A Chiral Pentadecanuclear Metallamacrocycle with a Sextuple Twisted Möbius Topology

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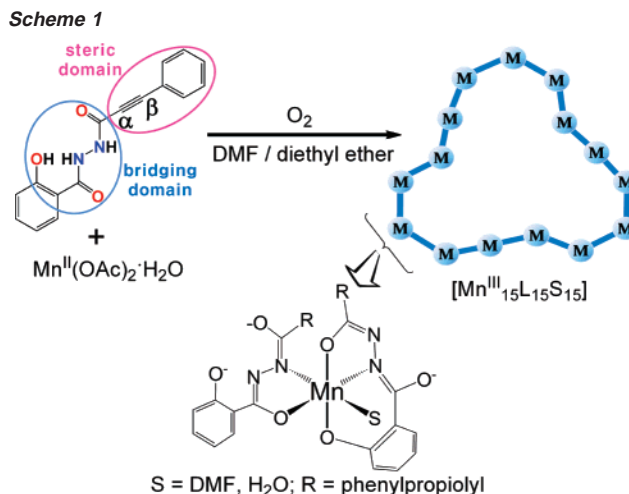Received August 8, 2007; E-mail: mslah@hanyang.ac.kr

Construction of cyclic molecules has received much attention in recent years because of both scientific curiosity and their potential use in applications such as magnetic materials, sensors for small molecules, and new classes of catalysts.[1] Although the possibility of forming molecules with a twisted cyclic band structure (Möbius molecules) was predicted theoretically among organic molecules such as polyenes and other conjugated aromatic systems,[2] only a few of such molecules have been realized experimentally.[3] Recently, an example of an inorganic Möbius strip of $NbSe_3$ crystal based on the coordination chemistry of inorganic elements has been reported.[4] A suitable design of the ligands and an appropriate choice of metal ions acting as connecting nodes can also lead to twisted cyclic architectures with a Möbius topology. The only metallamacrocycle of Möbius topology was obtained from a self-assembly of [Li_2(pyridyl-2,6-diphenyl)(tmeda)$_2$] (tmeda = N,N,N',N'-tetramethylethylene diamine) and a Au^I−diphosphane complex.[5] While several strategies exist to introduce multiple twists in conjugated cyclic polyenes or other aromatic systems,[6] none of these exhibits a twist greater than double twists (360° twists), which is probably due to the large strain that the cyclic system needs to accommodate. Metallamacrocycles that may experience lower strains around the metal centers due to the twist may be a convenient alternative for the generation of multiple twisted cyclic systems.

The pentadentate *N*-acylsalicylhydrazide can serve as an asymmetric ditopic bridging ligand between octahedral metal ions using its tridentate and bidentate binding modes to form metallamacrocycles (Scheme 1).[7] Depending on the influence of the N-terminal steric domain during self-assembly, the ligand chooses either Λ or Δ configuration around each metal center (Figure S1). In addition, it is also possible to modify the nuclearity of the macrocycle[8] and the stereochemistry of the metal centers.[9,10] A decrease in the steric volume near the Cα−Cβ region may increase the possibility of three or more successive metal centers having the same chiral configuration in the macrocycle that can induce multiple twists in the cycle.

Herein, we report on the self-assembly and characterization of a unique manganese-based pentadecanuclear metallamacrocycle from a manganese ion and a pentadentate ligand, *N*-phenylpropiolyl salicylhydrazide (H_3L), which has the smallest steric volume near the Cα−Cβ region (Scheme 1).

X-ray quality single crystals of the complex were grown from a DMF solution of the ligand, *N*-phenylpropiolyl salicylhydrazide, and manganese acetate by layering with diethyl ether. The pentadecanuclear metallamacrocycle with C_3 symmetry, [$Mn_{15}L_{15}S_{15}$] **1** (Figure 1), where S is either a DMF or a water molecule, crystallizes in the chiral space group $P6_3$, and the asymmetric unit contains five ligand units bound to five metal centers (Figure S2).

The steric requirements of the ethynyl phenyl group in the N-terminal steric domain restrain the chiral sequence to $\cdots\Delta\Delta\Delta\Delta\Lambda\cdots$

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Scheme 1

S = DMF, H_2O; R = phenylpropiolyl

around the metal center. The occurrence of successive metal centers of the same Δ configuration produces double twists (360° twists) in the metallamacrocycle along the direction of the propagation (Figure 2 and Figure S3). To obtain an insight into the nature and extent of the twist and its contribution to the overall geometry of the metallamacrocycle, we calculated the twist resulting from the chiral configuration at each metal center with respect to the ligand orientation. The consecutive twist angles calculated using the dihedral angle between the neighboring ligand planes were +90, +81, +99, +82, and −92°, where the direction and the extent of an individual twist is determined by the chiral sequence of four consecutive metal centers (Table S1). The five consecutive (+ + + + −) twists contribute a net twist of 360° (double twist) along the direction of propagation.[11]

The macrocycle makes a sharp turn at the metal center with a Λ configuration (Figure 2). Three such turns in the backbone lead to a C_3 symmetric pentadecanuclear metallamacrocycle. This results in a sum of six 180° twists in the overall cycle, creating a sextuple twisted metallamacrocycle (Figure S4).[12]

The double twist in the asymmetric unit orients the three salicyl moieties toward the inner core of the macrocycle on one face of the cycle (Figure S5). The chiral nature of the C_3 symmetric macrocycle[13] is exemplified by the fact that the inner core of the other face of the macrocycle has different residues, that is, three ethynyl phenyl groups.

Depending on the nature of the *N*-acyl residue, the chiral sequence of the metal centers is determined to minimize the unfavorable steric repulsion and to maximize the favorable weak interactions, such as the C−H···π and π···π stacking interactions. The macrocyclic assembly has a total of nine intramolecular C−H···O interactions between the N-terminal aromatic C−H's and oxygen atoms in the bridging domains of the different ligand units (Table S2). Three intramolecular C−H···π interactions between
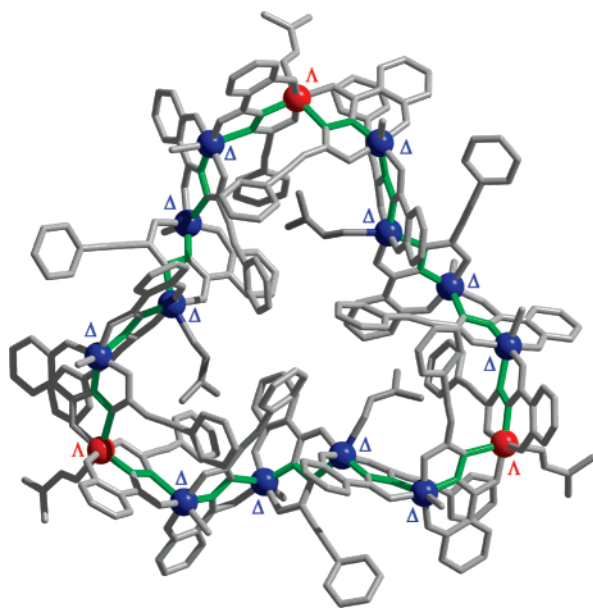
Figure 1. A stick diagram of chiral pentadecanuclear metallamacrocycle **1** with C_3 symmetry. The −N−N− connectivities are shown in green. The metal ions with Δ configuration appear as blue spheres, and the metal ions with Λ configuration appear as red spheres.
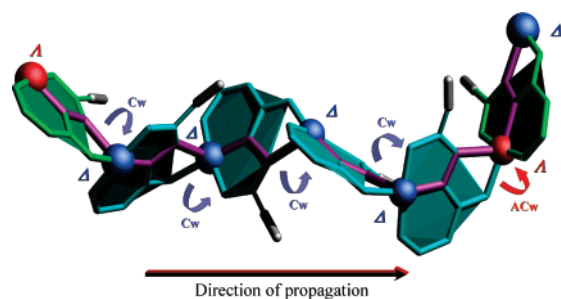

Figure 2. A section of the macrocyclic backbone that shows the double twist and the turn in the direction of propagation. The metal ions are shown as spheres and the ligand binding moieties as planes. The blue spheres have Δ configuration, and the red spheres have Λ configuration. The blue arrows represent a clockwise (+) rotation, and the red arrows represent an counterclockwise (−) turn for successive ligand planes.

the N-terminal phenyl groups and three other interactions between the salicyl C−H's and ethynyl phenyl groups are identified in the assembly. In addition, three intramolecular $\pi\cdots\pi$ stacking interactions between the ethynyl phenyl ring and the salicyl ring of neighboring ligand units, and extensive van der Waals interactions, support the assembly (Figure S6). One coordinated DMF molecule per crystallographic asymmetric unit is lodged in a small pocket created between the ligand frames of D- and B-labeled residues using van der Waals interactions (Figure S7 and Table S2). We believe that a rigid steric domain of the ligand with a narrow Cα−Cβ region near the bridging domain and a bulky aromatic phenyl end located away from the bridging domain induces the four consecutive Δ configurations for a double twist and the final Λ configuration for a turn in the propagation direction in the asymmetric unit. The combination of weak interactions, such as C−H⋯π and π⋯π stacking interactions, and extensive van der Waals interactions may be the reason for the stabilization of the sextuple twisted pentadecanuclear assembly forming.

In conclusion, we have constructed a unique C_3 symmetric pentadecanuclear metallamacrocycle using a pentadentate bridging ligand, *N*-phenylpropiolyl salicylhydrazide. The introduction of a

rigid ethynyl phenyl N-tail to the ligand minimized the steric interaction in the Cα−Cβ region and provided a moderate steric volume beyond this region. This led to the formation of four successive metal centers of the same Δ configuration, followed by a Λ, which resulted in a sextuple twisted chiral macrocycle. To the best of our knowledge, this is the first sextuple twisted high-nuclearity metallamacrocycle that has a Möbius topology.

Supporting Information Available: Synthesis of the ligand and **1**, crystallographic details of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) The total sum of the twist angles calculated from the dihedral angles between the two consecutive ligand planes in one asymmetric unit (∼260°) does not make up the 360° for double twist in the asymmetric unit along the propagation direction, as shown in Figure 2. This discrepancy is from the fact that the calculation was performed using the ligand planes that were not parallel to the direction of the propagation of the macrocyclic backbone. For a more accurate calculation, we need to calculate the best-fit straight line representing the propagation direction and the normal vector residing at the ligand planes, and the twist angles obtained using this information will form the required 360° for a double twist comprising four consecutive ∼120° clockwise twists and a ∼120° counterclockwise twist.
(12) The Möbius topology is only possible in a metallamacrocycle which does not contain any S_n symmetry. The metallamacrocycle having the chiral sequence related by an S_n symmetry leads to the same extent of twist but in an opposite direction, hence the net twist in an achiral metallamacrocycle is always zero regardless of the individual sequence.
(13) The Flack parameter of the crystal was found to be 0.20(3). However, the bulk crystals dissolved in chloroform did not show any CD activity, which suggests that metallamacrocycle **1** in bulk is not homochiral but racemic.

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