

Available online at www.sciencedirect.com

Mendeleev Commun., 2013, 23, 229–230

Mendeleev Communications

Construction of an unusual 2D_{chiral}/2D_{chiral}→2D_{achiral} network based on a V-shaped pyridyl ligand

Jin-Song Hu,*^{*a,b*} Zhang Lei,^{*a*} Hong-Long Xing,^{*a*} Xiao-Mei Zhang,^{*a*} Jian-Jun Shi^{*a*} and Jie He^{*a*}

^a School of Chemical Engineering, Anhui University of Science and Technology, Huainan 232001, P. R. China. E-mail: jshu@aust.edu.cn

^b State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P. R. China

DOI: 10.1016/j.mencom.2013.07.018

A new interpenetrating 2D coordination polymer $\{[Zn(dpb)(glu)]\}_n$ was prepared under hydrothermal conditions, and an X-ray diffraction study showed that it is an unusual ABAB stacked $2D_{chiral}/2D_{chiral} \rightarrow 2D_{achiral}$ network.

The rational design of coordination polymers (CPs) from various molecular building blocks connected by coordination bonds and supramolecular contacts have attracted great attention not only for their structural diversity^{1,2} but also for their explosive applications in photochemical areas,^{3,4} gas adsorption and separation,^{5,6} molecular magnetism^{7,8} and heterogeneous catalysis.^{9,10} Entangled systems are of considerable interest for supramolecular chemistry^{11,12} due to their esthetic architectures and topologies. Interpenetration as an important branch of entangled systems has attracted more and more attention, and a great number of interpenetrating nets have been reported.^{13,14} Interpenetration is an approach of nature to avoid voids or open space in a single network. The interpenetrating structure depends upon not only the metal coordination geometry but also the shapes and lengths of special ligands. Recently, a great deal of mixed-ligand CPs have been reported,^{15,16} but the design of the frameworks is still challenging, the occurrence of interpenetration sometimes requires that different bridging ligands match each other in shape and length.^{17,18} To continue our previous work with the V-shaped pyridyl ligand 1,3-dipyridylbenzene (1,3-dpb),¹⁹ we tried to explore the assembly of dpb and carboxylic acids. Here, we report a new $2D_{chiral}/2D_{chiral} \rightarrow 2D_{achiral}$ network based on dpb and flexible glutaric acid (H2glu).[†]

X-ray crystallography analysis[‡] reveals that the asymmetric unit of **1** contains an independent Zn^{II} cation, a dpb ligand and a glu^{2–} anion. As shown in Figure 1, Zn(1) has an octahedral coordination environment with two N atoms from two dpb and four O atoms from two glu^{2–}. The Zn–N bond lengths are 2.082(4) and 2.095(4) Å, and the Zn–O lengths are 2.075(4)–2.430(5) Å, which are similar to those in other Zn^{II} complexes containing the glu^{2–} anion ([Zn–O]: 1.918–2.574 Å). The dihedral angles

^{*} Crystal data. Crystal of 1 ($C_{21}H_{18}N_2O_4Zn$, M = 427.76) is monoclinic, space group $P2_1/c$, at 296 K: a = 7.7163(13), b = 14.477(3),



Figure 1 Coordination environment of 1. The hydrogen atoms are omitted for clarity. Symmetry codes: #1 = -x, -0.5 + y, 0.5 - z; #2 = 2 - x, 0.5 + y, 0.5 - z. Selected bond lengths (Å): Zn(1)-N(1#1) 2.082(4), Zn(1)-N(2) 2.095(4), Zn(1)-O(3) 2.133(4), Zn(1)-O(4) 2.272(4), Zn(1)-O(1#2) 2.075(4), Zn(1)-O(2#2) 2.430(5); selected bond angles (°): O(1#2)-Zn(1)-N(1#1) 139.86(15), O(1#2)-Zn(1)-N(2) 103.26(15), N(1#1)-Zn(1)-N(2) 94.07(14), O(1#2)-Zn(1)-O(3) 111.82(16), N(1#1)-Zn(1)-O(3) 103.66(16), N(2)-Zn(1)-O(3) 91.00(15), O(1#2)-Zn(1)-O(4) 91.65(15), N(1#1)-Zn(1)-O(4) 91.73(15), N(2)-Zn(1)-O(4) 148.69(15), O(3)-Zn(1)-O(4) 57.76(15), O(1#2)-Zn(1)-O(2#2) 94.43(16), N(1#1)-Zn(1)-O(2#2) 87.47(14), N(2)-Zn(1)-O(2#2) 94.43(16), O(3)-Zn(1)-O(2#2) 167.26(16), O(4)-Zn(1)-O(2#2) 116.57(17).

between phenyl and pyridyl rings are 23.8° and 41.0° , and the dihedral angle between pyridyl rings is 40.3° .

The neighbouring Zn(1) ions linked V-shaped dpb into an infinitely helical chain, the adjacent Zn(1)…Zn(1) distance is 8.622 Å. Glu^{2–} anions adopt *cis*-configuration, also linked Zn(1) ions to form an infinitely helical chain, the adjacent distance of Zn(1)…Zn(1) is 13.168 Å. These two kinds of helical chains further form a wavelike 2D layer by sharing the Zn^{II} ions. There are irregular windows in 2D layer, which has a 40-membered

and c = 17.439(3) Å, $\beta = 101.818(2)^\circ$, V = 1906.8(6) Å³, Z = 4, $d_{calc} = 1.490$ g cm⁻³, μ (MoK α) = 1.318 mm⁻¹, F(000) = 1248. 13122 reflections were measured and 3348 independent reflections ($R_{int} = 0.054$) were used in further refinement. The refinement converged to $wR_2 = 0.1624$ and GOF = 1.08 for all independent reflections [$R_1 = 0.0532$ was calculated against *F* for 2524 observed reflections with $I > 2\sigma(I)$]. The measurements were made on a Bruker Apex Smart CCD diffractometer with graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using full-matrix least-squares procedures based on F^2 values.²⁰ Hydrogen atom positions were fixed geometrically at calculated distances and allowed them to ride on the parent atoms.

CCDC 936250 contains 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. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2013.

[†] Commercial reagents and solvents were used as received. The IR absorption spectra of complexes were recorded in a range of 400–4000 cm⁻¹ on a Nicolet (Impact 410) spectrometer with KBr pellets (5 mg sample in 500 mg of KBr). C, H, and N analyses were carried out with a Perkin–Elmer 240C elemental analyzer.

General procedure for the preparation of compound **1**. A mixture of $Zn(NO_3)_2$ (0.15 mmol), 1,3-dpb and glu²⁻ (0.1 mmol) was dissolved in 8 ml of DMF–MeOH–H₂O (1:1:2, v/v). The final mixture was placed in a Parr Teflon-lined stainless steel vessel (15 ml) and heated at 110 °C for 3 days, colourless crystals were obtained (52% yield based on 1,3-dpb). IR (KBr, ν/cm^{-1}): 3425 (m), 3068 (w), 2848 (w), 2359 (m), 1580 (s), 1515 (s), 1394 (s), 1226 (s), 1156 (w), 1056 (s), 964 (w), 852 (w), 757 (m), 674 (m), 536 (m). Found (%): C, 59.06; H, 4.13; N, 6.41. Calc. for C₂₁H₁₈N₂O₄Zn (%): C, 58.96; H, 4.24; N, 6.55.



Figure 2 Neighbouring Zn^{II} ions linked dpb or glu^{2-} into infinitely helical chains, the helical directions of $(dpb-Zn-dpb)_n$ or $(glu-Zn-glu)_n$ chains are the same.

loop composed of four metal ions, two dpb linkers and two glu^{2–} anions. In this layer, the helical directions of all $(dpb-Zn-dpb)_n$ or all $(glu-Zn-glu)_n$ chains are the same, so the 2D layer can be regarded as a $2D_{chiral}$ layer (Figure 2).

In complex 1, a pair of adjacent 2D layers interpenetrated each other to generate a 2D + 2D \rightarrow 2D sheet (Figure 3); because the helical directions of two interpenetrating 2D layers are the same, the sheet can be regarded as $2D_{chiral} + 2D_{chiral} \rightarrow 2D_{chiral}$ sheet. The helical chains of (dpb–Zn–dpb)n and (glu–Zn–glu)_n in the interpenetrating 2D sheet coincide to form a double helical chain. The adjacent interpenetrating $2D_{chiral}$ sheets are stacked in an offset ABAB mode, the most striking feature is that the helical directions of sheet (A) and sheet (B) are reversed, so complex 1 is achiral 2D network (Figure 4). The interpenetration mode and the formation of the double helices benefit not only from the shape of the two bridging ligands but also from the match of two ligands in length.

In summary, a new $2D_{achiral}$ network has been synthesized under solvothermal conditions. Complex 1 is an interpenetrating $2D_{chiral} + 2D_{chiral} \rightarrow 2D_{chiral}$ sheet, which further stacked to generate a $2D_{achiral}$ network. The results demonstrate that the lengths and bendings of ligands can be well used as a structure-directing tool in the synthesis of unusual coordination frameworks.

This work was supported by the Natural Science Foundation of China (grant nos. 21271008 and 51173002), the Natural



Figure 3 2D + 2D \rightarrow 2D interpenetrating sheet constructed by two identical 2D layers.



Figure 4 Interpenetrating $2D_{chiral} + 2D_{chiral} \Rightarrow 2D_{chiral}$ sheet, which stacked in the ABAB manner to generate a $2D_{achiral}$ network.

Science Fund of Education Department of Anhui Province (grant no. KJ2011A091), the Natural Science Foundation of Anhui Province (grant no. 1308085QB34) and the Research Fund of Key Laboratory for Advanced Technology in Environmental Protection of Jiangsu Province (grant no. AE201107).

References

- H. Eshtiagh-Hosseini and M. Mirzaei, *Mendeleev Commun.*, 2012, 22, 323.
- 2 S. K. Chawla, M. Arora, K. Nättinen and K. Rissanen, *Mendeleev Commun.*, 2006, 88.
- 3 L. Rajput, D. Kim and M. S. Lah, CrystEngComm, 2013, 15, 259.
- 4 P. K. Thallapally, J. Tian, M. R. Kishan, C. A. Fernandez, S. J. Dalgarno, P. B. McGrail, J. E. Warren and J. L. Atwood, *J. Am. Chem. Soc.*, 2008, 130, 16842.
- 5 C. R. Tan, S. H. Yang, N. R. Champness, X. Lin, A. J. Blake, W. Lewis and M. Schröder, *Chem. Commun.*, 2011, 47, 4487.
- 6 J. R. Li and H. C. Zhou, Nat. Chem., 2010, 2, 893.
- 7 R. A. Agarwal, A. Aijaz, C. Sañudo, Q. Xu and P. K. Bharadwaj, *Cryst. Growth Des.*, 2013, **13**, 1238.
- 8 D. W. Ryu, W. R. Lee, J. W. Lee, J. H. Yoon, H. C. Kim, E. K. Koh and C. S. Hong, *Chem. Commun.*, 2010, 46, 8779.
- 9 A. Corma, H. García, F. X. Llabrés i Xamena, *Chem. Rev.*, 2010, **110**, 4606.
- 10 D. Bradshaw, A. Garai and J. Huo, Chem. Soc. Rev., 2012, 41, 2344.
- 11 J. H. He, D. R. Xiao, H.Y. Chen, S. W. Yan, D. Z. Sun, X. Wang, J. Yang, R. Yuan and E. B. Wang, *Inorg. Chem. Acta*, 2012, 385, 170.
- 12 Z. Z. Lu, R. Zhang, Y. Z. Li, Z. J. Guo and H. G. Zheng, J. Am. Chem. Soc., 2011, 133, 4172.
- 13 L. Carlucci, G. Ciani and D. M. Proserpio, *Coord. Chem. Rev.*, 2003, 246, 247.
- 14 J. S. Hu, L. F. Huang, X. Q. Yao, Y. Z. Li, Z. J. Guo, H. G. Zheng and Z. L. Xue, *Inorg. Chem.*, 2011, **50**, 2404.
- 15 S. K. Henninger, H. A. Habib and C. Janiak, J. Am. Chem. Soc., 2009, 131, 2776.
- 16 R. Patra, H. M. Titi and I. Goldberg, Cryst. Growth Des., 2013, 13, 1342.
- 17 D. Liu, N. Y. Li, F. Z. Deng, Y. F. Wang, Y. Xu, G. Y. Xie and Z. L. Zheng, J. Mol. Struct., 2013, 1034, 271.
- 18 M. H. Xie, X. L. Yang and C. D. Wu, Chem. Commun., 2011, 47, 5521.
- 19 J. S. Hu, X. H. Liu, J. J. Shi, H. L. Xing and J. He, *Chinese J. Inorg. Chem.*, 2012, 28, 381.
- 20 Bruker 2000, SMART (Version 5.0), SAINT-plus (Version 6), SHELXTL (Version 6.1), and SADABS (Version 2.03), Bruker AXS Inc., Madison, WI.

Received: 30th April 2013; Com. 13/4115