Inorg. Chem. **2005**, *44*, 3371–3373

Inorganic Chemistry

Communication

A Unique Cyanide-Bridged Three-Dimensional (3-D) Copper(II)–Copper(I) Mixed-Valence Polymer Containing 1-D Water Tapes with Cyclic Pentamer Units

Ji-Min Zheng,[*,†] Stuart R. Batten,[‡] and Miao Du[*,§,||]

Department of Chemistry, Nankai University, Tianjin 300071, P. R. China, School of Chemistry, P.O. Box 23, Monash University, Clayton, Victoria, 3800, Australia, College of Chemistry and Life Science, Tianjin Normal University, Tianjin 300074, P. R. China, and State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, P. R. China

Received November 22, 2004

A unique cyano-bridged copper(II)–copper(I) mixed-valence polymer, $\{[Cu_3(CN)_4(H_2O)_3](H_2O)_2\}_n$ (**1**), has been prepared and structurally determined by X-ray diffraction. The cyanide anions with (μ_2,η^2) and (μ_3,η^2) bridging modes connect the copper centers into a complicated zeolite-like 3-D network. Of further interest, coordinated and lattice water molecules in this structure form 1-D hydrogen-bonded water tapes consisting of linked cyclic pentamer clusters.

There is currently considerable and ever-increasing interest in crystal engineering of metal coordination polymers. These polymers may possess intriguing architectural complexity of network topologies and potential applications in the aspects of zeolite-like materials, molecular absorption, ion exchange, electrical conductivity, and new molecule-based magnets.[1,2] In this field, coordination polymers constructed from metal centers and pseudohalide ligands such as the classical cyanide, azide, and thiocyanate ligands have long been investigated,[3] and those based on larger dicyanamide and tricyanomethanide anions have also become a very hot topic recently.[4] On the other hand, the rational design and preparation of mixed-valence copper(II)–copper(I) coordination complexes, which are of great biological importance and interesting electronic properties, is still a challenge.[5] Of further interest is the fact that only a few such mixed-valence coordination polymers have been documented so far, predominantly via hydro(solvo) thermal approaches.[6]

Water is the most abundant and cheapest natural solvent and is of fundamental importance in almost all branches of natural sciences such as biological, chemical, and physical processes.[7] Although considerable attention has been devoted to the theoretical and experimental investigation of water clusters, including a variety of oligomers and polymers consisting of the basic cyclic water subunits, they are still

---

[*] Author to whom correspondence should be addressed. E-mail: dumiao@public.tpt.tj.cn. Fax: +86-22-2340315. Tel: +86-22-23538221.

[†] Department of Chemistry, Nankai University.

[‡] Monash University.

[§] Tianjin Normal University.

[||] State Key Laboratory of Elemento-Organic Chemistry, Nankai University.

(1) For examples see: (a) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460–1494. (b) Blake, A. J.; Champness, N.; Hubberstey, P.; Li, W.-S.; Withersby, A.; Schröder, M. *Coord. Chem. Rev.* **1999**, *183*, 117–138. (c) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629–1658. (d) Robson, R. *J. Chem. Soc., Dalton Trans.* **2000**, 3735–3744. (e) Carlucci, L.; Ciani, G.; Proserpio, D. M. *Coord. Chem. Rev.* **2003**, *246*, 247–289. (f) Brammer, L. *Chem. Soc. Rev.* **2004**, *33*, 476–489.

(2) For examples see: (a) Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2639–2684. (b) Kahn, O. *Acc. Chem. Res.* **2000**, *33*, 647–657. (c) Evans, O. R.; Lin, W. *Acc. Chem. Res.* **2002**, *35*, 511–522. (d) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705–714. (e) Janiak, C. *Dalton Trans.* **2003**, 2781–2804. (f) Rao, C. N. R.; Natarajan, S.; Vaidhyanathan, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 1466–1496. (g) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334–2375.

(3) For examples see: (a) Ohba, M.; Okawa, H. *Coord. Chem. Rev.* **2000**, *198*, 313–328. (b) Dunbar, K. R.; Heintz, R. A. *Prog. Inorg. Chem.* **1997**, *45*, 283–391. (c) Ribas, J.; Escuer, A.; Monfort, M.; Vicente, R.; Cortes, R.; Lezama, L.; Rojo, T. *Coord. Chem. Rev.* **1999**, *193–195*, 1027–1068. (d) Zhang, H.; Wang, X. M.; Zhang, K. C.; Teo, B. K. *Coord. Chem. Rev.* **1999**, *183*, 157–195.

(4) Batten, S. R.; Murray, K. S. *Coord. Chem. Rev.* **2003**, *246*, 103–130, and references therein.

(5) (a) LeCloux, D. D.; Davydov, R.; Lippard, S. J. *J. Am. Chem. Soc.* **1998**, *120*, 6810–6811. (b) House, R. P.; Young, V. G., Jr.; Tolman, W. B. *J. Am. Chem. Soc.* **1996**, *118*, 2101–2102. (c) Gamelin, D. R.; Williams, K. R.; LaCroix, L. B.; Houser, R. P.; Tolman, W. B.; Mulder, T. C.; de Vries, S.; Hedman, B.; Hodgson, K. O.; Solomon, E. I. *J. Am. Chem. Soc.* **1997**, *119*, 613–614. (d) George, S. D.; Metz, M.; Szilagyi, R. K.; Wang, H.; Cramer, S. P.; Lu, Y.; Tolman, W. B.; Hedman, B.; Hodgson, K. O.; Solomon, E. I. *J. Am. Chem. Soc.* **2001**, *123*, 5757–5767.

(6) For examples see: (a) Tao, J.; Zhang, Y.; Tong, M.-L.; Chen, X.-M.; Yuen, T.; Lin, C. L.; Huang, X.; Li, J. *Chem. Commun.* **2002**, 1342–1343. (b) Zhang, X.-M.; Tong, M.-L.; Chen, X.-M. *Angew. Chem., Int. Ed.* **2002**, *41*, 1029–1031. (c) Colacio, E.; Kivekas, R.; Lloret, F.; Sunberg, M.; Suarez-Varla, J.; Bardaji, M.; Laguna, A. *Inorg. Chem.* **2002**, *41*, 5141–5149. (d) Tong, M.-L.; Li, L.-J.; Mochizuki, K.; Chang, H.-C.; Chen, X.-M.; Li, Y.; Kitagawa, S. *Chem. Commun.* **2003**, 428–429. (e) Kang, Y.; Yao, Y.-G.; Qin, Y.-Y.; Zhang, J.; Chen, Y.-B.; Li, Z.-J.; Wen, Y.-H.; Cheng, J.-K.; Hu, R. F. *Chem. Commun.* **2004**, 1046–1047.

(7) Buck, U.; Huisken, F. *Chem. Rev.* **2000**, *100*, 3863–3890.

10.1021/ic0483491 CCC: $30.25

not fully understood.[8,9] Water pentamers were found to exist in large water clusters, liquid water, the surfaces of proteins, and DNA. However, solid structural studies are quite limited in comparison with those of the more common water tetramers or hexamers.[10] In this Communication, we will describe the preparation, structural characterization, and properties of a unique 3-D cyano-bridged $Cu^{II}-Cu^{I}$ polymer, $\{[Cu_3(CN)_4(H_2O)_3](H_2O)_2\}_n$ (**1**), in which novel 1-D water tapes consisting of cyclic pentamers were formed via hydrogen-bonding interactions of the coordinated and clathrated water molecules.

Complex **1** was grown in a gel medium through diffusion method and its composition was confirmed by elemental analyses and inductively coupled plasma (ICP).[11] The crystal structure was determined by X-ray diffraction.[12] The asymmetric unit contains three copper atoms, four cyanide ligands, three water ligands, and two clathrated water molecules. The Cu1 atom (Figure 1) is octahedral and thus clearly divalent, coordinating to three cyanide ligands arranged in a *mer* geometry (Cu−C/N = 1.958(4)−1.988(4) Å), and three *mer* water ligands (Cu−O = 1.952(4)−2.572(3) Å). This copper atom also shows classic Jahn−Teller distortion, with the two trans water ligands having significantly longer bond lengths (Cu−O2 = 2.431(4) and Cu−O3 = 2.572(3) Å) than the other four ligands (Cu−C/N/O = 1.952(4)−1.988(4) Å). The Cu2 and Cu3 atoms are tetrahedral and thus monovalent, coordinating to four cyanide ligands (Cu2−C/N = 1.923(6)−2.428(6) Å; Cu3−C/N = 1.969(6)−2.292(5) Å). For the cyanide ligands, each cyanide atom position was refined as being disordered equally between a carbon and a nitrogen atom, with equivalent thermal parameters. Three of the cyanide ligands show (μ_3,η^2) bridging modes, while the other adopts a (μ_2,η^2) coordination fashion. The CN1 ligand (which contains C1/N1′ and N1/C1′) coordinates to one Cu1 atom via a monodentate C/N atom, and to one Cu2 and one Cu3 atom via a μ-C/N atom. The same applies to CN2. The CN4 ligand is the same, except the μ-C/N atom coordinates to two Cu3 atoms, while the monodentate C/N atom coordinates to Cu2. Finally, the linear CN3 ligand bridges between the Cu1 and Cu2 atoms.

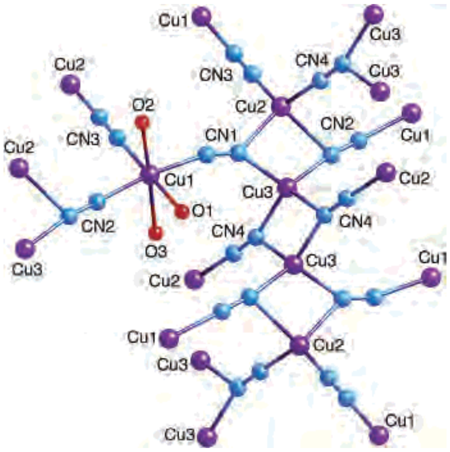

Figure 1. Portion of the 3-D polymeric framework of **1**, with selected atom numbering. The hydrogen atoms and clathrated water molecules are omitted for clarity. The cyanide ligands were refined as disordered, and thus the label CN*x* refers to the cyanide ligand containing both C*x*/N*x*′ and N*x*/C*x*′.

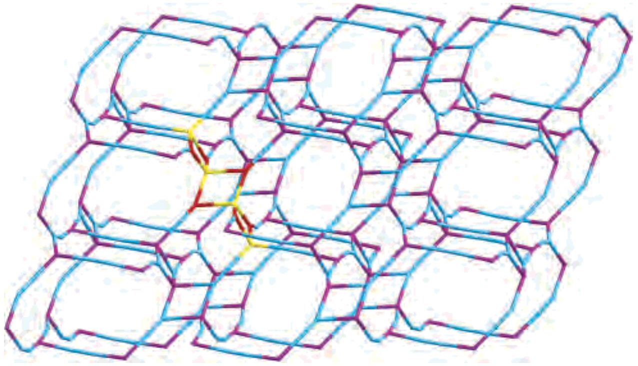

Figure 2. Zeolite-like 3-D network of **1**. Water ligands and lattice molecules are omitted for clarity. One tetranuclear subunit is highlighted in red and yellow (see text).

The copper atoms are bridged by the cyanide ligands to afford a complicated zeolite-like three-dimensional (3-D) network, which contains 3-connectors (Cu1, CN1, CN2, and CN4), 4-connectors (Cu2 and Cu3), and 2-connecting CN3 ligands. This 3,4-connected net can be thought of in terms of centrosymmetric, tetranuclear subunits containing three $Cu_2(C/N)_2$ "squares" (as highlighted in Figure 2). The two squares at either end contain a Cu2 and a Cu3 atom bridged by a single atom from a CN1 ligand and another from a CN2 ligand (Cu2···Cu3 = 2.5139(12) Å). The central square contains two Cu3 atoms bridged by a single atom from each of two CN4 ligands (Cu3···Cu3 = 2.5564(14) Å). These tetranuclear subunits are then connected into the final 3-D net by CN4 ligands and by Cu1(CN1)(CN2)(CN3) moieties (see Figure 2).

Further analysis of the crystal packing reveals that this structure also contains extensive hydrogen bonding between the coordinated (O1, O2, O3) and clathrated (O4, O5) water

---

(8) For examples see: (a) Head-Gordon, T.; Hura, G. *Chem. Rev.* **2002**, *102*, 2651−2669, and references therein. (b) Keutsch, F. N.; Cruzan, J. D.; Saykally, R. J. *Chem. Rev.* **2003**, *103*, 2533−2577, and references therein.

(9) For examples see: (a) Ghosh, S. K.; Bharadwaj, P. K. *Angew. Chem., Int. Ed.* **2004**, *43*, 3577−3580. (b) Ghosh, S. K.; Bharadwaj, P. K. *Inorg. Chem.* **2004**, *43*, 5180−5182. (c) Rodriguez-Cuamatzi, P.; Vargas-Diaz, G.; Hopfl, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 3041−3044. (d) Ma, B. Q.; Sun, H. L.; Gao, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 1374−1376. (e) Long, L. S.; Wu, Y. R.; Huang, R. B.; Zheng, L. S. *Inorg. Chem.* **2004**, *43*, 3798−3800. (f) Tao, J.; Ma, Z. J.; Huang, R. B.; Zheng, L. S. *Inorg. Chem.* **2004**, *43*, 6133−6135. (g) Ye, B. H.; Ding, B. B.; Weng, Y. Q.; Chen, X. M. *Inorg. Chem.* **2004**, *43*, 6866−6868.

(10) Ma, B. Q.; Sun, H. L.; Gao, S. *Chem. Commun.* **2004**, 2220−2221.

(11) The detailed preparation for **1**: An aqueous solution of $CuCl_2{\cdot}2H_2O$ (85 mg) and an aqueous solution containing $K_2[Cu(CN)_4]$ (60 mg) and KCN (35 mg) were placed in two arms of the U-tube set with gel, respectively. After an interval of 3 weeks at room temperature, single-crystals appeared at the bend portion of the U-tube. Yield: 20%. Found: C, 12.32; H, 2.64; N, 14.46; Cu, 49.46. Anal. Calcd for $C_4H_{10}Cu_3N_4O_5$: C, 12.49; H, 2.62; N, 14.56; Cu, 49.54. IR spectra (KBr, cm^{-1}): ν(O−H) 3577*s*, 3439*b*; ν(CN) 2167*s*, 2147*s*, and 2130*s* (Cu−CN), 2109*s* and 2091*s* (Cu−NC).

(12) Crystal data for **1**: triclinic, space group $P\bar{1}$, with $a = 6.720(2)$ Å, $b = 9.494(3)$ Å, $c = 10.682(3)$ Å, $\alpha = 111.979(4)°$, $\beta = 96.879(5)°$, $\gamma = 106.678(5)°$, $V = 585.3(3)$ Å^3, $Z = 2$, 2041 unique reflections measured with 145 parameters, final $R_1 = 0.0387$ and $wR_2 = 0.1041$. Data collection: Bruker Smart 1000 CCD diffractometer at room temperature. All non-H atoms were refined anisotropically. H atoms were first found in difference electron density maps, and then placed in the calculated sites and included in the final refinement in the riding model approximation with fixed thermal factors.

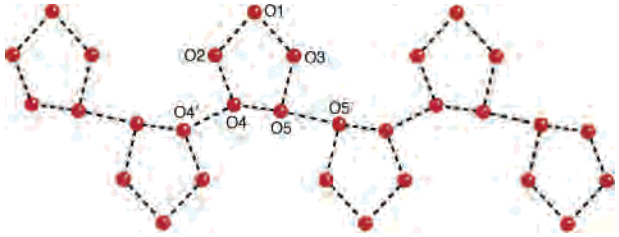

Figure 3. Representation of the 1-D water tape consisting of pentamers linked via water−water interactions.

molecules. The most significant of these are O1···O2 = 2.722 Å, O1···O3 = 2.714 Å, O2···O4 = 2.731 Å, O3···O5 = 2.846 Å, and O4···O5 = 2.654 Å, affording a five-membered cyclic motif. Within the pentamer, five oxygens are arranged in the expected pucker mode. Additional O4···O4 (2.619 Å) and O5···O5 (2.913 Å) water−water interactions extend these pentamers to form a unique 1-D tape (Figure 3). Normally, water clusters locate in organic molecular hosts or inorganic−organic hybrid frameworks. In this case, these water tapes may play a complementary role for stabilizing the network structure. Comparing this structure with other mixed valence copper−cyanide polymers with similar coligands, such as $Cu^{I}_2Cu^{II}(CN)_4(NH_3)_3$[13] and $Cu^{I}_4Cu^{II}(CN)_6(DMF)_4$,[14] we could observe that both polymers have network topologies quite different from that described in this work, suggesting that such water clusters can influence the final overall 3-D coordination frameworks (also see below for XRPD studies). To estimate the stability of the water tapes, thermal analysis experiments were carried out. The results (see Supporting Information) indicate that the weight loss of two guest water molecules occurs in the region of 65−200 °C and the loss of the aqua ligands is not observed before 300 °C where the decomposition of the framework starts, maybe due to their coordination to the Cu^{II} center. Powder X-ray diffraction studies of **1** before and after water expulsion (treated by heating the sample of **1** at 240 °C for 10 h) showed major changes in the diffraction patterns (see Supporting Information) which were attributed to the complete breakdown of the coordination framework on exclusion of water and also confirmed that the water clusters are significant for stabilization of the network structure.

Magnetic measurement of **1** was carried out in a magnetic field of 0.5 T with the temperature range of 2−300 K, and the results were given in the form of a $\chi_M T$ vs T plot (inset: χ_M vs T, see Supporting Information), in which χ_M is the corrected magnetic susceptibility per asymmetric $[Cu_3(CN)_4(H_2O)_3](H_2O)_2$ unit. The $\chi_M T$ value at room temperature is 0.406 $cm^3\ mol^{-1}$ K, corresponding to an isolated Cu^{II} ion without any coupling, and decreases slowly upon cooling, attaining a value of 0.36 $cm^3\ mol^{-1}$ K at 2 K. This global feature is characteristic of a very weak antiferromagnetic exchange interaction. Taking the structure into account, this behavior could be justified on the two contributions: one arising from the pure ground-state basis of the sum of configuration of Cu^{II} and the other one mediated by the $CN-Cu^{I}-CN$ diamagnetic bridge. The reduced molar magnetization per entity tends to 1.0 electron following the Brillouin formula and this feature further confirms the mixed-valence of Cu^{I}/Cu^{II} and above magnetic behavior.

In summary, we have identified a unique 3-D zeolite-like coordination network in which Cu^{II} and Cu^{I} centers are linked via CN bridges. The guest water molecules located in this net are trapped by water−water interactions with the coordinated water ligands binding to Cu^{II}, forming a rare 1-D water tape with cyclic pentamer units. This investigation will evidently advance our understanding of the formation of both mixed-valence coordination polymers and water clusters.

Acknowledgment. This work was financially supported by the National Natural Science Foundation of China (50242001), the Key Project of Tianjin Natural Science Foundation (to M.D.), and the Australian Research Council (to S.R.B.). We also gratefully acknowledge Prof. Hong-Gen Wang and Dr. Hai-Bin Song for X-ray data collection and helpful discussions.

Supporting Information Available: X-ray crystallographic file in CIF format, thermal analysis, XRPD patterns of **1** before and after water expulsion, magnetic diagrams and magnetization curve of **1** (pdf). This material is available free of charge via the Internet at http://pubs.acs.org.

IC0483491

---

(13) (a) Williams, R. J.; Cromer, D. T.; Larson, A. C. *Acta Crystallogr., Sect. B* **1971**, *27*, 1701−1706. (b) Vrabel, V.; Garaj, J.; Sivy, J.; Oktavec, D. *Acta Crystallogr., Sect. C* **1999**, *55*, 1381−1383.

(14) (a) Peng, S. M.; Liaw, D. S. *Inorg. Chim. Acta* **1986**, *113*, L11−L12. (b) Zhao, X.-J.; Batten, S. R.; Du, M. *Acta Crystallogr., Sect. E* **2004**, *60*, m1237−m1239.