11.2°, Table S2) adopt the expected trans,trans arrangement of the three coordinating N-donors, which minimizes dipole moments (Figure 2).

**Complexation and Speciation of L7 and L8 with Trivalent Lanthanide Triflates in Solution.** Electrospray ionization-mass spectrometric (ESI-MS) titrations of L7 (10−4 M in CH3Cl2/CH3CN (9:1)) with Eu(CF3SO3)3·3H2O (Eu:L7 = 0.1:3.0) exclusively shows the existence in the gas phase of the complexes [Eu2(L7)2(CF3SO3)2]·v(CH3CN)]=[v(x−y)+ (x = 2−4, y = 1−3) possessing a 2:2 stoichiometry, with the base peak of the spectra corresponding to [Eu2(L7)2(CF3SO3)2]3+. Parallel 1H NMR titrations of L7 (10−2 M in CDCl3/CD3CN (1:1)) with Lanthanide Triflates in Solution. Inorganic Chemistry, Vol. 49, No. 3, 2010 1255

Figure 2. Perspective view with numbering scheme of the molecular structure of L8 in the crystal structure of L8·3CHCl3. Ellipsoids are represented at the 50% probability level.

the first coordination sphere only occur for the single-stranded complexes $[\text{Ln}_2(L_7)]^{6+}$. Complementary $^{19}$F NMR data show a single signal for the counteranion CF$_3$SO$_3^-$ along the complete titrations, in line with either purely ionic behavior, or fast exchange in the first coordination sphere for both complexes. Very similar results are obtained for $L_8$ (Figures S8 and S9 and Table S4, Supporting Information), which establish the successive formation of the $D_2$-symmetrical double-stranded helicates $[\text{Ln}_2(L_8)]^{6+}$ followed by the planar $C_{2v}$-symmetrical complexes $[\text{Ln}_2(L_8)]^{6+}$. As expected, the treatment of $[\text{Ln}_2(L_8)]^{6+}$ with optically pure $\Delta$-Trisphat anion (6 equiv)$^{30}$ splits some aromatic $^1$H NMR signals (Figure S10, Supporting Information), which ultimately demonstrates the formation of equal quantities of the two

enantiomers of the $D_2$-symmetrical double-stranded helicate $\Delta,\Delta$-[L$_n$(L8)$_2$]$^{6+}$ and $\Lambda,\Lambda$-[L$_n$(L8)$_2$]$^{6+}$ in slow exchange on the NMR time scale. The formation of the alternative achiral $C_{2v}$-symmetrical side-by-side complex $\Delta,\Delta$-[L$_n$(L8)$_2$]$^{6+}$ (sometimes called mesocate) 31b can be thus excluded once and for all. The only remarkable difference between the complexation of L7 and L8 concerns the quantitative transformation of [L$_n$2(L7)$_2$]$^{6+}$ into [L$_n$2(L8)$_2$]$^{6+}$ for Ln:L8 = 2:1 for a total ligand concentration of 10 mM (Figure S9c, Supporting Information), while both complexes coexist in solution for L7 under the same conditions (Figure 3c).

The latter observation suggests different thermodynamic behaviors, which are unraveled by using spectrophotometric titrations of L7 or L8 (10$^{-4}$ M in CH$_2$Cl$_2$/CH$_3$CN 1:1) with Ln(CF$_3$SO$_3$)$_3$·xH$_2$O (Ln = La, Eu, Lu, Y; $x = 2$–4; Ln:Ln > 0.1–3.0; Figure 4). The variation of the absorption spectra, which mainly results from the electronic reorganization of the σ system upon trans,trans to cis,cis conformational change of the tridentate binding sites due to complexation to Ln(III), 32 systematically shows one pronounced end point for Ln:Lk = 1.0, followed by a smooth evolution for Ln:Lk > 1.0 (Figure 4). Factor analysis 33 indicates the interconversion of three absorbing species assigned to Lk, [L$_n$(Lk)$_2$]$^{6+}$, and [L$_n$(Lk)]$^{6+}$ in agreement with ESI-MS and NMR titrations. The global set of spectrophotometric data can be satisfyingly fitted with equilibrium (3) and (4) by using nonlinear least-squares techniques. 34 The associated cumulative stability constants $\beta_{2n,Lk}^{Ln}$ are collected in Table 1. 35

$$2Lk + 2[Ln(CH_3CN)_6]^{3+} = [Ln_2(Lk)_2(CH_3CN)_6]^{6+} + 12CH_3CN \quad \beta_{2,2}^{Ln,Lk}$$

(3)

$$Lk + 2[Ln(CH_3CN)_6]^{3+} = [Ln_2(Lk)(CH_3CN)]_{2}^{6+} + 6CH_3CN \quad \beta_{2,1}^{Ln,Lk}$$

(4)

For the all-nitrogen ligand L8, the calculated electronic absorption spectra of the complexes [L$_n$2(L8)$_2$]$^{6+}$ and [L$_n$(L8)]$^{6+}$ are sufficiently different for allowing acceptable noncorrelated values for $\beta_{2n,L8}^{Ln}$ and $\beta_{2n,L8}^{Ln}$, an assertion substantiated by the good match between direct integration of the experimental $^1$H NMR data recorded during titration at 10$^{-2}$ M and the computed speciation predicted by using the stability constants of Table 1 (entries 5 and 6 in Table 1 and Figure S11, Supporting Information). However, the situation is less favorable for L7, because the replacement of terminal benzimidazole groups with carboxamide units provides almost identical absorption spectra for [L$_n$2(L7)$_2$]$^{6+}$ and [L$_n$(L7)]$^{6+}$. Consequently, the fitted values obtained by spectrophotometry for $\beta_{2n,L7}^{Ln}$ and $\beta_{2n,L7}^{Ln}$ are strongly correlated and

Footnote 35: For the sake of simplicity when calculating symmetry numbers (Figure S13, Supporting Information), we consider that Ln(III) exists in acetonitrile strictly as the tricapped-trigonal-prismatic solvates [Ln(CH$_3$CN)$_6$]$^{3+}$, although it has been experimentally demonstrated that the main species in equilibrium for lanthanide triflate solutions in anhydrous acetonitrile are [Ln(OH)$_2$CH$_2$CN]$^{2+}$ and [Ln(OH)$_3$(CH$_3$CN)$_2$], see: Di Bernardo, P.; Choppin, G. R.; Portanova, R.; Zanonato, P. L. Inorg. Chim. Acta 1993, 207, 85–91. Alternative geometries have been considered, but the changes in symmetry numbers have very little effect on the final microscopic descriptors.
pseudoisosbestic points are indeed observed during the titration processes (Figure 4a). A detailed analysis of the nonlinear least-squares fit process shows that convergence is very sensitive to the values of $\beta_{2,2}^{L,7}$, which can be thus satisfactorily obtained from spectrophotometric data, but $\beta_{2,1}^{L,7}$ can be varied within a rather wide range without significantly influencing the fitting process. The comparison between direct integration of the experimental $^1$H NMR data recorded during titration at 10$^{-2}$ M (Figure S12a, Supporting Information) and the computed speciation obtained by using the stability constants of Table 1 (entries 2 and 3 in Table 1 and Figure S12b, Supporting Information) indeed shows considerable discrepancies. Fixing $\beta_{2,1}^{L,7}$ at their values obtained by spectrophotometry allows the fit of a second set of more reliable $\beta_{2,1}^{L,7}$ values by using the NMR data (entry 4 in Table 1), which eventually provides a very good match between experimental and computed speciations in the whole experimentally accessible concentration range (10$^{-4}$–10$^{-1}$ M; Figure S12c, Supporting Information). We are now in a position to reliably compare the stability constants found for the two different bis-tridentate ligands. First, $\beta_{2,1}^{L,7} \approx \beta_{2,1}^{L,8}$ obtained for the single-stranded binuclear complexes $[\text{Ln}_2(Lk)]^{6+}$ indicates that the intermolecular affinities of the tridentate N$_2$O or N$_3$ binding sites for Ln(III) are similar, as previously established by a thorough analysis of the triple-stranded helicates produced with ligands $\text{L1} - \text{L3}$.$^{9a,14}$ Second, $\beta_{2,2}^{L,7} > \beta_{2,2}^{L,8}$ (2 orders of magnitude) implies that the macrocyclization required for the formation of the double-stranded helicate is less favorable for the more bulky ligand $\text{L8}$, again in line with previous observations reported for related triple-stranded binuclear triple-stranded helicates fitted with the N$_2$O or N$_3$ binding units used in this work.$^{36}$ The different behavior between L7 and L8 is responsible for the concomitant observation of $[\text{Ln}_2(L7)]^{6+}$ and $[\text{Ln}_3(L7)]^{6+}$ complexes in solution by NMR for Ln :L7 = 2:1 (total ligand concentration 10$^{-2}$

Table 1. Experimental Cumulative Formation Constants log ($\beta_{2,1}^{L,7}$) ($k = 7, 8$) and log ($\beta_{2,2}^{L,7}$) ($k = 9, 10$) Obtained by Spectrophotometry According to Equilibria (3)-(4) and (7)-(9) for the Complexes $[\text{Ln}_2(Lk)]^{6+}$ ($k = 7, 8$) and $[\text{Ln}(Lk)]^{3+}$ ($k = 9, 10$; Ln = La, Eu, Y; $\text{CH}_3\text{CN}$, 298 K).

<table>
<thead>
<tr>
<th>Ln(III)</th>
<th>La</th>
<th>Eu</th>
<th>Y</th>
<th>Lu</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta_{2,2}^{La,L7}$</td>
<td>1.216</td>
<td>1.120</td>
<td>1.075</td>
<td>1.032</td>
</tr>
<tr>
<td>$\log \beta_{2,2}^{La,L7}$</td>
<td>18.74</td>
<td>19.46</td>
<td>19.76</td>
<td>19.69</td>
</tr>
<tr>
<td>$\log \beta_{2,1}^{La,L7}$</td>
<td>13.06</td>
<td>12.35</td>
<td>13.14</td>
<td>12.07</td>
</tr>
<tr>
<td>$\log \beta_{2,2}^{Eu,L7}$</td>
<td>11.53</td>
<td>11.03</td>
<td>11.23</td>
<td>11.03</td>
</tr>
<tr>
<td>$\log \beta_{2,1}^{Eu,L7}$</td>
<td>17.82</td>
<td>16.71</td>
<td>17.23</td>
<td>17.43</td>
</tr>
<tr>
<td>$\log \beta_{2,2}^{Eu,L8}$</td>
<td>12.01</td>
<td>10.91</td>
<td>11.28</td>
<td>11.23</td>
</tr>
<tr>
<td>$\log \beta_{2,1}^{Eu,L8}$</td>
<td>7.45</td>
<td>8.24</td>
<td>7.96</td>
<td>7.55</td>
</tr>
<tr>
<td>$\log \beta_{2,2}^{Y,L7}$</td>
<td>15.46</td>
<td>14.96</td>
<td>15.38</td>
<td>14.97</td>
</tr>
<tr>
<td>$\log \beta_{2,1}^{Y,L7}$</td>
<td>20.95</td>
<td>21.67</td>
<td>23.1</td>
<td>21.89</td>
</tr>
<tr>
<td>$\log \beta_{2,2}^{Y,L8}$</td>
<td>14.66</td>
<td>14.26</td>
<td>14.35</td>
<td>14.74</td>
</tr>
<tr>
<td>$\log \beta_{2,1}^{Y,L8}$</td>
<td>21.75</td>
<td>20.78</td>
<td>21.27</td>
<td>19.97</td>
</tr>
</tbody>
</table>

* Ionic radii for nine-coordinate trivalent lanthanides.$^{43}$

M; Figure 3c), while only $[\text{Ln}_3(L8)]^{6+}$ is detected under the same conditions (Figure S9c, Supporting Information). Finally, the most striking point concerns the nondetection of the saturated triple-stranded helicates $[\text{Ln}_2(Lk)]^{6+}$ ($k = 7, 8$) within the 10$^{-7}$–10$^{-4}$ M concentration range, although the latter complexes correspond to the only candidates satisfying simultaneously (i) the principle of maximum site occupancy and (ii) the principle of stereochemical matching.

### Thermodynamics, Effective Molarities, and Quantitative Deviations from the Standard Principles

Application of the site binding model (eq 2) to equilibria (3) and (4) gives eqs 5 and 6, in which a set of four different microscopic descriptors is involved ($f_{\text{Lk}}, u_{\text{Lk},\text{Lk}}, u_{\text{Lk},\text{Ln}}, u_{\text{Ln},\text{Ln}}$) and $\alpha_{\text{double}}$ with $k = 7, 8$; the statistical factors are calculated and reported in Figure S13 (Supporting Information).

$$
\beta_{2,2}^{Ln,Lk} = 72(f_{\text{Lk}}^{Ln})^4(u_{\text{Lk},\text{Lk}})^2(u_{\text{Lk},\text{Ln}})^2(u_{\text{Ln},\text{Ln}})^2(\alpha_{\text{double}}) (5)
$$

$$
\beta_{2,1}^{Ln,Lk} = 36(f_{\text{Lk}}^{Ln})^2(u_{\text{Ln},\text{Ln}}) (6)
$$

An elegant strategy for estimating experimental values for these parameters requires additional information obtained by the spectrophotometric determination of additional stability constants with ligands L9 and L10, which respectively possess tridentate N$_2$O and N$_3$ binding units identical with those found in L7 and L8 (Scheme 3, equilibrium 7–9, $k = 9, 10$, Table 1).

$$
\text{Lk} + [\text{Ln(CH}_3\text{CN)}_n]^{3+} \rightleftharpoons [\text{Ln(Lk)}]([\text{CH}_3\text{CN})_n]^{3+} + 3\text{CH}_3\text{CN} \beta_{1,n}^{\text{Lk,Lk}} (7)
$$

$$
2\text{Lk} + [\text{Ln(CH}_3\text{CN)}_n]^{3+} \rightleftharpoons [\text{Ln(Lk)}_2([\text{CH}_3\text{CN})_n]^{3+} + 6\text{CH}_3\text{CN} \beta_{1,2}^{\text{Lk,Lk}} (8)
$$

$$
3\text{Lk} + [\text{Ln(CH}_3\text{CN)}_n]^{3+} \rightleftharpoons [\text{Ln(Lk)}_3]^{3+} + 9\text{CH}_3\text{CN} \beta_{1,3}^{\text{Lk,Lk}} (9)
$$

Reasonably assuming that (i) a single average value for the intermetallic interaction ($\alpha_{\text{double}}$) is considered for

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[Ln$_2$(Lk)$_2$]$^{n+}$ and [Ln$_2$(Lk)$_3$]$^{n+}$, (ii) the absolute intermolecular affinities of the tridentate binding sites for Ln(III) ($f_{12}$) are identical for the L7/L9 ($f_{12} = f_{19} = f_{29}$) and L8/L10 ($f_{18} = f_{110} = f_{139}$) pairs, and (iii) so are the interligand interactions ($u_{2k,Ln} = u_{2k,Ln}$ and $u_{1k,Ln} = u_{1k,Ln}$, (37) the application of the site binding model to equbria 7–9 provides the six additional equations (10)–(15).

\[
\begin{align*}
\rho_{1,1}^{Ln,L9} &= 6f_{N2O} \quad (10) \\
\rho_{1,2}^{Ln,L9} &= 6(f_{N2O}^2 + 4f_{N2O,N2O}^2) \quad (11) \\
\rho_{1,3}^{Ln,L9} &= (f_{N2O}^3 + 4f_{N2O,N2O}^3) + 12(f_{N2O,N2O}^2 + f_{N2O,N2O}^2) \quad (12) \\
\rho_{1,1}^{Ln,L10} &= 6f_{N3} \quad (13) \\
\rho_{1,2}^{Ln,L10} &= 12(f_{N3}^2 + f_{N3,N3}^2) \quad (14) \\
\rho_{1,3}^{Ln,L10} &= 16(f_{N3}^3 + f_{N3,N3}^3) \quad (15)
\end{align*}
\]

The two parameters $u_{N2O,N2O}$ and $u_{N2O,N2O}$ in eqs 11 and 12 results from the lack of C$_2$ symmetry in L9. (38) which produces head-to-head (HH) or head-to-tail (HT) orientations when coordinated to the same metal ions. If we assume that there is no difference in energy between the two possible orientations, i.e. $u_{N2O,N2O} = u_{N2O,N2O}$, eqs 10–12 reduce to eqs 13–15 except for the replacement of $f_{N3}$ with $f_{N2O}$. Under these conditions, we expect purely entropic 1:1 ratios for HH-[Ln(L9)]$_{1+}$/HT-[Ln(L9)]$_{1+}$ and 1:3 ratios for HH-[Ln(L9)]$_{1+}$/HT-[Ln(L9)]$_{1+}$ isomers in solution, a distribution very close to the experimental speciations previously reported for these complexes in acetonitrile at 298 K. (39) Therefore, we finally performed simple multilinear least-squares fits of eqs 5, 6, and 13–15 (five equations) for each type of tridentate binding units (N$_2$O or N$_3$) in order to determine the two sets of four microscopic thermodynamic parameters collected in Table 2 and graphically shown in Figure 5.

First, the stability constant computed with eqs 5, 6, and 13–15 and using the microscopic parameters of Table 2 satisfyingly reproduce the experimental data (0.001 ≤ AF$_{Ln}$ ≤ 0.01). (39) Second, the interligand ($\Delta G_{inter}$) and intermetallic ({$\Delta E_{Ln,Ln}$}) interactions and the intermolecular connections $\Delta G_{inter} = -RT \ln f_{12}$ are very similar for both type of binding units (N$_2$O or N$_3$). Moreover, they do not significantly vary along the lanthanide series within experimental errors, as previously reported for the polynuclear triple-stranded helicates [Ln$_n$(Lk)$_3$]$^{n+}$. (39)

\(k = 1 – 3, m = 2 – 4\). (39) Though the interligand interactions are close to negligible (≤ $\Delta E_{k+}$ ≤ 6 kJ mol$^{-1}$), the average magnitude of the intermetallic interaction $\Delta E_{Ln,Ln} = 24(4)$ kJ mol$^{-1}$ found in [Ln$_2$(L7)]$^{n+}$ and [Ln$_2$(L8)]$^{n+}$ is much larger than $\Delta E_{Ln,Ln} = 4(1)$ kJ mol$^{-1}$ found for [Ln$_2$(L9)]$^{n+}$ (k = 1–3, m = 2–4) in acetonitrile, whereby the intermetallic distance amounts to 9 Å. (9a) Contrary to simple predictions solely based on the Coulomb equation, an increase in $\Delta E_{Ln,Ln}$ for solvated polynuclear helicates implies an increase in the intermetallic separation because of the reduction of the favorable free energies of solvation in larger molecular objects. (9b, 40) We thus predict that the Ln···Ln intrahelical distances significantly exceed 9 Å in [Ln$_2$(L7)]$^{n+}$ and [Ln$_2$(L8)]$^{n+}$. However, the most striking difference between the latter double-stranded helicates (n = 2) and the analogous triple-stranded complexes [Ln$_n$(Lk)$_3$]$^{n+}$ (k = 1–3, m = 2–4) relies on the minute values of the effect ive molarities (10$^{-6.3}$ ≤ EM$_{Ln,Ln}$ ≤ 10$^{-5.5}$ M and 10$^{-8}$ ≤ EM$_{Ln,Ln}$ ≤ 10$^{-6.6}$ M, Table 2), in comparison with the average values EM$_{Ln,Ln}$ = 10$^{-4.8}$ M previously estimated for the formation of multiple-stranded helicates [Ln$_n$(Lk)$_3$]$^{n+}$ (k = 1–3, m = 2–4; Figure 1a). (9a) We thus deduce that the replacement of the methylene spacer in L1 with a para-disubstituted phenyl ring in L7 and L8 reduces the preorganization for macrocyclization by 2–4 orders of magnitude, thus leading to intramolecular connection processes which are still significantly favorable for the N$_2$O binding units (10 ≤ $\Delta G_{intr}$ = -RT ln

Table 2. Fitted Microscopic Thermodynamic Parameters for [Ln$_n$(Lk)$_3$]$^{n+}$ (k = 7, 8, n = 1, 2) by Using Eqs 5, 6, and 13-15 (Ln = La, Eu, Y, Lu; CH$_2$Cl$_2$/CH$_3$CN 1:1, 298 K)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>La</th>
<th>Eu</th>
<th>Y</th>
<th>Lu</th>
</tr>
</thead>
<tbody>
<tr>
<td>AF$_{Ln}$</td>
<td>0.87</td>
<td>0.78</td>
<td>0.79</td>
<td>0.73</td>
</tr>
<tr>
<td>$\Delta G_{inter}$</td>
<td>-36.7</td>
<td>-35.2</td>
<td>-35.1</td>
<td>-35.4</td>
</tr>
<tr>
<td>$\Delta E_{Ln,Ln}$</td>
<td>24.4</td>
<td>24.1</td>
<td>23.2</td>
<td>23.9</td>
</tr>
<tr>
<td>$\Delta G_{intr}$</td>
<td>-10.4</td>
<td>-10.2</td>
<td>-10.3</td>
<td>-10.5</td>
</tr>
<tr>
<td>$\Delta E_{Ln,Ln}$</td>
<td>24.4</td>
<td>24.1</td>
<td>23.2</td>
<td>23.9</td>
</tr>
<tr>
<td>$\Delta G_{intr}$</td>
<td>-10.4</td>
<td>-10.2</td>
<td>-10.3</td>
<td>-10.5</td>
</tr>
<tr>
<td>$\Delta E_{Ln,Ln}$</td>
<td>24.4</td>
<td>24.1</td>
<td>23.2</td>
<td>23.9</td>
</tr>
<tr>
<td>$\Delta G_{intr}$</td>
<td>-10.4</td>
<td>-10.2</td>
<td>-10.3</td>
<td>-10.5</td>
</tr>
<tr>
<td>$\Delta E_{Ln,Ln}$</td>
<td>24.4</td>
<td>24.1</td>
<td>23.2</td>
<td>23.9</td>
</tr>
</tbody>
</table>

(37) The statistical factors for eqs (10)–(12) are derived in ref 16, and those for eqs (13)–(15) can be found in ref 20.


(39) Wilcott, M. R.; Lenkiski, R. E.; Davis, R. E. J. Am. Chem. Soc. 1972, 94, 1742–1744. AF$_{Ln}$ = [(\Sigma log $\rho_{Ln}^{N2O,N2O}$) – (\Sigma log $\rho_{Ln}^{N2O,N2O}$)]$^{1/2}$.


Article

(\frac{\Delta G_{\text{int}}}{R_T})_{\text{Ln},a} \leq -3 \text{ kJ mol}^{-1}; \text{Figure 5a}) but globally unfavorable for the N$_3$ binding units (\(-4 \leq \Delta G_{\text{int}} \leq -RT \ln(\beta_{\text{LD},a}) \leq +6 \text{ kJ mol}^{-1}; \text{Figure 5b}).

Once the microscopic thermodynamic parameters are at hand (Table 2), the stability of the missing saturated triple-stranded complexes [Ln$_2$(L)$_3$]$^{6+}$ (k = 7, 8, equilibrium 16) can be computed a posteriori with eq 17 (the statistical factors is calculated in Figure S13, Supporting Information):

$$3nk + 2[\text{Ln(CH$_3$CN)}_2]^{3+} \approx [\text{Ln}_2(\text{Lk})_3]^{6+} + 18\text{CH}_3\text{CN}$$

$$\beta_{\text{LD},a} = 96(\frac{\Delta G_{\text{int}}}{R_T})_{\text{Ln},a} \cdot (\frac{\Delta G_{\text{int}}}{R_T})_{\text{eff},a} \cdot (\frac{\Delta G_{\text{int}}}{R_T})_{\text{triple}}$$

As a first approximation, we can tentatively assume that the effective molarities for macrocyclization (i.e., transforming the single-stranded helicate [Ln$_2$(L)$_3$]$^{6+}$ into the double-stranded helicate [Ln$_2$(L)$_2$]$^{6+}$, EM$_\text{double}$) and for macrobirocyclization (i.e., transforming the double-stranded helicate [Ln$_2$(L)$_2$]$^{6+}$ into the triple-stranded helicate [Ln$_2$(L)$_3$]$^{6+}$, EM$_\text{triple}$) are comparable: EM$_\text{triple}$ \approx EM$_\text{double}$ (Table 3, entries 1 and 5). The introduction of the microscopic parameters of Table 2 into eq 17 thus predicts 25.4 \leq \log \beta_{\text{LD},a} \leq 28.3$ (Table 3, entry 2) and 21.2 \leq \log \beta_{\text{LD},a} \leq 23.0$ (Table 3, entry 6), which should result in the almost quantitative formation of the saturated triple-stranded helicate (for Ln:

The dotted lines are only guides for the eyes.

(Figure 5).

Figure 5. Plots of the four microscopic thermodynamic parameters in the form of free energies of interactions, in function of the inverse of nine-coordinate ionic radii for the assemblies of (a) [Ln$_{(L)}_9$]$^{1+}$ and [Ln$_{(L)}_7$]$^{1+}$ and (b) [Ln$_{(L)}_{10}$]$^{1+}$ and [Ln$_{(L)}_8$]$^{1+}$ (n = 1–3, p = 1, 2; 1:1 CH$_2$Cl$_2$/CH$_3$CN, 298 K). The dotted lines are only guides for the eyes.

(Figure 6).

Figure 6. Theoretical ligand speciation for the titration of L7 (10$^{-2}$ M in 1:1 CH$_2$Cl$_2$/CD$_3$CN) with La(CF$_3$SO$_3$)$_3$·4H$_2$O: (a) computed by using \(\log \beta_{\text{LD},a} \) estimated with EM$_\text{double}$ and (b) computed by using \(\log \beta_{\text{LD},a} \) estimated with EM$_\text{triple}$ (Table 3, entries 3 and 4).

\(\text{Lk} = 2:3\) during $^1$H NMR titration performed at 10$^{-2}$ M (Figure 6a and Figure S14a, Supporting Information), in complete disagreement with experimental data (Figures S4–S7 and S9, Supporting Information). Our tentative hypothesis is thus wrong, and the origin of this discrepancy can be assigned to EM$_\text{triple} \ll$ EM$_\text{double}$, which prevents the

Table 3. Values of log $\beta_{\text{LD},a}^{\text{Lk}}$ and log EM$_{\text{Lk}}$ for the Virtual Triple-Stranded Complexes [Ln$_2$(L)$_3$]$^{6+}$ (k = 7, 8) Computed by Using Eq 17 (Ln = La, Eu, Y, Lu; 1:1 CH$_2$Cl$_2$/CH$_3$CN, 298 K)

<table>
<thead>
<tr>
<th>Ligand L7: N$_2$O Binding Units</th>
<th>La</th>
<th>Eu</th>
<th>Y</th>
<th>Lu</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\log EM_{\text{double}})</td>
<td>(\log EM_{\text{triple}})</td>
<td>(\log EM_{\text{triple}})</td>
<td>(\log EM_{\text{triple}})</td>
<td>(\log EM_{\text{triple}})</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>6.3</td>
<td>-5.5</td>
<td>-6.2</td>
<td>-5.5</td>
<td></td>
</tr>
<tr>
<td>24.9</td>
<td>26.2</td>
<td>28.4</td>
<td>28.2</td>
<td></td>
</tr>
<tr>
<td>19.9</td>
<td>20.6</td>
<td>20.9</td>
<td>20.8</td>
<td></td>
</tr>
<tr>
<td>-11.3</td>
<td>-11.1</td>
<td>-13.7</td>
<td>-12.9</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Taken from Table 2. $^b$ Computed with eq 17 and data given in the previous row. $^c$ Maximum values estimated by using nonlinear least-squares simulation of the ligand speciation with the condition that the quantities of [Ln$_{(L)}_n$]$^{\text{a}}$ (k = 7, 8) in solution never exceed 5% of the ligand speciation for [Lk]$_{\text{tot}} = 10^{-2}$ M (see text and Figure 6b).
second intramolecular connection process to occur (i.e., the transformation of the double-stranded complexes into the triple-stranded helicates, Figure 7 and Figure S15, Supporting Information). Fixing a reasonable minimum limit for the $^{1}H$ NMR detection of $[Ln_{2}(L_{k})_{3}]^{6+}$ to 5% of the ligand speciation, we can estimate $21.2 \leq \log (\beta_{2,3}^{L_{7}}) \leq 23.0$ (Table 3, entry 3) and $17.9 \leq \log (\beta_{2,3}^{L_{8}}) \leq 19.0$ (Table 3, entry 7) by using nonlinear least-squares simulation of the ligand speciation in solution (Figure 6b and Figure S14b, Supporting Information), from which $10^{-13.7} \leq EM_{\text{triple}}^{L_{7}} \leq 10^{-11.1}$ M and $10^{-11.7} \leq EM_{\text{triple}}^{L_{8}} \leq 10^{-9.1}$ M can be calculated with eq 17 (Table 3, entries 4 and 8). The decrease by 3–6 orders of magnitude on going from $EM_{\text{double}}^{L_{k}}$ to $EM_{\text{triple}}^{L_{k}}$ is diagnostic for drastic enthalpic constraints originating from steric limitations encountered during ring closure, which eventually prevent the successive macrocyclization processes required for the formation of multiple-stranded helicates (Figure 7 and Figure S15, Supporting Information).

**The Ultimate Pieces of the Puzzle: Isolation and Structures of Double-Stranded Helicates in the Solid State.**

According to the speciations observed by $^{1}H$ NMR for titration of $L_{7}$ (Figure S12, Supporting Information) and $L_{8}$ (Figure S11, Supporting Information) at high concentrations (i.e., $[L_{k}]_{\text{tot}} = 10$ mM), the isolation of pure...
double-stranded helicates \([\text{Ln}_2(Lk)_2]^{6+}\) for \(\text{Ln:} Lk = 1.0\) is straightforward (yields 30–75%), as confirmed by the elemental analyses of the microcrystalline powders of \([\text{Ln}_2(Lk)_2](\text{CF}_3\text{SO}_3)_6 \cdot x\text{H}_2\text{O}\) (\(\text{Ln} = \text{La}, \text{Eu}, \text{Lu}, \text{Y}; k = 7, 8; x = 4–13]\); Table S5, Supporting Information). However, the observed mixtures of double-stranded \([\text{Ln}_2(Lk)_2]^{6+}\) and single-stranded \([\text{Ln}_2(Lk)]^{6+}\) for \(\text{Ln:} Lk = 2.0\) (Figures S11 and S12, Supporting Information) prevent the isolation of pure 2:1 complexes in the solid state with \(L_7\) (Table S5, Supporting Information). For \(L_8\), the minute effective molarities sufficiently destabilize the formation of the macrocyclic double-stranded helicates (Table 2), thus allowing the isolation of pure noncyclic single-stranded complexes \([\text{Ln}_2(L8)](\text{CF}_3\text{SO}_3)_6 \cdot x\text{H}_2\text{O}\) (\(\text{Ln:} Lk = 2.0\)) with the small lanthanides (\(\text{Ln} = \text{Y, Lu}\)). For the larger metals (\(\text{Ln} = \text{La}, \text{Eu}\)), contamination with 10–20% of \([\text{Ln}_2(L8)](\text{CF}_3\text{SO}_3)_4(\text{H}_2\text{O})_2\]2+ is unavoidable (Table S5, Supporting Information). Slow diffusion of tert-butyl methyl ether into a concentrated solution of \([\text{Lu}_2(L7)](\text{CF}_3\text{SO}_3)_6\) in acetonitrile gives fragile yellow X-ray-quality crystals of \([\text{Lu}_2(L7)](\text{CF}_3\text{SO}_3)_4(\text{H}_2\text{O})_2\]3\(\cdot\)3\(\text{CH}_3\text{CN}\) \(\cdot\)3\(\text{H}_2\text{O}\) (6). Due to the limited quality of the diffraction data (see the Experimental Section), we focus here on the shape and on the global metric of the binuclear double-stranded helical cation \([\text{Lu}_2(L7)](\text{CF}_3\text{SO}_3)_4\]2+, the solvent molecules and the two remaining ionic triflate anions being disordered. In agreement with \(^1\text{H}\) NMR data recorded in solution, the molecular structure of the cation shows the two ligands wrapped about a pseudo-2-fold axis passing through the two octa-coordinate Lu(III) atoms (Figure 8).

The Lu⋯Lu intrahelical distance of 13.26(2) \(\text{Å}\) greatly exceeds the 9.06(3) \(\text{Å}\) reported for the intermetallic separation in the triple-stranded helicate \([\text{Tb}_2(L1)]^{6+}\) and 9.05(3) \(\text{Å}\) found in the double-stranded side-by-side complex \([\text{Eu}_2(L1)](\text{CF}_3\text{SO}_3)_4(\text{H}_2\text{O})_2\]2+. This corresponds to a logical extension due to the replacement of the compact twisted methylene spacer in \(L_1\), with the larger linear \(p\)-phenyl in \(L_7\).

The main torsions in the ligand strands result from rotation about the interannular C–C bonds connecting the aromatic benzimidazole and phenyl rings, which are obtained at the expense of a reduced overlap between the aromatic \(\pi\) systems (interplanar angles = 33–42°; Table S6, Supporting Information). The helical arrangement of the two wrapped ligands thus produces a prolate ellipsoidal intermetallic cavity (occupied by one disordered water molecule; see the Experimental Section), with its long axis passing through the Lu atoms, while its short axis could be defined by the separation between the two central phenyl rings of the spacers (interplanar angle 7.2°, average interplanar distance 6.9 \(\text{Å}\); Table S6, Supporting Information). The geometrical characteristics of the double-stranded helix \([\text{Lu}_2(L7)](\text{CF}_3\text{SO}_3)_4\]2+ (total length \(L = 20.3\) \(\text{Å}\) for a total rotation of 1.15 turn, pitch \(P = 17.7\) \(\text{Å}/\)turn) are significantly different from those observed for the analogous, but triple-stranded helix \([\text{Tb}_2(L1)]^{6+}\) (total length \(L = 11.9\) \(\text{Å}\) for a total rotation of 0.81 turn, pitch \(P = 14.7\) \(\text{Å}/\)turn). However, we do

not detect strong constraints in the metallic coordination sphere, each Lu(III) atom being eight-coordinated by two tridentate N$_3$O binding units and by two monodentate triflate anions, thus forming slightly distorted dodecahedrons (Figure 8). The Lu–N and Lu–O bond lengths are standard (Table S6, Supporting Information), leading to ionic radii of R$_{\text{Lu-N}}$ = 0.97 Å and R$_{\text{Lu-O}}$ = 0.96 Å, which are close to the expected value for nonconstrained Lu(III) (0.977 Å).43

Conclusion

Inspired by the unusual crystal structures of lanthanide complexes with L$_5$ and L$_6$, in which the first coordination spheres are not saturated with tridentate binding units, we deliberately designed ligands L$_7$ and L$_8$ for investigating the thermodynamic parameters responsible for significant deviations from the principle of maximum site occupancy. The effective molarity EM, which contains both the enthalpic and entropic corrections required for transforming an intramolecular connection into its intramolecular counterpart (EM = $\Delta G_{\text{intral}}^{\text{m}} - \Delta G_{\text{intol}}^{\text{m}}$), indeed controls the number of favorable macrocyclization processes leading to stable oligomeric complexes. In L$_7$ and L$_8$, the rigid para-disubstituted phenyl spacer produces values for the effective molarities (EM$_{\text{triple}}$ = $10^{-8}$–$10^{-6}$ M, EM$_{\text{double}}$ = $10^{-3}$–$10^{-5}$ M) so low that intramolecular connections ($\Delta G_{\text{intral}}^{\text{m}} = \Delta G_{\text{intol}}^{\text{m}}$ – RT ln (EM$_{\text{triple}}$)) computed for standard state 1 M are only compatible with a single macrocyclization process and the assembly of the double-helicate complexes [Ln$_4$(L$_6$)$_2$]$^{2+}$ (k = 7, 8). The total lack of the triple-stranded helicates [Ln$_4$(L$_7$)$_2$]$^{2+}$ in solution, which however simultaneously satisfy the principle of maximum site occupancy and the principle of stereoechemical matching, can be thus eventually explained by the large decrease of EM for the second macrocyclization process (EM$_{\text{triple}}$ < EM$_{\text{double}}$). This phenomenon is probably at the origin of the discovery of several unexpected and often aesthetically appealing structures by serendipity, when constrained ligands with restricted degrees of freedoms are considered.8,19 Our results suggest that, except for some kinetically controlled interfaces of crystallization, which escape a thermodynamic rationalization, the manipulation and tuning of the effective molarities in coordination and supramolecular chemistry can be rationally exploited for better predicting the outcome of self-assembly processes without relying on chance and on statistics. As far as short-term applications are concerned, the deliberate design of systems displaying low values of EM are attractive for the preparation of stable single-stranded polynuclear lanthanide oligomers or polymers, for which the associated intermolecular complexation processes are easily amenable to thermodynamic modeling46 and predictions4 and to deliberate metal selection52 for the design of pure heterometallic f–f$^\pi$ luminescent complexes.53

Experimental Section

Chemicals were purchased from Fluka AG and Aldrich and used without further purification unless otherwise stated. The syntheses of the starting synthons 1 and 2 (Scheme 2) are described in the Supporting Information (Scheme S3). The ligands L$_9$ and L$_{10}$ were prepared according to literature procedures. The trifluoromethanesulfonate salts Ln(CF$_3$SO$_3$)$_3$·xH$_2$O were prepared from the corresponding oxide (Aldrich, 99.99%).44 The Ln content of the solid salt was determined by complexometric titrations with Triproline III (Merck) in the presence of urotropine and xylene orange.45 Acetonitrile and dichloromethane were distilled over calcium hydride. Silica gel plates Merck 60 F$_{254}$ were used for thin-layer chromatography (TLC), and Fluka silica gel 60 (0.04–0.063 mm) or Acros neutral activated alumina (0.050–0.200 mm) was used for preparative column chromatography.

Preparation of 3. To a cooled (0 °C, ice bath) 50 mL chloroform solution containing 1 (1.26 g, 3.73 mmol) and K$_2$CO$_3$ (0.77 g, 5.6 mmol) was slowly added phenyltriflimide (O-N(Tf)$_2$, 1.89 g, 5.48 mmol) in chloroform (40 mL) under an inert atmosphere. The resulting mixture was then refluxed for 20 h, diluted with dichloromethane (150 mL), and washed with aqueous half-saturated NH$_4$Cl (200 mL). The separated organic layer was dried (Na$_2$SO$_4$) and filtered and the solvent removed under reduced pressure to give a pale yellow oil. The crude material was then purified by column chromatography (silica gel, 98:2 CH$_2$Cl$_2$/CH$_3$OH to give 3 as a yellow viscous oil (1.73 g, 3.69 mmol, yield 99%).1 H NMR (CDCl$_3$; 400 MHz): 1.06 (t, J = 7 Hz, 3H), 1.27 (t, J = 7 Hz, 3H), 1.47 (t, J = 7 Hz, 3H), 3.53 (q, J = 7 Hz, 2H), 3.60 (q, J = 7 Hz, 2H), 4.77 (q, J = 7 Hz, 2H), 7.26 (dd, J = 9 Hz, J = 2.4 Hz, 1H), 7.8 (d, J = 9 Hz, 1H), 7.57 (d, J = 8 Hz, 1H), 7.74 (d, J = 2 Hz, 1H), 7.97 (t, J = 8 Hz, 1H), 8.38 (d, J = 8 Hz, 1H). ESI-MS: m/z 470.5 ([M$^+$ + H]$^+$), 941.7 ([2M$^+$ + H]$^+$).

Preparation of 4. To a cooled (0 °C, ice bath) 50 mL chloroform solution containing 2 (3.0 g, 7.8 mmol) and K$_2$CO$_3$ (1.52 g, 11.0 mmol) was slowly added phenyltriflimide (O-N(Tf)$_2$, 3.9 g, 10.9 mmol) in chloroform (25 mL) under an inert atmosphere. The resulting mixture was then refluxed for 6 h, diluted with dichloromethane (300 mL), and washed with aqueous half-saturated NH$_4$Cl (200 mL). The separated organic layer was dried (Na$_2$SO$_4$) and filtered and the solvent removed under reduced pressure to give a pale yellow oil. The crude material was then purified by column chromatography (silica gel, 100:0 → 99:1 CH$_2$Cl$_2$/CH$_3$OH) to give 4 as a yellow viscous oil (4.0 g, 7.8 mmol, yield 100%).1 H NMR (CDCl$_3$; 400 MHz): 0.1 39 (t, J = 7 Hz, 3H), 1.40 (t, J = 7 Hz, 3H), 4.80 (q, J = 7 Hz, 2H), 4.83 (q, J = 7 Hz, 2H), 7.31 (dd, J = 9 Hz, J = 2 Hz, 1H), 7.47 (d, J = 9 Hz, 1H), 7.52 (d, J = 9 Hz, 1H), 7.70 (d, J = 7 Hz, 1H), 7.89 (d, J = 8 Hz, 1H), 8.09 (J = 8 Hz, 1H), 8.35 (d, J = 8 Hz, 1H), 8.40 (d, J = 8 Hz, 1H). ESI-MS: m/z 516.5 ([M$^+$ + H]$^+$), 1031.6 ([2M$^+$ + H]$^+$).

Preparation of 5. A 20 mL THF solution of 1,4-dibromobenzene (4.72 g, 20 mmol) was added dropwise to a suspension of magnesium shavings (1.06 g, 43.6 mmol) in dry THF (10 mL) under an inert atmosphere. The mixture was refluxed for 24–48 h until a gray precipitate appeared. Trimethylborate (5 mL, 4.66 g, 44.8 mmol) in THF (50 mL) was added and the mixture refluxed for 2 h. The white gel was poured onto aqueous hydrochloric acid (2 M, 200 mL) and stirred for 1 h at room temperature. The clear solution was extracted with diethyl ether (4 × 200 mL), and the combined organic phases were dried (Na$_2$SO$_4$), filtered, and evaporated to dryness. Recrystallization from hot water (200 mL) gave 5 as transparent crystals (1.6 g, 9.6 mmol, 48%).1 H NMR (d$_6$-acetone; 400 MHz): δ 7.86 (s, 4H), 7.13 (s, 4H). ESI-MS (negative mode/CH$_2$OH): m/z 165.3 ([M – H]$^-$).

Preparation of L$_7$. Compounds 3 (0.94 g, 2.0 mmol) and 5 (166 mg, 1.0 mmol) were dissolved in degassed dioxane/ethanol (30 mL/20 mL) containing cesium fluoride (610 mg, 4.0 mmol)
under an inert atmosphere. The Pt(PPh3)4 catalyst (100 mg, 0.09 mmol) was added, and the resulting dark solution was stirred for 20 min at room temperature and finally refluxed for 24 h. After evaporation to dryness, the solid residue was partitioned between dichloromethane and aqueous half-saturated NaCl (150 mL/200 mL). The aqueous phase was separated and extracted with dichloromethane (200 mL), and the combined organic phases were dried (Na2SO4), filtered, and evaporated to dryness. The crude brown solid was purified by column chromatography (silica gel, 99.5:0.5 → 96:5:3:0.5 CH2Cl2/CH3OH/NEt3) to give a pale yellow solid, which was recrystallized from dichloromethane/methanol to eventually provide L8 as a microcrystalline yellow powder (0.5 g, 0.68 mmol, yield 68%).

1H NMR (CDCl3; 400 MHz): δ 1.08 (t, J = 7 Hz, 6H), 1.29 (t, J = 7.1 Hz, 6H), 1.51 (t, J = 7.1 Hz, 4H), 3.62 (q, J = 7.1 Hz, 4H), 4.85 (q, J = 7 Hz, 4H), 7.53 (d, J = 8.6 Hz, 2H), 7.56 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 8.2 Hz, 2H), 7.78 (s, 4H), 7.96 (t, 3H), 3.36 (q, J = 8 Hz, 2H), 8.18 (d, 4H). ESI-MS: m/z = 360.6 ([L7 + 2H]+).

Preparation of L8. Compounds 4 (1.3 g, 2.61 mmol) and 5 (216 mg, 1.30 mmol) were dissolved in degassed dioxane/ethanol (30 mL/20 mL) containing cesium fluoride (1 g, 6.58 mmol) under an inert atmosphere. The Pt(PPh3)4 catalyst (150 mg, 0.13 mmol) was added, and the resulting dark solution was stirred for 20 min at room temperature and finally refluxed for 4 h. After evaporation to dryness, the solid residue was partitioned between dichloromethane and aqueous half-saturated NaCl (150 mL/200 mL). The aqueous phase was separated and extracted with dichloromethane (200 mL), and the combined organic phases were dried (Na2SO4), filtered, and evaporated to dryness. The crude brown solid was purified by column chromatography (silica gel, 99.5:0.5 → 96:5:3:0.5 CH2Cl2/CH3OH/NEt3) to give a pale yellow solid, which was recrystallized from dichloromethane/methanol to eventually provide L8 as a microcrystalline yellow powder (0.76 g, 0.92 mmol, yield 70%). X-ray-quality prisms of L8·3CHCl3 were obtained by slow diffusion of hexane into a concentrated solution of L8·3CHCl3 in acetonitrile (1 mL). The resulting clear solutions were stirred for 1 h and filtered, and microcrystalline powders were deposited upon slow diffusion of diethyl ether. The resulting solids were collected by filtration and dried in vacuo to give [L8(L)](CF3SO3)4·3CHCl3·3CH3CN·3H2O (x = 4, 5; 28 μmol for 2:2 complexes and 56 μmol for 2:1 complexes) in acetonitrile (1 mL). The resulting clear solutions were stirred for 1 h and filtered, and microcrystalline powders were deposited upon slow diffusion of diethyl ether. The resulting solids were collected by filtration and dried in vacuo to give [La(L8)](CF3SO3)4·xH2O (x = 1–13; Table S5). Spectroscopic Measurements. Spectrophotometric titrations were performed with a J&M diode array spectrometer (Tidas series) connected to an external computer. In a typical experiment, 50 mL of ligand in 1:1 CH2Cl2/CH3CN (10−4 M) was titrated at 298 K with a solution of Ln(OTf)3·xH2O (10−3 M) in 1:1 CH2Cl2/CH3CN under an inert atmosphere. After each addition of 0.2 mL, the absorbance was recorded using Hellma optrodes (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.134 H, 19F, and 13C NMR spectra were recorded at 298 K on Bruker Avance 400 MHz and Bruker DRX 500 MHz spectrometers. Chemical shifts are given in ppm with respect to TMS. Pneumatically assisted electrospary (ESI-MS) mass spectra were recorded from 10−4 M solutions on an Applied Biosystems API 150EX LC/MS system equipped with a Turbo Ionspray source. Least-squares fits were performed with Excel. Elemental analyses were performed by Dr. H. Eder from the Microchemical Laboratory of the University of Geneva.

X-ray Crystallography. A summary of crystal data, intensity measurements, and structure refinements for S6, L8·3CHCl3, and [Lu(L7)]3(CF3SO3)4·CH3CN·3H2O (6) are collected in Table S7 (Supporting Information). 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 calculations were performed with ShelX97 (47) and ShelXL97 (48). XTAL (S6) systems, and ORTEP49 programs. CCDC-753961 and 753962 contain the supplementary crystallographic data for S6 and L8·3CHCl3, respectively. The CIF files can be obtained free of charge via ccdc.cam.ac.uk or retrieved from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax (+44) 1223-336-033, e-mail deposit@ccdc.cam.ac.uk. The CIF file of [Lu(L7)]3(CF3SO3)4·CH3CN·3H2O (6) is given in the Supporting Information.

Comments on the Crystal Structure of S6. All non-hydrogen atoms (20) were refined with anisotropic atomic displacement parameters. Except for the hydrogen atoms of the methyl group C8 (refined with restriction on bond angles and bond angles), all other coordinates of hydrogen atoms were calculated.

Comments on the Crystal Structure of L8·3CHCl3. All non-hydrogen atoms (74) were refined with anisotropic atomic displacement parameters. The hydrogen atoms were observed and refined with isotropic atomic displacement parameters. The maximum residual electron density was located in the vicinity of the disordered chloroform molecule, while the two other solvent molecules did not show significant disorder.

Comments on the Crystal Structure of [L8(L7)]3(CF3SO3)4·CH3CN·3H2O (6). The double-stranded cationic complexes [L8(L7)]3(CF3SO3)4·CH3CN·3H2O (6) were arranged in polymer-like chains along the direction of their helical axis, via short contact interactions involving the two disordered ionic triadine anions. These chains were further packed into parallel planes and separated by large voids filled with highly disordered solvent molecules (Figure S16, Supporting Information). This mainly explained the very poor quality of the best diffraction data that we were able to obtain. We performed “SQUEEZE”.

calculations, and the final refinements were performed using the resulting “solvent-free” $F_o^2$ data (details given in the associated CIF file). The residual disorder and the poor quality of the data were not compatible with deposition of this crystal structure in the CCDC database, but its importance for the ultimate confirmation of the global double-stranded helical structure adopted by the binuclear lanthanide complexes was crucial for this contribution. The 12 terminal ethyl groups were refined isotropically. Hydrogen atoms were calculated and constrained for bond lengths and bond angles. The triflate units were refined isotropically with restraints on bond lengths and bond angles, except for one triflate (S1TC1T) coordinated to Lu1, which was refined without restraints. One triflate, coordinated to Lu1, displayed positional disorder and was refined on two different sites (population parameters: PP = 0.47/0.53). The coordinated oxygen atoms of these triflate anions (O10P and O10T) were almost superimposed and did not distort the coordination polyhedra around Lu1. Two ionic triflates were located on special positions and were disordered about inversion centers, each accounting for 0.5 anion. The second ionic triflate showed quite large $U_{iso}$ values, but attempts to refine it on different sites increased the number of refined parameters without significantly improving the quality of the fit. Three interstitial water molecules were found from the residual electronic density map, two of them displaying large $U_{iso}$ values. We noticed the presence of one water molecule in the cavity inside the helical complex, located between the approximately parallel phenyl rings. The distances between encapsulated $O_{water}$ and the two centroids of these phenyl ring centroids were $\sim 3.5\AA$.

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**Supporting Information Available:** Geometric parameters and crystal data for the crystal structures of S6, L8·3CHCl₃, and [Lu₂(L₇)₂(CF₃SO₃)₃]·(CF₃SO₃)₂·CH₃CN·3H₂O (6) (Tables S1, S2, S6, and S7, Figures S2, S3, and S16, and CIF files), $^1$H NMR data (Tables S3 and S4 and Figures S4–S10), elemental analysis data (Table S5), experimental synthetic procedures for S6 (Scheme S1) and for synthons 1 and 2 (Scheme 3), illustration of previous self-assembly of unsaturated helicates (Figure S1) and representation of conformational isomers (Scheme S2), species distribution curves (Figures S11, S12, and S14) and statistical factors (Figure S13), and the thermodynamic self-assembly process of [Lu₂(L₈)₆]$^{14+}$ (Figure S15). This material is available free of charge via the Internet at http://pubs.acs.org.