Chiral Frameworks

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Chiral 3D Architectures with Helical Channels Constructed from Polyoxometalate Clusters and Copper–Amino Acid Complexes**

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Chiral inorganic–organic materials have received much attention, not only because of their numerous potential applications in nonlinear optics, enantioselective catalysis,

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and medicine, but also owing to their intriguing variety of architectures and topologies.[1–3] In recent years, much progress has been made in the design of zeolite and metal–phosphate systems with chiral structures.[4] In contrast, only a few compounds containing polyoxoanions and organic ligands/metal coordination complexes have been reported to have chiral features.[5] Polyoxometalates (POMs),[6,7] as anionic early-transition-metal oxide clusters, bear many properties that make them attractive for applications in catalysis, biology, magnetism, optics, and medicine.[8] Because of their importance in the areas of medicine and asymmetric catalysis, in particular, there has been increasing interest in the construction of enantiomerically pure architectures from POM clusters.[9] Two main approaches have been developed for the formation of chiral POM-based frameworks. The first method is based on the direct connection of POM clusters with chiral organic ligands. A few interesting studies on this approach have been performed by the groups of Pope, Yamase, and Kortz.[10] The second method, which is far less developed than the first, uses a chiral metal–organic complex as a template, which can transfer the chirality of the organic ligands to the whole framework through the bonding of the metal centers to the POM cluster. Using this approach, Hill's group has synthesized a fascinating, enantiomerically pure polytungstate that consists of two units of lacunary $[P_2W_{15}O_{56}]^{12-}$ ion bridged by a chiral zirconium–tartrate coordination complex.[11] However, the preparation of enantiomerically pure high-dimensional frameworks constructed from POM units remains largely unexplored, although they may be of practical use in catalysis and separation. Therefore, the search for suitable chiral organic molecules, metal cations, and POM building units to be applied in the construction of chiral 3D open frameworks is one of the most challenging issues in synthetic chemistry and material science.

The remarkable, chiral multidentate ligand, proline, first seized our attention because: 1) it can act as an enantioselective catalyst in many reactions, and as an amino acid, it is a basic building unit in proteins for study in medical applications;[12] 2) it has a relatively small volume and has versatile coordination behavior,[13] which allows extensive cross-linking between the metal–organic moieties and the oxygen-rich POM units to yield high-dimensional architectures.

Among the many different types of POMs, the most well known are the Keggin heteropolyanions.[14] Although it has been amply demonstrated that these clusters can be linked into low-dimensional (0D, 1D, or 2D) structures by using metal cations or their coordination complexes as linkers,[15] the process of assembling Keggin POMs into 3D frameworks is still in its infancy,[16] perhaps owing to the steric demands of the POMs and the deficient charge density at their surface oxygen atoms. Furthermore, reports of enantiomerically pure assemblies of Keggin POMs are rare.[17] Therefore, our focus is the production of 3D chiral networks based on metal–proline coordination complexes as linkers and Keggin polyoxoanions as achiral building units. Herein, we choose the Keggin cluster $[BW_{12}O_{40}]^{5-}$ as the building block, because of its high charge density and its potential applications.[18] We describe two new enantiomerically pure 3D POM-based frameworks with helical channels, D-**1** and L-**1**. The frameworks are built up from homochiral intertwined double helices. The circular dichroism (CD) spectra of compounds D-**1** and L-**1** in the solution state show significant induced optical activity in the POM moieties, as a result of chirality transfer from the chiral proline molecules to the whole framework.

$KH_2[(D\text{-}C_5H_8NO_2)_4(H_2O)Cu_3][BW_{12}O_{40}] \cdot 5\,H_2O$ D-**1**

$KH_2[(L\text{-}C_5H_8NO_2)_4(H_2O)Cu_3][BW_{12}O_{40}] \cdot 5\,H_2O$ L-**1**

We adopted standard synthetic techniques for the preparation of compound D-**1** by the reaction of $K_5[BW_{12}O_{40}]\cdot 15\,H_2O$[19] with copper(II) and D-proline in a molar ratio of 1:2:2 in water. Compound L-**1** was prepared from L-proline under similar synthetic conditions. Single-crystal X-ray diffraction analyses revealed that compounds D-**1** and L-**1** are enantiomers;[20] their unit-cell dimensions, volumes, related bond distances, and angles are only slightly different. The structures of D-**1** and L-**1** exhibit a unique 3D chiral open framework assembled from $[BW_{12}O_{40}]^{5-}$ polyoxoanions and copper–proline coordination polymer chains. D-**1** crystallizes in the chiral space group $P4_32_12$, and L-**1** in the space group $P4_12_12$, each with one $[BW_{12}O_{40}]^{5-}$ unit, three copper atoms, four proline ligands, one potassium atom, two protons, and six water molecules in the asymmetric unit. The $[BW_{12}O_{40}]^{5-}$ cluster is a classic Keggin structure, which consists of a central BO_4 tetrahedron surrounded by four vertex-sharing W_3O_{13} trimers (Figure 1). Each W_3O_{13} group is composed of three WO_6 octahedra linked in a triangular arrangement by sharing edges. There are four types of oxygen atoms with different coordination modes in the cluster: terminal oxygen atoms Ot, terminal oxygen atoms linked to copper(II) Ot′, bridging oxygen atoms Ob, and central oxygen atoms Oc. Thus, the W–O bond lengths fall into four classes: W–Ot 1.667(13)–1.731(9), W–Ot′ 1.694(12)–1.738(12), W–Ob 1.853(13)–1.970(12), and W–Oc 2.318(8)–2.410(8) Å. The central B–O distances vary from 1.463(16) to 1.591(16) Å, and the O-B-O angles are in the range of 106.4(9)–111.7(10)°, indicating that the BO_4 tetrahedra are distorted.

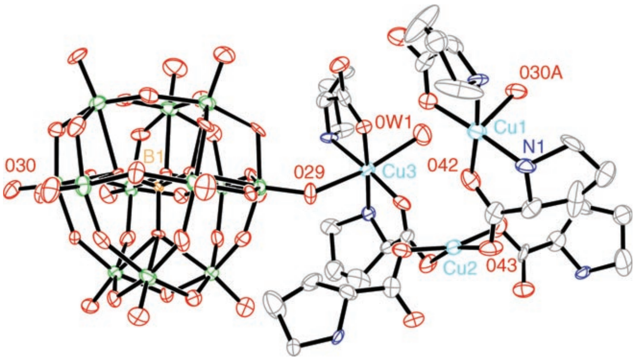

Figure 1. ORTEP drawing of D-**1** with thermal ellipsoids set at 50% probability; B yellow, C gray, N dark blue, O red, Cu blue, W green. Hydrogen and potassium atoms, and solvated water molecules are omitted for clarity. Atom O30A is generated through the symmetry transformation: $y, x-1, -+1$.

There are three crystallographically independent copper(II) centers, each having a different coordination sphere (Figure 1). Cu1 centers a distorted square pyramid, defined by two carboxy oxygen atoms and two nitrogen atoms from two different proline molecules, and one terminal oxygen atom from a Keggin polyoxoanion [Cu1–O30A 2.508(10) Å in D-**1**; 2.470(12) Å in L-**1**]. Cu2 is coordinated by four carboxy oxygen atoms from four different proline molecules in a square-planar geometry. Cu3 has a slightly distorted octahedral coordination environment, formed by two carboxy oxygen atoms and two nitrogen atoms from two different proline molecules, one oxygen atom from a water molecule [Cu3–OW1 2.337(10) Å in D-**1**; 2.364(16) Å in L-**1**], and one terminal oxygen atom from a polyoxoanion [Cu3–O29 2.560(7) Å in D-**1**; 2.515 (12) Å in L-**1**]. Each of the four crystallographically independent proline molecules acts as a tridentate chelating ligand, coordinating to two neighboring copper atoms using its carboxy oxygen atoms and nitrogen atom.

As shown in Figure 2, the copper(II) centers are linked together by proline ligands to yield a 1D coordination polymer chain. Each chain consists of moieties in which four copper atoms are bridged by four carboxylate groups from four different proline ligands. The planes of adjacent tetracopper units are nearly perpendicular to one another (see Supporting Information). The copper–proline polymer chains are further covalently bonded to terminal oxo groups of the Keggin clusters by the Cu1 and Cu3 sites of each tetracopper moiety, to form a unique 3D open framework (Figure 3). Each Keggin unit acts as a bidentate ligand, coordinating to two adjacent polymer chains through its terminal oxygen atoms (see Supporting Information). This kind of connection mode results in the formation of channels along the *c* axis. Interestingly, each channel is enclosed by two intertwined helices of the same handedness (Figure 4). Each of these double helices in D-**1** is built up from two identical right-handed single-helical chains with a pitch of 26.201 Å. The helical chains, which are generated around the crystallographic 4_3 axis, are composed of copper–proline subunits bridging four-coordinate boron and six-coordinate tungsten atoms. Differing from D-**1**, the channels of L-**1** are enclosed by two intertwined left-handed helices with a pitch of 26.124 Å, which are generated around the crystallographic 4_1 axis. Such chiral intertwined double helices are rare in inorganic–organic materials. The dimensions of the channels are approximately 10.6 × 7.2 Å in cross section in both compounds (Figure 3b). Water molecules fill the channels and participate in extensive hydrogen-bonding interactions with the polyoxoanions and ligands. The observed chirality of D-**1** and L-**1**, indicated by their chiral space groups, can be understood in terms of chirality transfer from the small chiral proline molecules to the whole framework.

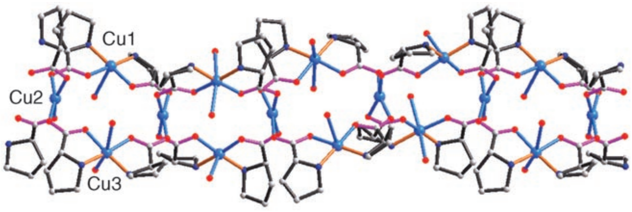

Figure 2. View of the one-dimensional copper–proline coordination polymer chain in D-**1**, showing the carboxylate-bridged tetracopper moieties; C gray, N dark blue, O red, Cu blue.

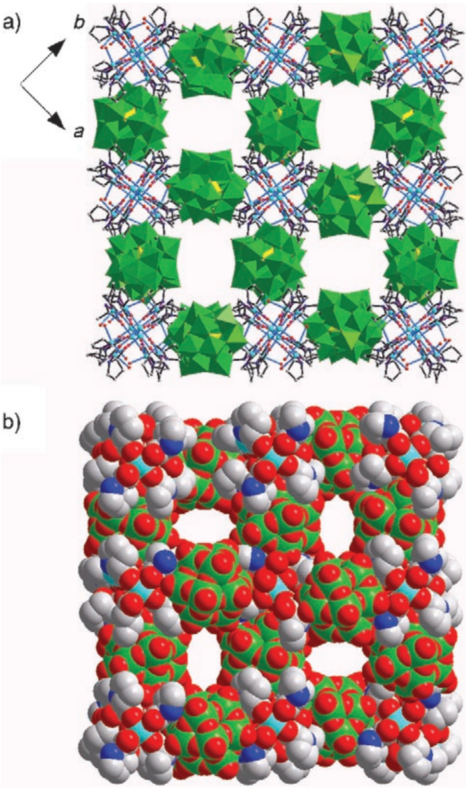

Figure 3. The 3D open-framework structure of D-**1**, which is composed of copper–proline polymer chains covalently linked to Keggin polyoxoanions, viewed along the *c* axis, a) as a polyhedral and ball-and-stick representation, and b) as a space-filling diagram; B yellow, C gray, N dark blue, O red, Cu blue, W green. Hydrogen and potassium atoms, and solvated water molecules are omitted for clarity.

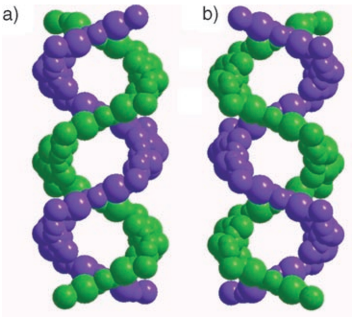

Figure 4. Space-filling diagrams of a) the two intertwined right-handed helices that enclose the channels in D-**1**, and b) the two intertwined left-handed helices in L-**1**.

To examine the chiroptical and stable activities of both enantiopure compounds in the solution state, the CD spectra of compounds D-**1** and L-**1** in water were investigated

(Figure 5). The CD spectra of D-**1** and L-**1** are mirror images of one another, and conclusively demonstrate that D-**1** and L-**1** are enantiomers. Compared with the CD spectra of D-proline (Figure 5, inset), that of D-**1** shows different Cotton effects in the wavelength range of 200–400 nm. The spectrum of the D-proline molecule exhibits only a single negative Cotton effect at 213 nm, while the spectrum of D-**1** exhibits Cotton effects at 225 and 272 nm. In fact, the spectrum of D-**1** displays strong Cotton effects up to 272 nm, the spectral region characteristic of the oxygen-to-tungsten charge-transfer bands of Keggin polyoxoanions.[21] The induced circular dichroism (ICD) in the POM clusters can be clearly seen in the CD spectra,[22] because the chirality transfer from the chiral proline ligands to the POM clusters through the copper bridges leads to a lowering of the symmetry of the Keggin polyoxoanion. The CD and UV/Vis spectra of compounds D-**1** and L-**1** are virtually unchanged with time, indicating that both compounds are enantiomerically stable in aqueous solution.

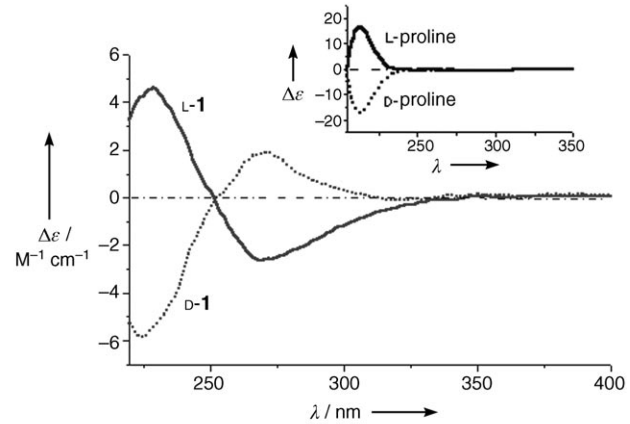

Figure 5. CD spectra in water of D-**1** and L-**1**, and their precursors, D- and L-proline (inset).

In summary, we have developed a rational approach to the synthesis of chiral POM-based materials utilizing enantiopure proline ligands, copper cations, and Keggin-type $[BW_{12}O_{40}]^{5-}$ polyoxoanions as building blocks. To our knowledge, compounds D-**1** and L-**1** represent the first examples of homochiral 3D open-framework POM-based compounds with helical channels. The CD spectra of D-**1** and L-**1** in water reveal significant induced optical activity in the POM moieties. It is believed that chirality transfer from the small chiral ligands to the achiral POM units occurs through the copper centers that link them. The successful synthesis of both compounds not only provides novel examples of enantiomerically pure architectures, but also may open up possibilities for the design of new chiral POM-based materials with particular functions.

Experimental Section

D-**1**: D-Proline (0.0576 g, 0.5 mmol) and $CuCl_2\cdot 2H_2O$ (0.0852 g, 0.5 mmol) were dissolved in water (30 mL). The pH value of the mixture was carefully adjusted with a dilute NaOH solution (1 M) to approximately 4.50 and then stirred for 2 h. Then a solution of $K_5[BW_{12}O_{40}]\cdot 15H_2O$ (0.8306 g, 0.25 mmol) in water (30 mL) was added, and the resulting solution was heated for 2 h at 80 °C. The filtrate was kept for one month at ambient conditions, and blue block crystals of compound D-**1** were isolated in 18 % yield (0.110 g, based on copper). Elemental analysis (%) calcd for $C_{20}H_{46}BCu_3KN_4O_{54}W_{12}$: C 6.57, H 1.26, Cu 5.22, K 1.07, N 1.53, W 60.39; found: C 6.83, H 1.01, Cu 5.07, K 0.98, N 1.64, W 60.49. IR (KBr pellet): $\tilde{\nu} = 3441$(m), 3260(m), 1561(s), 1451(w), 1325(w), 1185(w), 999(m), 955(s), 904 (s), 821(vs), 532(m), and 424 cm^{-1}(w). $[\alpha]_D^{20} = +43.3$ ($c = 1.0$ M, H_2O). $[M]_D = +1581.9$. UV/Vis ($c = 1.26\times10^{-5}$ M, H_2O): $\lambda_{max} = 256$ nm. CD ($c = 5.0\times10^{-4}$ M, H_2O): 225 ($\Delta\varepsilon = -5.9$), 272 nm ($\Delta\varepsilon = 1.9$).

L-**1**: The synthesis of compound L-**1** was carried out as described above for compound D-**1**, but starting with L-proline. Yield: 20 % (based on copper). Elemental analysis (%) calcd for $C_{20}H_{46}BCu_3KN_4O_{54}W_{12}$: C 6.57, H 1.26, Cu 5.22, K 1.07, N 1.53, W 60.39; found: C 6.78, H 1.03, Cu 5.01, K 1.00, N 1.64, W 60.55. IR (KBr pellet): $\tilde{\nu} = 3468$(m), 3260(m), 1560(s), 1455(w), 1377(w), 1326(w), 1184(w), 999(m), 955(s), 904 (s), 821(vs), 533(m), and 423 cm^{-1}(w). $[\alpha]_D^{20} = -44.6$ ($c = 1.0$ M, H_2O). $[M]_D = -1629.4$. UV/Vis ($c = 1.31\times10^{-5}$ M, H_2O): $\lambda_{max} = 256$ nm. CD ($c = 4.9\times10^{-4}$ M, H_2O): 229 ($\Delta\varepsilon = 4.6$), 269 nm ($\Delta\varepsilon = -2.6$).

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[20] Crystal data for D-**1** ($KH_2[(D\text{-}C_5H_8NO_2)_4(H_2O)Cu_3][BW_{12}O_{40}]\cdot 5\,H_2O$): $M_r = 3653.34$, tetragonal, space group $P4_32_12$, $a = 23.944(3)$, $b = 23.944(3)$, $c = 26.201(5)$ Å, $V = 15022(4)$ Å^3, $Z = 8$, $\rho_{calcd} = 3.227$ g cm^{-3}, $R_{int} = 0.0660$, final $R_1 = 0.0288$ ($wR_2 = 0625$) for 11833 independent reflections [$I > 2\sigma(I)$]. Crystal data for L-**1** ($KH_2[(L\text{-}C_5H_8NO_2)_4(H_2O)Cu_3][BW_{12}O_{40}]\cdot 5\,H_2O$): $M_r = 3653.34$, tetragonal, space group $P4_12_12$, $a = 23.897(3)$, $b = 23.897(3)$, $c = 26.124(5)$ Å, $V = 14919(4)$ Å^3, $Z = 8$, $\rho_{calcd} = 3.253$ g cm^{-3}, $R_{int} = 0.1208$, final $R_1 = 0.0401$ ($wR_2 = 0.0783$) for 11783 independent reflections [$I > 2\sigma(I)$]. Data were collected on a Bruker Smart-Apex CCD diffractometer with $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å) at 293 K using the ω-scan technique. Empirical absorption corrections were applied. The structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXTL-97 software. The Flack parameters of −0.014(9) and 0.003(13) for D-**1** and L-**1** indicate that the absolute configurations are correct. In both compounds, one achiral carbon atom of a proline molecule (C9 in D-**1**; C4 in L-**1**) is disordered. CCDC-285623 (D-**1**) and CCDC-285624 (L-**1**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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