

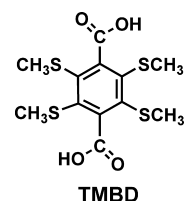
Coordination Networks from a Bifunctional Molecule Containing Carboxyl and Thioether Groups

Xiao-Ping Zhou,[†] Zhengtao Xu,^{*,†} Matthias Zeller,[‡] Allen D. Hunter,[‡] Stephen Sin-Yin Chui,[§] and Chi-Ming Che[§]

Department of Biology and Chemistry, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong, China, Department of Chemistry, Youngstown State University, One University Plaza, Youngstown, Ohio 44555, and Department of Chemistry and HKU-CAS Joint Laboratory on New Materials, The University of Hong Kong, Pokfulam Road, Hong Kong, China

Received May 26, 2008

The bifunctional molecule tetrakis(methylthio)-1,4-benzenedicarboxylic acid (TMBD) interacts with the increasingly harder metal ions of Cu^I, Cd^{II}, and Zn^{II} to form the coordination networks of Cu₂TMBD, CdTMBD, and Zn₄O(H₂O)₃(TMBD)₃, where the carboxyl group consistently bonds to metal ions, while the softer methylthio group binds with preference to the softer metal ions (i.e., chelation to Cu⁺, single-fold coordination to Cd²⁺, and nonbonding to Zn²⁺). Diffuse-reflectance spectra show that the metal–thioether interaction is associated with smaller electronic band gaps of the solid-state networks.



This paper builds on tetrakis(methylthio)-1,4-benzenedicarboxylic acid (TMBD), as part of an effort to combine the carboxyl and thioether groups within metal–organic frameworks (MOFs). The potential advantages of such a bifunctional building block are manifold. For example, the robustness from the carboxylate–metal bonds, combined with the electronic communication mediated by the thioether–metal interaction, could lead to strong porous networks with enhanced electronic properties. Also, the thioether S atom can be conveniently anchored to various other groups (e.g., alkyls and aryls), so as to modify the volume as well as the functionality of the molecular building block. Presented here are a number of networks based on TMBD and the ions of Cu⁺, Cd²⁺, and Zn²⁺ (see the Supporting Information for synthetic procedures) with varying chemical hardness η_A values of 6.3, 10.3, and 10.8, respectively.⁶ Together these networks exhibit the salient features of simultaneous bonding of the carboxyl and thioether groups to metal centers and extensive decoration of a channel structure with free-standing thioether groups, features that have remained unexplored in MOF systems and could open new possibilities for functionalizing these solid-state materials.

Simultaneous bonding of the carboxyl and thioether groups is observed in compounds Cu₂TMBD (**1**) and CdTMBD (**2**).⁷ Compound **1** crystallizes in *P2₁/n*, with TMBD adopting a

In the field of coordination networks,¹ carboxylic acids² and thioethers³ represent two distinct classes of widely used molecular building blocks. The chemically hard carboxylate unit bonds to metal centers with distinct ionic character, and the resultant frameworks are often robust enough to sustain extensive porosity; the electronic systems of the metal centers and the organic core are, however, largely isolated from each other, and the overall electronic properties of the networks often remain similar to those of the individual building blocks. By comparison, the thioether S atom is soft and more polarizable and interacts with metal centers in more pliant coordination modes; the resultant networks are thus more soluble in polar organic solvents (e.g., acetone and tetrahydrofuran). Recent works also indicate that the metal center and the organic π -electron system can be electronically coupled via the thioether site, while the solubility of the metal–thioether network allows for solution processing of the potential semiconductor network.⁴ Overall, thioethers and other sulfated molecules⁵ figure prominently in the field of organic electronics.

* To whom correspondence should be addressed. E-mail: zhengtao@cityu.edu.hk.

[†] City University of Hong Kong.

[‡] Youngstown State University.

[§] The University of Hong Kong.

(1) (a) Janiak, C. *Dalton Trans.* **2003**, 2781. (b) James, S. L. *Chem. Soc. Rev.* **2003**, 32, 276. (c) Kesanli, B.; Lin, W. *Coord. Chem. Rev.* **2003**, 246, 305. (d) Maspoeh, D.; Ruiz-Molina, D.; Veciana, J. *Chem. Soc. Rev.* **2007**, 36, 770. (e) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, 37, 1461. (f) Tanaka, D.; Kitagawa, S. *Chem. Mater.* **2008**, 20, 922.

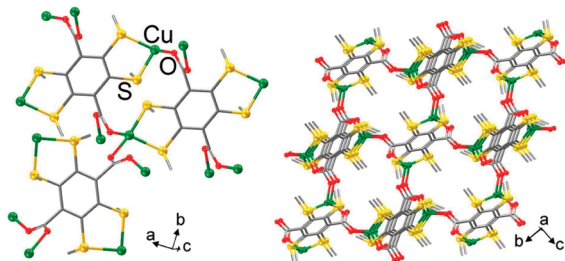


Figure 1. Local coordination environment of ligand TMBD and Cu^{I} centers (left) and an overview of the 3D coordination network of **1** (right).

centrosymmetric conformation. The O and S atoms of the TMBD molecule are fully engaged in coordinating to the Cu^{I} center (Figure 1, left). Specifically, each TMBD dianion is bonded with six Cu^{I} ions: two are chelated by the methylthio groups ($\text{Cu}-\text{S}$ distances, 2.328 and 2.242 Å), and the other four are bonded to carboxyl O atoms in a single-fold coordination mode ($\text{Cu}-\text{O}$ distances, 1.999 and 2.093 Å). Overall, the six Cu^{I} ions form an octahedral geometry around the TMBD molecule, and the individual Cu^{I} ion features a tetrahedral geometry consistent with its d^{10} electronic configuration. With chelation between the Cu^{I} ion and the S atoms treated as a single connection, the network in **1** can be rationalized as a rutile-like (TiO_2) net, with each TMBD molecule acting as the six-connected node and the Cu ion as the three-connected node (see Figure 1, right, and Figure S4 in the Supporting Information).

With the harder Cd^{II} , the thioether–metal interaction in **2** becomes less extensive: whereas all S atoms are bonded to the Cu^{I} ions in **1**, only half of the S atoms from TMBD are bonded to the Cd^{II} ion. The $\text{Cd}-\text{S}$ bond acts in concert with one nearby carboxyl O atom to form a 2-fold chelation motif

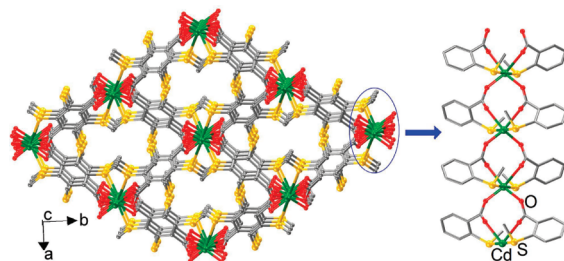


Figure 2. 3D coordination network of **2** (left) and the chainlike coordination motif of TMBD and the Cd^{II} centers (right).

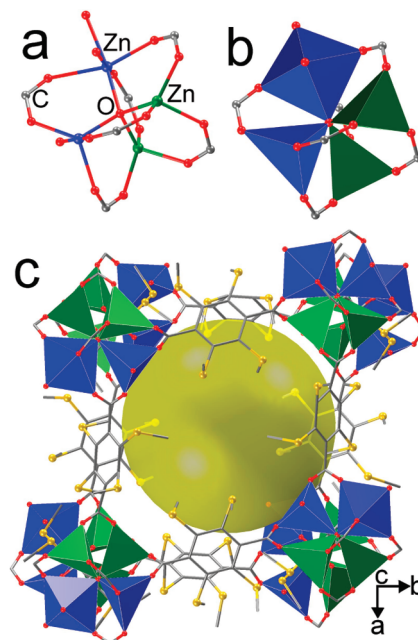


Figure 3. Crystal structure of **3**: (a) $\text{Zn}_4\text{O}(\text{H}_2\text{O})_3(\text{COO})_6$ cluster as a ball-and-stick model; (b) same cluster with the ZnO_4 tetrahedra in green and the hydrated Zn^{2+} centers as blue polyhedra; (c) coordination net of **3**, with a large yellow sphere highlighting the 3D feature.

(Figure 2). Each Cd^{II} center entertains two sets of such chelation interactions ($\text{Cd}-\text{S}$ distances, 2.672 and 2.723 Å; $\text{Cd}-\text{O}$ distances, 2.368 and 2.324 Å). The Cd^{II} further bonds to two O atoms from a neighboring chelation unit to complete an octahedral geometry made of two axial (trans) S atoms and four equatorial O atoms. The Cd atoms are thus integrated into a linear chain (see Figure 2, right), which is then linked into a 3D net through the phenylene units. Treating the above O–Cd–S chelation mode as a single rod, one can denote TMBD and the Cd center as two types of four-connected nodes, and the resultant net is topologically equivalent to PtS. No substantial porous feature or fluorescence was observed in the crystal structures of **1** and **2**, and both compounds are stable in air.

By contrast, the even harder Zn^{2+} ion bonds exclusively to the carboxyl groups of TMBD, leading to the 3D framework $\text{Zn}_4\text{O}(\text{H}_2\text{O})_3(\text{TMBD})_3$ (**3**) with channels decorated by the free-standing methylthio groups. Complex **3** crystallizes in the space group $I4_1/acd$ and features an unusual water-containing $\text{Zn}_4\text{O}(\text{H}_2\text{O})_3(\text{COO})_6$ cluster (Figure 3) as its secondary building block. Unlike the more common $\text{Zn}_4\text{O}(\text{COO})_6$ cluster (T_d symmetric, with the Zn ions tetrahedrally bonded to the central $\mu_4\text{-O}$ and each

- (2) (a) Li, H.; Eddaoudi, M.; O’Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276. (b) Chen, B. L.; Eddaoudi, M.; Hyde, S. T.; O’Keeffe, M.; Yaghi, O. M. *Science* **2001**, *291*, 1021. (c) Chae, H. K.; Siberio-Perez, D. Y.; Kim, J.; Go, Y. B.; Eddaoudi, M.; Matzger, A. J.; O’Keeffe, M.; Yaghi, O. M. *Nature* **2004**, *427*, 523. (d) Sudik, A. C.; Millward, A. R.; Ockwig, N. W.; Cote, A. P.; Kim, J.; Yaghi, O. M. *J. Am. Chem. Soc.* **2005**, *127*, 7110. (e) Bradshaw, D.; Prior, T. J.; Cussen, E. J.; Claridge, J. B.; Rosseinsky, M. J. *J. Am. Chem. Soc.* **2004**, *126*, 6106. (f) Ma, S.; Sun, D.; Ambrogio, M.; Fillinger, J. A.; Parkin, S.; Zhou, H.-C. *J. Am. Chem. Soc.* **2007**, *129*, 1858. (g) Wang, X.-S.; Ma, S.; Sun, D.; Parkin, S.; Zhou, H.-C. *J. Am. Chem. Soc.* **2006**, *128*, 16474. (h) Chen, B.; Liang, C.; Yang, J.; Contreras, D. S.; Clancy, Y. L.; Lobkovsky, E. B.; Yaghi, O. M.; Dai, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 1390. (i) Chen, B.; Yang, Y.; Zapata, F.; Lin, G.; Qian, G.; Lobkovsky, E. B. *Adv. Mater.* **2007**, *19*, 1693.
- (3) (a) Gan, X.; Munakata, M.; Kuroda-Sowa, T.; Maekawa, M. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 3009. (b) Inoue, M. B.; Inoue, M.; Bruck, M. A.; Fernando, Q. *Chem. Commun.* **1992**, 515. (c) Zhong, J. C.; Misaki, Y.; Munakata, M.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Konaka, H. *Inorg. Chem.* **2001**, *40*, 7096. (d) Suenaga, Y.; Konaka, H.; Kitamura, K.; Kuroda-Sowa, T.; Maekawa, M.; Munakata, M. *Inorg. Chim. Acta* **2003**, *351*, 379. (e) Li, K.; Xu, Z.; Xu, H.; Carroll, P. J.; Fetting, J. C. *Inorg. Chem.* **2006**, *45*, 1032. (f) Fu, Y.-T.; Lynch, V. M.; Lagow, R. J. *Chem. Commun.* **2004**, 1068. (g) Do, L.; Halper, S. R.; Cohen, S. M. *Chem. Commun.* **2004**, 2662. (h) Chen, B.; Lee, S.; Venkataraman, D.; DiSalvo, F. J.; Lobkovsky, E.; Nakayama, M. *Cryst. Growth Des.* **2002**, *2*, 101.
- (4) (a) Li, K.; Xu, Z.; Xu, H.; Ryan, J. M. *Chem. Mater.* **2005**, *17*, 4426. (b) Li, K.; Xu, H.; Xu, Z.; Zeller, M.; Hunter, A. D. *Inorg. Chem.* **2005**, *44*, 8855.
- (5) (a) Gingras, M.; Raimundo, J.-M.; Chabre, Y. M. *Angew. Chem., Int. Ed.* **2006**, *45*, 1686. (b) Shirota, Y.; Kageyama, H. *Chem. Rev.* **2007**, *107*, 953. (c) Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99. (d) Briseno, A. L.; Miao, Q.; Ling, M.-M.; Reese, C.; Meng, H.; Bao, Z.; Wudl, F. *J. Am. Chem. Soc.* **2006**, *128*, 15576.
- (6) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512.

carboxyl group bridging two Zn ions along the tetrahedral edge),^{2a} the $\text{Zn}_4\text{O}(\text{H}_2\text{O})_3(\text{COO})_6$ cluster is based on two four-coordinated and two hydrated Zn^{2+} centers: the former bonds to three carboxyl O atoms and the central O atom and resembles the Zn^{2+} environment in $\text{Zn}_4\text{O}(\text{COO})_6$; the latter have additional aqua ligands (Zn–O distances, 2.07 and 2.40 Å) to furnish five- and six-coordinated Zn^{2+} centers. Consequently, the Zn_4O tetrahedron is distorted, featuring two Zn–Zn distances of 3.08 and 3.32 Å and two Zn–O distances of 1.92 and 1.98 Å. The current case provides another water-containing zinc carboxylate cluster⁸ and might offer additional clues to the hydrolysis mechanism of the widely reported $\text{Zn}_4\text{O}(\text{COO})_6$ -based networks.⁹

The $\text{Zn}_4\text{O}(\text{H}_2\text{O})_3(\text{COO})_6$ cluster (as a slightly distorted octahedral node) and TMBD (as a linear rod) build up a 3D net topologically equivalent to that of the familiar MOF-5 and α -Po (Figure 3c).^{2a} The methylthio groups of TMBD do not coordinate to the Zn^{2+} ions, and they remain free-standing in the void space of compound **3** (solvent-accessible volume: about 40.6% of the unit cell, calculated with the Platon software). Although the crystals of **3** are stable in a mother liquor, they lose crystallinity within a few minutes in air. The making of thioether-decorated porous structures with enhanced stability is needed for advanced applications such as selective absorption of heavy-metal species.

As part of our ongoing study on the impact of metal–thioether interaction on solid-state electronic properties,^{4,10} we here present the diffuse-reflectance spectra of **1–3** (Figure S6 in the Supporting Information). By fitting of the steepest slope on the absorption edge (wherein the Kubelka–Munk function is proportional to the absorption coefficient α) versus the photon energy and extrapolation to $\alpha = 0$, the band gaps

(E_g) of 2.349, 2.973, and 3.165 eV were obtained for **1–3**, respectively. This band-gap order fits well with the decreasing order of metal–thioether interactions in **1–3**, indicating that the metal–thioether interactions serve to enhance the electronic interaction in the solid state and reduce the band gap as a result. In addition, the shoulders and the slow slopes in the absorption spectra of **1–3** suggest that indirect interband transitions might significantly contribute to the absorption edge features, as is commonly observed in other indirect band-gap semiconductors (e.g., Ge).¹¹ Further electronic structure studies are, however, needed to reveal more details regarding the mechanisms of the optical transitions observed here.

Taken together, the decreasing hardness in Cu^{I} , Cd^{II} , and Zn^{II} correlates well with the steadily lesser participation of the soft thioether groups in the coordination motifs of **1–3**, although in future studies the coordination behavior of the thioether groups might also be susceptible to other factors such as the reaction medium, crystal packing forces, and chemical environment around the thioether groups. Such bonding flexibility points to the rich structural diversity that could potentially be achieved in coordination networks from the carboxyl–thioether combination. For example, a porous robust system with extensive thioether–metal interaction may enhance the electronic properties in the solid state, whereas a thioether-decorated pore could selectively take up metal (e.g., Pd, Ru, Hg) salts for applications such as catalysis and sensing.

Acknowledgment. This work is supported by City University of Hong Kong (Project No. 7002119) and the Research Grants Council of HKSAR [Project 9041109 (CityU 102406)]. The diffractometer was funded by NSF Grant 0087210, by Ohio Board of Regents Grant CAP-491, and by Youngstown State University.

Supporting Information Available: Crystallographic data in CIF format, synthetic procedures for TMBD and **1–3**, topologies of **1** and **2**, and powder X-ray diffraction patterns, optical absorption spectra, and crystal data and structure refinement for **1–3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC800952Z

- (7) Crystal data for **1**: $\text{C}_6\text{H}_6\text{CuO}_2\text{S}_2$, $M_r = 237.77$, $P2_1/n$, $a = 6.751(2)$ Å, $b = 12.758(4)$ Å, $c = 9.911(3)$ Å, $\beta = 107.818(5)^\circ$, $V = 812.6(4)$ Å³, $Z = 4$, $\rho = 1.943$ g cm⁻³, GOF = 1.147, $R_1 = 0.0411$, $wR_2 = 0.1423$ [$I > 2\sigma(I)$]. Crystal data for **2**: $\text{C}_{12}\text{H}_{12}\text{CdO}_4\text{S}_4$, $M_r = 460.86$, $P2_1/c$, $a = 9.844(2)$ Å, $b = 15.658(4)$ Å, $c = 9.567(2)$ Å, $\beta = 92.187(6)^\circ$, $V = 1473.5(6)$ Å³, $Z = 4$, $\rho = 2.077$ g cm⁻³, GOF = 1.157, $R_1 = 0.0784$, $wR_2 = 0.2090$ [$I > 2\sigma(I)$]. Crystal data for **3**: $\text{C}_{18}\text{H}_{21}\text{O}_8\text{S}_6\text{Zn}_2$, $M_r = 688.55$, $I4_1/acd$, $a = b = 25.519(1)$ Å, $c = 50.910(5)$ Å, $V = 33154(4)$ Å³, $Z = 32$, $\rho = 1.104$ g cm⁻³, GOF = 1.079, $R_1 = 0.1037$, $wR_2 = 0.3181$ [$I > 2\sigma(I)$].
- (8) Ma, S.; Wang, X.-S.; Collier, C. D.; Manis, E. S.; Zhou, H.-C. *Inorg. Chem.* **2007**, *46*, 8499.
- (9) (a) Greathouse, J. A.; Allendorf, M. D. *J. Am. Chem. Soc.* **2006**, *128*, 10678. (b) Huang, L.; Wang, H.; Chen, J.; Wang, Z.; Sun, J.; Zhao, D.; Yan, Y. *Microporous Mesoporous Mater.* **2003**, *58*, 105.
- (10) Sun, Y.-Q.; Tsang, C.-K.; Xu, Z.; Huang, G.; He, J.; Zhou, X.-P.; Zeller, M.; Hunter, A. D. *Cryst. Growth Des.* **2008**, *8*, 1468.

- (11) (a) Li, J.; Chen, Z.; Wang, X.; Proserpio, D. M. *J. Alloys Compd.* **1997**, *262* (263), 28. (b) Seeger, K. *Semiconductor Physics*; Springer: Berlin, 2004.