Supramolecular Chemistry

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Multiple Lanthanide Helicate Clusters and the Effects of Anions on Their Configuration**

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Helices are the central structural motif in biological molecules.[1] Except for some familiar helices (single, double, and triple), the plasmid DNA has a cyclic structure,[2] and the biologically significant multi-stranded nucleic acid configuration is quadruplex.[3] Helices and circular helices have been fundamental topological targets for chemical synthesis for the past two decades, and much effort has been made in the design and synthesis of artificial helical molecules.[4] Helical–metal coordination compounds (helicates), have been extensively investigated;[5] however, the formation of the cyclic helicate, a higher nuclearity variant of the helicate, is conversely less well understood.[6] Controlling the structure of assemblies of helicates is one of the leading challenges for supramolecular chemists. The ingenuity of Lehn and coworkers occupies a prominent position, and they have reported a series of helicates/circular helicates, leading to further improvements in this field.[7] Although this challenging task has been quite successfully accomplished with transition metals,[8] the polynuclear helicates with lanthanides have not been developed to such an extent because of the fact that trivalent lanthanide ions display high kinetic lability and a lack of stereochemical preference.[9] Despite some evolution, the ability to predict and control supramolecular assembly is seriously restricted by the bewildering structure-directing factors;[10] in particular, the anion-controlled self-assembly of lanthanide helicates is rare.

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Furthermore, it is necessary to investigate nitrates because of the importance of nitrate ions in environmental and biological systems. Primary nitrate response is the best known nitrate-induced response, in which genes encoding the nitrate assimilatory enzymes and nitrate transporters are rapidly induced by nitrate; moreover, transcriptomic studies have indicated that many other genes for diverse biological processes, including amino acid and nucleic acid metabolism, protein folding, RNA processing, and hormone biosynthesis, could also be rapidly induced or repressed by nitrate.[11]

Herein, we discuss the design and synthesis of a flexible dentate-bridging ligand, $H_2\mathbf{L}$, which has two amide-containing NO_3 tetradentate chelators positioned at the two termini (Figure 1). This linear amide-containing ligand is highly effective in the construction of supramolecular lanthanide complexes. The self-assembly process depends strongly on anion templates, tetrahedral ClO_4^- and trigonal-planar NO_3^- anions, to induce the formation of novel hexanuclear lanthanum circular helicate and tetranuclear quadruple-stranded helicate complexes, respectively. Moreover, the lanthanum complexes dynamically converted from a circular helicate structure into a quadruple-stranded helicate structure upon NO_3^- anion stimulus, which suggests that NO_3^- is the more potent structure regulator.

Adding a solution of $La(ClO_4)_3{\cdot}6H_2O$ in methanol to a light yellow and transparent solution of $H_2\mathbf{L}$ and LiOH (2 equiv) in methanol led to the formation of $[La_6\mathbf{L}_6(CH_3O)_3(CH_3OH)_3](ClO_4)_3$ (**1**). Brown rhombohedral crystals of **1**, which were suitable for X-ray diffraction analysis, were obtained in good yield by slow evaporation of the solution in air over four weeks. X-ray crystallographic studies revealed that the crystal belongs to the monoclinic space group *C*2/*c*.

Perchlorate complex **1** consists of a cationic cyclic helicate $[La_6\mathbf{L}_6(CH_3O)_3(CH_3OH)_3]^{3+}$ (Figure 1a, right), and three ClO_4^- counter anions. In the asymmetric unit, each La^{III} ion is coordinated with three salicylaldehyde–hydrazone domains from three different ligands, three methanol molecules bridge La1–La6, La2–La3, and La4–La5, whereas La1, La3, and La5 are coordinated with three additional deprotonated methanol molecules. Consequently, La1, La3, and La5 are ten-coordinate and lie in a slightly distorted bicapped square antiprism coordination environment (La–N: 2.559(4)–2.826(4) Å, La–O: 2.193(3)–2.916(3) Å), whereas the other three (La2, La4, La6) are nine-coordinate and the coordination polyhedras can be described as slightly distorted monocapped square antiprisms. The six deprotonated ligands wrapped around six La^{III} ions yield a cyclic helicate structure with a charged central cave. As can be seen in Figure 1a, left (see also the Supporting Information, Table S3), the two ClO_4^- anions

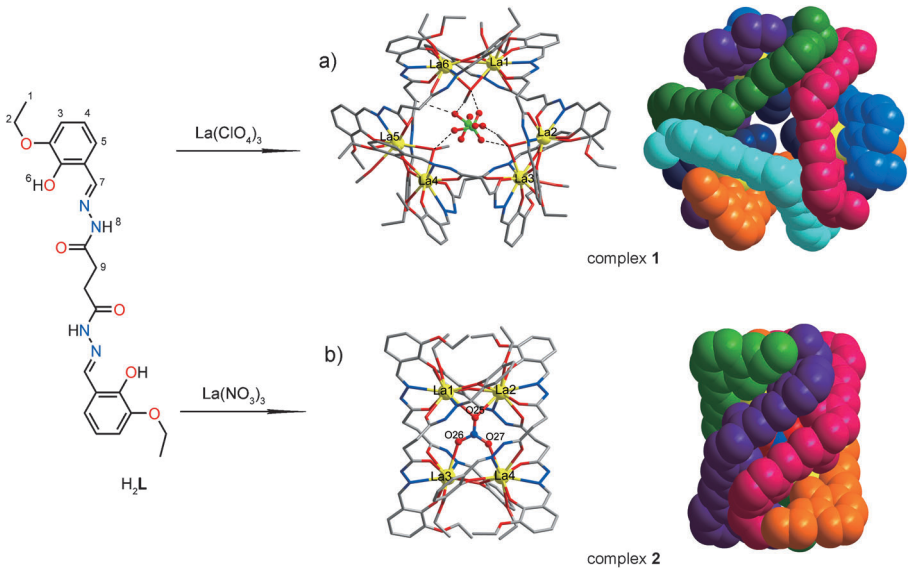

Figure 1. Anion templated assembly of circular helicate and quadruple-stranded helicate structures. a) Crystal structure of **1**: ball-and-stick model with the ClO_4^- ion shown (left; Cl green, La yellow, N blue, O red) and space-filling modeln (right). In the space filling model, each ligand is shown in a different color, with the lanthanum ions represented by yellow spheres and coordinated CH_3O^- and CH_3OH in dark blue. b) Crystal structure of **2**: ball-and-stick model (left; La yellow, N blue, O red) with the NO_3^- ion shown, and space-filling model (right) . In the space filling model, each ligand is shown in a different color, with the lanthanum ions represented by yellow spheres. Hydrogen atoms, external counteranions, and solvent molecules are omitted for clarity.

occupy the center of the helix and interact with three coordinated MeOH molecules and a ligand through three O–H···O and three C–H···O hydrogen bonds with the following properties: O···O distances 2.727(4)–3.148(4) Å (average 2.962 Å), O–H···O angles 145.0–156.0° (average 151.0°); C···O distances 3.111(4)–3.171(4) Å (average 3.137 Å), C–H···O angles 120.0–132.0° (average 124.7°). To the best of our knowledge, complex **1** is the first example of a hexanuclear lanthanide cyclic helicate.

Using $La(NO_3)_3{\cdot}6H_2O$ in the synthetic procedure gave $[La_4\mathbf{L}_4(NO_3)](NO_3)_3$ (**2**), which crystallizes in the monoclinic space group $P2_1/n$. The $[La_4\mathbf{L}_4(NO_3)]^{3+}$ cation is comprised of four lanthanum ions together with four deprotonated ligands and a nitrate anion, which forms a complete supramolecular cluster (Figure 1b). Each La^{III} ion is nine-coordinated and surrounded by two nitrogen atoms together with seven oxygen atoms, coming from three $\mathbf{L}^{2-}$ and the NO_3^- encapsulated in the center (La–N: 2.706(6)–2.769(6) Å, La–O: 2.302(5)–2.818(5) Å). Thus, the coordination polyhedra around the four lanthanum ions are slightly distorted monocapped square antiprisms. Four La^{III} ions form a twisted rectangle (Figure S4), instead of arranging in an aligned fashion to form the linear tetranuclear helicates as previously reported,[12] and four deprotonated ligands wrap around the four La^{III} ions in a helical fashion, resulting in the formation of a tetranuclear quadruple-stranded helicate structure. This arrangement has, to the best of our knowledge, not been previously reported.

Another important feature of this structure is the encapsulated distorted NO_3^- anion at the center of the cage; the anion uses oxygen atoms coordinated to the inner lanthanum ions in a μ_4-η^1:η^1:η^2 bridging mode (Figure 1b, left). The symmetry of cluster **2** forces the NO_3^- ligands to lie in a peculiar hexagonal architecture, with the oxygen atoms (O25, O26, O27) in the nitrate ligand each disordered over two sites with 50% occupancy factors, and consequently, nitrate templates the formation of cyclic hexagonal arrangements.[13] The presence of NO_3^- anions is critically important, and they serve as the nucleation site for the formation of $[La_4\mathbf{L}_4(NO_3)]^{3+}$ clusters.

High-resolution electrospray ionization mass spectra (HRESI-MS) of **1** and **2** were measured to provide evidence for the formation of stable hexanuclear lanthanum cyclic helicate and tetranuclear quadruple-stranded helicate structures in solution. The presence of the intense peaks at $m/z = 918.5907$ and $m/z = 942.6085$ with isotopic distribution patterns separated by (0.25 ± 0.005) Da in the HRESI-MS of **1**, demonstrated the presence of positively charged species $[La_6\mathbf{L}_6(ClO_4)_2]^{4+}$ and $[La_6\mathbf{L}_6(ClO_4)_2(CH_3OH)_3]^{4+}$, respectively; their isotopic distributions were in good agreement with theoretical expectations, and indicated the successful assembly of a similar La-based $M_6\mathbf{L}_6$ molecular circular helicate in solution (Figure S5a). The mass spectrum of assembly **2** showed $[La_4\mathbf{L}_4(NO_3)]^{3+}$ and $[La_4\mathbf{L}_4(NO_3)–H]^{2+}$ peaks at $m/z = 793.0986$ and $m/z = 1189.1423$, with the isotopic distribution patterns separated by a distance of (0.33 ± 0.005)–(0.5 ± 0.005) Da, which is in good agreement with the theoretical isotopic distribution (Figure S5b).

The different conformations induced by different anions suggest that the anion template plays a leading role during the self-assembly process. When a nitrate salt, such as $(TBA)NO_3$ (TBA = tetrabutylammonium), $NaNO_3$, or NH_4NO_3, was added to the methanol solution of **1**, the quadruple-stranded helicate **2** was obtained and confirmed by X-ray diffraction analysis, thus indicating that **1** changed into **2** when induced by the NO_3^- template (Figure 2). The IR spectra of $H_2\mathbf{L}$, **1**, **2**, and $\mathbf{1} + NO_3^-$ are shown in Figure S6. Strong new peaks are observed at 1143, 1113, 1090, and 631 cm^{-1} in **1**, which are attributed to the asymmetric and symmetric stretching frequencies of ClO_4^-. Whereas strong nitrate-based vibrations at approximately 1385 cm^{-1} were observed in **2** and $\mathbf{1} + NO_3^-$, which are different from the ligand.[14] The presence of the coordinating NO_3^- ion in $\mathbf{1} + NO_3^-$ was further confirmed by solid-state ^{15}N NMR spectroscopy, which shows one low-intensity peak at $\delta = 368.25$ ppm that can be assigned to the encapsulated NO_3^- ion (Figure S11). Further evidence for the templating effect of NO_3^- was examined; when other anions, including $(TBA)H_2PO_4$, (TBA)AcO (Ac = acetyl), $(TBA)HCO_3$, $(TBA)HSO_4$,

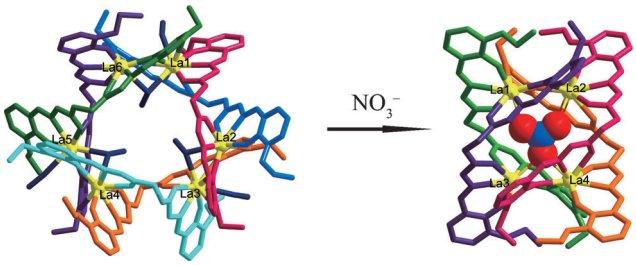

Figure 2. Conversion from **1** into **2**.

(TBA)F, (TBA)Cl, (TBA)Br, and (TBA)I, were added into a methanol solution of **2**, only the quadruple-stranded helicate crystallized. This reveals strong specific binding of the complexes with NO_3^- in methanol solution.

The fact that the composition changes based on the presence of NO_3^- anions was confirmed by ^{1}H NMR studies. The ^{1}H NMR spectrum of a methanol solution of $[La_6\mathbf{L}_6(CH_3O)_3(CH_3OH)_3](ClO_4)_3$ in CD_3OD (Figure 3a) shows the presence of one major set of 13 signals, which are assigned to the protons of the six ligands, whereas $[La_4\mathbf{L}_4(NO_3)](NO_3)_3$ shows the presence of one major set of 21 signals (Figure 3c). The addition of 0.17–0.67 equiv of $NaNO_3$ to the 1.26 mM

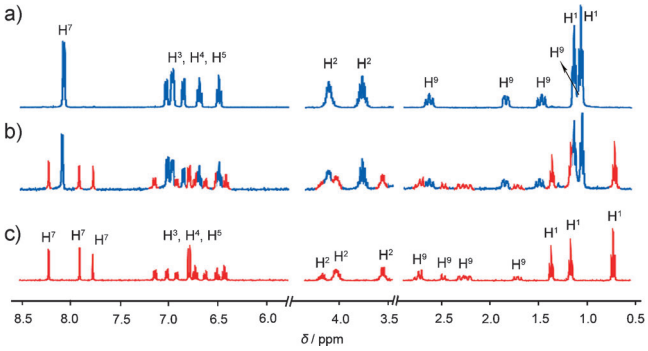

Figure 3. Partial ^{1}H NMR ([D$_4$]MeOH, 600 MHz) spectra. a) Complex **1**. b) $NaNO_3$ (0.33 equiv) in a solution of complex **1** (1.26 mM, NO_3^-/ClO_4^- 1:1) at 298 K for 4 d. c) Complex **2**.

solution of **1** (NO_3^-/ClO_4^- 1:2–2:1) in CD_3OD resulted in the progressive disappearance of the NMR signals assigned to **1** and to the appearance of the signals assigned to **2** (Figure S10). The addition of excess $NaNO_3$ led to the crystallization of $[La_4\mathbf{L}_4(NO_3)](NO_3)_3$, and did not lead to the formation of additional species (Figure S10d), which suggests that the quadruple-stranded helicate is the only thermodynamically favored assembly in solution.

In conclusion, we have successfully designed and synthesized the first examples of hexanuclear circular helicate, and quadruple-stranded helicate lanthanide complexes by employing a butanedihydrazide-bridged bis(3-ethoxysalicylaldehyde) ligand ($H_2\mathbf{L}$) and lanthanide ions. Interestingly, the lanthanide complexes can adjust the different structures of the product, owing to the different anion templates. In the presence of the larger tetrahedral anion ClO_4^-, the larger circular helicate is favored; in contrast, the smaller trigonal-planar geometry and stronger coordination effect of the NO_3^- anion leads to the compact quadruple-stranded helicate. The size, shape, and binding modes of the anions are the key factors that determine the stereochemistry of the product. The transformation of the configuration from circular helicate to quadruple-stranded helicate was also achieved by the addition of NO_3^- anions, which suggests that NO_3^- is the more potent structure regulator. We are in the process of evaluating the properties of these complexes and developing related f-based helical structures.

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