Inorg. Chem. **2007**, *46*, 5814–5816

Inorganic Chemistry
Communication

Assembly of Trigonal and Tetragonal Prismatic Cages from Octahedral Metal Ions and a Flexible Molecular Clip

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Received November 29, 2006

Reaction of a semirigid ligand with two octahedral metal ions with restricted coordination symmetry afforded metalated container complexes showing trigonal or tetragonal outer shapes and inner cavities.

Self-assembly of metalated container molecules by utilizing directional metal−ligand dative bonds is a highly topical area of current research in supramolecular chemistry.[1] With predetermined shapes and sizes, such molecular containers hold promising functionalities such as selective recognition, sensing, catalysis, and acting as molecular reaction vessels.[2] Three types of metalated molecular architectures, classified according to the ways in which the regular polygons are assembled to enclose space, are most interesting: (1) the Platonic solids with all faces being identical regular polygons, such as an octahedron, (2) the Archimedean solids made up of at least two types of regular polygons, such as a truncated octahedron, and (3) the prisms composed of two regular *n*-gons perpendicular to a *n*-fold rotation axis, such as trigonal and tetragonal prisms (see the Supporting Information). The first two types, often called polyhedra, have received intense attention[1−3] compared to the last one, partly because of the fact that the high symmetry of polyhedra can limit the formation of structural isomers caused by different orientations of the ligand in the self-assembly process.[1d] By contrast, the molecular prisms, which do not possess multiple *n*-fold rotation axes, are of relatively lower symmetry.

Therefore, assembly of prismatic architectures requires relatively more deliberate predesign and judicious choice of the components. However, the low-symmetry hosts are expected to show enhanced guest selectivity, especially toward planar guests.[4] To achieve convergent assembly of molecular prisms by preventing the appearance of more than one *n*-fold axis during the self-assembly process, we have utilized a *ligand-directed symmetry-interaction* approach[4b] in which the modular assembly of prismatic architectures was directed by a shape-defined molecular clip.[4a] Because the molecular clip has a symmetry no higher than 2-fold, the combination of the molecular clips with two axial centers will give rise to *n*-gonal prisms determined by *n*-fold symmetry of the axial centers (C_n). Typically, square centers afford a tetragonal molecular prism,[4b,5] and triangular centers[4b,6] afford a trigonal prism. In this paper, we report a rare example in which a molecular clip can adapt to different coordination directions of the octahedral centers, leading to the formation of both dicapped trigonal- and tetragonal-shaped molecular cage complexes.

The ditopic, semirigid ligand that contains a long central base and two pyridyl coordinating rings linked by methylene groups, 2,6-bis(pyridin-3-ylmethyl)hexahydro-4,8-ethenopyrrolo[3,4-*f*]isoindole-1,3,5,7-tetrone (Scheme 1, **L**), was prepared from a replacement reaction of 3-(aminomethyl)-pyridine with bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic acid dianhydride in *N*,*N*-dimethylformamide. The reaction of **L** with hydrated $Zn(CF_3SO_3)_2$ in an EtOH−$CHCl_3$ solution afforded complex $[Zn_2\mathbf{L}_3(H_2O)_6]\cdot(CF_3SO_3)_4\cdot CHCl_3$ (**1**), and the reaction of **1** with hydrated $Cu(ClO_4)_2$, $Cu(NO_3)_2$, and a

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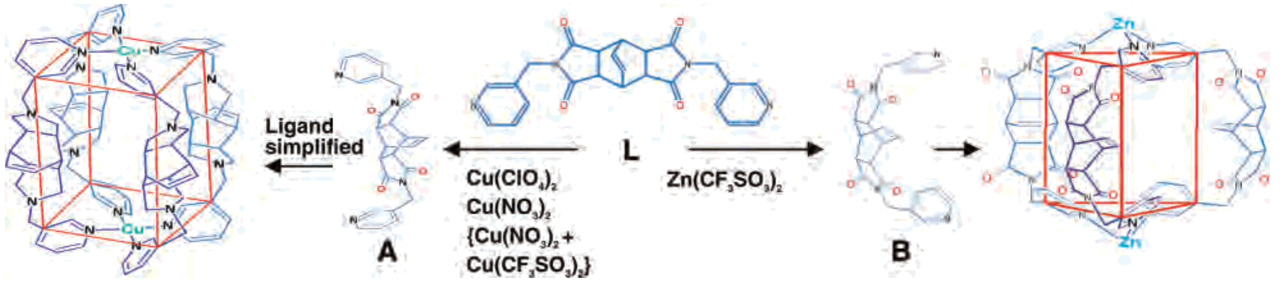
10.1021/ic062270+ CCC: $37.00

Scheme 1



1:1 mixture of $Cu(NO_3)_2$ and $Cu(CF_3SO_3)_2$ in an MeOH−$CHCl_3$ solution afforded complexes $[Cu_2\mathbf{L}_4(ClO_4)_4]\cdot 6CHCl_3$ (**2**), $[Cu_2\mathbf{L}_4(NO_3)_4]\cdot 5CHCl_3\cdot 3MeOH$ (**3**), and $[Cu_2\mathbf{L}_4(NO_3)_2(CF_3SO_3)_2]\cdot 8CHCl_3$ (**4**), respectively. The detailed characterization of all complexes by means of elemental analysis, IR, ^1H NMR, electrospray ionization mass spectrometry, and X-ray powder diffraction is described in the Supporting Information.

The single-crystal X-ray diffraction analysis (see the Supporting Information) unambiguously revealed a dicapped trigonal-prismatic structure for **1** and tetragonal-prismatic structures for **2**−**4**. Figure 1 shows molecular structures of **1** and **4** in the asymmetric unit with an atomic labeling scheme. In both structures, **L** acts as a di-monodentate bridging ligand to connect two metal ions that have similar octahedral coordination geometry. In **1**, each Zn^{2+} ion is coordinated by three different ligands and three water molecules, resulting in a N_3O_3 environment, where three N atoms and three O atoms are arranged in a *fac* conformation, allowing 3-fold rotation symmetry (C_3). Three Zn−N bonds and three Zn−O bonds are identical individually with normal distances of 2.154(3) and 2.153(2) Å, respectively. In **4**, the Cu^{2+} ions are six-coordinated by four N atoms from different ligands and two O atoms from one NO_3^- anion and one $CF_3SO_3^-$ anion. Four pyridyl N atoms occupy the equatorial positions and two O atoms lie in the axial positions, resulting in a N_4O_2 environment, allowing for apparent 4-fold rotation symmetry (C_4). Four Cu−N bond distances are comparable, falling in the range of 2.019(3)−2.025(3) Å, and two Cu−O bonds show the known Jahn−Teller effect, giving rise to two elongated distances of 2.394(3) and 2.521(3) Å. The complexes **2** and **3** show essentially the same coordination environment as that of **4**, only replacing the NO_3^- and $CF_3SO_3^-$ anions by two ClO_4^- or NO_3^- anions.

The most striking feature is that in **1** two $[Zn(H_2O)_3]^{2+}$ motifs, where three water molecules occupy one face of the octahedron, can connect three ligands to form an $M_2\mathbf{L}_3$ dicapped trigonal-prismatic molecule while in **2**−**4** two $[Cu(anion)_2]^{2+}$ motifs, where two anions occupy the axial sites, can connect four ligands to form $M_2\mathbf{L}_4$ tetragonal-prismatic molecules. As shown in Figure 2, the $M_2\mathbf{L}_3$ molecule contains a trigonal cage in which a disordered $CHCl_3$ guest molecule is hosted. All $CF_3SO_3^-$ anions reside outside the cage. The molecule possesses an exact C_{3h} point symmetry with a C_3 rotation axis passing through two Zn^{2+} atoms and a mirror plan bisecting the molecule. By contrast, the $M_2\mathbf{L}_4$ molecules contain tetragonal cages in which two anions are located. Outside the cages, the other two anions sit on the top and bottom of the prisms. Because all anions and Cu^{2+} atoms are aligned in the axial positions, the crystallographically imposed C_4 rotation symmetry is thereof destroyed, leaving virtually only an inversion center in the middle of the cages. The cavity is about 360 Å^3 inside the trigonal cage **1** and about 380 Å^3 inside the tetragonal cages **2**−**4** estimated by the *WINGX* program.

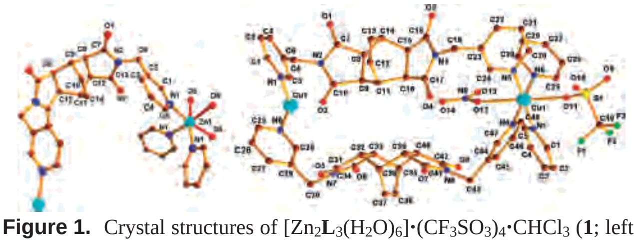


Figure 1. Crystal structures of $[Zn_2\mathbf{L}_3(H_2O)_6]\cdot(CF_3SO_3)_4\cdot CHCl_3$ (**1**; left) and $[Cu_2\mathbf{L}_4(NO_3)_2(CF_3SO_3)_2]\cdot 8CHCl_3$ (**4**; right) showing the asymmetric unit and coordination geometry of metal centers.

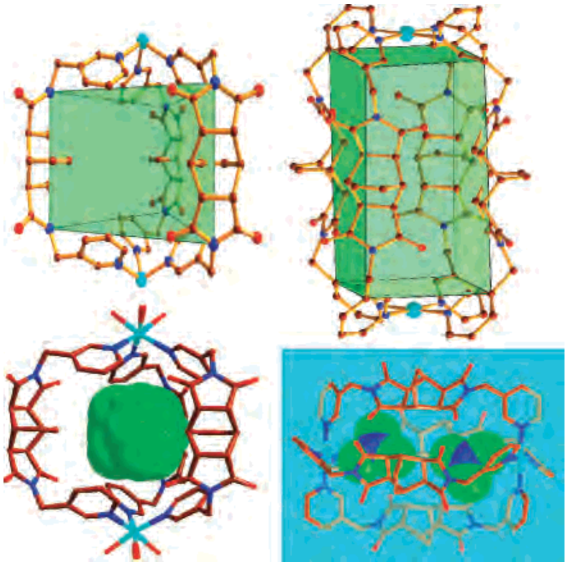
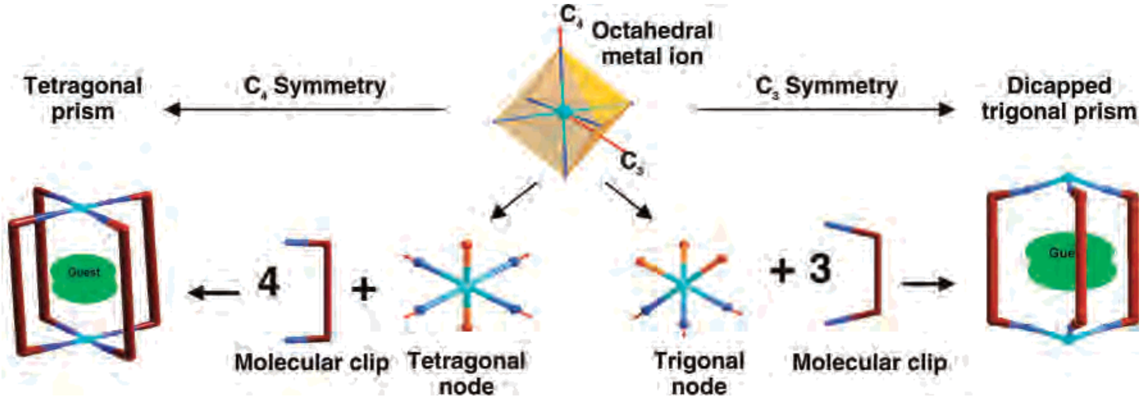


Figure 2. Prismatic architectures of **1** and **4** containing trigonal and tetragonal cages (top, shown in transparent green prisms) and encapsulation of small molecules (bottom, shown in space-filling mode).

It is noticeable that the intrinsic O_h symmetry of the octahedral centers has been degraded to lower C_n symmetry in **1** (C_3) and **2**−**4** (pseudo-C_4) because of nonequivalent coordination environments as discussed above. The octahedral metal ions are known to provide versatile coordination geometries that play important roles in the engineering of both infinite coordination polymers[7] and discrete molecular architectures.[3] However, their potential application in the construction of molecular prisms has so far been mainly realized in tetragonal prisms.[5] As depicted in Scheme 2, the utilization of four equatorial sites can afford a C_4 tetragonal node, while a C_3 trigonal node can be produced if three *fac*-

Scheme 2. Schematic Representation Showing the Assembly Process of Trigonal and Tetragonal Molecular Prisms by a Combination of Different Coordination Symmetries of the Octahedral Metal Ions with a Conformation Adaptive Molecular Clip



coordination sites are blocked. By the design of such facial blocked octahedral metal centers, a few cubelike cage structures have been successfully assembled.[8] These C_4 tetragonal and C_3 trigonal nodes offer good axial centers required for the formation of tetragonal and dicapped trigonal prisms in combination with the appropriate molecular clips, as shown in Scheme 2. In addition, using such a facial blocked trigonal node may be helpful in preventing the formation of a helical twist, which is often observed when the octahedral metal ions are directly used to assemble with the bis(bidentate) ligands; in such cases, elegant helicates or polyhedra instead of molecular prisms are constructed.[3] Therefore, octahedral metal ions could become an abundant source to construct prismatic molecular architectures following the *ligand-directed symmetry-interaction* approach[4b] if their C_n symmetry can be properly retained, providing an alternative way of creating new members in the well-established molecular prism family.[9−11]

From Scheme 2, it is also noticeable that the formation of dicapped trigonal and tetragonal prisms by using blocked octahedral metal centers actually requires different geometries of the molecular clips. The tetragonal nodes need molecular clips with vertex angles close to 90°, while the trigonal nodes demand vertex angles of molecular clips larger than 90°. Therefore, it is necessary for the molecular clip to have conformational flexibility to form both dicapped trigonal and tetragonal prisms. This geometric requirement is properly met by the present ligand. The semirigid nature of the ligand permits two types of preferred conformations, of which the cis,cis conformation shows a cliplike feature. Furthermore, two 3-substituted pyridyl donor groups and the nonplanar central base linked by the flexible $-CH_2-$ groups facilitate the geometrical adjustment to offer two slightly different cis,cis conformations, **A** and **B** as depicted in Scheme 1. Conformation **A** satisfies the geometric requirement of the tetragonal nodes, and conformation **B** matches well with the trigonal nodes. Therefore, this ligand exhibits a good conformational adaptation to cooperate with the blocked octahedral metal ions in different C_n symmetries. On the other hand, the Zn^{2+} ion is typical of normal octahedral coordination geometry, while the Cu^{2+} ion more prefers tetragonal geometry, characteristic of elongated octahedral geometry. This may be the reason that **1** gave the dicapped trigonal structure while **2**−**4** afforded tetragonal molecules. Another important role for the formation of closed structures may be the template effect. In **1**, all coordination sites are occupied and the C_{3v} symmetric $CHCl_3$ molecule represents a suitable guest rather than the linear $CF_3SO_3^-$ anion, but in **2**−**4**, the free axial sites choose the small weakly coordinating NO_3^- or ClO_4^- anions. However, the linear $CF_3SO_3^-$ anion seems still not preferred, as is evident in **4**. Assembly with mixing NO_3^- and $CF_3SO_3^-$ anions caused encapsulation of NO_3^- rather than $CF_3SO_3^-$.

Complex **1** is air-stable while **2**−**4** effloresce quickly because of the escape of $CHCl_3$ molecules from the crystal lattice. A thermogravimetric analysis (TGA) study indicates that cage **1** is stable up to 360 °C, losing the guest molecules before 200 °C, while cage **2** has a lower thermal stability up to 280 °C.

In summary, two coordination prismatic structures, dicapped trigonal $M_2\mathbf{L}_3$ and tetragonal $M_2\mathbf{L}_4$ molecules, have been assembled from the same ligand, which displays an adaptive conformation, and blocked octahedral centers, which display different coordination symmetries, indicative of a potential *ligand-directed symmetry-interaction* approach to assemble coordination prismatic structures by using the plentiful and versatile octahedral metal ions and the shape-defined molecular clips.

Acknowledgment. This work was supported by the National Science Funds for Distinguished Young Scholars of China (Grant 20525310), the NSF of China (Grants 20303027 and 20673147), and the NSF of Guangdong Province (Grant 04205405).

Supporting Information Available: X-ray crystallographic data (CIF), TGA curves of **1** and **2**, and experimental details for the synthesis and characterization of **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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