Inorg. Chem. **2007**, *46*, 6852–6854

Inorganic Chemistry
Communication

Unprecedented (3,10)-Connected 2-D Metal–Organic Framework Constructed from Octanuclear Cobalt(II) Clusters and a New Bifunctional Ligand

Wen-Qiang Zou,[†,‡] Ming-Sheng Wang,[†] Yan Li,[†,‡] A-Qing Wu,[†,‡] Fa-Kun Zheng,*,[†] Qi-Yong Chen,[†,‡] Guo-Cong Guo,*,[†] and Jin-Shun Huang[†]

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China, and Graduate School, Chinese Academy of Sciences, Beijing 100039, People's Republic of China

Received April 29, 2007

A metal–organic framework with the highest connectivity of 2-D topology was first assembled from an octacobalt(II) cluster as a 10-connected node and a new bifunctional ligand 1-(3,5-dicarboxyphenyl)-4-phenyl-1*H*-1,2,3-triazole as a 3-connected node as well as "double bridge" linkers.

The past decade has witnessed a rapid growth of interest in the field of metal−organic frameworks (MOFs) because of their potential applications as functional materials as well as their intriguing variety of molecular architectures and topologies.[1] On the basis of the knowledge of both the metal coordination preferences and ligand geometries, diverse 2-D and 3-D structures have been engineered.[2] The most common structural types found in MOFs exhibit 3-, 4-, and 6-connected topologies.[1,2] Examples of 7- and 8-connected MOFs are relatively scarce,[3] and MOFs with connectivities higher than 8 are still extremely rare.[4] Structures with connectivities higher than 4 normally adopt 3-D topologies,[3,4] and there are few examples of 5- and 6-connected topologies having 2-D structures.[5] The only 2-D MOF with a connectivity larger than 6 reported thus far is an 8-connected 2-D bilayered structure.[3e] The construction of highly connected MOFs, especially for 2-D structures, is still a challenge in crystal engineering because of the limited coordination numbers of metal centers and the steric hindrance of most commonly used organic ligands.[3c] Recently, the utilization of metal clusters as nodes in place of single metal ions has provided a promising pathway toward the generation of highly connected MOFs.[4] Compared with single metal ions, nodes based on metal clusters generally have large surface areas, indicating more coordination sites but smaller steric hindrance when linked by organic ligands.

An effective approach for building highly connected MOFs is the rational design of organic ligands, which should have the ability of prompting core aggregation and feasibly linking discrete clusters into an extended network. The carboxylate- and 1,2,3-triazole-containing ligands have extensively been shown to possess excellent coordination capabilities and flexible coordination manners.[6,7] In this context, we designed

---

* To whom correspondence should be addressed. E-mail: zfk@fjirsm.ac.cn.

[†] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences.

[‡] Graduate School, Chinese Academy of Sciences.

(1) (a) Moulton, B.; Lu, J.-J.; Hajndl, R.; Hariharan, S.; Zaworotko, M. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 2821−2824. (b) Huang, X.-C.; Lin, Y.-Y.; Zhang, J.-P.; Chen, X.-M. *Angew. Chem., Int. Ed.* **2006**, *45*, 1557−1559. (c) Chen, B.; Eddaoudi, M.; Hyde, S. T.; O'Keeffe, M.; Yaghi, O. M. *Science* **2001**, *291*, 1021−1023. (d) Abrahams, B. F.; Batten, S. R.; Grannas, M. J.; Hamit, H.; Hoskins, B. F.; Robson, R. *Angew. Chem., Int. Ed.* **1999**, *38*, 1475−1477.

(2) (a) Wang, Z.-Q.; Kravtsov, V. C.; Zaworotko, M. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 2877−2880. (b) Abrahams, B. F.; Egan, S. J.; Robson, R. *J. Am. Chem. Soc.* **1999**, *121*, 3535−3536. (c) Eddaoudi, M.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2002**, *124*, 376−377. (d) Liu, Y.-L.; Kravtsov, V. C.; Beauchamp, D. A.; Eubank, J. F.; Eddaoudi, M. *J. Am. Chem. Soc.* **2005**, *127*, 7266−7267.

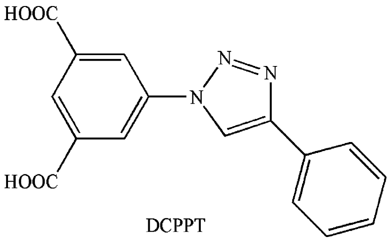
(3) Most recent and representative references: (a) Chun, H.; Kim, D.; Dybtsev, D. N.; Kim, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 971−974. (b) Luo, T.-T.; Tsai, H.-L.; Yang, S.-L.; Liu, Y.-H.; Yadav, R. D.; Su, C.-C.; Ueng, C.-H.; Lin, L.-G.; Lu, K.-L. *Angew. Chem., Int. Ed.* **2005**, *44*, 6063−6067. (c) Fang, Q.-R.; Zhu, G.-S.; Jin, Z.; Xue, M.; Wei, X.; Wang, D.-J.; Qiu, S.-L. *Angew. Chem., Int. Ed.* **2006**, *45*, 6126−6130. (d) Long, D.-L.; Blake, A. J.; Champness, N. R.; Wilson, C.; Schröder, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 2443−2447. (e) Long, D.-L.; Hill, R. J.; Blake, A. J.; Champness, N. R.; Hubberstey, P.; Proserpio, D. M.; Wilson, C.; Schröder, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 1851−1854. (f) Wang, X.-L.; Qin, C.; Wang, E.-B.; Su, Z.-M. *Chem.*—*Eur. J.* **2006**, *12*, 2680−2691.

(4) (a) Wang, X.-L.; Qin, C.; Wang, E.-B.; Su, Z.-M.; Li, Y.-G.; Xu, L. *Angew. Chem., Int. Ed.* **2006**, *45*, 7411−7414. (b) Wang, S.-N.; Xing, H.; Li, Y.-Z.; Bai, J.-F.; Pan, Y.; Scheer, M.; You, X.-Z *Eur. J. Inorg. Chem.* **2006**, 3041−3053. (c) Li, D.; Wu, T.; Zhou, X.-P.; Zhou, R.; Huang, X.-C. *Angew. Chem., Int. Ed.* **2005**, *44*, 4175−4178. (d) Zhang, X.-M.; Fang, R.-Q.; Wu, H.-S. *J. Am. Chem. Soc.* **2005**, *127*, 7670−7671. (e) Jia, J.-H.; Lin, X.; Wilson, C.; Blake, A. J.; Champness, N. R.; Hubberstey, P.; Walker, G.; Cussena, E. J.; Schröder, M. *Chem. Commun.* **2007**, 840−842.

(5) (a) Hill, R. J.; Long, D.-L.; Turvey, M. S.; Blake, A. J.; Champness, N. R.; Hubberstey, P.; Wilson, C.; Schröder, M. *Chem. Commun.* **2004**, 1792−1793. (b) Williams, C. A.; Blake, A. J.; Hubberstey, P.; Schröder, M. *Chem. Commun.* **2005**, 5435−5437. (c) Li, J.-R.; Zhang, R.-H.; Bu, X.-H. *Cryst. Growth Des.* **2004**, *2*, 219−221. (d) Bu, X.-H.; Weng, W.; Li, J.-R.; Chen, W.; Zhang, R.-H. *Inorg. Chem.* **2002**, *41*, 413−415. (e) Su, C.-Y.; Cai, Y.-P.; Chen, C.-L.; Kang, B.-S. *Inorg. Chem.* **2001**, *40*, 2210−2211.

10.1021/ic700820d CCC: $37.00

Chart 1. Chemical Diagram of DCPPT



DCPPT

and synthesized a new bifunctional ligand, 1-(3,5-dicarboxyphenyl)-4-phenyl-1*H*-1,2,3-triazole (DCPPT;[8] Chart 1), with a 1,2,3-triazole ring and two carboxylate groups providing multidentate metal-binding centers, which may favor the goal of constructing highly connected MOFs. Herein, we report an unprecedented (3,10)-connected 2-D network, $[Co_8(DCPPT)_6(\mu_3\text{-}OH)_4(H_2O)_4]\cdot 5H_2O$ (**1**), utilizing octanuclear cobalt(II) clusters as 10-connected nodes and the ligands DCPPT as 3-connected nodes as well as "double-bridge" linkers. The obtained polymer possesses a structure motif never observed before in MOFs and, to the best of our knowledge, for the first time defines a 2-D MOF with connectivity larger than 8.

The hydrothermal reaction of $Co(NO_3)_2\cdot 6H_2O$, DCPPT, NaOH, and H_2O at 180 °C for 3 days afforded purple-red crystals of **1**,[9] which is air-stable and insoluble in water and most common used organic solvents. The purity of **1** was independently confirmed by elemental analysis and similarities between simulated and experimental powder X-ray diffraction (PXRD; Figure S1 in the Supporting Information). The thermogravimetric analysis (TGA) curve of **1** (Figure S2 in the Supporting Information) reveals that the gradual weight loss of 5.4% from 30 to 125 °C corresponds to the loss of five lattice and four coordinated water molecules (calcd 6.3%). The decomposition of **1** happened above 285 °C.

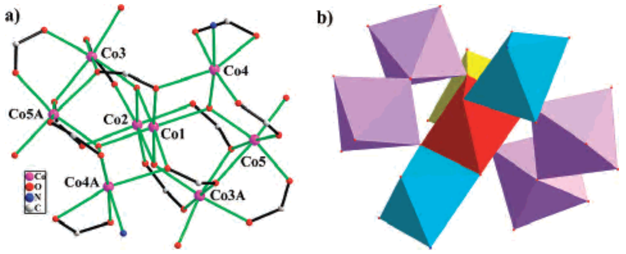


Figure 1. (a) View of one of the $[Co_8N_2(\mu_3\text{-}OH)_4(CO_2)_{12}(H_2O)_4]$ SBUs in **1** and (b) polyhedral view of the octanuclear cluster. Color code: Co1, red; Co2, yellow; Co4, light blue; Co3 and Co5, purple-pink. Symmetry code: A, $0.5 - x$, $-0.5 + y$, $0.5 - z$.

X-ray structural analysis[10] reveals that **1** crystallizes in the centrosymmetric space group $C2/c$ with an octanuclear cobalt(II) cluster $[Co_8N_2(\mu_3\text{-}OH)_4(CO_2)_{12}(H_2O)_4]$ as the secondary building unit (SBU; Figure 1), which has the crystallographically imposed 2-fold axis passing through Co1 and Co2 atoms. The SBU represents an initial example of the $[Co_8(\mu_3\text{-}OH)_4]$ core[11] and is built up with 4 μ_3-OH groups, 2 N atoms (on Co4 and Co4A), and 12 carboxylate groups of DCPPT as well as 4 terminal H_2O molecules (on Co3, Co3A, Co5, and Co5A). Each of the five independent Co atoms shows a distorted octahedral geometry, and especially the Co4 octahedron is most distorted, resulting from its coordination accomplished by the chelating carboxylate group (Figure S3 in the Supporting Information). The Co1 octahedron shares three cis edges with three neighboring octahedra (Co2, Co4, and Co4A) forming an ideal planar triangular tetramer. A pair of symmetry-related dimers of edge-sharing octahedra (Co3 and Co5), above and below the tetrameric plane, respectively, graft onto the tetramer by sharing a corner (μ_3-OH) of each octahedron, with the Co1 octahedron producing the octanuclear cluster. The formed configuration is significantly different from those in the other reported octanuclear cobalt(II) clusters, which display a Co_8 cage, a ring, or irregular arrangements or consist of Co_4O_4 cubane fragments.[11]

The coordination modes of the three symmetry-independent DCPPT in **1** can be characterized as 3.1111, 5.2111, and 7.22111 in the Harris notation[12] (Figure S3 in the Supporting Information). Of further interest are the four different coordination modes of the carboxylate groups (Scheme S1 in the Supporting Information): one terminal chelating η^1:η^1 mode, one doubly bridging *syn,syn*-η^1:η^1:μ_2 mode, one triply bridging *syn,syn,syn*-η^1:η^2:μ_3 mode, and one unusual quadruply bridging *syn,syn,syn,syn*-η^2:η^2:μ_4 mode.[13] The coexistence of such four coordination modes of car-

---

(6) (a) Guillou, N.; Livage, C.; Beek, W. V.; Noguès, M.; Férey, G. *Angew. Chem., Int. Ed.* **2003**, *42*, 643−647. (b) Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, D. T.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2003**, *300*, 1027−1029. (c) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319−330.

(7) (a) Low, D. M.; Jones, L. F.; Bell, A.; Brechin, E. K.; Mallah, T.; Riviére, E.; Teat, S. J.; McInnes, E. J. L. *Angew. Chem., Int. Ed.* **2003**, *42*, 3781−3784. (b) Tangoulis, V.; Raptopoulou, C. P.; Terzis, A. *Inorg. Chem.* **1998**, *37*, 3142−3153. (c) Jones, L. F.; Brechin, E. K.; Collison, D.; Raftery, J.; Teat, S. J. *Inorg. Chem.* **2003**, *42*, 6971−6973.

(8) Zou, W.-Q.; Li, Y.; Zheng, F.-K.; Guo, G.-C.; Huang, J.-S. *Acta. Crystallogr.* **2006**, *E62*, o3591−o3593.

(9) A mixture of DCPPT (78 mg, 0.25 mmol), NaOH (10 mg, 0.25 mmol), and H_2O (8 mL) was heated at 180 °C for 12 h in a Teflon-lined vessel and then cooled to 20 °C. $Co(NO_3)_2\cdot 6H_2O$ (146 mg, 0.50 mmol) was added, and the mixture was heated at 180 °C for 3 days. Purple-red crystals of **1** were recovered by filtration, washed with distilled water, and dried in air. Yield: 38% (based on DCPPT). Anal. Calcd (%) for $Co_8C_{96}H_{76}N_{18}O_{37}$: C, 45.30; H, 3.01; N, 9.91. Found: C, 44.54; H, 3.16; N, 9.65. IR (KBr, cm^{-1}): 3450s, 3147w, 3070w, 2920w, 2843w, 1620m, 1575s, 1485w, 1433m, 1380s, 1240w, 1083w, 1040w, 1018w, 915w, 855w, 779m, 760m, 701m, 501s, 450s.

(10) Crystal data for **1**: $Co_8C_{96}H_{76}N_{18}O_{37}$, $M_r = 2545.19$, monoclinic, $C2/c$, $a = 40.580(7)$ Å, $b = 11.021(2)$ Å, $c = 22.269(4)$ Å, $\beta = 95.430(4)°$, $V = 9914(3)$ Å^3, $Z = 4$, $\rho = 1.705$ g cm^{-3}, $\mu = 1.404$ mm^{-1}, $F(000) = 5160$, GOF = 1.018. A total of 37 099 reflections were collected and 11 261 are unique ($R_{int} = 0.0423$). R1/wR2 = 0.0505/0.1305 for 11 261 reflections [$I > 2\sigma(I)$] and 717 parameters.

(11) (a) Langley, S. J.; Helliwell, M.; Sessoli, R.; Rosa, P.; Wernsdorfer, W.; Winpenny, R. E. P. *Chem. Commun.* **2005**, 5029−5031. (b) Beattie, J. K.; Hambley, T. W.; Klepetko, J. A.; Masters, A. F.; Turner, P. *Chem. Commun.* **1998**, 45−46. (c) Akine, S.; Dong, W.; Nabeshima, T. *Inorg. Chem.* **2006**, *45*, 4677−4684. (d) Dimitrou, K.; Sun, J.-S.; Folting, K.; Christou, G. *Inorg. Chem.* **1995**, *34*, 4160−4166.

(12) Coxall, R. A.; Harris, S. G.; Henderson, D. K.; Parsons, S.; Tasker, P. A.; Winpenny, R. E. P. *J. Chem. Soc., Dalton Trans.* **2000**, 2349−2356.

(13) (a) Schmitt, W.; Hill, J. P.; Juanico, M. P.; Caneschi, A.; Costantino, F.; Anson, C. E.; Powell, A. K. *Angew. Chem., Int. Ed.* **2005**, *44*, 4187−4192. (b) Fondo, M.; Ocampo, N.; Garcia-Deibe, A. M.; Vicente, R.; Corbella, M.; Bermejo, M. R.; Sanmartín, J. *Inorg. Chem.* **2006**, *45*, 255−262.

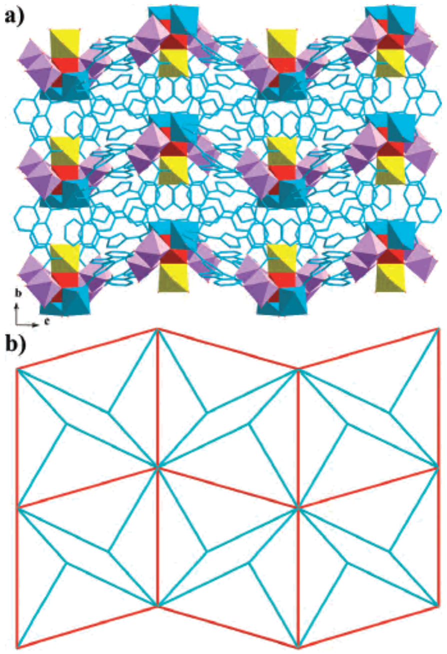


Figure 2. (a) 2-D framework of **1** viewed from the *a* axis and (b) its topology. Color code: light blue, the $CdCl_2$ net; red, the (4,4) net constructed with “double bridges”.

boxylate groups in one complex is rather rare and plays an important role in the formation of the octanuclear cluster.

One of the most striking features of **1** lies in its network topology. As shown in Figure 2a, each $[Co_8N_2(\mu_3\text{-}OH)_4(CO_2)_{12}(H_2O)_4]$ SBU is surrounded by 14 DCPPT to form a 2-D net parallel to the *bc* plane. The 8 doubly bridging DCPPTs (Harris notation: 3.1111 and 5.2111), with each pair connecting two SBUs, form 4 “double bridges”,[3d] and each of them is considered as one connection (Figure S4 in the Supporting Information).[14] Thus, with each SBU acting as a 10-connected node and each triply bridging DCPPT (Harris notation: 7.22111) as a 3-connected node, **1** defines a 2-D (3,10)-connected net of vertex type $[(3^2.4)_2(3^8.4^{14}.5^{12}.6^{11})]$ (Figure 2b), which represents the highest connected topology of 2-D MOFs to date and has not been reported in any known structures. The coexistence of four “double bridges” in 2-D MOFs is comparatively rare, especially in highly connected structures owing to the steric hindrance of organic ligands. This unprecedented 2-D topology can be considered as being composed of a (3,6)-connected $CdCl_2$ net (light blue part in Figure 2b) formed by the SBUs and the triply bridging DCPPT and a (4,4) net (red part in Figure 2b) constructed by “double bridges”. The 2-D nets are stacked along the *a* direction with interlayer $\pi-\pi$ interactions between the triazole and phenyl rings (Figure S5 in the Supporting Information).

The variable-temperature magnetic susceptibility χ_M for the powder sample of **1** was investigated in the 5−300 K range in a 1.0 T field (Figure 3). Above 50 K, the magnetic susceptibility follows Curie−Weiss law with $C = 27.8$ cm^3 mol^{-1} K and $\theta = -71.7$ K. The Curie constant is significantly higher than the expected spin-only value of eight isolated high-spin Co^{II} ions (15.0 cm^3 mol^{-1} K), in accordance with the well-documented orbital contribution of octahedral Co^{II} ions. The negative Weiss constant and the decrease of $\chi_M T$ indicate an overall strong antiferromagnetic interaction and/or spin-orbital coupling between the Co^{II} ions. The more remarkable decrease from 5.3 cm^3 mol^{-1} K at 10 K to 3.7 cm^3 mol^{-1} K at 5 K may be caused by the zero-field splitting of the ground state of the cluster, which is typically large for complexes containing high-spin six-coordinate Co^{II} ions.[15] Because the octanuclear clusters are quite well isolated by large DCPPT ligands, the magnetic behavior is interpreted as being due to antiferromagnetic coupling within the octanuclear cobalt(II) clusters.

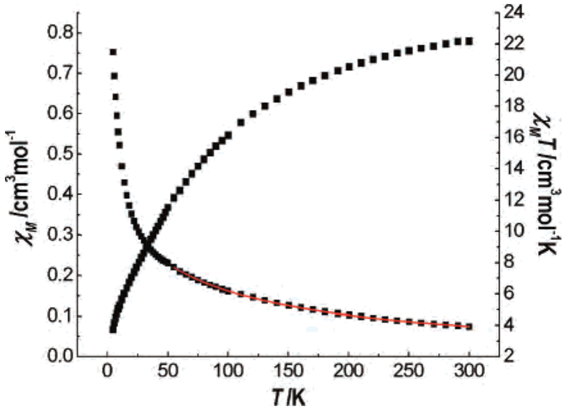


Figure 3. Temperature dependence of χ_M and $\chi_M T$ of **1** in the range 5−300 K in the field of 1.0 T.

In summary, a novel 2-D MOF **1** with a topology that defines the highest connectivity of known 2-D nets has been constructed by using octanuclear cobalt clusters as 10-connected nodes and organic ligands as 3-connected nodes as well as “double-bridge” linkers. Our study not only provides an intriguing example of chemical topology but also confirms the concept of using metal clusters as building blocks for constructing new highly connecting solid-state materials.

Acknowledgment. This work was financially supported by the 973 Program (Grant 2006CB932900), National Natural Science Foundation of China (Grant 20671091), and Fujian Province (Grants A0420002, 2005I017, and 2004J039).

Supporting Information Available: Crystallographic data for **1** in CIF format, materials and measurements, crystal structure analyses, and figures of TGA curve, coordination modes of DCPPT ligands, the (4,4) net constructed by the “double bridges”, the interlayer $\pi-\pi$ interactions in **1**, and PXRD diagrams of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC700820D

---

(14) Vodak, D. T.; Braun, M. E.; Kim, J.; Eddaoudi, M.; Yaghi, O. M. *Chem. Commun.* **2001**, 2534−2535.

(15) Boudalis, A. K.; Raptopoulou, C. P.; Abarca, B.; Ballesteros, R.; Chadlaoui, M.; Tuchagues, J.-P.; Terzis, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 432−435.