Topological Networks

Twelve-Connected Net with Face-Centered Cubic Topology: A Coordination Polymer Based on [Cu$_{12}$(μ$_4$-SCH$_3$)$_6$]$^{6+}$ Clusters and CN$^-$ Linkers**

Dan Li,* Tao Wu, Xiao-Ping Zhou, Rui Zhou, and Xiao-Chun Huang

In recent years, the analysis of topological networks of metal–organic coordination polymers has been a topical area of research in crystal engineering, not only as an important tool for simplifying complicated supramolecular coordination polymers, but also in the rational design of some functional materials with unique properties.[1–3] Considerable effort has been invested in the characterization and design of such coordination polymers.[4] O'Keeffe et al. identified five regular nets, one quasiregular net, and fourteen semiregular three-periodic nets by transitivity *pqrs*.[5] Of these nets, the face-centered cubic net (fcu) is the only quasiregular net with transitivity 1112, which exhibits the highest coordination number (12). It has been suggested that among the numerous topological nets, the most important and plausible targets for designed synthesis are those with "simple, high-symmetry" structures.[6] Although many coordination polymers with different topological networks containing 3~8-connected nodes are known,[7] synthetically prepared examples of higher connected and higher symmetry nets, such as fcu, have not been reported to date.

Significant interest has also arisen in organic and coordination chemistry for the design and synthesis of novel coordination polymers with ligands generated in situ.[8] We have previously reported[9] the reaction of CuSCN with acetonitrile and methanol under solvothermal conditions, which yielded a novel 3D polymeric photoluminescent complex, {[Cu(μ$_3$-SCH$_3$)$_2$(CN)]$_2$[Cu$_{10}$(μ$_3$-SCH$_3$)$_4$(μ$_4$-SCH$_3$)$_2$]}$_n$, in which the methyl mercaptide is generated in situ. The complex contains dodecanuclear copper(ı) clusters, which can be rationalized in terms of an α-Po simple cubic net (pcu), by defining the decanuclear copper cluster [Cu$_{10}$(μ$_3$-SCH$_3$)$_4$(μ$_4$-SCH$_3$)$_2$] as a node and [Cu(μ$_3$-SCH$_3$)$_2$(CN)] as a

[*] Prof. Dr. D. Li, T. Wu, X.-P. Zhou, Dr. X.-C. Huang
Department of Chemistry, Shantou University
Shantou, Guangdong 515063 (P. R. China)
Fax: (+86) 754-290—2767
E-mail: dli@stu.edu.cn

R. Zhou
Department of Chemistry, Medical College,
Shantou University
Shantou, Guangdong 515063 (P. R. China)

© 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

linker. In our ongoing research, we have found that the complex can also be obtained by reaction of $Cu(NO_3)_2 \cdot 3H_2O$ or $Cu(CH_3COO)_2 \cdot 2H_2O$ and NaSCN in the presence of acetonitrile and methanol under the same solvothermal conditions (140°C). Interestingly, when the reaction temperature was increased to 160°C, a very different product, namely, $[Cu_{12}(\mu_4\text{-}SCH_3)_6(CN)_6]_n \cdot 2H_2O$ (**1**), was obtained in low yield. This compound is very stable in air at ambient temperature, and relatively insoluble in common solvents.

X-ray single-crystal analysis[10] revealed that the crystal structure of **1** is composed of a 3D neutral microporous framework based on the highly symmetrical, spherical dodecanuclear copper(I) cluster $[Cu_{12}(\mu_4\text{-}SCH_3)_6]^{6+}$ connected by CN^- ligands and guest water molecules, with space group $F\text{m}\bar{3}\text{m}$. The basic spherical unit (Figure 1) contains a cen-

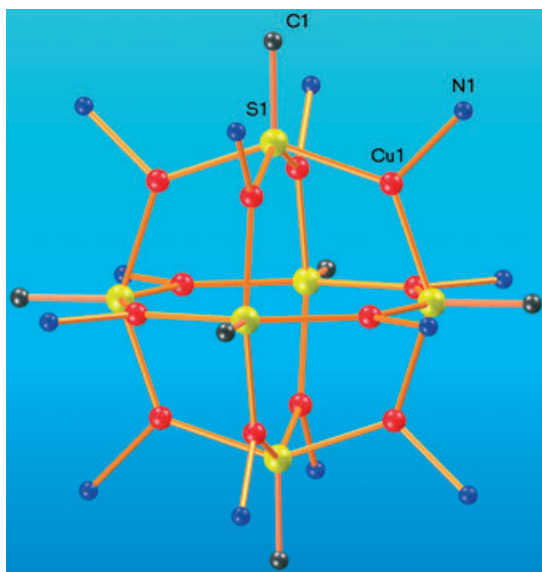***Figure 1.*** Structure of the basic globular $Cu_{12}(SCH_3)_6(CN)_6$ unit with a center of symmetry at the center of the S_6 cage; hydrogen atoms are omitted for clarity.

trosymmetric Cu_{12} cubo-octahedron, involving a regular octahedron of sulfur atoms with each edge bridged by a CuX unit (X = C or N) from the CN^- ligand. All methyl groups point outwards. Three mutually perpendicular, coplanar, eight-membered Cu_4S_4 rings intersect at the sulfur atoms to generate an globular configuration. Each Cu^I center lies in a planar and trigonal coordination sphere and binds to two bridging $\mu_4\text{-}SCH_3$ ligands and to one N or C atom of the CN^- ligand (S–Cu 2.2284(17), Cu–X 1.889(15), C–N 1.17(3) Å, S-Cu-S 127.1(2), S-Cu-X 116.44(12)°). The coordination environment of all the sulfur atoms in μ_4 bridging mode is a square-pyramidal $CSCu_4$ unit, with one carbon atom at the apex and four copper atoms in the equatorial plane. The C–S bond lengths are all 1.81(2) Å, similar to those in other mercaptanes.[11] While μ_2- and μ_3-thiolate bridging modes are relatively common, symmetric μ_4-thiolates remain scarce.[11] Three adjacent Cu^I atoms bridged by three sulfur atoms form an equilateral triangle with a Cu···Cu distance of 2.987(2) Å that indicates a weak Cu···Cu interaction. The corresponding

bond angles and lengths are equal, and thus an ideal 32-face polyhedron results: eight equilateral triangles and 24 isosceles triangles (see Supporting Information).

A polymer $[Cu_{13}Cl_{13}(SCH_2CH_2NH_3)_6 \cdot H_2O]_n$ containing $(Cu_{12}S_6)$ clusters with a similar globular configuration has been previously reported[11a] in which the corresponding bond angles and lengths in each cluster are non-equivalent, for example, Cu–S bond lengths range from 2.221 to 2.300 Å. In this complex, $^-SCH_2CH_2NH_3^+$ is a neutral ligand, and the clusters act as 4-connected nodes linked by CuCl subunits and chloride ions to form a 2D framework. In contrast, each $[Cu_{12}(\mu_4\text{-}SCH_3)_6]^{6+}$ unit in complex **1**, which has higher symmetry, is connected to twelve adjacent clusters by twelve cyanide ions to give a 3D microporous supramolecular framework (Figure 2). Approximately 20.3% of the crystal volume is occupied by free water molecules with a volume of about 748.1 Å^3 in each cell unit.
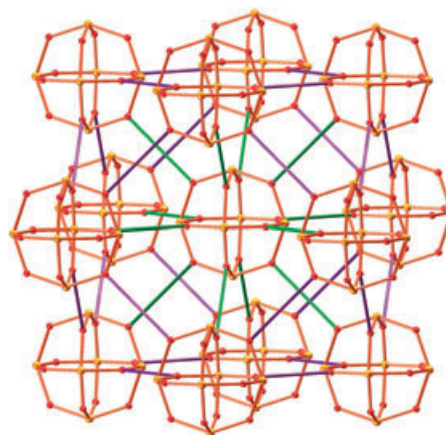

Figure 2. The site of each $Cu_{12}S_6$ cluster in the cell unit.

The 3D framework can be rationalized as a face-centered cubic net (fcu) with Schläfli symbol ($3^{24}4^{36}5^6$) by assigning the dodecanuclear copper(I) cluster $[Cu_{12}(\mu_4\text{-}SCH_3)_6]^{6+}$ as a node and the CN^- ligand as a linker (Figure 3), in accordance with the quasiregular net structure defined by O'Keeffe. In each
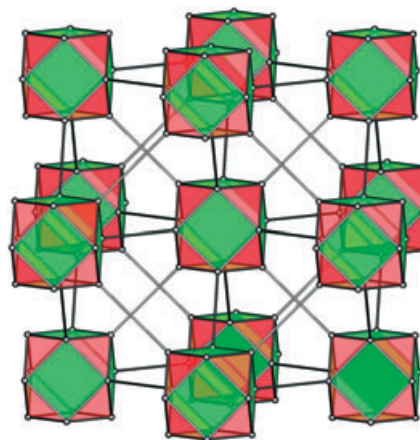

Figure 3. The 3D, 12-connected augmented fcu topological network.

cell unit, the central node or the center of the central cluster is located at (0.5, 0.5, 0.5), and the other adjacent twelve nodes are located at the center of each edge of the cube, respectively (Figure 2). Eight water molecules occupy the center of the tetrahedron. The distance from the center of each spherical unit to adjacent units is $a/\sqrt{2}$ (10.918 Å), and each spherical unit resides at a crystallographic inversion center. To the best of our knowledge, this is the first fcu topological network observed in coordination polymers, and represents the highest connected topology of any known coordination network.

Thermogravimetric analysis of **1** showed that the structural skeleton remains stable up to 190 °C (see Supporting Information). Initial loss of guest water molecules is followed by the abrupt loss of organic components (CH_3 and CN) from 190 to 275 °C (found weight loss 21.9 %, calcd 22.8 %; see Supporting Information).

Another interesting feature of **1** is the in situ generation of SCH_3^- and CN^- ligands. We have previously shown that the sulfur atom in SCH_3^- originates from SCN^- and the methyl group from methanol rather than acetonitrile.[9] In an attempt to understand the mechanism for the transformation of inorganic sulfur into organic sulfur, we identified the following experimental phenomena: 1) the colorless residual solution has a characteristically pungent smell and quickly becomes green after the reactor is opened to air; this indicates reduction of Cu^{2+} to Cu^+ and production of CH_3SH or H_2S in the reactions; 2) yellow α-CuSCN single crystals and yellow S_8 single crystals were found in the residual solid in two analogous reactions.[12] Even though it cannot be found in the present reactions, we assume that H_2S acts indirectly as the sulfurization reagent, which is generated by the reaction of S with H_2O, and which can then react with CH_3OH to form SCH_3^-. Possibly, S from the decomposition of SCN^- and CuSCN from redox reaction of Cu^{2+} and SCN^- are two important intermediates in the present reactions. Moreover, it is likely that the frameworks of the two complexes were determined by the reaction temperature. The precise mechanism and the effect of the temperature on the reactions warrant further investigation.

In conclusion, a novel microporous polymer containing a face-centered cubic (fcu) topological network with the highest connectivity, based on a dodecanuclear copper(I) cluster as a twelve-connected node, was synthesized by a simultaneous redox, sulfurization, and self-assembly reaction under solvothermal conditions. The concept of using a cluster as a building block to construct high-connectivity networks is therefore feasible, and the reactions confirm the transformation of inorganic into organic sulfur. The result provides a new avenue for designing and generating new solid-state materials based on networks of high-coordinate nodes linked by bridging ligands.

Experimental Section

1: A mixture of $Cu(NO_3)_2\cdot3H_2O$ (0.241 g, 1.0 mmol), NaSCN (0.081 g, 1.0 mmol), methanol (5.0 mL), and acetonitrile (5.0 mL) was stirred for 1 min in air, then transferred and sealed in a 25 mL teflon-lined reactor, which was heated in an oven to 160 °C for 72 h and then

cooled to room temperature at a rate of 5 °C h^{-1}. Yellow cubic crystals were obtained in 4.5 % yield based on $Cu(NO_3)_2\cdot3H_2O$.

Elemental analysis (%) calcd for **1** ($C_{12}H_{22}Cu_{12}N_6O_2S_6$): H 1.79, C 11.65, N 6.79 %; found: H 1.82, C 11.59, N 6.82 %; IR (KBr, cm^{-1}): 2920s, 2825w, 2127s, 1418m, 1305m, 957s, 689w, 645m, 463w.

[1] a) B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629–1658; b) M. Eddaoudi, D. B. Moler, H.-L. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319–330; c) P. J. Hagrman, D. Hagrman, J. Zubieta, *Angew. Chem.* **1999**, *111*, 2798–2848; *Angew. Chem. Int. Ed.* **1999**, *38*, 2639–2684; d) S. R. Batten, R. Robson, *Angew. Chem.* **1998**, *110*, 1558–1595; *Angew. Chem. Int. Ed.* **1998**, *37*, 1460–1494.

[2] a) B. F. Abrahams, S. R. Batten, M. J. Grannas, H. Hamit, B. F. Hoskins, R. Robson, *Angew. Chem.* **1999**, *111*, 1538–1540; *Angew. Chem. Int. Ed.* **1999**, *38*, 1475–1477; b) B. F. Abrahams, P. A. Jackson, R. Robson, *Angew. Chem.* **1998**, *110*, 2801–2804; *Angew. Chem. Int. Ed.* **1998**, *37*, 2656–2659; c) L. Carlucci, G. Ciani, D. M. Proserpio, S. Rizzato, *Chem. Commun.* **2001**, 1198–1199; d) J.-C. Dai, X.-T. Wu, Z.-Y. Fu, S.-M. Hu, W.-X. Du, C.-P. Cui, L.-M. Wu, H.-H. Zhang, R.-Q. Sun, *Chem. Commun.* **2002**, 12-13.

[3] a) L. Carlucci, G. Ciani, P. Macchi, D. M. Proserpio, *Chem. Commun.* **1998**, 1837-1838; b) M. Eddaoudi, J. Kim, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2002**, *124*, 376–377; c) T.-Y. Niu, X.-Q. Wang, A. J. Jacobson, *Angew. Chem.* **1999**, *111*, 2059–2062; *Angew. Chem. Int. Ed.* **1999**, *38*, 1934–1937; d) S. A. Barnett, A. J. Blake, N. R. Champness, C. Wilson, *Chem. Commun.* **2002**, 1640–1641; e) B. Rather, B. Moulton, R. D. B. Walsh, M. J. Zaworotko, *Chem. Commun.* **2002**, 694–695; f) L. Carlucci, N. Cozzi, G. Ciani, M. Moret, D. M. Proserpio, S. Rizzato, *Chem. Commun.* **2002**, 1354–1355; g) B. Moulton, H. Abourahma, M. W. Bradner, J.-J. Lu, G. J. McManus, M. J. Zaworotko, *Chem. Commun.* **2003**, 1342–1343; h) S. Banfi, L. Carlucci, E. Caruso, G. Ciani, D. M. Proserpio, *Cryst. Growth Des.* **2004**, *4*, 29–32.

[4] a) R. M. Barrer, H. Villiger, *Z. Kristallogr.* **1969**, *128*, 352–370; b) A. F. Wells, *Three-Dimensional Nets and Polyhedra*, Wiley, New York, **1977**; c) A. F. Wells, *Further Studies of Three-Dimensional Nets*, Am. Crystallogr. Assoc. Monogr. **1979**, No. 8; d) S. J. Chung, T. Hahn, W. E. Klee, *Acta Crystallogr. Sect. A* **1985**, 40, 42–50; e) J. V. Smith, *Chem. Rev.* **1988**, *88*, 149–182; f) D. E. Akporiaye, G. D. Price, *Zeolites* **1989**, *9*, 23–32; g) M. O'Keeffe, *Z. Kristallogr.* **1991**, *196*, 21–37; h) M. O'Keeffe, *Acta Crystallogr. Sect. A* **1992**, 48, 670–673; i) M. O'Keeffe, *Acta Crystallogr. Sect. A* **1995**, 51, 916–920; j) M. O'Keeffe, N. E. Brese, *Acta Crystallogr. Sect. A* **1992**, 48, 663–669; k) O. Delgado Friedrichs, A. W. M. Dress, D. H. Huson, J. Klinowsky, A. L. Mackay, *Nature* **1999**, *400*, 644–647; l) O. Delgado Friedrichs, D. H. Huson, *Discrete Comput. Geom.* **2000**, *4*, 279–292.

[5] a) O. Delgado Friedrichs, M. O'Keeffe, O. M. Yaghi, *Acta Crystallogr. Sect. A* **2003**, 59, 22–27; b) O. Delgado Friedrichs, M. O'Keeffe, O. M. Yaghi, *Acta Crystallogr. Sect. A* **2003**, 59, 515–525.

[6] a) M. O'Keeffe, M. Eddaoudi, H.-L. Li, T. Reineke, O. M. Yaghi, *J. Solid State Chem.* **2000**, *152*, 3–20; b) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705–714.

[7] a) R. J. Hill, D.-L. Long, M. S. Turvey, A. J. Blake, N. R. Champness, P. Hubberstey, C. Wilson, M. Schröder, *Chem. Commun.* **2004**, 1792–1793; b) J. U. Schutze, R. Eckhardt, R. D. Fischer, D. C. Apperley, N. A. Davies, R. K. Harris, *J. Organomet. Chem.* **1997**, *534*, 187–194; c) S. M. F. Lo, S. S. Y. Chui, L. Y. Shek, Z. Y. Lin, X. X. Zhan, G. H. Wen, I. D. Williams, *J. Am. Chem. Soc.* **2000**, *122*, 6293–6294; d) D.-L. Long, A. J. Blake, N. R. Champness, C. Wilson, M. Schröder, *Angew. Chem.* **2001**, *113*, 2509–2513; *Angew. Chem. Int. Ed.* **2001**, *40*, 2444–2447; e) D.-L. Long, R. J. Hill, A. J. Blake, N. R. Champness, P. Hubberstey, D. M. Proserpio, C. Wilson, M. Schröder, *Angew. Chem.* **2004**, *116*, 1887–1890; *Angew. Chem. Int. Ed.* **2004**, *43*, 1851–1854; f) L. Pan, H. Liu, X. Lei, X. Huang, D. H. Olson, N. J. Turro, J. Li, *Angew. Chem.* **2003**, *115*, 560–564; *Angew. Chem. Int. Ed.* **2003**, *42*, 542–546; g) Q. Fang, X. Shi, G. Wu, G. Tian, G. Zhu, R. Wang, S. Qiu, *J. Solid State Chem.* **2003**, *176*, 1–4; h) B. Moulton, J.-J. Lu, R. Hajndl, S. Hariharan, M. J. Zaworotko, *Angew. Chem.* **2002**, *114*, 2945–2948; *Angew. Chem. Int. Ed.* **2002**, *41*, 2821–2824; i) G. J. McManus, Z.-Q. Wang, M. J. Zaworotko, *Cryst. Growth Des.* **2004**, *4*, 11–13.

[8] a) E. C. Constable, *Metals and Ligand Reactivity*, VCH, Weinheim, **1996**; b) R. A. Michelin, M. Mozzon, R. Bertani, *Coord. Chem. Rev.* **1996**, *147*, 299–338; c) V. Y. Kukushkin, A. J. L. Pombeiro, *Chem. Rev.* **2002**, *102*, 1771–1802; d) J.-P. Zhang, S.-L. Zheng, X.-C. Huang, X.-M. Chen, *Angew. Chem.* **2004**, *116*, 208–211; *Angew. Chem. Int. Ed.* **2004**, *43*, 206–209; e) Z. P. Demko, K. B. Sharpless, *Angew. Chem.* **2002**, *114*, 2214–2217; *Angew. Chem. Int. Ed.* **2002**, *41*, 2110–2113; f) J.-K. Cheng, Y.-G. Yao, J. Zhang, Z.-J. Li, Z.-W. Cai, X.-Y. Zhang, Z.-N. Chen, Y.-B. Chen, Y. Kang, Y.-Y. Qin, Y.-H. Wen, *J. Am. Chem. Soc.* **2004**, *126*, 7796–7797.

[9] D. Li, T. Wu, *Inorg. Chem.* **2005**, *44*, 1175–1177.

[10] Crystal data for **1**: $C_{12}H_{22}Cu_{12}N_6O_2S_6$, cubic, space group $Fm\bar{3}m$ (no. 225), $M_r = 1237.20$, $a = 15.4410(19)$, $b = 15.4410(19)$, $c = 15.4410(19)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 3681.5(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.232$ g cm^{-3}, $\mu = 7.137$ mm^{-1}, $F(000) = 2384$, $T = 296(2)$ K; $R1 = 0.0634$, $wR2 = 0.1897$ for all data. Data collection was performed on a Bruker Smart Apex CCD diffractometer (Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å) by using frames of 0.3° oscillation ($4.56 \leq 2\theta \leq 50°$). The structure was solved by direct methods, and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares methods on F^2 by using the SHELXTL program.[13] The hydrogen atoms were generated geometrically.

[11] a) R. V. Parish, Z. Salehi, R. G. Pritchard, *Angew. Chem.* **1997**, *109*, 276–278; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 251–253; b) R. G. Pritchard, R. V. Parish, Z. Salehi, *J. Chem. Soc. Dalton Trans.* **1999**, 243–250; c) W.-P. Su, R. Cao, M.-C. Hong, J.-T. Chen, J.-X. Lu, *Chem. Commun.* **1998**, 1389–1340; d) Z. Salehi, R. V. Parish, R. Z. Pritchard, *J. Chem. Soc. Dalton Trans.* **1997**, 4241–4246; e) G. W. Adamson, N. A. Bell, H. M. M. Shearer, *Acta Crystallogr. Sect. B* **1982**, *38*, 462–465; f) M. D. Janssen, A. L. Spek, D. M. Grove, G. van Koten, *J. Am. Chem. Soc.* **1996**, *118*, 4081–4084.

[12] Heating a mixture of CuSO$_4$, CH$_3$CN, and CH$_3$OH in a sealed reactor at 180 °C gave yellow single crystals of α-CuSCN (crystal data at 293 K: orthorhombic, $a = 7.2535(6)$, $b = 6.6842(6)$, $c = 11.0466(9)$ Å, $V = 535.58(8)$ Å^3). Heating a mixture of Cu(NO$_3$)$_2$·3H$_2$O, NaSCN, CH$_3$OH, and *m*-phenylenediacetonitrile in a sealed reactor at 180 °C gave pale yellow crystals of S$_8$ (crystal data at 293 K: orthorhombic, $a = 10.4612(10)$, $b = 12.8619(12)$, $c = 24.486(2)$ Å, $V = 3294.7(5)$ Å^3).

[13] G. M. Sheldrick, SHELXTL 6.10, Bruker Analytical Instrumentation, Madison, Wisconsin, USA, **2000**.