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Spontaneously Resolved Chiral Interpenetrating 3-D Nets with Two Different Zinc Coordination Polymers

Masaaki Sasa,[†] Kentaro Tanaka,[†] Xian-He Bu,[‡]
Motoo Shiro,[§] and Mitsuhiko Shionoya*[,†]

Department of Chemistry
Graduate School of Science
The University of Tokyo, Hongo, Bunkyo-ku
Tokyo 113-0033, Japan
Department of Chemistry, Nankai University
Tianjin 300071, P. R. China
Rigaku Corporation, 3-9-12 Matsubaracho
Akishima, Tokyo 196-8666, Japan

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A net-based approach to metal coordination polymers using ligands with a range of proper geometries and connectivities has been expected to develop new functionalized materials with useful electronic, magnetic, electrochemical, optical, or catalytic properties.[1] Among different types of net-assembled molecular frameworks reported so far, interpenetrating networks are of particular interest concerning the topological types of three-dimensional (3-D) nets postulated by Wells.[2] For example, "3-D racemates"[3−5] consisting of two topologically equivalent but enantiomeric interpenetrating networks have attracted much attention with regard to asymmetric induction of supramolecular chirality in network assembly.

2,4-Di-(4-pyiridyl)-1,3,5-triazine (DPT),[6] an angular dipyridine ligand, has attracted our attention in connection with structural control of discrete or divergent coordination networks. This ligand has a rigid 120° angle between the central triazine ring and the two 4-pyridine *N*-donors and therefore could potentially provide both discrete (e.g., hexagonal macrocycles) and divergent (e.g., one-dimensional zigzag polymer) products upon metal complexation under appropriate conditions. Recently, Champness et al. have independently reported a net-based approach with a DPT ligand providing a doubly interpenetrated 4.8^2 2-D cadmium sheet and a one-dimensional zinc (or cadmium) polymer.[7] We report here the synthesis and X-ray crystal structure of a novel zinc-DPT coordination polymer **1** which consists of an interpenetrating pair of 3-D nets of different composition. The most striking feature of this complex is that each single crystal is spontaneously resolved in the solid state. Such completely stereospecific self-assembly without any chiral auxiliary in self-assembly[8] would offer a useful tool for chiral molecular recognition and asymmetric catalysis.

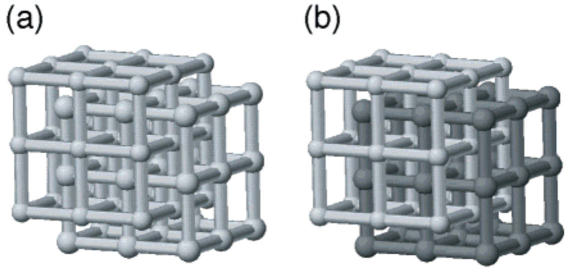

Figure 1. Schematic representation of potential interpenetrating structures resulting from two topologically equivalent 3-D nets of (a) identical composition and (b) different composition.

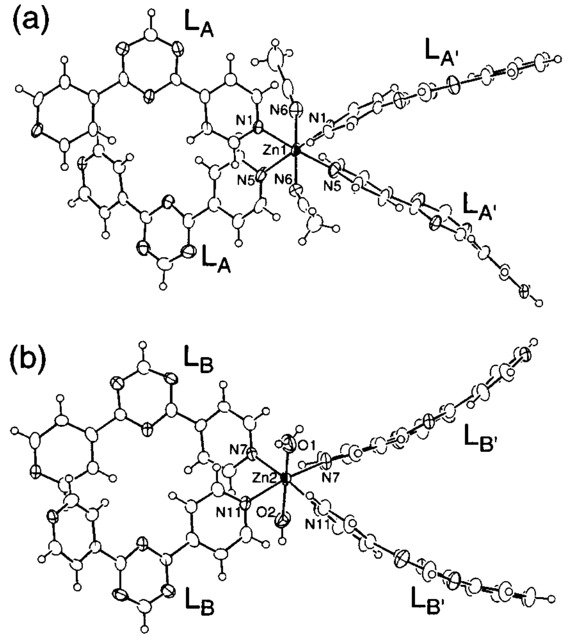

Figure 2. ORTEP views of the zinc centers for (a) net **A** and (b) net **B** in complex **1** with 50% thermal ellipsoids. Selected bond distances (Å) and angles (deg): for net **A**, Zn(1)−N(1), 2.163(5); Zn(1)−N(5), 2.165(5); Zn(1)−N(6), 2.270(6); N(1)−Zn(1)−N(1), 88.6(2); N(1)−Zn(1)−N(5), 89.7(2); N(1)−Zn(1)−N(6), 91.9(2); N(1)−Zn(1)−N(5), 176.8(2); N(1)−Zn(1)−N(6), 88.7(2); N(5)−Zn(1)−N(6), 88.6(2); N(5)−Zn(1)−N(6), 90.8(2); N(6)−Zn(1)−N(6), 179.1(3), for net **B**, Zn(2)−O(1), 2.052(8); Zn(2)−O(2), 2.406(7); Zn(2)−N(7), 2.124(5); Zn(2)−N(11), 2.184(5); O(1)−Zn(2)−N(7), 94.2(2); O(1)−Zn(2)−N(11), 95.6(2); O(2)−Zn(2)−N(7), 85.8(2); O(2)−Zn(2)−N(11), 84.4(2); N(7)−Zn(2)−N(7), 171.5(3); N(7)−Zn(2)−N(11), 87.3(2); N(7)−Zn(2)−N(11), 91.9(2).

The reaction of $Zn(ClO_4)_2{\cdot}6H_2O$ with DPT in a 1:1 ratio in a $CH_3CN{-}CHCl_3$ solvent mixture afforded $[Zn(DPT)_2(H_2O)_2][Zn(DPT)_2(CH_3CN)_2](ClO_4)_4{\cdot}(CH_3CN)_2$ **1** as colorless prisms in 47% yield (Scheme 1).[9] Complex **1** crystallizes in the chiral space group, $P4_12_12$, which was confirmed on the basis of the Flack's parameter, 0.00(2).

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* Author for correnpondence. E-mail: shionoya@chem.s.u-tokyo.ac.jp.

[†] The University of Tokyo.

[§] Nankai University.

[‡] Rigaku Corporation.

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(9) Complex **1** was prepared by layering a solution of $Zn(ClO_4)_2{\cdot}6H_2O$ (37 mg, 0.1 mmol) in CH_3CN (5 mL) carefully onto a solution of DPT (24 mg, 0.1 mmol) in $CHCl_3$ (5 mL) at ambient temperature. The solution was kept standing, and then colorless prisms of **1** suitable for X-ray diffraction study were obtained in 47% yield. The structural determination was made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo Kα radiation at −150 ± 1 °C to a maximum 2θ value of 60.0°. The structure was solved by direct methods (SIR97) and expanded using Fourier techniques (DIRDIF). The non-hydrogen atoms were refined anisotropically. *Crystal data* for **1**: FW = 834.90, crystal size 0.25 mm × 0.10 mm × 0.05 mm, primitive tetragonal, space group $P4_12_12$, $a = b = 12.3804(7)$ Å, $c = 46.505(2)$ Å, $V = 7128.0(7)$ Å^3, $Z = 8$, $\mu = 9.1$ cm^{-1}, $D_c = 1.56$ g cm^{-3}, min/max transmission = 0.82/0.96. $2\theta < 60.03$, $R(R_w) = 0.109$ (0.168) for 5978 ($R_{int} = 0.121$) independent reflections out of a total of 66616 reflections with $I > -3.00\ \sigma(I)$ and 489 parameters. The space group, $P4_12_12$, was confirmed based on the Flack's parameter, 0.00(2). The good-of-fit on F^2 is 1.098, and the residual electron density (min/max) is −0.88/1.38 e$^-$/Å.

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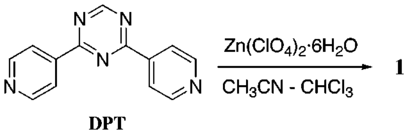
Scheme 1



Interpenetration of topologically equivalent 3-D nets potentially generates homomeric (Figure 1a) or heteromeric (Figure 1b) nets which are of identical or different composition, respectively. Interestingly, the structural determination of a single crystal revealed that complex **1** consists of an interpenetrating pair of 3-D nets (**A** and **B**) which are of different chemical composition (Figure 1b). Each zinc(II) ion is coordinated by four neutral DPT bridging ligands (for convenience, classified as L_A and $L_{A'}$ in net **A**, and L_B and $L_{B'}$ in net **B** in Figure 2) at the equatorial positions and therefore acts as a four-connecting node. Furthermore, two CH_3CN molecules (net **A**) or two water molecules (net **B**) are axially bound to each zinc center in a slightly distorted octahedral coordination environment (Figure 2).

Figure 3 shows a view of the doubly interpenetrating structure of nets **A** and **B**. Ligands L_A in net **A** (drawn with brown-yellow balls (zinc) and sticks (DPT)) along the *a*-axis are connected by zinc atoms to form a one-dimensional right-handed helical network (see the right-handed arrow in Figure 3). One helical pitch includes two zinc atoms and two DPT ligands. In addition, these helices are interlinked with the ligands $L_{A'}$ to form a large right-handed helical structure in which one helical pitch contains six zinc atoms and six DPT ligands, and the axis is parallel to that of the aforementioned smaller helices. Interestingly, ligands L_B and $L_{B'}$ and zinc atoms (drawn with blue-green balls (zinc) and sticks (DPT)) similarly form two types of helical structures, but the handedness is opposite to that with net **A** (see the left-handed arrow for the smaller helical network in net **B**).[10] It should be noted that interpeneration of heteromeric nets (composed of homochiral units) with the opposite handedness possibly produce chiral nets, whereas an interpenetrating enantiomorphic pair of nets produces a "3-D racemate". Indeed, each single crystal of complex **1** is spontaneously resolved with the chiral space group.

Taken all together, these two interpenetrating nets are of different chemical composition as well as of the opposite handedness. The structural feature led to spontaneous resolution, and thus each individual crystal has proved to consist of a single enantiomer in the solid state. As far as we know, this is the first example for *interpenetration of two different metal coordination 3-D nets leading to spontaneous resolution*.[11,12]

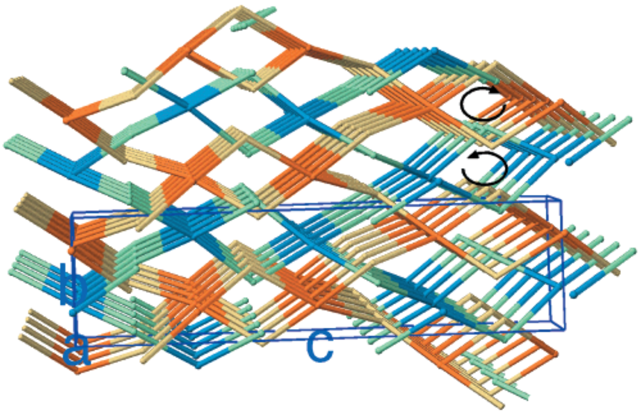


Figure 3. A view of the doubly interpenetrating nets **A** (brown-yellow) and **B** (blue-green) in complex **1**. The axial ligands, CH_3CN molecules (net **A**) or water molecules (net **B**), bound to each zinc center are omitted for clarity.

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Supporting Information Available: Crystallographic data for **1** (crystallographic information, atomic coordinates, bond lengths and angles, and structure factors); X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[10] The interaction observed between the two interpenetrating nets is aromatic face-to-face stacking which totally stabilizes the interpenetrating structure.

[11] A few examples for interpenetrating nets of different chemical composition have been reported: for instance, (a) Sleight, A. W. *Inorg. Chem.* **1968**, *7*, 1704. (b) Kim, K.-W.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1992**, *114*, 4878. (c) Soma, T.; Iwamoto, T. *Acta Crystallogr. Sec. C* **1996**, 1200. It should be also noted that a similar type of chirality has been observed in a noninterpenetrating net involving chemically distinct helical motifs, see: Blake, A. J.; Champness, N. R.; Cooke, P. A.; Nicolson, J. E. B. *Chem. Commun.* **2000**, 665.

[12] Such spontaneous resolution was also observed with cadmium−DPT complex, where, except for axial coordination, cadmium ions and DPT ligands assembled in a fashion similar to complex **1**. The results will be reported elsewhere in detail together with other metal complexes with DPT.