Inorganic Chemistry
Communication

*Inorg. Chem.* **2009**, *48*, 8653–8655 **8653**
DOI: 10.1021/ic900611u

# A 12-Connected Dodecanuclear Copper Cluster with Yellow Luminescence

**Xi Liu* and Kun-Lin Huang**

*Key Laboratory of Functional Materials, College of Chemistry, Chongqing Normal University, Chongqing 400047, People's Republic of China*

Received March 31, 2009

The 3-D 12-connected metal−organic framework $[Cu_{12}Br_2(CN)_{6/2}(SCH_3)_6][Cu(SCH_3)_2]$, containing dodecanuclear copper clusters, has been solvothermally synthesized and exhibits efficient yellow luminescence. The emission mechanism was studied in detail to elucidate the relationship of the luminescent properties and crystal structures, which is helpful for the design and synthesis of more efficient luminescent materials.

The analysis of metal−organic framework structures with a topological method is of great current interest in the crystal engineering field recently because of applications not only as important tools for simplifying complicated coordination polymers but also in the rational design of some functional materials with special properties.[1] The classifications of structures by Wells and O'Keeffe et al. lay the foundation for the general understanding of inorganic solids as well as metal−organic frameworks.[2] Among these structure types, many coordination polymers with 3−8-connected topological networks in which d- and f-block ions act as nodes are known,[1,3] while a connectivity larger than eight remains unknown in the metal−organic frameworks, probably because of the limited coordination numbers of metal centers and steric hindrance of the organic ligands.[3c,f] Compared with d- or f-block ions, metal clusters commonly have larger sizes and more coordination sites but smaller steric hindrance when coordinated by organic ligands and have been used as nodes for high-connected metal−organic frameworks recently.[4,5]

Besides the curiosity in the construction of frameworks with metal clusters as design elements, an interest in the special luminescent properties of filled-shell $d^{10}$ metal cyanide complexes drives us to synthesize $d^{10}$ metal cluster−cyanide complexes. According to others'[6,7] and our[8,9] recent studies, the $d^{10}$ metal complexes formed with cyanide groups as bridging ligands and halide ions as ancillary ligands have been shown to be highly luminescent materials with abundant optical transitions. In the present communication, we report the synthesis and luminescent properties of a 12-connected dodecanuclear copper cluster with a pseudo-primitive cubic (pseudo-pcu) topology, $[Cu_{12}Br_2(CN)_{6/2}(SCH_3)_6][Cu(SCH_3)_2]$ (**1**).

---

*To whom correspondence should be addressed. E-mail: xliu@cqnu.edu.cn. Fax: +86-23-65910306.

(1) For reviews, see: (a) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629–1658. (b) Eddaoudi, M.; Moler, D. B.; Li, H.-L.; Chen, B.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319–330. (c) Carlucci, L.; Ciani, G.; Proserpio, D. M. *Coord. Chem. Rev.* **2003**, *246*, 247–289. (d) Hill, R. J.; Long, D.-L.; Champness, N. R.; Hubberstey, P.; Schröder, M. *Acc. Chem. Res.* **2005**, *38*, 337–350.

(2) (a) Wells, A. F. *Three-Dimensional Nets and Polyhedra*; Wiley: New York, 1977. (b) Wells, A. F. *Further Studies of Three-Dimensional Nets*; American Crystallographic Association Monograph 8; American Crystallographic Association: Buffalo, NY, 1979. (c) O'Keeffe, M. *Z. Kristallogr.* **1991**, *196*, 21–37. (d) O'Keeffe, M.; Brese, N. E. *Acta Crystallogr., Sect. A* **1992**, *48*, 663–669. (e) O'Keeffe, M. *Acta Crystallogr., Sect. A* **1992**, *48*, 670–673. (f) O'Keeffe, M. *Acta Crystallogr., Sect. A* **1995**, *51*, 916–920. (g) Friedrichs, O. D.; O'Keeffe, M.; Yagh, O. M. *Acta Crystallogr., Sect. A* **2003**, *59*(22−27), 515–525. (h) Friedrichs, O. D.; O'Keeffe, M. *J. Solid State Chem.* **2005**, *178*, 2480–2485.

(3) For examples, see: (a) Lo, S. M. F.; Chui, S. S. Y.; Shek, L. Y.; Lin, Z. Y.; Zhan, X. X.; Wen, G. H.; Williams, I. D. *J. Am. Chem. Soc.* **2000**, *122*, 6293–6294. (b) Long, D.-L.; Blake, A. J.; Champness, N. R.; Wilson, C.; Schröder, M. *J. Am. Chem. Soc.* **2001**, *123*, 3401–3402. (c) Long, D.-L.; Blake, A. J.; Champness, N. R.; Wilson, C.; Schröder, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 2443–2447. (d) Moulton, B.; Lu, J.-J.; Hajndl, R.; Hariharan, S.; Zaworotko, M. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 2821–2824. (e) Pan, L.; Liu, H.; Lei, X.; Huang, X.; Olson, D. H.; Turro, N. J.; Li, J. *Angew. Chem., Int. Ed.* **2003**, *42*, 542–546. (f) 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.

(4) (a) Chun, H.; Kim, D.; Dybtsev, D. N.; Kim, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 971−974 and references cited therein. (b) Hao, Z.-M.; Fang, R.-Q.; Wu, H.-S.; Zhang, X.-M. *Inorg. Chem.* **2008**, *47*, 8197–8203. (c) Morris, J. J.; Noll, B. C.; Henderson, K. W. *Inorg. Chem.* **2008**, *47*, 9583–9591. (d) Wang, X.-L.; Qin, C.; Lan, Y.-Q.; Shao, K.-Z.; Su, Z.-M.; Wang, E.-B. *Chem. Commun.* **2009**, 410–412.

(5) (a) Zhang, X.-M.; Fang, R.-Q.; Wu, H.-S. *J. Am. Chem. Soc.* **2005**, *127*, 7670–7671. (b) Li, D.; Wu, T.; Zhou, X.-P.; Zhou, R.; Huang, X.-C. *Angew. Chem., Int. Ed.* **2005**, *44*, 4175–4178.

(6) (a) Horváth, A.; Stevenson, K. L. *Inorg. Chim. Acta* **1991**, *186*, 61–66. (b) Horváth, A.; Stevenson, K. L. *Inorg. Chem.* **1993**, *32*, 2225–2227. (c) Horváth, A.; Wood C. E.; Stevenson, K. L. *Inorg. Chem.* **1994**, *33*, 5351−5354 and references cited therein.

(7) (a) Bowmaker, G. A.; Hartl, H.; Urban, V. *Inorg. Chem.* **2000**, *39*, 4548–4554. (b) Hibble, S. J.; Eversfield, S. G.; Cowley, A. R.; Chippindale, A. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 628–630.

(8) (a) Liu, X.; Guo, G.-C.; Wu, A.-Q.; Cai, L.-Z.; Huang, J.-S. *Inorg. Chem.* **2005**, *44*, 4282–4286. (b) Liu, X.; Guo, G.-C.; Fu, M.-L.; Zou, J.-P.; Zheng, F.-Q.; Huang, J.-S. *Inorg. Chim. Acta* **2006**, *359*, 1643–1649. (c) Liu, X.; Guo, G.-C. *Cryst. Growth Des.* **2008**, *8*, 776–778.

(9) (a) Liu, X.; Guo, G.-C.; Fu, M.-L.; Chen, W.-T.; Zhang, J.-Z.; Huang, J.-S. *Dalton Trans.* **2006**, 884–886. (b) Liu, X.; Guo, G.-C.; Fu, M.-L.; Chen, W.-T.; Wang, M.-S.; Huang, J.-S. *Inorg. Chem.* **2006**, *45*, 3679–3685. (c) Liu, X.; Guo, G.-C. *Aust. J. Chem.* **2008**, *61*, 481–483.

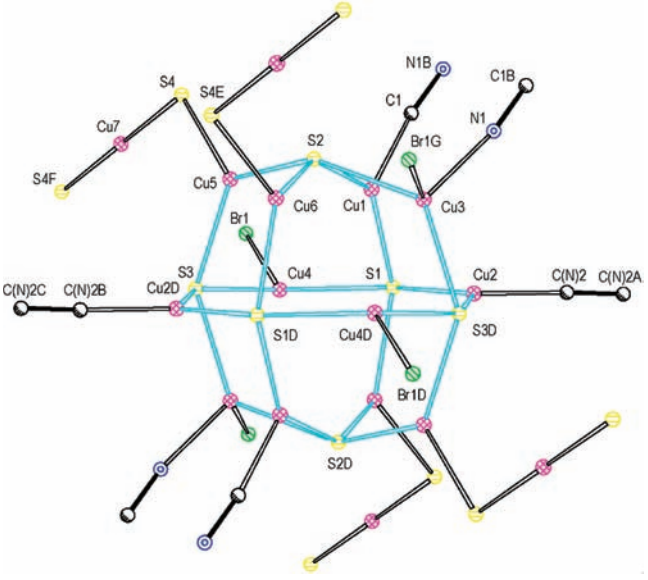

**Figure 1.** Coordination environments of Cu atoms in **1**. Methyl groups of methyl mercaptide groups are omitted for clarity. Symmetry codes: A, $-x, 1-y, 2-z$; B, $1-x, 1-y, 2-z$; C, $1+x, y, -1+z$; D, $1-x, 1-y, 1-z$; E, $2-x, 1-y, 2-z$; F, $2-x, -y, 1-z$; G, $x, 1+y, z$.

The solvothermal reaction[10] of copper(I) thiocyanate (CuSCN) and tetrabutylammonium bromide in acetonitrile and methanol produced complex **1**, which was characterized by X-ray single-crystal structural analysis,[11] elemental analysis, and Fourier transform infrared (FT-IR) spectroscopy.[12]

The structure of **1** exhibits a 3-D 12-connected framework with pseudo-pcu topology based on spherical dodecanuclear copper(I) clusters $[Cu_{12}(\mu_4\text{-}SCH_3)_6]^{6+}$ connected by cyanide groups, bromide anions, and $[Cu(SCH_3)_2]^-$ subunits. The structure has no isolated guest molecules and no residual solvent-accessible void (calculation by *PLATON*), showing a closest-packed structure. As shown in Figure 1, there are seven unique Cu$^I$ ions in the asymmetric unit. The three-coordinate Cu1, Cu2, Cu4, Cu5, and Cu6 ions are all in a distorted trigonal-planar coordination environment with CuS2C1, CuS2C(N)1, CuS2Br1, CuS3, and CuS3 coordination geometry, respectively; The four-coordinate Cu3 atom is approximately tetrahedrally coordinated by one $\mu$-Br atom, one cyanide ($\mu$-CN$^-$) N atom, and two S atoms from two methyl mercaptide groups ($\mu_4$-SCH$_3$), while the two-coordinate Cu7 is linearly connected by two S atoms from two methyl mercaptide groups ($\mu_3$-SCH$_3$) to form a subunit of $\mu_4$-$[Cu(\mu_3\text{-}SCH_3)_2]^-$ with a S−Cu−S bond angle of 180°. Interestingly, two-, three-, and four-coordinate Cu$^I$ atoms coexist in **1**, which is the second example[8a] according to the survey of the Cambridge Crystallographic Database. S atoms in methyl mercaptide groups adopt two different kinds of bridging modes: S1, S2, and S3 in $\mu_4$-S and S4 in $\mu_3$-S. To our knowledge, the $\mu_4$-S bridging mode is rare and mainly occurs in silver complexes[13] but scarcely in copper(I) complexes.[5b,14] Two adjacent centrosymmetric sets of S1, S2, and S3 atoms bridge two adjacent centrosymmetric sets of Cu1, Cu2, Cu3, Cu4, Cu5, and Cu6 atoms to form a spherical dodecanuclear copper(I) cluster $[Cu_{12}(\mu_4\text{-}SCH_3)_6]^{6+}$, in which the 12 Cu$^I$ atoms display a Cu$_{12}$ cuboctahedron-like configuration and all S atoms reside in the approximate square-pyramidal CSCu$_4$ environment with one C atom at the apex and four Cu$^I$ atoms in the equatorial plane. The Cu$\cdots$Cu separation in the cluster varies from 2.7961(8) to 3.001(1) Å, suggesting weak Cu−Cu interactions, while the Cu−S bond distances range between 2.243(1) and 2.381(1) Å. Accordingly, the $[Cu_{12}(\mu_4\text{-}SCH_3)_6]^{6+}$ cluster in **1** is different from that in the reported $[Cu_{12}(CN)_6(\mu_4\text{-}SCH_3)_6]\cdot 2H_2O$,[5b] in which the corresponding bond angles and lengths are equivalent.

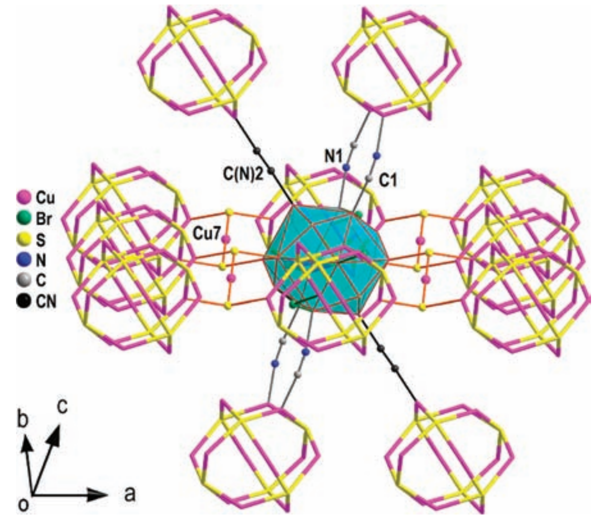

**Figure 2.** Spherical $[Cu_{12}(SCH_3)_6]^{6+}$ cluster (represented as a turquoise polyhedron) connecting 12 adjacent clusters through four $[Cu(SCH_3)_2]^-$ subunits (orange), four $\mu$-Br atoms (green), four $\mu$-cyanide groups (gray), and two symmetry-related disordered $\mu$-cyanide groups (black).

Each spherical $[Cu_{12}(\mu_4\text{-}SCH_3)_6]^{6+}$ cluster connects eight adjacent clusters through four $\mu_4$-$[Cu(SCH_3)_2]^-$ subunits and four $\mu$-Br atoms to form a 2-D layer along the *a* and *b* directions and further links four similar clusters by four $\mu$-CN$^-$ groups along the *c* direction and two symmetry-related disordered $\mu$-CN$^-$ groups along the [−1 0 1] direction to generate a 3-D closest-packed framework (Figure 2 and Figure S1 in the Supporting Information). Thus, each spherical $[Cu_{12}(\mu_4\text{-}SCH_3)_6]^{6+}$ cluster connects 12 adjacent clusters through four $\mu_4$-$[Cu(SCH_3)_2]^-$ subunits, four $\mu$-Br atoms, four $\mu$-CN$^-$ groups, and two symmetry-related disordered

---

[10] (10) A mixture of CuSCN (243 mg, 2 mmol) and Bu$_4$NBr (161 mg, 0.5 mmol) in 5 mL of acetonitrile and 5 mL of methanol was sealed in a 25 mL poly(tetrafluoroethylene)-lined stainless steel container under autogenous pressure and heated at 160 °C for 3 days, followed by cooling at 2 °C/h to room temperature. The resulting orange crystals $[Cu_{10}(SCH_3)_6][Cu(CN)(SCH_3)_2]_2$ (crystal data at 293 K: triclinic, $P\bar{1}$, $a$ = 8.5492(5) Å, $b$ = 9.1668(2) Å, $c$ = 11.813(1) Å, α = 74.16(2)°, $\beta$ = 74.16(2)°, $\gamma$ = 65.31(2)°, $V$ = 806.43(1) Å$^3$, reported by Li and Wu[14b]) and red crystals **1** (ca. 10% yield, based on copper) were collected and separated manually.

[11] (11) Crystal data of **1**: triclinic, $P\bar{1}$, $a$ = 9.2047(5) Å, $b$ = 9.570(1) Å, $c$ = 9.8376(5) Å, α = 83.39(1)°, $\beta$ = 71.06(1)°, $\gamma$ = 85.89(2)°, $V$ = 813.6(1) Å$^3$, $Z$ = 1, $M_r$ = 1440.65, $\rho$ = 2.940 g cm$^{-3}$, $F$(000) = 686, $\mu$(Mo Kα) = 11.282 mm$^{-1}$, $\theta_{max}$ = 25.03°, 5162 measured reflections, 2830 independent reflections. R1 (wR1) = 0.0604 (0.1417) for 2315 reflections $[I > 2\sigma(I)]$ and 170 parameters. GOF = 1.002. Crystal dimensions: 0.17 × 0.15 × 0.10 mm$^3$.

[12] (12) Anal. Calcd for **1**, $C_{11}H_{24}Br_2Cu_{13}N_3S_8$: C, 9.17; H, 1.68; N, 2.92. Found: C, 9.15; H, 1.62; N, 2.99. FT-IR (KBr, cm$^{-1}$): 3377 (br, s), 3039 (w), 2948 (m), 2873 (m), 2826 (w), 2378 (w), 2344 (m), 2271 (w), 2128 (m), 1654 (w), 1497 (w), 1478 (w), 1352 (m), 1106 (s), 952 (w), 679 (w), 614 (m), 481 (m), 417 (w). $\nu$(CN): 2128 (m).

[13] (13) (a) Su, W.-P.; Cao, R.; Hong, M.-C.; Chen, J.-T.; Lu, J.-X. *Chem. Commun.* **1998**, 1389–1390. (b) Hong, M.-C.; Su, W.-P.; Cao, R.; Zhang, W.-J.; Lu, J.-X. *Inorg. Chem.* **1999**, *38*, 600–602. (c) Su, W.-P.; Hong, M.-C.; Weng, J.-B.; Cao, R.; Lu, S.-F. *Angew. Chem., Int. Ed.* **2000**, *39*, 2911–2914.

[14] (14) (a) Prichard, R. G.; Parish, R. V.; Salehi, Z. *J. Chem. Soc., Dalton Trans.* **1999**, 243. (b) Li, D.; Wu, T. *Inorg. Chem.* **2005**, *44*, 1175–1177.

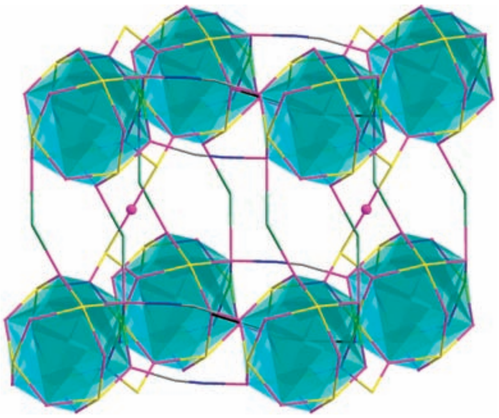

**Figure 3.** View of the simple cubiclike packing pattern of the spherical $[Cu_{12}(SCH_3)_6]^{6+}$ clusters.

$\mu$-$CN^-$ groups to generate a 3-D 12-connected framework. The topology of the 3-D framework can be rationalized in terms of a pseudo-pcu net by defining the dodecanuclear $[Cu_{12}(\mu_4\text{-}SCH_3)_6]^{6+}$ clusters as 12-connected nodes and $\mu$-Br, $\mu$-$CN^-$, and $\mu_4$-$[Cu(SCH_3)_2]^-$ subunits as linkers (Figure 3 and Scheme S1 in the Supporting Information).

Another feature of **1** is in situ generation of $CN^-$ and $SCH_3^-$ groups through the solvothermal reaction of CuSCN with acetonitrile and methanol, whose reaction mechanism has been reported by Li.[14b] The C−N bond lengths in the $CN^-$ groups are found to be 1.142(6) or 1.161(7) Å, which was verified through an FT-IR spectrum because there is a medium peak at 2128 cm$^{-1}$, corresponding to the C≡N stretching vibration of the cyanide groups.[8a]

Compound **1** displays a strong broad yellow-luminescent emission band in the solid state at 575 nm upon photoexcitation at 386 nm (Figure 4), and its lifetime was measured as 4.9 ns (see the Supporting Information), suggesting it to be a good candidate for luminescent material. The emission peak is similar to that of the byproduct $[Cu_{10}(SCH_3)_6][Cu(CN)(SCH_3)_2]_2$.[14b] Density functional theory calculation of the electronic band structure of **1** along with density of states was carried out with the CASTEP code.[15] The results indicate that the origin of the emission band may be mainly ascribed to the coupling of metal-to-ligand charge transfer, where the electrons are transferred from the copper (Cu 3d states, VBs) to unoccupied $\pi^*$ orbitals of cyanide groups ($C_{cyanide}$ 2p and $N_{cyanide}$ 2p states, CBs) and metal-centered transitions ($Cu^I$, ds/dp) of the type $3d^{10} \rightarrow 3d^94s$ and $3d^{10} \rightarrow 3d^94p$ on the copper(I) center (Figure S2 and its explanation in the Supporting Information).

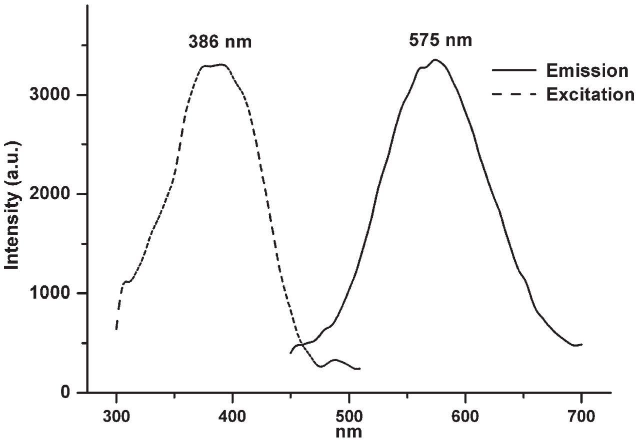

**Figure 4.** Solid-state electronic excitation ($\lambda_{ex}$ = 386 nm) and emission ($\lambda_{em}$ = 575 nm) of **1** at room temperature.

In conclusion, we have synthesized a 3-D 12-connected pseudo-pcu topological metal−organic framework containing dodecanuclear copper clusters and exhibiting efficient yellow luminescence. The results are significant not only for validating the feasibility of using a cluster as a building block to construct high-connectivity networks but also for elucidating the relationship of the luminescent properties and crystal structures in $d^{10}$ metal cyanide complexes, which may be helpful for the design and synthesis of more efficient luminescent materials.

**Acknowledgment.** We gratefully acknowledge financial support by the NNSF of China (Grant 20701041), the NSF of Chongqing (Grant CSTC2007BB4234), the SP of Chongqing Municipal Education Commission (Grant KJ070812), and the MSF of Chongqing Normal University (Grant 08XLZ09).

**Supporting Information Available:** X-ray crystallographic file in CIF format, theoretical approach methodology and the corresponding calculated results, and a luminescence spectrum. This material is available free of charge via the Internet at http://pubs.acs.org.

---

(15) (a) Segall, M.; Linda, P.; Probert, M.; Pickard, C.; Hasnip, P.; Clark, S.; Payne, M. *Materials Studio CASTEP*, version 2.2; Accelrys: San Diego, CA, 2002. (b) Segall, M.; Linda, P.; Probert, M.; Pickard, C.; Hasnip, P.; Clark, S.; Payne, M. *J. Phys.: Condens. Matter* **2002**, *14*, 2717–2744.