Dodecanuclear Hexagonal-Prismatic $M_{12}L_{18}$ Coordination Cages by Subcomponent Self-assembly

Kiu-Chor Sham, Shek-Man Yiu, and Hoi-Lun Kwong*

Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong SAR

ⓢ Supporting Information

ABSTRACT: Dodecanuclear hexagonal-prismatic $M_{12}L_{18}$ cages were prepared by a subcomponent self-assembly process with commercially available pyridinecarboxaldehyde, m-xylenediamine, and cadmium(II) perchlorate or manganese(II) perchlorate. The NMR spectrum of the Cd cage shows that there are three independent ligand sets, and the X-ray crystal structure of the Mn cage reveals that the structure has both fac-Δ- and mer-Λ-configured metal centers in a 1:1 ratio. The cage structure also has a large cavity that contains five perchlorate anions.

Polyhedral coordination cages have attracted considerable attention because of their elegant structures as well as their interesting host–guest properties.[1–5] Their construction usually involves self-assembly between metal ions and ligands, and cages of different geometries have been reported.[6–12] Although many different types of assembly processes are possible, two types of metal–ligand combinations are often used. One of them is a monodentate ditopic ligand with a square-planar metal ion, and the other is a bidentate ditopic ligand with an octahedral metal ion.[13–15] When monodentate ligands are used, metal centers act like vertices of geometrical figures and ligands act as the connecting edges.[1,16] The situation is a bit different when bis-bidentate ligands are used.

Depending on the orientation of the binding domains of the bis-bidentate ligands, chelation of bidentate ligands to an octahedral metal ion makes the metal ion a stereocenter having both facial/meridonal and Δ/Λ stereoisomerisms.[17–19] The metal centers of a cage are no longer simple vertices of a geometric figure but are variable to control the self-assembly process. For example, in an octanuclear cuneane-like coordination cage, while seven of the eight metal centers are homochiral, all of them have the same meridonal ligand arrangement.[20] On the other hand, in an octanuclear cubic cage, the eight metal centers are in a different situation, a combination of mer-Δ/mer-Λ/fac-Δ/fac-Λ in a 3:3:1:1 ratio.[21]

Numerous polyhedral coordination cages using a bis-bidentate ligand and an octahedral metal ion have been reported so far. All of them have a metal/ligand ratio of 2:3, and most of them resemble the geometry of a tetrahedron (M_4L_6),[6,9,22] which is a platonic solid having all faces formed by identical polygons.[23] Cages of other geometries are rarer. Cube (M_8L_{12}), also a platonic solid,[21,24–26] cuneane (M_8L_{12}),[20] a truncated tetrahedron $(M_{12}L_{18})$,[27,28] a skewed truncated tetrahedron $(M_{16}L_{24})$,[29,30] and n-gonal-prismatic cages, which have two n-gons and n squares as faces, like a trigonal prism (M_6L_9),[29,31] a

pentagonal prism $(M_{10}L_{15})$,[32] and a hexagonal prism $(M_{12}L_{18})$,[33] are some examples. In this Communication, we report a new $M_{12}L_{18}$ hexagonal-prismatic cage type. Of D_3 symmetry, this cage type using 1,3-bis(2-pyridylmethyleneaminomethyl)benzene[34] as ligand **L** is chiral and has both facial- and meridonal-configured metal centers of opposite chirality in a 1:1 ratio.

The self-assembly process was carried out by stirring, in acetonitrile, commercially available 2-pyridinecarboxyaldehyde, m-xylenediamine, and either manganese(II) or cadmium(II) perchlorate, in a 6:3:2 ratio (Scheme 1). After precipitation with

**Scheme 1. Subcomponent Self-assembly of Manganese and Cadmium Complexes**
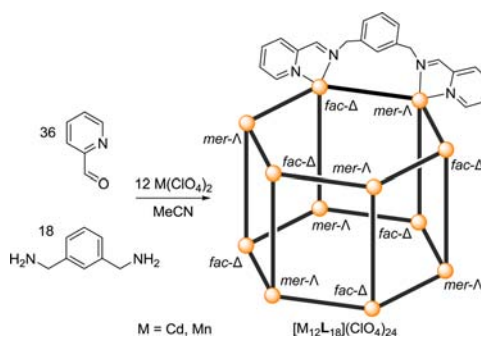
diethyl ether, manganese(II) and cadmium(II) complexes, in yields of 79% and 71%, respectively, were isolated by filtration. Electrospray ionization mass spectrometry (ESI-MS) spectra of the manganese complex (Figure 1) show signals at m/z 1641.0, 1350.9, and 1143.5, which correspond to multicharged species $[M_{12}L_{18}](ClO_4)_{19}^{5+}$, $[M_{12}L_{18}](ClO_4)_{18}^{6+}$, and $[M_{12}L_{18}](ClO_4)_{17}^{7+}$, respectively. The same multicharged species are also observed with the cadmium complex at m/z 1778.6, 1466.1, and 1242.2 (Figure S1 in the Supporting Information, SI). These observations suggest the formation of polynuclear metal complexes $[M_{12}L_{18}](ClO_4)_{24}$ from a self-assembly process involving 90 components.

Two $M_{12}L_{18}$ cages have been reported previously, a truncated tetrahedron[27,28] and a hexagonal prism.[33] We first thought that our cage complexes had similar structures, but the ^1H NMR spectrum of the isolated cadmium complex is quite different from that expected of a truncated tetrahedron of T symmetry or a hexagonal prism of D_6 symmetry (Figure 2). Protons on the pyridyl rings are indistinguishable; however, most of the signals
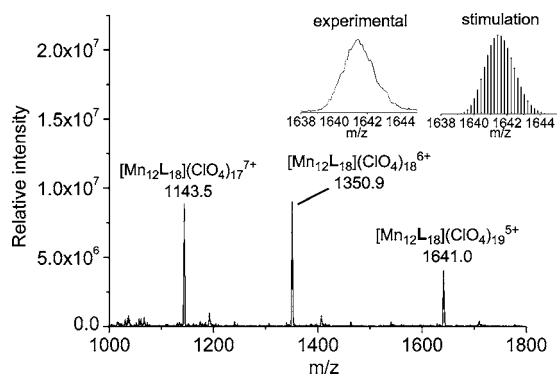
Figure 1. ESI-MS spectrum of $[Mn_{12}L_{18}](ClO_4)_{24}$. Inset: isotopic distribution of $[Mn_{12}L_{18}](ClO_4)_{19}{}^{5+}$.
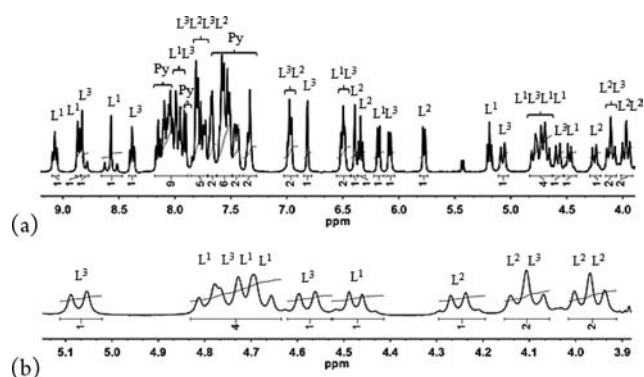
Figure 2. ^1H NMR spectrum (400 MHz) of $[Cd_{12}L_{18}](ClO_4)_{24}$ in CD_3CN: (a) full spectrum with signals corresponding to three independent ligands, L^1–L^3 [the overlapped pyridine signals (Py) are not individually assigned]; (b) expanded spectrum (5.2–3.9 ppm) with methylene protons assigned.

can be assigned with the help of COSY and NOESY spectra (Figures S2 and S3 in the SI). A total of 12 doublet signals with large coupling constants (J = 11.2–14.0 Hz) are observed from 5.2 to 3.9 ppm. They are assigned to protons of six methylene groups. Together with the observation of signals from three different phenyl rings, it is suggested that the observed signals are coming from three independent ligands (L^1–L^3) having no internal symmetry. In addition, the ^{113}Cd NMR spectrum of the Cd cage shows two signals, at −414 and −418 ppm, with the same integration. These results suggest that the symmetry of the cadmium complex does not agree with the reported $M_{12}L_{18}$ cages.

Evidence of the structure finally came from X-ray crystal structure characterization of the manganese cage complex. Crystallization of the manganese cage by ether diffusion into an acetonitrile solution gave bright-yellow crystals. Figure 3a shows the crystal structure of this manganese cage. In a hexagonal space group $R\bar{3}$ with a large unit cell (V = 34318 Å^3), it is a dodecanuclear complex $[Mn_{12}L_{18}](ClO_4)_{24}$ with hexagonal prismlike geometry and a large cavity that captures five perchlorate anions. The cage is composed of two Mn_6L_6 hexagons. Mn ions on each hexagon are not exactly on the same plane. They are puckered, giving a chairlike structure similar to cyclohexane. One of the Mn_6L_6 hexagons is shown in Figure 3b. Within the hexagon, the separations between the Mn ions are in the range 8.624–8.925 Å and the Mn–Mn–Mn angles are in the range 96.84–136.12°. The ligands can be divided into two groups that are not related by symmetry. This
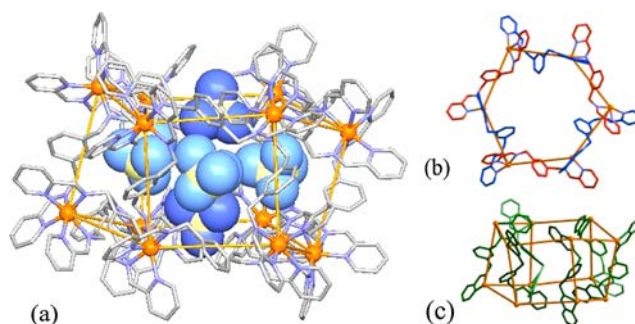
Figure 3. (a) X-ray crystal structure of $[Mn_{12}L_{18}](ClO_4)_{24}$. Mn ions are shown as orange spheres, the orange lines outline the connection of the metal ion array by the ligands, and anions are shown in the space-filling model. (b) Top view showing one of the M_6L_6 hexagons in the structure. (c) View showing six ligands bridging the two hexagon layers.

coordination of ligands results in two different types of Mn centers: Λ- and Δ-configured. These two types of Mn centers appear alternately within the hexagon. With each Mn center having two ligands coordinated already, there is one more cis-coordination site on each metal. The cis-coordination sites are occupied by a third group of six ligands that bridge the upper hexagon to the lower hexagon to complete the structure (Figure 3c). Each bridging ligand links a Λ-configured Mn center of one hexagon with a Δ-configured Mn center of another hexagon. Connections of these bridging ligands generate six squarelike faces, and within the square, the separations between the Mn ions are in the range 8.843−8.925 Å and the Mn−Mn−Mn angles are in the range 80.30−95.24°.

Coordination of bridging ligands leads to mer-Λ- and fac-Δ-configured Mn centers. To form a hexagonal-prismatic structure, the two types of Mn centers are oriented in a stereochemical pattern shown in Figure 4a. The mer-Λ- and fac-Δ-configured
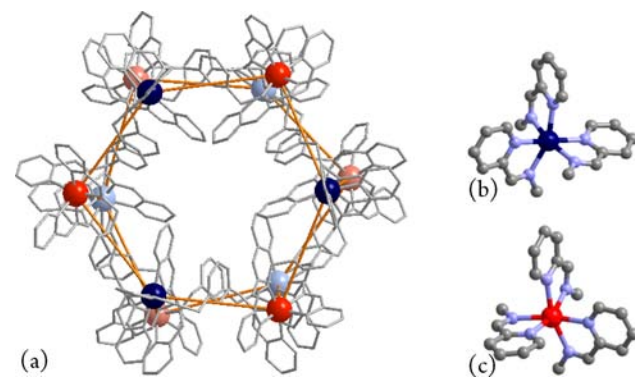
Figure 4. (a) Top view of $[Mn_{12}L_{18}]^{24+}$ emphasizing the arrangement of two different types of metal centers within the structure; mer-Λ-configured Mn centers in blue and fac-Δ-configured Mn centers in red. (b) mer-Λ-configured Mn center. (c) fac-Δ-configured Mn center.

Mn centers appear alternately within the hexagonal prism. This arrangement is significantly different from the reported truncated tetrahedral[27,28] and hexagonal-prismatic $M_{12}L_{18}$ cages.[33] Parts b and c of Figure 4b show the mer-Λ and fac-Δ metal centers. With the presence of both mer-Λ and fac-Δ metal centers in a 1:1 ratio, the hexagonal prism can be considered pseudomeso. Because only one enantiomer is observed in the crystal structure (Flack parameter = 0.073(8)), it is an example of spontaneous resolution. However, when a piece of crystal is dissolved in solution, interestingly, no signals are observed in the CD

spectrum (Figure S4 in the SI). Because polyhedral cages are not likely to undergo fast exchange,[35] this observation may come from the cancelation of absorption between the Δ and Λ Mn centers.

The five captured anions can be divided into two groups, two located at the two hexagonal faces and three located at three of the six square faces. At the hexagonal face, the aromatic C−H···O distance and angle of 2.409 Å and 136.26°, respectively, and at the rectangular face, the aromatic C−H··O distance and angle of 2.528 Å and 142.94°, respectively, are observed, which indicates that there are hydrogen-bonding interactions between the anions and cage. An anion template is curial to the formation of a particular structure in some self-assembly systems.[36] When manganese triflate was used as the starting material, peaks corresponding to $[Mn_{12}L_{18}](OTf)_{24-n}{}^{n+}$ were observed in ESI-MS (Figure S5 in the SI). ^1H and ^{113}Cd NMR spectra of the cadmium complex with triflate anions also showed signals of three independent ligands (Figure S6 in the SI) and two ^{113}Cd signals of the same integration, respectively, suggesting the formation of a hexagonal prism cage. With these results, we believe that a perchlorate anion is not essential to the formation of the hexagonal prism cage.

In summary, we have reported novel $M_{12}L_{18}$ hexagonal prismatic cages of Cd and Mn. These cages are easily synthesized by subcomponent self-assembly with inexpensive readily available starting materials. The ligand is formed in situ during the coordination-driven self-assembly process. In the structure of the $Mn_{12}L_{18}$ cage, 12 Mn centers adopt a unique stereochemical pattern. The cage has a large cavity that captures five anions. Further experiments are underway to investigate its chemistry and potential application.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data in CIF format, experimental details, ESI-MS spectra of $[Cd_{12}L_{18}](ClO_4)_{24}$ and $[Mn_{12}L_{18}](OTf)_{24}$, COSY and NOESY spectra of $[Cd_{12}L_{18}](ClO_4)_{24}$, an NMR spectrum of $[Cd_{12}L_{18}](OTf)_{24}$, and CD and UV−vis spectra of $[Mn_{12}L_{18}]$-$(ClO_4)_{24}$ and $[Cd_{12}L_{18}](ClO_4)_{24}$. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: bhhoik@cityu.edu.hk. Fax: 852 3442 4706. Tel: 852 3442 7304.

Notes

The authors declare no competing financial interest.

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