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Polyoxometalatocyclophanes: Controlled Assembly of Polyoxometalate-Based Chiral Metallamacrocycles from Achiral Building Blocks

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The chemistry of metallamacrocycles, a versatile class of ringlike coordination compounds composed of organic fragments and at least one endocyclic metal center, has received much attention in recent years because of their peculiar nanosized molecular architectures and interesting properties and many potential applications, including catalysis, ion exchange, molecular recognition, absorption and separation, sensing, and nanoelectronics.[1] They are generally synthesized by self-assembly of simple metal ions or metal complexes containing suitably oriented substitution sites with ditopic ligands in a one-pot reaction. To date, a variety of amazingly complex cyclic structures such as metallocenophanes,[2] molecular squares and rectangles,[3] molecular wheels,[4] and metallacrowns[5] have been fabricated in this way. Recently, mesoscopic metallocycles with cavities up to 22 nm in diameter have also been prepared by expeditious stepwise directed assembly via cyclization of metal- and ligand-terminated oligomers under kinetic control.[6] However, to the best of our knowledge, almost all of the reported metallamacrocycles are composed of bridged mononuclear metallic centers. Besides one dinuclear cluster,[7] there are few metallamacrocyclic compounds formed by bridging polynuclear complexes, including polyoxometalate (POM) clusters,[8] with suitable organic ligands. Building up polymetallic-cluster-based metallamacrocycles is still a formidable challenge.

POMs are early-transition-metal oxide clusters with the extensive capability of attaching organic groups onto the surface of the cluster.[9] If suitable bidentate organic ligands are available, they can be exploited to make polyoxometalatocyclophanes, a class of POM-based metallamacrocycles, by the replacement of two neighboring oxo groups. As can be expected, such monocyclic [*n*]-polyoxometalatocyclophanes should be chiral if the incorporated organic ligand is nonplanar. Inspired by the heuristic work of Errington, Maatta, and Roesner,[10] we report here novel POM-based chiral macrocycles formed in a controllable manner from the achiral Lindqvist hexamolybdate and bisarylamines bearing *o*-alkoxy chain substituents using the DCC protocol for preparing diorganoimido-substituted POMs.[11] Unexpectedly, some of the metallamacrocycles undergo spontaneous resolution upon crystallization. This work not only opens a new strategy for preparing chiral metallamacrocycles[1g,12] but also provides an alternative route to the development of novel chiral POM architectures[13] that is totally different from the pioneering work of Hill, Kortz, Pope, Wang, Yamase, and other groups.[14−20]

Refluxing reactions of $[N(n\text{-}Bu)_4]_4[\alpha\text{-}Mo_8O_{26}]$, bisarylamine [1,4-bis(*o*-aminophenoxy)butane (C_4), 1,6-bis(*o*-aminophenoxy)hexane (C_6), or 1,8-bis(*o*-aminophenoxy)octane (C_8)] and its hydrochloride, and *N*,*N*′-dicyclohexylcarbodiimide (DCC) in a mole ratio of 6:5:3:20 in dry acetonitrile proceeded smoothly and afforded the chiral hexamolybdatocyclophanes $[N(n\text{-}Bu)_4]_2[Mo_6O_{17}(2,2'\text{-}NC_6H_4OC_nH_{2n}OC_6H_4N)]$ [$n = 4$ (**1**), 6 (**2**), 8 (**3**)] in 20−40% yield.

The molecular structures of compounds **1**, **2**, and **3** were determined by single-crystal X-ray diffraction (XRD) investigations, and ORTEP drawings of their cluster anions are shown in Figure 1. They crystallize in the monoclinic space groups $P2_1/n$ and $P2_1$ and the triclinic space group $P\bar{1}$, respectively. The asymmetric unit of each of these compounds contains a novel diorganoimido-functionalized hexamolybdate in which two cis terminal oxo groups have been replaced to form a POM-based metallamacrocycle with a perimeter of 2.286, 2.604, and 2.876 nm in **1**, **2** and **3**, respectively. The most distinctive feature is that the organic ligand has a flexible alkyl chain that is long enough to reach the POM, thus making a cycle. Because both ends are fixed by Mo−N bonds, the alkyl chain cannot rotate freely, and this loss of freedom of rotation destroys the mirror symmetry of the mother Lindqvist anion, resulting in the formation of chiral metallamacrocycles. In these compounds, the metrical parameters of the Mo−N bonds (1.729−1.744 Å) and Mo−N−C angles (167.47−178.54°) indicate substantial $Mo{\equiv}N$ triple-bond character. The angles between the two aromatic planes in the same anion range from 20.6 to 90.5°.

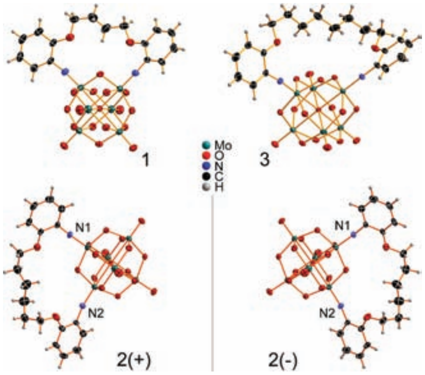

Figure 1. ORTEP drawings of the macrocyclic anions of compounds **1**, **2**, and **3**. Thermal ellipsoids are set at 30% probability.

Hydrogen bonds between hydrogen atoms of the organic ligands and oxygen atoms of the next hexamolybdate are present in these compounds. In compound **1**, two neighboring homochiral macrocycles are linked by a hydrogen bond between H5A and O14 (C5−H5A···O14, 3.269 Å, 152.24°) to form a 1D chain (Figure S1a in the Supporting Information). There is similar hydrogen bonding in compound **3** (C5−H5A···O2, 3.341 Å, 150.99°). The two-direction macrocyclic anions of **1** alternate in the chain, while there is a 1D channel along the *a* axis in the structure of **3** (Figure S1a). The neighboring homochiral metallamacrocycle chains are a pair of enantiomers, which results in racemic crystals. In comparison with compounds **1** and **3**, there are more abundant hydrogen bonds in the crystal structure of **2**, forming a 2D undee netlike layer (C7−H7A···O9, 3.143 Å, 126.61°; C12−H12A···O17, 3.259 Å, 141.57°) (Figure S1b). Interestingly, packing of such macrocyclic anions in crystals can generate supramolecular chiral nanochannels (Figure S1c).

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Single-crystal XRD analyses also definitively confirmed that the enantiopure compounds **2**(+) and **2**(−) were isolated by spontaneous resolution upon crystallization without any outside chiral influence; they both crystallize in the chiral space group $P2_1$ with the same crystal data within experimental error. Moreover, the corresponding torsion angles related to the alkyl chains in the pair of enantiomers are exactly inverse within experimental error (Table 1).

Table 1. Selected Torsion Angles (deg)

compound	C11−O19−C16−C17	C17−C18−C9−C8	C8−C7−O18−C2
2(+)	−74.3(6)	−149.6(6)	173.2(4)
2(−)	74.5(6)	149.6(6)	−172.9(4)

The chirality of these POM-based macrocycles was further substantiated by circular dichroism (CD) studies. The CD spectra of compounds **2**(+) and **2**(−)(Figure 2) are almost mirror images of each other, indicating that the pair of compounds are enantiomers of each other. The crystals are designated as (+) and (−) on the basis of the sign of the ellipticity at $\lambda \approx 196$ and 296 nm.

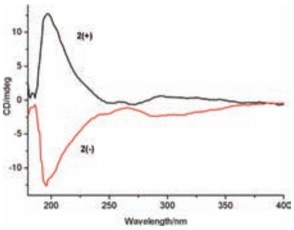

Figure 2. Solid-state CD spectra of **2**(+) and **2**(−). A mixture of a single crystal (~120 μg) and 100 mg of KBr was ground well and compacted into a disk with a radius of 13 mm for the measurement.

The ^{1}H NMR spectra of compounds **1**−**3** show clearly resolved signals, all of which can be unambiguously assigned (Figure S2). Comparison with the ^{1}H NMR spectra of the corresponding bisaromatic amines showed that the signal of the amino group at ~4.5 ppm had vanished completely in these metallamacrocycles, indicating that the two amino groups in the ligand had been deprotonated and new bonds had formed. Furthermore, other protons of the ligands exhibited downfield chemical shifts due to the stronger electron-withdrawing power of the incorporated hexamolybdate cage.

Their IR spectra not only closely resemble that of the hexamolybdate parent but also include features from the cis direplacement and the organic ligands. In the approximation of separate Mo−O_t and Mo−N vibrations, the strong band at ~944 cm^{-1} should be assigned to the ν_{as}(Mo−O_t) mode, whereas the less intense band (a shoulder peak) at ~964 cm^{-1} might associate principally with the Mo−N vibrator, implying that these compounds essentially belong to cis diorganoimido derivatives.[21] Two weak absorption bands at ~1280 and 1240 cm^{-1} can be assigned to the asymmetric stretching vibration of the *ar*C−O−*al*C moiety, which shows that the organic ligand has been anchored onto these compounds.

The lowest-energy electronic transition in the UV−vis absorption spectra exhibits a significant bathochromic shift from 325 nm in $[Mo_6O_{19}]^{2-}$ to ~370 nm in these compounds. This indicates that the Mo−N bond is formed and that the π electrons are delocalized from the organic conjugated system onto the hexamolybdate skeletons.[22] Electrospray ionization mass spectrometry (ESI-MS) data also show that these macrocycles can retain the integrity of organoimido POM derivatives in MeCN (Figure S3).

In summary, bisarylamines bearing *o*-alkoxy chain substituents are effective ligands for synthesizing semirigid metallamacrocycles when polyoxometalates are bridged to act as the endocyclic metal centers. These POM-based metallamacrocycles have attractive chirality and can pack into homochiral nanochannels. This work has provided a new protocol for preparing chiral POMs, especially chiral metallamacrocyles, directly from achiral building blocks. Further studies of their redox properties, resolution, and potential applications in catalysis, absorption and separation, and NLO materials are underway in our laboratory.

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Supporting Information Available: Synthetic details and characterization data, including ESI-MS, IR, UV−vis, and ^{1}H NMR data and X-ray crystallographic data (CIF), for compounds **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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