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Homochiral Zn and Cd Coordination Polymers Containing Amino Acid−Tetrazole Ligands

Zhi-Rong Qu,[†] Hong Zhao,[†] Xi-Sen Wang,[†] Yong-Hua Li,[†] Yu-Mei Song,[†] Yu-juan Liu,[†] Qiong Ye,[†] Ren-Gen Xiong,[*,†] Brendan F. Abrahams,[‡] Zi-Ling Xue,[§] and Xiao-Zeng You[†]

Coordination Chemistry Institute, The State Key Laboratory of Coordination Chemistry, Nanjing University, 210093 Nanjing, P. R. China, School of Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia, and Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996

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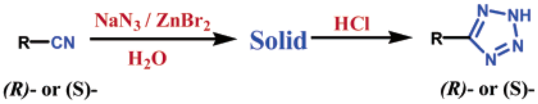
The reactions of (*S*)-3-cyanophenylalanine with NaN_3 in the presence of H_2O and Lewis acids ($ZnCl_2$ and $CdCl_2$) afford two unprecedented 3D homochiral networks, mono[(*S*)-5-(3-tetrazoyl)-phenylalaninato]zinc(II) (**1**) and mono[(*S*)-5-(3-tetrazoyl)-phenylalaninato]cadmium(II) monoaqua(II) (**2**), respectively. The two compounds are isostructural with noninterpenetrated $SrAl_2$ topology. The structure of these coordination polymers gives new insight into Sharpless’ reaction of chiral 5-substituted 1H-tetrazole and homochiral supramolecular array constructions.

The in situ generation of bridging ligands through the employment of hydrothermal techniques has proven to be a successful approach for the synthesis of coordination polymers in the form of high quality single crystals.[1] In recent times we have employed this technique to form coordination polymers that use tetrazole-based ligands to link metal centers.[2] Our interest in this area was prompted by reports by Sharpless et al. on the metal ion assisted synthesis of tetrazoles through the 2 + 3 cycloaddition reactions of nitriles with azide in aqueous solution (Scheme 1).[3] We were particularly interested in a solid intermediate product that we believed was likely to be a coordination polymer. Investigations of this type of reaction under hydrothermal conditions with zinc or cadmium salts were particularly fruitful and yielded a rich variety of coordination networks.[2]

Scheme 1



Encouraged by our success in generating tetrazole-based coordination polymers, we considered that this approach may succeed in yielding homochiral polymers if the nitrile employed in the hydrothermal reaction was chiral and enantiomerically pure. Our interest in synthesizing homochiral metal−organic polymers stems from the fact that they often exhibit desirable optical properties and have potential applications in the areas of chiral catalysis, enantioseparation, and chemical sensing.[4−8]

In this present investigation, we have reacted (*S*)-3-cyanophenylalanine ((*S*)-3-CNPHA) and NaN_3 with either $ZnCl_2$ or $CdCl_2$ under hydrothermal conditions. The coordination polymers, mono[(*S*)-5-(3-tetrazoyl)phenylalaninato]-zinc(II), [Zn((*S*)-TPA)] (**1**) and mono[(*S*)-5-(3-tetrazoyl)-phenylalaninato]cadmium(II) monoaqua(II) [Cd((*S*)-TPA)(H_2O)]

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[*] To whom correspondence should be addressed. E-mail: xiongrg@netra.nju.edu.cn. Fax: (+86) 25 3317761 or (+86) 25 3314502.

[†] Nanjing University.

[‡] University of Melbourne. E-mail: bfa@unimelb.edu.au. Fax: 61-3-9347-5180.

[§] University of Tennessee. E-mail: Xue@ukt.edu.

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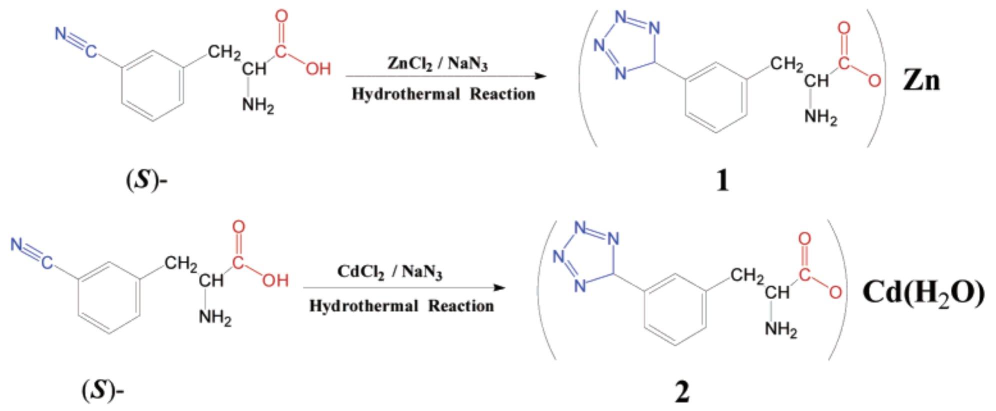
Scheme 2



(**2**), were isolated from these reaction mixtures (Scheme 2). The IR spectra of **1** and **2** show the absence of a cyano peak in the 2100 cm^{-1} region, which supports the proposed reaction between the nitrile and the azide. The formation of a tetrazole group is supported by the emergence of a peak at ca. 1400 cm^{-1}. Strong peaks at 1590−1600 cm^{-1} are consistent with the presence of a carboxylate group (see Supporting Information).

The crystal structure determination of **1** (Zn((S)-TPA)) reveals a complex, chiral, 3-D coordination polymer that contains one unique ligand and one zinc center.[9] The zinc centers are coordinated by four (*S*)-TPA ligands, one of which is chelating. This results in a 5-coordinate metal center with a trigonal bipyramidal coordination geometry (Figure 1). The complex structure of this polymer is a consequence of the unusual coordination mode of the pentadentate ligand which is coordinated to 4 different Zn(II) centers.

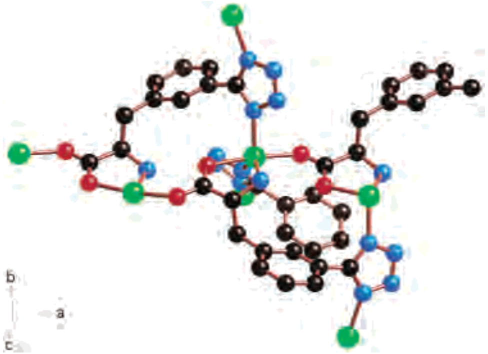


Figure 1. Part of the structure of **1** showing the 5-coordinate zinc center bound to four ligands and the ligand attached to four zinc(II) centers (Zn, green; O, red; N, blue; C, black; H atoms were removed for clarity).

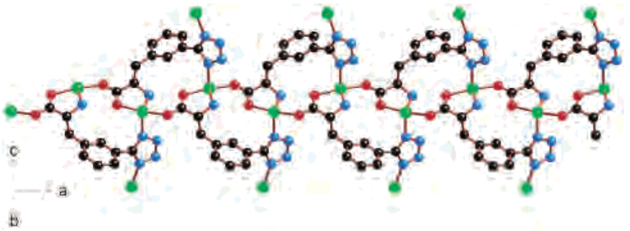


Figure 2. Zigzag chain of zinc atoms linked by bridging amino acid ligands (Zn, green; O, red; N, blue; C, black; H atoms were removed for clarity). Hydrogen bonds are indicated by the striped bonds.

The complex structure of the network is perhaps best understood by considering zigzag chains of zinc(II) centers that extend in the *a*-direction. As can be seen in Figure 2, each ligand links 3 metal centers within this chain. Neighboring ligands that lie either side of the zigzag chain in Figure 2 are linked by hydrogen bonds that extend from the amino group of one ligand to the carboxylate group of the other ligand.

The described chain links to four equivalent parallel chains through bridging tetrazole groups. The tetrazole groups directed upward in Figure 2 link to one parallel chain while the tetrazoles directed downward link to another. Tetrazole groups belonging to two other parallel chains complete the coordination environment of the Zn(II) centers shown in Figure 2.

The full structure is represented in Figure 3 which shows the view down the *a* axis. To aid in the identification of the chains, individual chains are represented by either blue spheres or red spheres. Inspection of Figure 3 reveals that each blue chain connects to four red chains and each red chain connects to four blue chains. To the best of our knowledge, **1** is the first structurally characterized homochiral tetrazole-based metal coordination polymer.[10]

Interestingly, compound **2**, formulated as [Cd((*S*)-TPA)](H$_2$O), is essentially isostructural with **1**. Part of the 3-D structure of **2** is represented in Figure 4. A minor difference

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(9) Crystal data for **1**, $C_{10}H_9N_5O_2Zn$: $M = 296.59$, orthorhombic, $P2_12_12_1$, $a = 9.9723(13)$ Å, $b = 10.4851(13)$ Å, $c = 10.5565(14)$ Å, $V = 1103.8(2)$ Å^3, $Z = 4$, $D_c = 1.785$ Mg m^{-3}, R1 = 0.0290, wR2 = 0.0850, $T = 296$ K, $\mu = 2.226$ mm^{-1}, $S = 0.716$. Flack $\chi = 0.008$-(16). For **2**, $C_{10}H_{11}N_5O_3Cd$: $M = 361.64$, orthorhombic, $P2_12_12_1$, $a = 9.9969(9)$ Å, $b = 10.8731(10)$ Å, $c = 10.8731(10)$ Å, $V = 1181.88$-(15) Å^3, $Z = 4$, $D_c = 2.032$ Mg m^{-3}, R1 = 0.0306, wR2 = 0.0886, $T = 296$ K, $\mu = 1.861$ mm^{-1}, $S = 0.761$, Flack $\chi = -0.04(4)$.

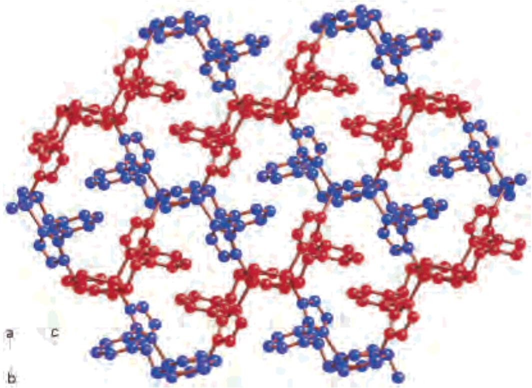

Figure 3. View down the *a* axis of the extended structure of **1** with the chains extending in the direction of the *a* axis. Each blue chain connects to four red chains, and each red chain connects to four blue chains.

Figure 4. Part of the structure of **2** showing the slightly distorted trigonal bipyramidal coordination geometry of the cadmium center.

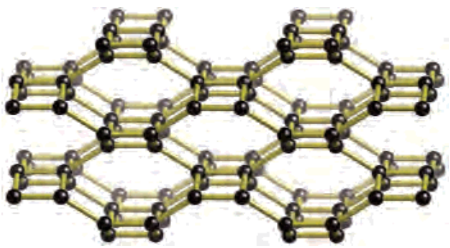

Figure 5. Topological representation of the network in **1** and **2**. Individual black spheres represent either the ligand or the metal center. Zigzag ladders extend into the page.

between compounds **1** and **2** is the inclusion of water within the intranetwork voids of **2** (see Supporting Information).

The connectivity of the networks in **1** and **2** can be simplified if the 4-connecting ligands and the 4-connecting metal centers are represented by single nodes. If this simplification is made, the chains depicted in Figure 2 become simple ladders. Within a ladder, each "metal center" node is connected to three "ligand" nodes, and each ligand node is connected to three metal center nodes. From a topological viewpoint, the nodes representing ligands and metal centers are equivalent. In addition to the intraladder connections, each node of the ladder is linked to one of four equivalent ladders that extend in the same direction. This net, which is represented in Figure 5, shows ladders extending into the page and linking to neighboring parallel ladders. In keeping with the traditional representation of this net, the ladders are represented by zigzag ladders. This network which was characterized by Wells[11] as a 4^26^38-a net has been referred to by Smith[12] as the ABW tetrahedral net in Li-A(BW) zeolite while O'Keeffe and Hyde[13] refer to it as the $SrAl_2$ net. In addition to the Li-A(BW) zeolite and $SrAl_2$ structures, the net is also apparent in the structures of $CeCu_2$ and KHg_2.[14] To the best of our knowledge, **1** and **2** represent the first example of a homochiral inorganic−organic hybrid coordination polymer network with such net topology.[14]

The open channels make it possible to remove the guest molecules from [Cd((*S*)-TPA)](H_2O) (**2**). The TGA curve of **2** showed that one discrete weight loss (4.79%) occurred at 120−280 °C, corresponding to the removal of one molecule of water per formula unit (4.97% calculated) while there is no weight loss observed in the temperature range 280−390 °C, suggesting the polymer is stable up to 390 °C. The resulting solid [Cd((*S*)-TPA)] retains the framework and crystallinity, as supported by the consistent XRD patterns of **1** and **2**. The porous nature of [Cd((*S*)-TPA)] was further demonstrated by their ability to absorb water vapor to form **2**. The dehydration and rehydration processes were reversible. Furthermore, the frameworks of **1** and **2** are stable before 400 °C (see Supporting Information). Preliminary investigation of powdered samples **1** and **2** indicates they are second harmonic generation active with an approximate estimation of 1.02 times than that of urea.

The results presented here demonstrate the value of hydrothermal approaches in the generation of novel coordination polymers. In particular, the in situ formation of homochiral tetrazole-based ligands provides further encouragement that the Sharpless-based approach to ligand formation has the potential to lead to a wide variety of network structures.

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Supporting Information Available: X-ray CIF data. Experimental section. This material is available free of charge via the Internet at http://pubs.acs.org.

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