A Novel Microporous Cluster Polymer $\{[Et_4N]_2[WS_4Cu_4(CN)_4]\}_n$ with Cyanide-Bridged Three-Dimensional Open-Framework

Chi Zhang, Guocheng Jin, Yan Xu, Hoong-Kun Fun,† and Xinquan Xin*
State Key Laboratory of Coordination Chemistry, Department of Chemistry, Nanjing University, Nanjing 210093, P. R. China
†X-Ray Crystallography Unit, School of Physics, Universiti Sains Malaysia 11800, USM, Penang, Malaysia

(Received February 3, 2000; CL-000122)

Reaction of $(Et_4N)_2WS_4$ with CuCN (molar ratio of 1:4) in pyridine affords an interesting three-dimensional cluster polymer with open-framework. The crystal structure determination shows that the anionic WS_4Cu_4 units bridged by cyanide produce three-dimensional channels running down the crystallographic *a* axis.

The cluster chemistry of transition-metal-sulfur has been attracting considerable attention[1] because these clusters with interesting electronic, optical, structural and catalytic properties are of important biological and industrial significance in advance materials, biological processes, and catalyiic reaction.[2~4] Previously, the discrete Mo(W)/S/Cu(Ag) complexes had been extensively investigated, while the molecular construction of extended structure represents the subject of current research interest. The reported cluster polymers of this type are polynuclear chain polymers $\{[MoOS_3Cu_3(CN)(py)_3]\}_n$, $\{[W_4Ag_5S_{16}][Nd(DMF)_8]\}_n$, $\{[W_4Ag_4S_{16}][2Ca(DMSO)_6]\}_n$ and $\{[M_3Ag_3S_{12}][Nd(DMSO)_8]\}_n$ (M=Mo, W);[5] dinuclear infinite chain clusters $[AgMS_4(\gamma\text{-MepyH})]_n$, $[AgMS_4(\alpha\text{-MepyH})]_n$, $\{[MoS_4Ag]^-\}_n$, $\{[H_3NC(CH_2OH)_3R][WS_4Ag]\}_n$ (R=2DMF, H_2O), $[MS_4Tl]_n$;[6] tetranuclear open polymers $\{[(CuNCS)_3WS_4]^{2-}\}_n$;[7] pentanuclear open polymers $\{[(CuL)_4MoS_4]^{2-}\}_n$ (L=Br, NCS) $\{[Cu_4(NCS)_5MoS_4]^{2-}\}_n$;[8] heptanuclear net-work polymers $[MS_4Cu_6X_4(py)_4]_n$.[9] However, the cluster polymers with three-dimensional framework in Mo(W)/S/Cu(Ag) system are very rare. Moreover, the new kinds of inorganic materials with crystalline microporous open-framework other than aluminosilicate zeolites, aluminophosphate materials, started to emerge only in recent years.[10] The driving force behind the research is to engineer open-framework materials with desired chemical and catalytic reactivities. Herein, the synthesis and structural characteristic of an interesting microporous heterothiobimetallic cluster polymer $\{[Et_4N]_2[WS_4Cu_4(CN)_4]\}_n$ **1** [11] with cyanide-bridged three-dimensional open-framework are firstly reported.

The cluster polymer **1** was synthesized by reaction of $(Et_4N)_2WS_4$(0.573 g, 1 mmol) with CuCN (0.358 g, 4 mmol) in pyridine (20 cm^3) in inert atmosphere. The resulting orange-red solution was filtrated and laid with *i*-PrOH (20 cm^3) to stand in air at room temperature for about a month. Orange-red polyhedral crystals of cluster **1** with suitable quality for X-ray diffraction were obtained (0.220 g, yield 24% based on W). Found: C, 25 62; H 4 21; N 9 23%. Calcd for $C_{20}H_{40}N_6S_4Cu_4W$ **1**: C, 25.80; H, 4.33; N, 9.03%. The IR (KBr pellets) spectrum of cluster **1** exhibited intense bands at 2121 cm^{-1} attributed to ν(C-N), and feature at 447 cm^{-1} characteristic of $\nu(W\text{-}\mu_3\text{-}S)$. The elemental analysis and IR spectrum confirmed the formula of cluster **1**.

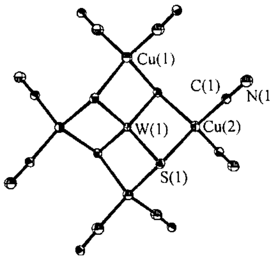

Figure 1. ORTEP diagram of a section of the crystal structure of **1** (30% displacement ellipsoids).

The crystal structure of cluster **1** consists of one crystallographic independent $[(CuCN)_4WS_4]^{2-}$ anion with the ORTEP diagram shown in Figure 1, and two Et_4N^+ cations, while the polymeric anion is constructed from WS_4Cu_4 units bridged by cyanide ligands. Each W atom of the structure is at the center of an essentially tetrahedral WS_4 unit in which the four W-S bond lengths are all quite similar to each other. Four edges of the WS_4 tetrahedron are coordinated by Cu atoms with W-Cu distances ranging from 2.7636(8) Å to 2.7926(8) Å, are longer than the corresponding separations observed in other discrete $WS_4(CuX)_n^{2-}$ (n=1-3) anions and the homogeneous constructions $WS_4(CuX)_4^{2-}$ anions. Within the WCu_4 core, five metal atoms are perfectly co-planar with Cu-W-Cu angle (180°) concerning the two mutually *trans* Cu atoms, which leads to an ideal crystallographic D_{2d} symmetry for the WS_4Cu_4 aggregate. Two *cis* Cu atoms, Cu(1) and Cu(2), both have a distorted-tetrahedral geometry with their tetrahedral apices occupied by two triply bridged S atoms and two cyanide bridged C atoms or N atoms, forming a CuS_2C_2 unit and a CuS_2N_2 unit respectively. These tetrahedra are mutually linked by bridged cyanide ligands thus constructing a polymeric three-dimensional anion of basic formula $[WS_4(CuCN)_4]_n^{2-}$. Comparing with the analogous cluster polymer $[WS_4(CuSCN)_4]_n^{2-}$ with bridging thiocyanate groups,[8] which exhibit a significant deviation of Cu-NCS and Cu-SCN angles, the polymeric anions bridged by the cyanide are very slightly bend with Cu-C-N=175.9(4)° and Cu-N-C=174.4(4)°. The corresponding cyanide ligands are involved in interaggregate linear bridges between Cu atoms of the next WS_4Cu_4 unit, forming a three-dimensional open-framework, and displaying no layering but particular directionality. The bond distances of Cu-N and Cu-C are 1.967(4) Å and 1.961(4) Å respectively, while the bond angles of C(1)-Cu(2)-C(1a)(-x-5/4, y, -z+3/4) and N(1a)(-x-3/2, -y, -z+1/2)-Cu(1)-N(lb)(x+1/4, y-1/4, -z+1/2) are 111.4(3)° and 112.0(2)° separately. Owing to different coordination of Cu(1) and Cu(2) atoms, the Cu(2)-S(1) bond length (2.3346(11) Å) is slightly shorter than the Cu(1)-S(1a)(x, -y- 1/4, -z+3/4) bond length (2.3521(11) Å).

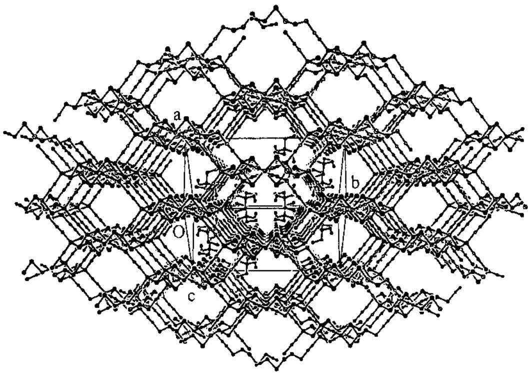

Figure 2. Packing drawing of cluster polymer **1** viewed along *a* axis.

The packing drawing of the unit cell depicted in Figure 2. The unit shown in Figure 1 is then fused together tetrahedrally, resulting in an anionic open-framework containing a three-dimensional intersecting channel system, where the channels run parallel to the crystallographic directions of [100] and [010]. These channels are occupied by the Et_4N^+ cations, which appear to induce the polymeric structure and presumable help to balance the cluster anions. An alternative way to view this framework is in terms of the diamond structure, where C has been alternately replaced by WS_4Cu_4 aggregate and C-C by cyanide bridging ligands. However, unlike the diamond lattice, microporous is created as a consequence of the larger size of the inorganic clusters compared to carbon atoms. In these intersecting channels, the shortest distances between Cu atoms along *b* axis and *c* axis are 15.22 Å and 8.11 Å respectively.

In summery, a novel microporous three-dimensional open-framework cluster polymer $\{[Et_4N]_2[WS_4Cu_4(CN)_4]\}_n$ with anionic WS_4Cu_4 units bridged by cyanide ligands has been synthesized and its single-crystal structure determined. The previous efforts to prepare this kind of cluster polymer are all frustrated by using $(NH_4)_2MS_4$ (M=Mo, W) as starting materials in the same reaction system. It is partly attributed to the NH_4^+ cations for their low solublity and too small in volume to sustain those intersecting channels. Whereas the Et_4N^+ cations can induce the polymeric structure and occupy the channels of the three-dimensional open-framework as well as help to achieve the charge balance in the cluster polymer.

This work was supported by the National Science Foundation of China (No. 29631040) and the research grant R&D (No. 190-9609-2801) of the Malaysian Government and Universiti Sains Malaysia.

References and Notes

1 a) "Transition Metal Sulfur Chemistry: Biological and Industrial Significance" ed by E. I. Stiefel and K. Matsumoto, American Chemical Society, Washington, DC (1996). b) I. G. Dance and K. Fisher, *Prog. Inorg. Chem.*, **41**, 637 (1994). c) S. C. Lee and R. H. Holm, *Angew. Chem., Int. Ed. Engl.*, **29**, 840 (1990).

2 a) S. Shi, W. Ji, S. H Tang, J. P. Lang, and X. Q. Xin, *J. Am. Chem. Soc.*, **116**, 3615 (1994). b) S. Shi, W. Ji, and X. Q. Xin, *J. Phys. Chem.*, **99**, 894 (1995). c) P. E. Hoggard, H. W. Hou, X. Q. Xin, and S. Shi, *Chem. Mater.*, **8**, 2218 (1996). d) M. K. M. Low, H. W. Hou, H. G. Zheng, W. T. Wong, G. X. Jin, X. Q. Xin, and W. Ji, *Chem. Commun.*, **1998**, 505.

3 a) J. B. Howard and D. J. Low, *Chem. Rev.*, **96**, 2965 (1996). b) R. H. Holm, *Adv. Inorg. Chem.*, **38**, 1 (1992). c) D. Coucouvanis, *Acc. Chem. Res.*, **24**, 1 (1991). d) T. Shibahara, *Coord. Chem. Rev.*, **123**, 73 (1993). e) B. C. Wiegand and C. M. Friend, *Chem. Rev.*, **92**, 491 (1992).

4 a) A. Muller, E. Diemann, and H. Bogge, *Angew. Chem., Int. Ed. Engl.*, **20,** 934 (1981). b) H. W. Hou, X. Q. Xin, and S. Shi, *Coord. Chem. Rev.*, **153**, 25 (1996). c) S. Sarkar and S. B. S. Mishra, *Coord. Chem. Rev.*, **59**, 239 (1984). d) J. Guo, X. T. Wu, W. J. Zhang, T. L. Sheng, Q. Huang, P. Lin, Q. M. Wang, and J. X. Lu, *Angew. Chem., Int. Ed. Engl.*, **36,** 2464 (1997).

5 a) H. W. Hou, H. G. Zheng, H. G. Ang, Y. T. Fan, M. K. M. Low, Y. Zhu, W. L. Wang, X. Q. Xin, W. Ji, and W. T. Wong, *J. Chem. Soc., Dalton Trans.*, **1999**, 2953. b) Q. Huang, X. T. Wu, Q. M. Wang, T. L. Sheng, and J. X. Lu, *Angew. Chem., Int. Ed. Engl.*, **35**, 868 (1996). c) Q. Huang, X. T. Wu, and J. X. Lu, *Inorg. Chem.*, **35**, 7445 (1996). d) Q. Huang, X. T. Wu, and J. X. Lu, *Chem. Commun.*, **1997**, 703. e) H. Yu, W. J. Zhang, X. T. Wu, T. L. Sheng, Q. M. Wang, and P. Lin, *Angew. Chem., Int. Ed. Engl.* , **37**, 2520 (1998).

6 a) J. P. Lang, S.A. Bao, X. Q. Xin, and K. B. Yu, *Polyhedron*, **12**, 801 (1993). b) A. Muller, W. Jaegermann, and W. Hellmann, *J. Mol. Struct.*, **100**, 559 (1983). c) Q. Huang, X. T. Wu, T. L. Sheng, and Q. M. Wang, *Inorg. Chem.*, **34**, 4931 (1995). d) J. P. Lang, K. Tatsumi, H. Kawaguchi, J. M. Lu, P. Ge, W. Ji, and S. Shi, *Inorg. Chem.*, **35**, 7924 (1996). e) J. P. Lang, J. Liu, M. Q. Chen, J. M. Lu, G. Q. Bian, and X. Q. Xin, *J. Chem. Soc., Chem. Commun.*, **1994**, 2665.

7 J. M. Manoli, C. Potvin, F. Secheresse, and S. Marzak, *Inorg. Chim. Acta*, **44**, 170 (1988).

8 a) J. R. Nicholson, A. C. Flood, C. D. Garner, and W. Clegg, J. Chem. Soc., *Chem. Commun.*, **1983**, 1179. b) C. Potvin, J. M. Manoli, F. Secheresse, and S. Marzak, *Inorg. Chem.*, **26,** 4370 (1987). c) J. M. Manoli, C. Potvin, F. Secheresse, and S. Marzak, *J, Chem. Soc., Chem. Commun.*, **1986**, 1557. d) J. M. Manoli, C. Potvin, F. Secheresse, and S. Marzak, *Inorg. Chim. Acta*, **150**, 257 (1988).

9 H. W. Hou, Y. T. Fan, C. X. Du, Y. Zhu, W. L. Wang, X. Q. Xin, M. K. M. Low, W. Ji, and H. G. Ang, *Chem. Commun.*, **1999**, 647.

10 P. J. Hagrman, D. Hagrman, and J. Zubieta, *Angew. Chem., Int. Ed. Engl.* , **38**, 2638 (1999) and references therein.

11 Crystal data for cluster polymer **1** $C_{20}H_{40}N_6S_4Cu_4W$, M =930. 83, Orthorhombic, space group F_{ddd}, a=10.8968(1) Å, b=23.0553(3) Å, c=23.2870(1) Å, $\alpha=\beta=\gamma=90°$, U=5850.37(10) $Å^3$ Z=8, Dc=2.114 g/cm^3 F(000)=3648, Mo-Kα radiation, λ=0.71073 Å, μ=7.086 mm^{-1}. An orange-red polyhedral crystal with dimensions of 0.34x0.28x0.24 mm was mounted on a glass fiber. Diffiaction data were collected at 293(2) K on a Siemens Smart CCD area-detecting diffractometer in the range 4.48° ≤ 2θ ≤ 59.60° by using an ω-scan technique. Among the total 10354 reflections, 1975 unique reflections with $I_o \geq 2\sigma(I_o)$ were used for structure refinement. An empirical absorption correction based on ψ scans was applied. All the metal atoms and S atoms were obtained by direct method and other non-hydrogen atoms were located from the difference Fourier maps. The structure of cluster **1** was solved by direct method and refined with full-matrix least-squares on F^2 using the SHELXTL 97 (Version 5.1) package of crystallographic software, giving the value of R=0.0353 and wR=0.0917. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in their calculated positions (C-H, 0.96 Å), assigned fixed isotropic thermal parameters (1.2 times for CH_2 and 1.5 times for CH_3 they attached) and allows to ride on their respective parent atoms. The contributions of these hydrogen atoms were included in the structure factors calculations. Atomic coordinates, bond lengths and angles, and terminal parameters have been sent to the Cambridge Crystallographic Data Center (CCDC).