



Chiral metal–organic and supramolecular interpenetrating 3-D frameworks constructed by one angular ligand and 4,4'-dipyridine

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Abstract

The self-assembly of 1,3,4-thiadiazole-2,5-di-4-pyridyl (L^1), 4,4'-dipyridyl (L^2) with Zn(II), Cu(II) salts afforded one unusual coordination polymer with left-handed homo-chiral 3-D open MOFs in which supramolecular left-handed methanol helices were selectively formed, and one 2-D coordination polymer where two-fold interpenetrated 3-D supramolecular frameworks were constructed by hydrogen bonds.

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The design and self-assembly of interpenetrating networks have attracted great interests not only for their potential new or special characteristics as functional materials, but also for their fascinating architectures and topologies [1,2]. Meanwhile, constructing chiral coordination polymers have also attracted great attention because of their special utilities in enantioselective separation, asymmetric syntheses, nonlinear optical materials, as well as the processes of chiral self-organization being universal in life [3,4]. Therefore, they are two hot research topics of crystal engineering in recent years. However, the smaller in number of coordination polymers with chiral or interpenetrated frameworks suggests that exploring new coordination polymers with novel architecture is still one of the major challenges in the pursuit of special functional materials [5,6].

Using rigid multipyridyl ligands to build interesting porous or interpenetrated networks is a long-lasting goal

of our group. As our continuous work, longer biting spacer 2,5-bis(4-pyridyl)-1,3,4-thiadiazole (L^1) [7] which is expected to be an excellent pillar to bridge metal nodes to chains, helices, porous or interpenetrated frameworks has been synthesized and used to assemble with zinc(II) and copper(II) salts, etc. We report herein the two resultant coordination polymers $\{[Zn(L^1)(H_2O)(SO_4)](CH_3OH)_{0.5}(H_2O)_{0.5}\}_n$ (**1**) and $\{[Cu(L^2)_2(H_2O)_2](L^1)_2(H_2O)_2(PF_6)_2\}_n$ (**2**) [8]. Their crystal structures determined by X-ray diffraction [9] exhibit unusual 3-D chiral MOFs (**1**) and interpenetrated supramolecular networks (**2**), respectively.

For compound **1**, each zinc centre is based on a distorted octahedral symmetry coordinating to one oxygen atom [O(5)] from one water molecule, three oxygen atoms [O(1), O(2), O(4)] from three distinct SO_4^{2-} anions and two nitrogen atoms [N(1), N(4)] from pyridyl rings of two distinct L^1 . The obvious distortion is reflected in differences of bond distances and deviations of bond angles from 90° relating to zinc(II) metal centres (Fig. 1a).

The compound **1** crystallized in the chiral space group $P2_12_12_1$ is a 3-D chiral coordination polymer possessing three types of homo-chiral helices. The first

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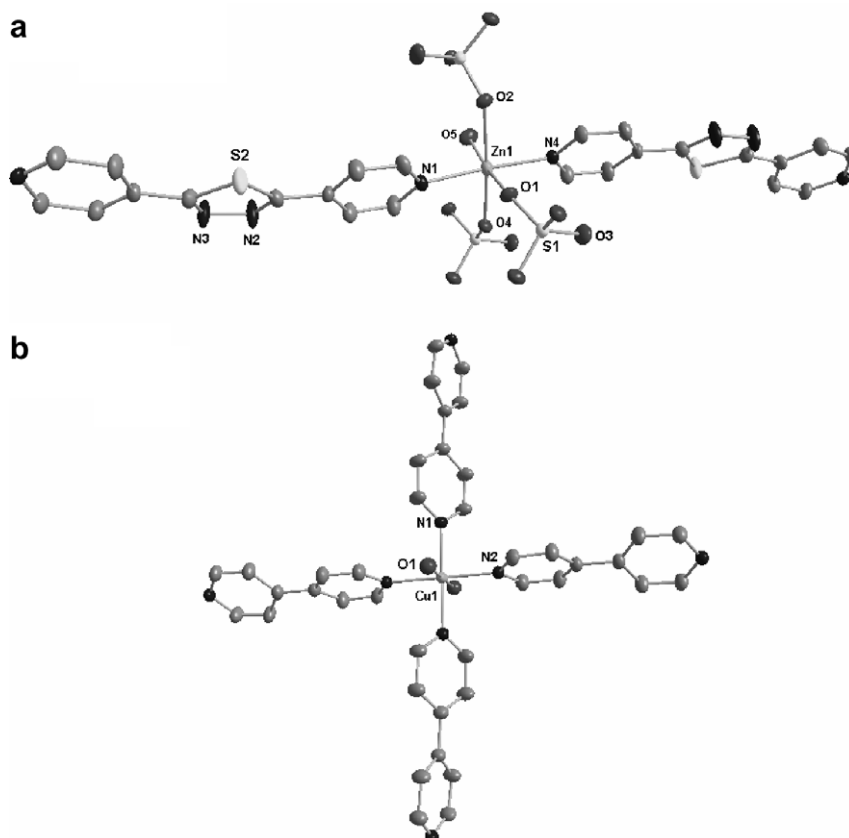


Fig. 1. The local coordination around metal centres in **1** (a) and **2** (b). Selected bond lengths (Å) and angles (°): (a) Zn(1)–O(1), 2.183(2), Zn(1)–O(2), 2.198(2), Zn(1)–O(4), 2.171(3), Zn(1)–O(5), 2.076(3), Zn(1)–N(1), 2.126(3), Zn(1)–N(4), 2.121(3), O(5)–Zn(1)–N(4), 90.88(12), O(5)–Zn(1)–N(1), 96.69(12), O(5)–Zn(1)–O(4), 87.56(10), N(1)–Zn(1)–O(4), 89.40(11), N(1)–Zn(1)–O(1), 83.90(12), O(5)–Zn(1)–O(2), 84.39(9), N(1)–Zn(1)–O(2), 90.48(11), O(4)–Zn(1)–O(1), 101.33(10), O(5)–Zn(1)–O(1), 171.10(10), N(4)–Zn(1)–N(1), 172.31(12); (b) Cu(1)–N(1), 2.062(3), Cu(1)–N(2), 2.079(3), Cu(1)–O(1), 2.380(3), N(1)–Cu(1)–N(2), 88.03(10), N(1)–Cu(1)–O(1), 90.23(10), N(2)–Cu(1)–O(1), 89.68(10).

mentioned is the chiral inorganic 2-D layers consisting of μ_3 -SO₄^{2−} bridging Zn(II) centres. There are characteristic IR bands of the SO₄^{2−} anions at 1040–1140 cm^{−1}, indicating its tridentate coordination feature. Through two oxygen atoms [O(2), O(4)], each sulfate anion bridges two Zn(II) ions to form infinite left-handed helical –Zn–O–S–O–Zn– chains along the crystallographic *b*-axis. The short distance of Zn···Zn bridged by a sulfate anion is about 5.555 Å and the pitch of the helix is about 10.364 Å. These helices are further connected into a chiral 2-D ZnSO₄ layer by oxygen atoms [O(1)] of sulfates (Fig. 2). Along the crystallographic *c*-axis, L¹, however, bridge two Zn(II) ions by two pyridyls' nitrogen atoms, forming another left-handed –Zn–L¹–Zn– helix. Thus all parallel inorganic layers are linked into a chiral 3-D framework containing two distinct homo-chiral helices. As shown in Fig. 3, the inorganic layers are supported by rigid pillars L¹ to form two-sorted dimension-different square channels.

The striking feature of this polymer is that the larger square chiral channel (about 14 × 6 Å²) embodies the third homo-chiral left-handed helix guest, which is a methanol supramolecule assembled by intermolecular hydrogen interactions C–H···O (Fig. 3) [10]. This suggests that achi-

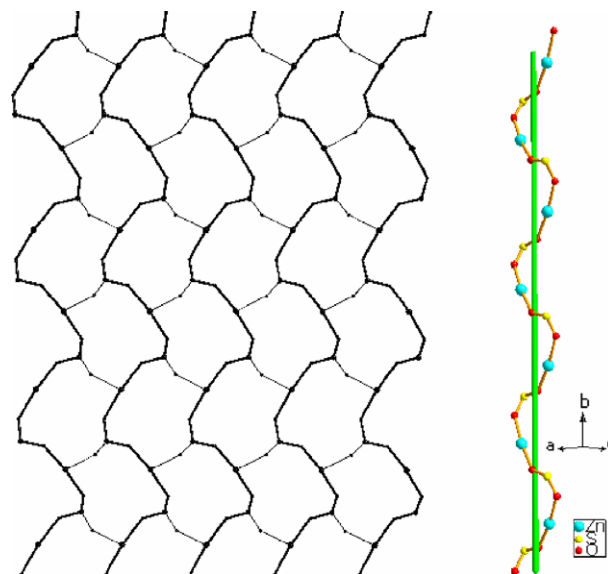


Fig. 2. The 2-D inorganic layer structure formed by left-hand helices (left) and a view of cylindrical left-hand helix (right) of ZnSO₄ of the complex **1**.

ral organic molecules can be selectively assembled into chiral supramolecular helices under a chiral environment such as a chiral channel.

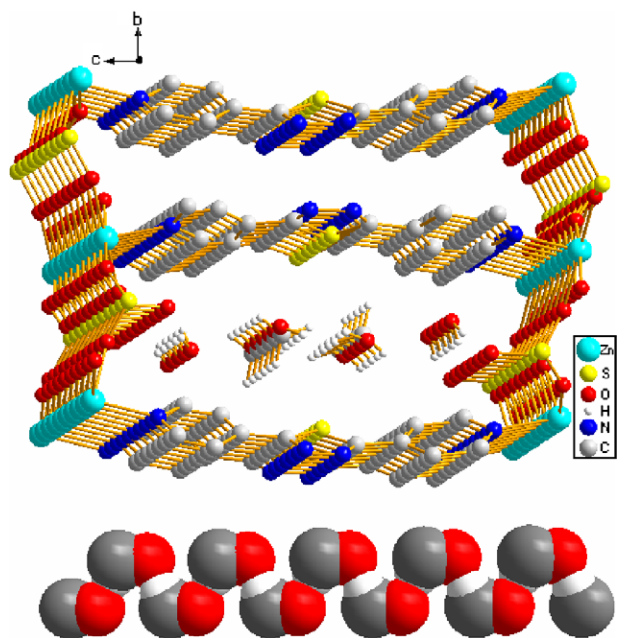


Fig. 3. A diagram showing methanol molecules as guests in the larger channels of 3-D metal–organic framework (up) and a space-filling view of the left-hand supramolecular methanol helix (down).

For compound **2**, the metal centre Cu(II) is six-coordinated to four nitrogen atoms from four distinct L^2 molecules and two oxygen atoms from two distinct water molecules to form a slightly distorted octahedral symmetry where bond distances of Cu–O are longer than those of Cu–N. Four nitrogen atoms are located in the equatorial plane and two oxygen atoms in two axial positions (Fig. 1b). L^1 molecules do not act as bridging ligand as in compound **1** but play another role of guests hosted in the metal–organic square grid. Each (4,4) grid with the dimensions of $11.2108 \times 11.2108 \text{ \AA}^2$ is constructed by four copper ions bridged by four L^2 ligands (Fig. S1).

It is noteworthy that there are medium π – π stacking interactions between two antiparallel neighbouring L^1 molecules in one grid with the central to central distance 3.7218 \AA and dihedral angle 0° . The two packing L^1 molecules can be considered as one bridge which connects two 2-D layers up and down the 2-D layer penetrated by L^1 molecules through hydrogen bondings between nitrogen atoms (acceptors) from L^1 molecules and oxygen atoms (donors) from coordinating and non-coordinating water molecules [O(1)–H(1W) \cdots N(4), $2.757(4) \text{ \AA}$; O(2)–H(3W) \cdots N(3), $2.852(5) \text{ \AA}$; O(1)–H(2W) \cdots O(2), $2.734(4) \text{ \AA}$] (Fig. 4). This type of linkage can be applied to every L^1 molecule and 2-D layer. So all 2-D layers are penetrated by double L^1 molecules and all separate 2-D layers are linked by L^1 linkers. Thus, an interesting two-fold supramolecular interpenetrating network is generated (Fig. 5).

Finally, from the structural information of the two coordination polymers, it can be inferred that the angular dipyriddy ligand L^1 can either act as bridging ligand linking

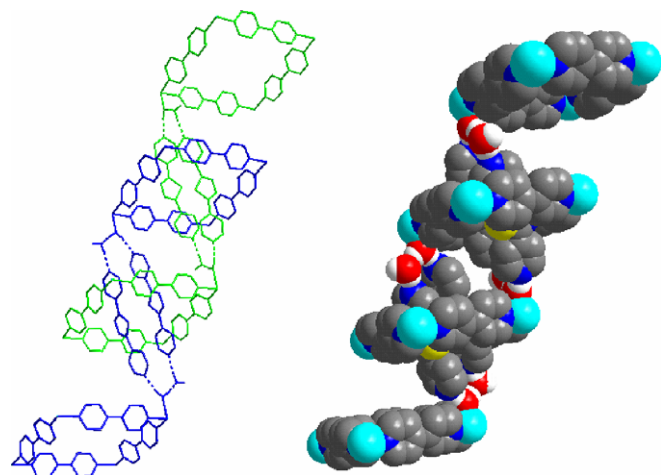


Fig. 4. A firework (left) and a space-filling (right) diagrams showing the supramolecular interpenetration (dotted line standing for hydrogen bondings).

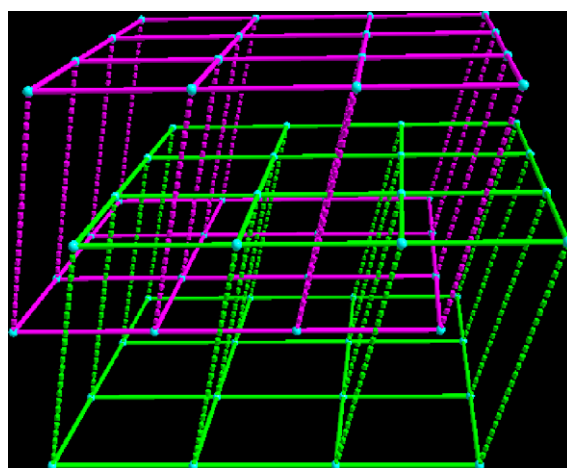


Fig. 5. A diagram showing the 3-D supramolecular interpenetrating network of the compound **2** (the dotted line standing for linkages of double L^1 molecules by hydrogen bondings).

metal nodes to construct metal–organic frameworks or be used to construct supramolecular structures through non-covalent interactions such as hydrogen bondings.

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Appendix A. Supplementary material

CCDC 622165 and 627043 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. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.inoche.2007.12.038](https://doi.org/10.1016/j.inoche.2007.12.038).

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- [8] *Synthesis of 1.* To a solution of **L**¹ (0.024 g, 0.1 mmol) and **L**² (0.016 g, 0.1 mmol) in the mixed solvent (5 mL chloroform, 10 mL methanol) was added ZnSO₄ · 7H₂O (0.029 g, 0.1 mmol) in methanol (15 mL). The mixture was stirred for 20 min, and then filtered. The filtrate was allowed to slowly evaporate the solvents at room temperature and about 40 days later suitable single crystals (colourless needle) were obtained. Yield: about 25%. Anal. Calcd % (found %) for C_{12.50}H₁₃N₄O₆S₂Zn: C, 33.75 (34.12); H, 2.95 (2.96); N, 12.60 (12.57). IR_{ν_{KBr}} (cm⁻¹): 3444b, 2930w, 1616s, 1560w, 1435s, 1402m, 1333w, 1261w, 1225m, 1139s, 1078m, 1032m, 1004w, 977w, 829m, 712m, 608s, 536w, 484w. *Synthesis of 2.* To a solution of **L**¹ (0.024 g, 0.1 mmol) and **L**² (0.016 g, 0.1 mmol) in the mixed solvent (5 mL chloroform, 10 mL methanol) was added Cu(CH₃COO)₂ · H₂O (0.02 g, 0.1 mmol) in methanol (10 mL). NH₄PF₆ (0.033 g, 0.2 mmol) in water (5 mL) was added to the mixture after it was stirred for 20 min. After being stirred for another 5 min the mixture was filtered. The filtrate was allowed to slowly evaporate the solvents at room temperature and about 20 days later suitable single crystals (blue block) were obtained. Yield: about 32%. Anal. Calcd % (found %) for C₄₄H₄₀CuF₁₂N₁₂O₄P₂S₂: C, 43.37 (43.54); H, 3.31 (3.28); N, 13.79 (13.62). IR_{ν_{KBr}} (cm⁻¹): 3111w, 1609 s, 1558w, 1535w, 1492w, 1428s, 1331w, 1259w, 1223s, 1101w, 1071m, 997w, 844vs, 736w, 698m, 639w, 611w, 560s, 495w.
- [9] X-ray diffraction data for single crystals were collected at 291 K on a Bruker SMART APEX-II CCD diffractometer equipped with a graphite crystal and incident beam monochromator using Mo Kα radiation (λ = 0.71073 Å). Crystal data for **1**: C_{12.50}H₁₃N₄O₆S₂Zn, *M* = 444.79, Orthorhombic, space group *P*2₁2₁2₁ (No. 19), *a* = 5.5225(6), *b* = 10.3642(11), *c* = 29.725(3) Å, *V* = 1701.3(3) Å³, *Z* = 4, μ(Mo Kα) = 1.728 mm⁻¹, final *R* indices [*I* > 2σ(*I*): *R*₁ = 0.0323, *wR*₂ = 0.0728, *R* indices (all data): *R*₁ = 0.0377, *wR*₂ = 0.0757. Crystal data for **2**: C₄₄H₄₀F₁₂N₁₂O₄P₂S₂Cu, *M* = 1218.48, Monoclinic, space group *P*2(1)/*m* (No. 11), *a* = 11.0886(10), *b* = 16.4333(15), *c* = 14.9897(13) Å, *V* = 2570.1(4) Å³, β = 109.790(1), *Z* = 2, μ(Mo Kα) = 0.668 mm⁻¹, final *R* indices [*I* > 2σ(*I*): *R*₁ = 0.0524, *wR*₂ = 0.1410, *R* indices (all data): *R*₁ = 0.0672, *wR*₂ = 0.1543.
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