

Largest Discrete Supramolecular Architecture Based on a Lanthanide Ion: [Lanthanum(III)₁₈{*N,N'*-bis(2-pyridylmethyl)-*N,N'*-1,2-ethanediybis(D-alaninate)}₁₈(H₂O)₃₆]¹⁸⁺

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The largest discrete octadecameric architecture based on a lanthanide ion has been found in the crystal structure of a La- $\{N,N'$ -bis(2-pyridylmethyl)-*N,N'*-1,2-ethanediybis(D-alaninate)} complex.

Construction of metal-based supramolecular systems of nanosize continues to attract considerable attention in connection to the development of functional materials. Various molecular architectures including inorganic–organic infinite frameworks have been reported.¹ In contrast to predictable structures of d-metal ion-based systems in well-designed syntheses, the structures of lanthanide-based systems are hardly predictable and often quite peculiar. This originates from the variable coordination numbers (CNs) and flexible geometries of lanthanide ions.² With regard to discrete molecular cluster complexes, while remarkably large clusters have been reported for those d-metal ions,³ there are a few higher nuclearity clusters in the case of those with lanthanide ions. Such examples include unique pentadecanuclear lanthanide clusters consisting of five vertex-sharing [Ln(μ^3 -OH)₄]⁸⁺ cubane substructures as reported by Zheng and co-

workers.⁴ Analogous architectures have also been successively reported.⁵ Other examples are a monocyclic wheel-shaped octamer⁶ and a cagelike icosahedral dodecamer.⁷

Here we report an unprecedented cagelike lanthanide cluster $\{[La^{III}_{18}(D-bpba)_{18}(H_2O)_{36}]Cl_{18} \cdot nH_2O$ (guest water, $n \approx 69$), **1** with a spherical aspect, revealed by X-ray crystallographic analysis.^{8,9} The ligand D-bpba {D-bpba = *N,N'*-bis(2-pyridylmethyl)-*N,N'*-1,2-ethanediybis(D-alaninate)} is hexadentate with two identical tridentate units: a hydrophobic (2-pyridylmethyl) and a hydrophilic optically active D-alaninate group. To the best of our knowledge, **1** is the largest lanthanide cluster so far reported not only in the number of metal ions but also in the size of cluster (the maximum diameter of the overall molecule is ca. 3.2 nm, and that of the La^{III}₁₈ cluster core is ca. 1.9 nm).

Figure 1 shows the structure of the cationic part of **1**. The crystal contains six independent La^{III}(D-bpba) complexes labeled from 1 to 6, which are extended to 1'–6' and 1''–6'' by the crystallographic 3-fold axis, eventually forming an octadecameric structure.

The most intriguing feature is that two different coordination modes are involved in the crystal structure. One mode is found in the six complexes labeled 1, 2, 1', 2', 1'', and 2'', and the other is found in the 12 complexes labeled 3–6,

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- (9) We have been studying the properties of lanthanide-bpba complexes as chiral shift reagents for an aqueous solution. La- and Ce(bpba) complexes resolve the enantiomer signals of α -amino acids and their *N*-acetyl derivatives. Ce(bpba) differentiates the chirality of the peptide C terminus. These results will be published elsewhere.

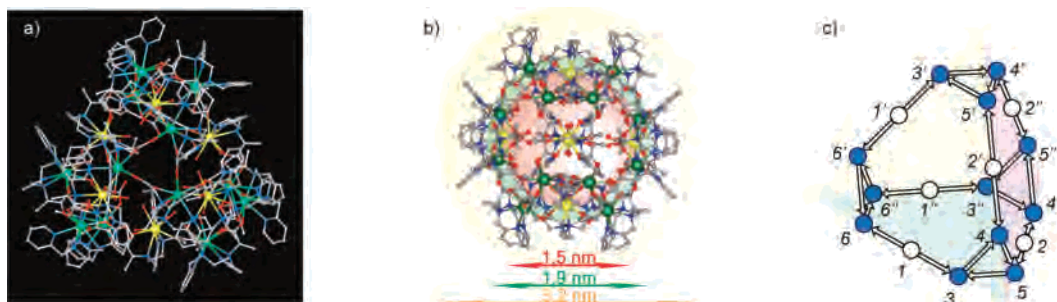


Figure 1. Structure of the cationic part of **1** with tetrahedral architecture. Top view (a) and side view (b): La^{III}(cis) in green, La^{III}(trans) in yellow, C in gray, O in red, and N in blue. (c) Schematic view: La^{III}(cis) in blue and La^{III}(trans) in white. Each arrow shows a carboxylate moiety bridging two complex units [\rightarrow : (La)–O–C=O \cdots (La)].

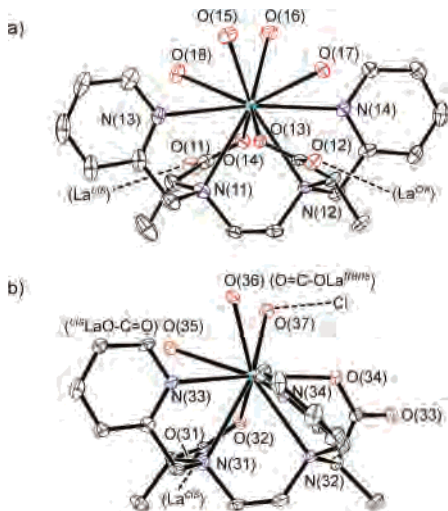


Figure 2. ORTEP drawings of the trans and cis complexes. The thermal ellipsoids are drawn with 30% probability, and H atoms are omitted for clarity. The trans complex adopts a bicapped square-antiprism: one square [N(11), O(14), O(15), and O(18)] capped by N(13) and the other [N(12), O(12), O(16), and O(17)] capped by N(14). The cis complex adopts an irregular and distorted monocapped square-antiprism: one square [N(31), N(32), N(33), and N(34)] and the other [O(32), O(34), O(36), and O(37)] capped by O(35).

3'–6', and 3''–6''. ORTEP drawings of the two complexes are shown in Figure 2. The former have four coordinating water molecules in addition to the hexadentate bpba ligand. The La^{III} ion is 10-coordinate (CN = 10) with an almost regular bicapped square-antiprismatic structure. The bpba ligand coordinates to the La^{III} ion with its pyridine rings in the trans position, and the absolute configurations of the two N(sp³) atoms are the same (described here as the trans complex). By contrast, the latter (cis complex) has the bpba ligand in the cis position with respect to the two pyridines. In this complex, one water molecule and two carbonyl O atoms (one from the cis complex and the other from the trans complex) coordinate to the La^{III} ion (CN = 9) with an irregular and distorted monocapped square-antiprismatic structure. The absolute configurations of the two N(sp³) atoms are opposite.

Each complex is connected principally in the mode of La–O–C=O \cdots La, where the bridging carbonyl O atom is provided by the coordinated bpba ligand. This bridging mode assembles the cis complexes into a cyclic trinuclear core. Complexes 6, 6', and 6'' are imposed by the crystallographic 3-fold axis, and complexes 3–5 are also related by a 3-fold

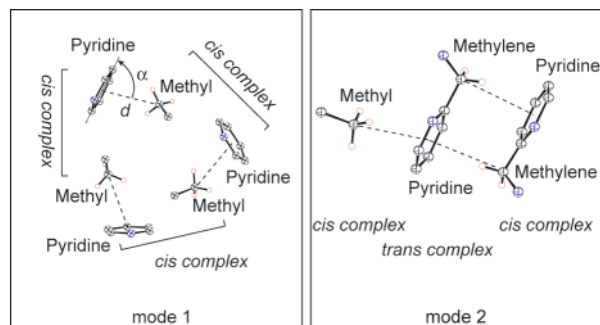


Figure 3. Two modes of the CH– π interactions. Mode 1 appears in the trinuclear core, and mode 2 exits in the trans complex and two sides of the cis complexes. The effect of the CH– π interaction can be described in terms of the distance (d) of the C atoms and the center of the aromatic ring and the inclination angle (α) from the ring plane; their average values are $d = 3.48$ Å and $\alpha = 72^\circ$ for the methyl group and $d = 3.42$ Å and $\alpha = 84^\circ$ for the methylene group.

pseudoaxis; thus, a total of four trinuclear cores exist in **1**. The trans complexes act as a bridge between two trinuclear cores by utilizing the trans-oriented carboxylate groups, thereby constructing a macroring with an octadecameric structure. The three C₂ pseudoaxes exist through two La^{III} ions in trans complexes such as 1 and 2''. Consequently, the overall structure of the cationic part of **1** can be described as a pseudotetrahedron in which the centers of the four triangles are the apexes. In fact, the distances of the La^{III} ions from the center of the tetrahedron are almost equal (9.43–9.52 and 7.39–7.43 Å for La^{III}(cis) and La^{III}(trans) ions, respectively). Thus, the La^{III}₁₈ core has a tetrahedral symmetry in which the outer diameter is ca. 19 Å and the inner diameter is ca. 15 Å (Figure 1b).

Each bpba ligand of the complex is oriented toward the outside of the cluster. In particular, all of the pyridine rings locate at the outer surface of the octadecamer core, and as a result, the surface is hydrophobic. This arrangement appears to be supported by the abundance of CH– π interactions; every pyridine ring of bpba participates in CH– π interactions in one of two ways, as shown in Figure 3. One mode can be seen in the trinuclear cores of the cis complexes, in which the methyl groups and pyridine ring are close to each other. The other occurs between a trans complex and two cis complexes, where there are one methyl–pyridine interaction and two methylene–pyridine interactions. The distance (d) and angle (α) between a C atom of the methyl or methylene and the centroid of the pyridine ring are in the range of those

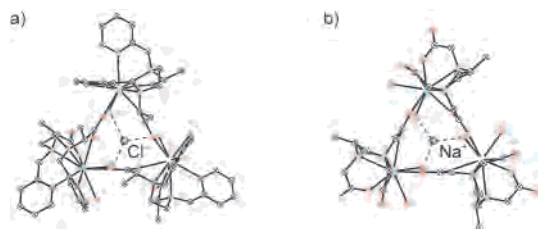


Figure 4. Structures of the trinuclear cores: (a) $\text{La}^{\text{III}}(\text{cis-bpba})$ and (b) $\text{Eu}^{\text{III}}(\text{pdta})$. The common features are that the ligand is chiral, the lanthanide ion adopts a mon capped square-antiprismatic geometry with $\text{CN} = 9$, and one counterion (Cl or Na) locates at the center of the trinuclear core.

found in favorable $\text{CH}-\pi$ interactions.¹⁰ In particular, the second mode that exists between the cis and trans complexes should play an important role in completing the macroring of the octadecameric structure. By contrast, the inside of the core is hydrophilic, in which the carboxylate moieties of the ligand and the coordinating water molecules are located. In addition, 4 Cl ions and 15 guest water molecules are included in a cavity of the cluster. These molecules interact with the polar coordinating groups of the complexes, forming a network of H bonds. The four Cl ions form H bonds with the water molecules coordinating to the La^{III} ions in the trinuclear cores with distances of 3.063–3.081(7) Å, possibly contributing to this assembly (Figure 4a).

The flexibility of the coordination geometry of the La^{III} ion is thought to reduce the structural stress resulting from the smallest assembled unit by utilizing the carboxylate-bridging mode. Such an example is found only in our previously reported complex $\text{Na}[\text{Eu}^{\text{III}}(\text{pdta})]$ (**2**, where pdta = propylenediamine-*N,N,N',N'*-tetraacetate; Figure 4b).¹¹ Given that $\text{Ln}(\text{edta})$ (edta = ethylenediamine-*N,N,N',N'*-tetraacetate) complexes with the same structure as that of **2** do not form a trinuclear core,¹² the chirality of the ligand may be a prerequisite for this assembly or at least may facilitate the construction of the trinuclear core.

The important force driving the formation of the fairly spherical shape of the octadecamer appears to be the separation of the hydrophobic and hydrophilic moieties outside and inside the octadecamer, respectively. The octadecameric structure is the smallest possible aggregation resulting in effective separation. Therefore, the use of a bifunctional ligand with hydrophobic pyridyl and hydrophilic carboxylate moieties in addition to the bridging ability of the latter is the key to the successful construction of the unique giant cluster assembly of our complex. The flexible coordination geometry of La^{III} complexes is also very relevant because, if complex formation were limited to one of the stable isomers between the trans and cis complexes, then the formation of the octadecamer would not be realized.

In conclusion, the reported octadecamer results from the various interactions described above. We postulate that the following three features contribute to the construction of this peculiar, highly organized system. (1) The ligand contains both hydrophobic and hydrophilic groups. (2) Both carboxylate groups and pyridyl groups interact with neighboring complexes. (3) La^{III} ions have a variable CN and coordination geometry. The involvement of the flexible backbone composed of sp^3 atoms, especially the existence of configurationally variable $\text{N}(\text{sp}^3)$ atoms, allows great flexibility and is also very relevant. In other words, the flexibility of these $\text{La}^{\text{III}}(\text{bpba})$ complexes allows self-assembly into **1**. This implies that a combination of different functional groups in a structurally flexible ligand and a metal ion with flexible coordination geometries would be very useful for creating new functional polynuclear cages and other types of assemblies.

Supporting Information Available: X-ray crystallographic file (in CIF format) and experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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