Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2014, **24**, 180–181

Mendeleev Communications

A trilaminar cobalt coordination network with trinuclear and uninuclear building units

Ming-Dao Zhang,*[a] Bao-Hui Zheng,[b] Yan Jiao[a] and Min-Dong Chen*[a]

[a] *Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control, Jiangsu Collaborative Innovation Center for Atmospheric Environment & Equipment Technology, School of Environmental Science and Engineering, Nanjing University of Information Science & Technology, Nanjing 210044, Jiangsu, P. R. China. E-mail: matchlessjimmy@163.com; chenmd@nuist.edu.cn*

[b] *Institute of Chemical Materials, Chinese Academy of Engineering Physics, Mianyang 621999, Sichuan, P. R. China. E-mail: zhengbaohui305@126.com*

DOI: 10.1016/j.mencom.2014.04.020

The new coordination polymer $\{[Co_4(DPDBT)_5(fuma)_4(H_2O)_2](NO_3)_4(H_2O)_7\}_n$, where DPDBT is 2,8-di(pyridin-4-yl)dibenzo[*b*,*d*]thiophene and fuma is fumarate dianion, was prepared; X-ray diffraction analysis revealed that it exhibits a 2D *gek*2 network with the coexistence of trinuclear and uninuclear building units.

Mixed-ligand coordination polymers are of interest due to their intriguing aesthetic structures[1–3] and potential applications in photochemistry, molecular magnetism, gas adsorption, gas separation and heterogeneous catalysis.[4–8] Pyridyl ligands, which possess excellent coordination ability to meet the requirement of coordination geometries of metal ions, have been widely used in the synthesis of coordination polymers.[9–12]

We designed and synthesized a new V-shape pyridyl ligand, 2,8-di(pyridin-4-yl)dibenzo[*b*,*d*]thiophene (DPDBT),[†] which can be regarded as a rigid ligand. We adopted fumaric acid (H_2fuma)[11,13] as a co-ligand to react with DPDBT and bivalent metal salts. Then, a new coordination polymer with intriguing structure was obtained under solvothermal conditions, namely, $\{[Co_4(DPDBT)_5(fuma)_4(H_2O)_2](NO_3)_4(H_2O)_7\}_n$ **1**.[†]

The crystal structure determination[14,15] revealed that complex **1** crystallizes in monoclinic crystal system *I*2/*m*.[‡] The asymmetric unit of **1** contains four Co^{3+} ions, five DPDBT molecules, four fuma^{2-} anions, two coordinated water molecules, four NO_3^- anions and seven lattice water molecules. The valence states of Co in **1** were confirmed by the PLATON program.[15]

Unusually, there are two kinds of building units around the Co^{3+} ions in **1** (Figure 1). Each Co(1) atom coordinates to four oxygen atoms from four distinct fuma^{2-} anions and two nitrogen

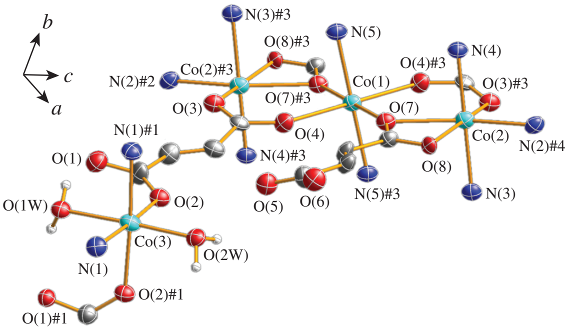

Figure 1 Coordination environments of complex **1**. The hydrogen atoms are omitted for clarity. Symmetry codes: #1 = *x*, –*y*, *z*; #2 = 0.5 + *x*, 0.5 + *y*, –0.5 + *z*; #3 = –*x* + 1/2, –*y* + 1/2, –*z* + 3/2; #4 = –*x*, –*y*, –*z* + 2. Selected bond lengths (Å): Co(1)–O(7) 2.061(2), Co(1)–O(7)#3 2.061(2), Co(1)–N(5) 2.205(3), Co(1)–N(5)#3 2.205(3), Co(1)–O(4) 2.281(2), Co(1)–O(4)#3 2.281(2), Co(2)–O(3)#3 2.047(2), Co(2)–N(2)#4 2.136(3), Co(2)–N(4) 2.138(3), Co(2)–O(8) 2.1419(19), Co(2)–N(3) 2.193(3), Co(2)–O(7) 2.259(2), Co(3)–O(2W) 2.035(3), Co(3)–O(2) 2.155(2), Co(3)–O(2)#1 2.155(2), Co(3)–N(1)#1 2.189(3), Co(3)–O(1W) 2.193(3).

[†] Reagents and solvents employed were commercially available and used as received.

Synthesis of DPDBT. A mixture of 2,8-dibromodibenzo[*b*,*d*]thiophene (3.42 g, 10 mmol), $Pd(PPh_3)_4$ (0.580 g, 0.5 mmol), pyridine-4-boronic acid (2.93 g, 24 mmol), 1 mM K_2CO_3 (25 ml, 25 mmol) and 1,4-dioxane (100 ml) was refluxed under N_2 for 24 h. After cooling to room temperature, the mixture was extracted by $CHCl_3$ (3×100 ml). The combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated *in vacuo*. The residue was purified by silica gel column chromatography with EtOAc as eluent to give the target compound DPDBT as yellow solid (2.84 g, 84%). ^{1}H NMR (500 MHz, DMSO-d_6) δ: 7.96 (d, 4H, *J* 5.5 Hz), 8.03 (d, 2H, *J* 8.5 Hz), 8.22 (d, 2H, *J* 8.5 Hz), 8.72 (d, 4H, *J* 5.5 Hz), 9.11 (s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 121.28, 121.82, 124.33, 126.25, 134.42, 136.31, 140.60, 147.15, 150.74. MS (ESI-MS), *m*/*z*: 339.38 $[M+H]^+$ (calc. for $C_{22}H_{14}N_2S$, *m*/*z*: 338.09).

Synthesis of complex **1**. A mixture of $Co(NO_3)_2\cdot 6H_2O$ (29.1 mg, 0.1 mmol), DPDBT (33.8 mg, 0.1 mmol) and fumaric acid (11.6 mg, 0.1 mmol) was dissolved in 15 ml of DMF–H_2O (1:1). The final mixture was placed in a Parr Teflon-lined stainless steel vessel (25 ml) under autogenous pressure and heated at 95 °C for 3 days. Red crystals of **1** were collected in 73% yield (based on DPDBT ligand). IR (KBr, ν/cm^{-1}): 3422 (s), 2362 (s), 1664 (s), 1610 (s), 1469 (m), 1380 (s), 1288 (m), 1226 (m), 1091 (m), 1036 (m), 1009 (m), 839 (w), 805 (s), 776 (w), 677 (s), 635 (w), 569 (w), 503 (m).

[‡] *Crystallographic data for* **1**. $C_{126}H_{96}Co_4N_{14}O_{37}S_5$ (M = 2794.19) is monoclinic, space group *I*2/*m*, at 296 K: a = 19.0377(19), b = 28.6840(3) and c = 25.7190(3) Å, β = 98.295(3)°, V = 13897.6(17) Å^3, Z = 4, d_{calc} = = 1.335 g cm^{-3}, μ(MoKα) = 0.624 mm^{-1}, F(000) = 5736. 47358 reflections were measured and 16320 independent reflections (R_{int} = 0.0258) were used in further refinement. The refinement converged to wR_2 = 0.1457 and GOF = 1.090 for all independent reflections [R_1 = 0.0503 was calculated against F for 8583 observed reflections with $I > 2\sigma(I)$]. The measurements were made on a Bruker Apex Smart CCD diffractometer with graphite-monochromated MoKα radiation (λ = 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.[14] Hydrogen atoms positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms.

CCDC 959829 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2014.

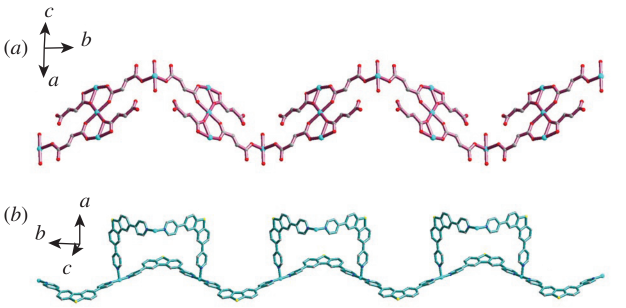

Figure 2 (*a*) 1D chain linked by fuma^{2-} and Hfuma^{-} anions and Co^{2+} ions; (*b*) 1D chain linked by DPDBT ligands and Co^{2+} ions.

atoms from two distinct DPDBT molecules. On the both sides of each Co(1) atom, there is one Co(2) atom coordinated to three oxygen atoms from two fuma^{2-} anions and three nitrogen atoms from three distinct DPDBT molecules. Then, the trinuclear cobalt building unit $[Co_3(COO)_4]^{5+}$ in compound **1** is generated (Figure 1).[16] The adjacent distance of Co(1)···Co(2) is 3.68 Å. Another kind of building unit is uninuclear: each Co(3) atom coordinates to two oxygen atoms from two distinct fuma^{2-} anions, two nitrogen atoms from two distinct DPDBT molecules, and two oxygen atoms from two water molecules.

For each fuma^{2-} anion in the asymmetric unit of **1**, one carboxylate group [O(7), O(8)] coordinates to two Co atoms with μ^3-chelating mode, while another carboxylate group [O(5), O(6)] does not participate in coordination. For another fuma^{2-} anion in the asymmetric unit of **1**, two carboxylate groups coordinate to Co atoms with bidentate and monodentate modes, forming a kind of 1D chains [Figure 2(*a*)]. Meanwhile, other 1D chains are created from the coordination of DPDBT molecules with Co atoms [Figure 2(*b*)]. The N(1)–S(1)–N(2), N(3)–S(2)–N(3), N(4)–S(3)–N(4) and N(5)–S(4)–N(5) angles are 81.308°, 79.709°, 80.871° and 81.395°, respectively. The above two kinds of 1D chains link each other by Co^{3+} ions, giving rise to a 2D trilaminar network (Figure 3). Complex **1** contains a small solvent accessible void space of 20.0% of the total crystal volume, as calculated by the PLATON program.[15] Previously, 2D coordination networks containing cavities or channels attracted much attention due to their function in finely tuning the shape and size of cavities.[16]

Better insight into this intricate network can be accessed by a topological method. The trinuclear cobalt cluster unit $[Co_3(COO)_4]^{5+}$ and Co(3) atom can be regarded as six-connected and four-connected nodes, respectively. DPDBT ligands and fuma^{2-} anions can be regarded as linkers (distances Co···Co linked by DPDBT ligands are 14.342 and 14.565 Å; distances Co···Co linked by fuma^{2-} anions are 9.099 Å), thus forming a 4,6-c network [Figure 4(*a*)]. The Schläfli symbol for this binodal net is $\{3^2.4^4\}\{3^4.4^2.6^4.7^5\}$, and the topology type of this net is *gek2*. The adjacent *gek*2 networks in **1** do not entangle with each other [Figure 4(*b*)].

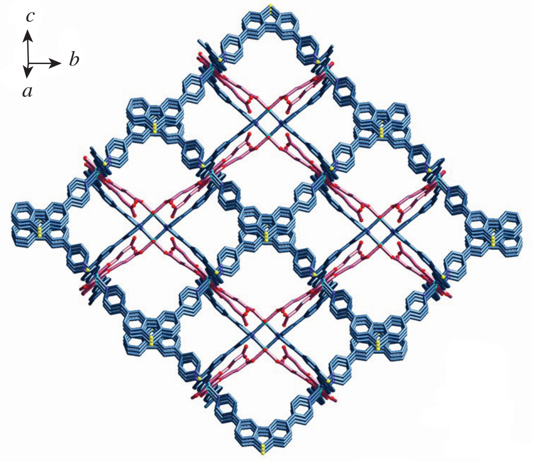

Figure 3 2D trilaminar network of complex **1**.

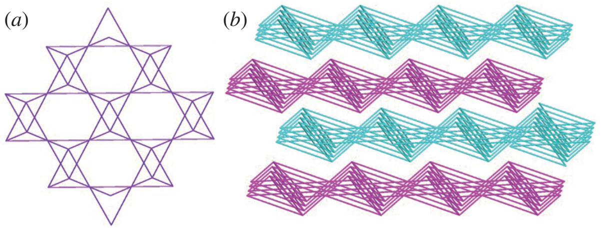

Figure 4 (*a*) Perspective view of the single 2D network of **1** (DPDBT ligand and fuma^{2-} anions were simplified into linkers); (*b*) packing drawing of a simplified structure of **1**.

In conclusion, the new fascinating 2D cobalt trilaminar coordination polymer $\{[Co_4(DPDBT)_5(fuma)_4(H_2O)_2](NO_3)_4(H_2O)_7\}_n$, which simultaneously includes trinuclear and uninuclear building units, was prepared based on fumaric acid and the V-shaped pyridyl ligand 2,8-di(pyridin-4-yl)dibenzo[*b*,*d*]thiophene (DPDBT) under hydrothermal conditions.

This work was supported by the Natural Science Foundation of China (grant no. 21272118), the Natural Science Foundation of Jiangsu, China (grant no. BK20130986) and the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

References

1 J.-S. Hu, X.-M. Zhang, H.-L. Xing, J. He and J.-J. Shi, *Mendeleev Commun.*, 2013, **23**, 231.
2 A. K. Eckert, O. N. Trukhina, M. S. Rodríguez-Morgade, E. A. Danilova, M. K. Islyaikin and T. Torres, *Mendeleev Commun.*, 2010, **20**, 192.
3 V. M. Kovrugin, V. V. Gurzhiy, S. V. Krivovichev, I. G. Tananaev and B. F. Myasoedov, *Mendeleev Commun.*, 2012, **22**, 11.
4 L. L. Johnston, J. H. Nettleman, M. A. Braverman, L. K. Sposato, R. M. Supkowski and R. L. LaDuca, *Polyhedron*, 2010, **29**, 303.
5 B. Xu, X. Lin, Z. He, Z. Lin and R. Cao, *Chem. Commun.*, 2011, **47**, 3766.
6 L. J. Murray, M. Dincâ and J. R. Long, *Chem. Soc. Rev.*, 2009, **38**, 1294.
7 L. Qin, J. S. Hu, M. D. Zhang, Z. J. Guo and H. G. Zheng, *Chem. Commun.*, 2012, **48**, 10757.
8 Z. L. Liao, G. D. Li, M. H. Bi and J. S. Chen, *Inorg. Chem.*, 2008, **47**, 4844.
9 Z. Z. Lu, R. Zhang, Y. Z. Li, Z. J. Guo and H. G. Zheng, *J. Am. Chem. Soc.*, 2011, **133**, 4172.
10 M. D. Zhang, C. M. Di, L. Qin, X. Q. Yao, Y. Z. Li, Z. J. Guo and H. G. Zheng, *Cryst. Growth Des.*, 2012, **12**, 3957.
11 B. Chen, S. Ma, F. Zapata, F. R. Fronczek, E. B. Lobkovsky and H. C. Zhou, *Inorg. Chem.*, 2007, **46**, 1233.
12 J.-S. Hu, Z. Lei, H.-L. Xing, X.-M. Zhang, J.-J. Shi and J. He, *Mendeleev Commun.*, 2013, **23**, 229.
13 F. Meng, L. Qin, M. Zhang and H. Zheng, *CrystEngComm*, 2014, **16**, 698.
14 *Bruker 2000, SMART (Version 5.0), SAINT-plus (Version 6), SHELXTL (Version 6.1), and SADABS (Version 2.03)*, Bruker AXS Inc., Madison, WI, 2000.
15 A. L. Spek, *Acta Crystallogr., Sect. A*, 1990, **46**, 194.
16 K. Biradha, M. Aoyagi and M. Fujita, *J. Am. Chem. Soc.*, 2000, **122**, 2397.

Received: 16th September 2013; Com. 13/4203