

Olive-Shaped Chiral Supramolecules: Simultaneous Self-Assembly of Heptameric Lanthanum Clusters and Carbon Dioxide Fixation**

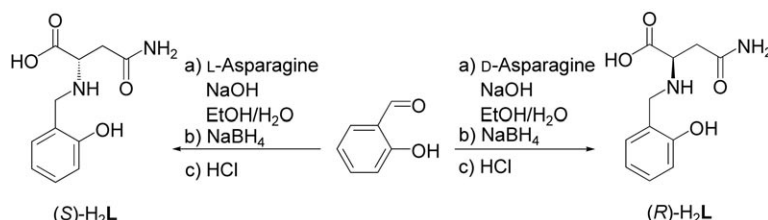
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Lanthanide-based high-nuclearity clusters have received considerable attention because of their fascinating self-assembled structures and potential applications in magnetic, optical, electronic, and catalytic processes.^[1,2] More and more geometrically intriguing supramolecules, for example, molecular polygons,^[3] cages,^[4] helicates,^[5] wheel-shaped clusters,^[6] and polynuclear clusters with different numbers of lanthanide ions^[7] have been successfully obtained, which may ultimately extend the range of new materials.^[2] However, the precise prediction and control of such lanthanide polynuclear clusters needs to be explored further because of the variable and high (8, 9, or more) coordination numbers that can exist, as well as the weak stereochemical preferences of lanthanide ions.^[2d,8] Moreover, cell-like heptanuclear lanthanide clusters that can effectively fix carbon dioxide under mild conditions have not been reported to date.

There has been a long-standing interest in the capture, fixation, and activation of CO₂ for the chemical conversion of CO₂ into various carbonates, formic acid, and other C₁ feedstock chemicals.^[9] Part of such work has dealt with the insertion of CO₂ from the atmosphere, particularly into coordination complexes as the carbonate anion.^[10] Several Zn^{II}, Cu^{II}, and Ni^{II} complexes are well known to perform this reaction, which results in the different bridging modes of the CO₃²⁻ ion.^[11] Despite intensive studies, the only example of CO₂ insertion into lanthanide complexes to date was reported by Jeong et al., and comprises a pair of lanthanide-based polynuclear clusters that are associated with CO₃²⁻ ions at high temperature.^[12b] In this class of

complexes, the CO₃²⁻ ion adopts a rare bridging mode and is incorporated into a triangular arrangement of lanthanides. However, the design and synthesis of these extended lanthanide complexes still represent a formidable challenge.^[10,12]

We have investigated the reaction of chiral amino acids with a variety of lanthanide salts. As multidentate ligands, two enantiomorphous amino acid containing reduced Schiff bases, (R)-H₂L and (S)-H₂L in optically pure form (Scheme 1) not only retain the chirality of the amino acids but also show improved metal-bridging capability. We report herein a pair of unique enantiopure heptanuclear lanthanide clusters, which are self-assembled with the aid of CO₃²⁻ ions and



Scheme 1. Preparation of ligands (S)-H₂L and (R)-H₂L.

possess olive-shaped nanostructures, by a one-step growth process under mild conditions. In addition, the overall structure of the chiral ligands in the cluster represents a new class of homochiral triple helix.

The clusters were synthesized by the addition of a solution of La(NO₃)₃·6H₂O in methanol to a transparent solution of (S)-H₂L and two equivalents of Li(OH)·H₂O in methanol. Colorless rhombohedral crystals of [La₇{(S)-L}₆(CO₃)(NO₃)₆(OCH₃)(CH₃OH)₇]:2CH₃OH·5H₂O (**1**) suitable for X-ray diffraction were obtained in good yield by slow evaporation of the solution in air over two weeks. X-ray crystallographic studies revealed that the crystal belongs to the monoclinic space group *P*2₁.^[13] The asymmetric unit, [La₇{(S)-L}₆(CO₃)(NO₃)₆(OCH₃)(CH₃OH)₇], which contains seven La^{III} ions and six (S)-L²⁻ linking ligands, forms a complete supramolecular cluster (Figure 1 a).

In the cluster, which has five La^{III} ions as apexes, La(2) ... La(6) form an elongated trigonal bipyramid with La ... La distances that range between 5.063 Å and 5.304 Å. La(2) and La(6) occupy the axial sites of the bipyramid and the rest lie in the equatorial plane. The other two La^{III} ions, La(1) and La(7), are symmetrically located on the axis at both sides of the trigonal bipyramid. The distances La(1) ... La(2) and La(6) ... La(7) are 3.768 Å and 3.763 Å, respectively. Thus, seven La^{III} ions extend over a trigonal bipyramidal geometry and are linearly arranged in the mode 1:1:3:1:1 to form an olive-

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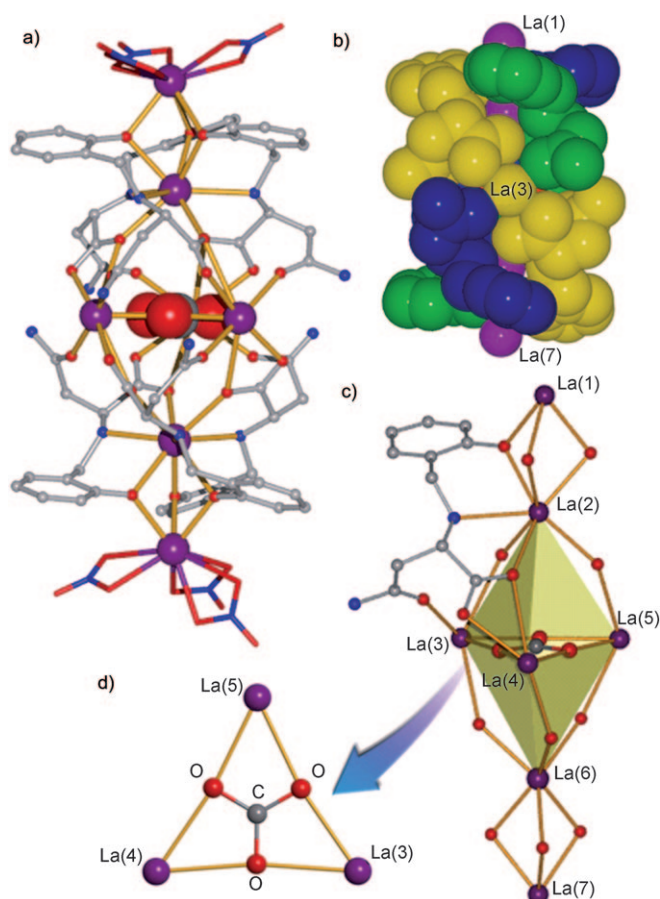


Figure 1. a) Molecular structure of lanthanide-based cluster **1** containing seven La^{III} ions and six $(S)\text{-L}^{2-}$ ligands. The CO_3^{2-} ion is encapsulated by La^{III} ions and shown in a space-filling representation. Hydrogen atoms and solvent molecules are omitted for clarity. b) Space-filling representation of **1** with a chiral helical arrangement of six $(S)\text{-L}^{2-}$ ligands. Hydrogen atoms, nitrate groups, and solvent molecules are omitted for clarity. Each $\{[(S)\text{-L}]\text{-La}[\text{-(S)-L}]\}$ unit is represented in a different color. c) The simplified structure of **1**. All La^{III} ions are bridged by oxygen atoms and form extended trigonal bipyramidal structures. d) The μ_3 -tridentate bridging mode of the CO_3^{2-} ion in the center of the cluster core. C gray, O red, N blue, La violet.

shaped cluster unit (Figure 1c). This arrangement has, to the best of our knowledge, not been reported to date.

One of the most notable structural features of **1** in the core of the cluster is that three equatorial La^{III} ions are trigonally arranged and bonded by the central CO_3^{2-} ion, which adopts a rare $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$ -tridentate bridging mode.^[12b] As shown in Figure 1d, each of the three oxygen atoms of the carbonate ion acts as a donor unit with an angle of around 170° , and the La^{III} ion acts as an acceptor unit with an angle of around 52° . All $\text{La}\text{-O}$ bonds are almost equal and the average bond length is 2.544 \AA . This bridging mode makes the carbon atom of CO_3^{2-} lie on the extended bipyramidal quasi- C_3 axis and the CO_3^{2-} ligand symmetrically fixed in the center of the cluster. From another point of view, the La^{III} ions are in close contact and the supramolecular structure is further stabilized by the introduction of the CO_3^{2-} ion.

In addition to the bridging of the CO_3^{2-} ion by three equatorial La^{III} ions, six bridging ligands play important roles in linking all the La^{III} ions to construct the cluster. The carboxylate anion of the ligand bridges two metal ions in a $\mu_2\text{-}\kappa^1\text{O}; \kappa^2\text{O}, \text{O}'$ fashion, and a phenolic oxygen atom also bridges two La^{III} ions (Figure 1c). As a result, each $(S)\text{-L}^{2-}$ group bridges four La^{III} ions, and thus acts in different coordination modes: 1) as a monodentate ligand for polar $\text{La}(1)$ or $\text{La}(7)$ through the $\text{O}_{\text{phenoxo}}$ atom, and through the O_{amide} atom for the equatorial La^{III} ions; 2) as a bidentate ligand for equatorial La^{III} ions through the carboxylate ion; and 3) as a tridentate ligand for $\text{La}(2)$ or $\text{La}(6)$ through the $\text{O}_{\text{phenoxo}}$, N_{amino} , and $\text{O}_{\text{carboxylate}}$ atoms. Furthermore, in order to saturate the coordination sphere of the lanthanide ions, a methanol molecule and three nitrate groups coordinate to $\text{La}(1)$ or $\text{La}(7)$ in a bidentate mode, and two solvent molecules coordinate to each equatorial La^{III} ion. Thus, most La^{III} ions in the cluster unit have a coordination number of ten, except $\text{La}(2)$ and $\text{La}(6)$, which have a coordination number of 9.

Interestingly, the whole framework of the cluster exists as a homochiral helix (Figure 1b). In order to understand the structure further, the cluster molecule can be disassembled schematically into three equatorial $\{[(S)\text{-L}]\text{-La}[\text{-(S)-L}]\}$ units, which are related by quasi- C_3 molecular symmetry (Figure 2). The units are interconnected by the central CO_3^{2-} and four La^{III} ions on the major axis of the cluster $\{\text{La}(1), \text{La}(2), \text{La}(6), \text{La}(7)\}$ to form a completely integrated triple M helix. The pitch length of the major axis $\{\text{La}(1) \cdots \text{La}(7)\}$ is about 16.15 \AA . The intrinsic structural information that is encoded in the discrete helical units reflects the direct relationship between the chiral ligand and supramolecular structure of the cluster. That is, the chirality of the organic ligand, with the aid of lanthanide ions, is reproduced in the outer chiral helical cluster, which is a remarkable chirality transfer process.

To further confirm the formation of CO_3^{2-} ions in the cluster core and understand the chirality transfer process from the ligand to the supramolecular structure, the chiral counterpart of **2**, $[\text{La}_7\{(R)\text{-L}\}_6(\text{CO}_3)(\text{NO}_3)_6(\text{OCH}_3)(\text{CH}_3\text{OH})_5\text{-(H}_2\text{O)}_2]\cdot 2\text{CH}_3\text{OH}\cdot 4\text{H}_2\text{O}$ was prepared by employing $(R)\text{-}$

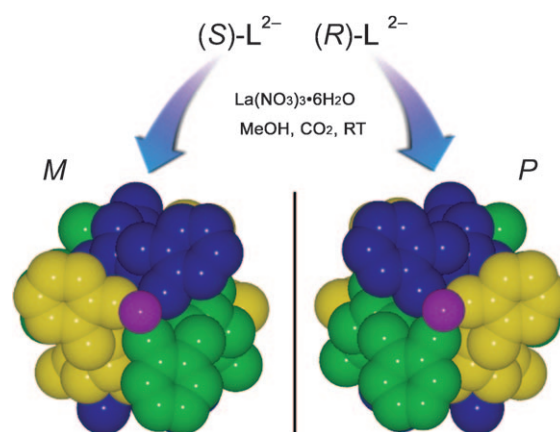


Figure 2. Preparation of the two lanthanide-based enantiomeric clusters **1** and **2**, which are shown in a space-filling representation. Hydrogen atoms, nitrate groups, and solvent molecules are omitted for clarity. Each (S) or $(R)\text{-L}^{2-}$ ligand is represented in a different color, while the lanthanide ions are shown in violet.

H_2L in place of $(S)\text{-H}_2\text{L}$.^[13] During the crystal growth, the mixed solution was placed in a sealed tank full of CO_2 and colorless rhombohedral crystals were successfully obtained over two days, thus showing how the carbonate core can be efficiently introduced. As expected, **2** also belongs to chiral space group $P2_1$, and, as in **1**, the six ligands form a triple helix that surrounds the CO_3^{2-} ion, but with the opposite P helical arrangement. As confirmed by solid-state CD spectroscopy, the chirality of the ligands is preserved in the crystals (Figure 3). Crystals of both **1** and **2** in KBr pellets give mirror-image CD spectra with opposite signs, that is, each crystal comprises helices of only one sense.

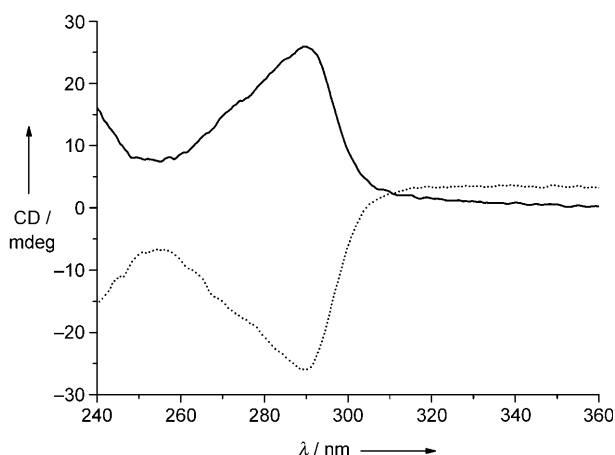


Figure 3. CD data obtained from a transparent disk with a radius of 5 mm made from a mixture of **1** or **2** (3 mg) and KBr (100 mg). Dotted line: complex **1**, solid line: complex **2**.

The presence of the CO_3^{2-} ion in the cluster core and the reaction of the ligands with CO_2 were further investigated by using IR and NMR spectroscopy. The IR spectra of the ligands and crystals were measured in the solid state. Strong carbonate-based vibrations, which are not observed for the ligands, are present at approximately 1450 cm^{-1} in the spectra of both **1** and **2**.^[14,15] The presence of the CO_3^{2-} ion in **1** was further confirmed by the solid-state ^{13}C NMR spectrum,^[15] which shows one low-intensity peak at $\delta = 170.77\text{ ppm}$ that can be assigned to the encapsulated CO_3^{2-} ion.^[16] To determine the origin of the CO_3^{2-} ion in the clusters, the same reactions of $(S)\text{-L}^{2-}$ with $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were carried out in methanol under an inert atmosphere (Ar or N_2). Then, CO_2 was slowly bubbled into the methanolic solution and the process was monitored by using UV/Vis spectrophotometry.^[15] Obvious changes in the UV absorption spectrum show the formation of the carbonate complexes. Thus, CO_2 molecules from the atmosphere are efficiently captured and fixed by these clusters through chemical conversion.

These results clearly suggest that the CO_3^{2-} anion plays an important role as a template in the formation of the heptameric lanthanum cluster. Moreover, six chiral ligands self-assemble and transfer their chirality to produce a new chiral supramolecular structure. We subsequently investigated the response of the system to different anions. We examined the optical rotation of a mixture of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $(S)\text{-L}^{2-}$ in deionized water in the presence of the F^- , Cl^- ,

Br^- , I^- , NO_3^- , SO_4^{2-} , ClO_4^- , and CO_3^{2-} ions. The results indicate that only the CO_3^{2-} ion can efficiently change the optical rotation of the system (Figure 4). Thus, optical rotation analysis of the chiral ligands can be successfully applied to anion-selective recognition. This method is simple and sensitive, which has not been reported to date.

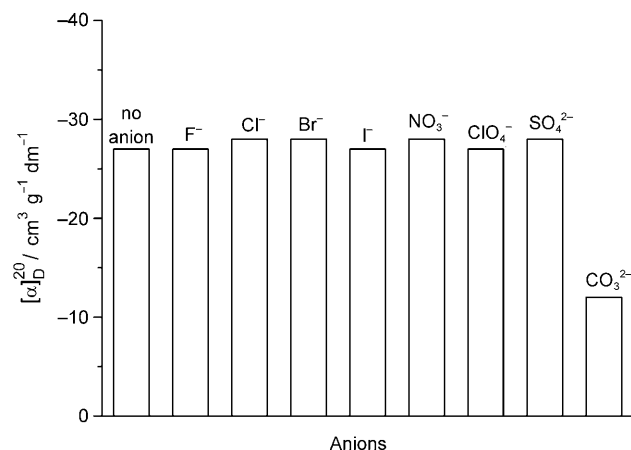


Figure 4. Optical rotation responses of the $\text{La}(\text{NO}_3)_3\text{-(S)-L}^{2-}$ system to different anions in water. $\lambda = 589\text{ nm}$, $[(S)\text{-L}^{2-}] = [\text{La}(\text{NO}_3)_3] = 6 \times [\text{anion}] = 0.028\text{ M}$.

In conclusion, we have described the preparation and structural characterization of a pair of novel supramolecular clusters **1** and **2**, in each of which six ligands bind seven lanthanum ions to form an olive-shaped nanocluster. Furthermore, the supramolecules not only inherit the chirality of the enantiomerically pure ligands, which are derived from amino acids, but also possess triple-helical structures that form homochiral crystals. In the core of the cluster, a CO_3^{2-} ion, which is derived from atmospheric CO_2 , adopts a rare tridentate bridging mode to link three lanthanum ions, thus allowing the clusters to efficiently fix CO_2 . Optical rotation analysis demonstrates that the system, which includes the chiral ligand L^{2-} and La^{III} ions, has an excellent ability to selectively recognize CO_3^{2-} in water. The properties and applications of these nanoparticles will be the subjects of future studies.

Experimental Section

Procedures for the preparation of ligands $(S)\text{-H}_2\text{L}$ and $(R)\text{-H}_2\text{L}$ are described in the Supporting Information.

Synthesis of 1: A mixture of $\text{LiOH} \cdot \text{H}_2\text{O}$ (8.4 mg, 0.2 mmol) and $(S)\text{-H}_2\text{L}$ (23.8 mg, 0.1 mmol) in methanol (3 mL) was stirred for 5 min to obtain a transparent solution. Then a solution of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (43.3 mg, 0.1 mmol) in methanol (2 mL) was added and the mixture was rapidly stirred for 10 min. Colorless rhombohedral crystals suitable for X-ray analysis were obtained in 67% yield by slow evaporation of methanol over two weeks at room temperature in air. The crystals were soluble in water but insoluble in common organic solvents. Elemental analysis calcd (%) for $\text{C}_{75}\text{H}_{103}\text{N}_{18}\text{O}_{33}\text{La}_7$ (non-coordinated solvent molecules were lost upon drying): C 29.27, H 3.37, N 8.19; found: C 29.81, H 3.28, N 8.29.

Synthesis of **2**: This complex was synthesized following the same procedure as described for **1** but with (*R*)-H₂L (23.8 mg, 0.1 mmol) instead of (*S*)-H₂L. The crystals were obtained in 59% yield by slow evaporation of methanol over two days in a sealed tank filled with CO₂. Elemental analysis calcd (%) for **2** C₇₃H₉₉N₁₈O₅₃La₇ (non-coordinated solvent molecules were lost upon drying): C 28.76, H 3.27, N 8.27; found: C 29.18, H 3.21, N 8.16.

Crystallographic data for complexes **1** and **2** were collected with a Siemens P4 four-circle diffractometer at (287 ± 2) K and a Bruker Smart APEX II CCD diffractometer at (294 ± 2) K using graphite-monochromatized MoK_α radiation (λ = 0.71073 Å), respectively. The structure of **1** was solved by Patterson methods and the structure of **2** was solved by direct methods. All non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares methods on F² by using the program package SHELXS-97.^[17] Hydrogen atoms, except those of the water molecules, were generated geometrically. CCDC 701060 (**1**), and 701061 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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