Inorg. Chem. **2006**, *45*, 10155–10161

Inorganic Chemistry
Article

Synthesis and Crystal Structures of Multidimensional Coordination Polymers Based on W/Cu/S Clusters with Flexible Imidazole Ligands

Li Song,[†,‡] Jianrong Li,[†] Ping Lin,[†] Zhihua Li,[†] Tao Li,[†] Shaowu Du,*,[†] and Xintao Wu[†]

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fujian, Fuzhou 350002, P. R. China, and Graduate School of the Chinese Academy of Sciences, Beijing 100039, P. R. China

Received June 23, 2006

Reactions of $[WES_3]^{2-}$ (E = S, O) with CuX (X = NCS, CN, I) in the presence of bix (bix = 1,4-bis(imidazole-1-ylmethyl)benzene) in DMF or CH_3CN resulted in the formation of two novel 2D $\rightarrow$3D interpenetrating coordination polymers $[S_2W_2S_6Cu_4(bix)_2]_n$ (**1**) and $\{[WS_4Cu_4(NCS)_2(bix)_3]\cdot CH_3CN\}_n$ (**2**), a noninterpenetrating 3D polymer $\{[WS_4Cu_2(bix)]\cdot DMF\}_n$ (**3**), and two 2D sheet polymers $[WS_4Cu_3(CN)(bix)]_n$ (**4**) and $\{[OWS_3Cu_3(bix)_2][I]\cdot DMF\cdot 2H_2O\}_n$ (**5**), depending on the reaction temperature and the reagents used. Compound **1** contains a hexagonal prism of $W_2Cu_4S_6$ cluster core, which serves as a 4-connecting node to link equivalent nodes via bix ligands, forming a 2D (4,4) net. In **2**, a WCu_4S_4 core, which also acts as a 4-connecting node, connects the neighboring nodes either through single or double bix bridges, affording a different 2D (4,4) sheet. Inclined interpenetration occurs between two stacks of 2D sheets in the total structure of **1**, while **2** involves a parallel interpenetration between the adjacent layers, both creating a 3D network. Compounds **1** and **2** represent the first examples of interpenetrating (4,4) frameworks with clusters as nodes and bidentate pyridyl-based ligands as linkers. Unlike **1** and **2**, compound **3** has a noninterpenetrating 3D network, which is composed of the inorganic 1D $(WS_4Cu_2)_n$ chains linked by cis and trans bix ligands. Compound **4** features an inorganic 1D $(WS_4Cu_3)_n$ chain structure, which is linked by CN groups and bix ligands to form an infinite 2D network. Compound **5** is a 2D layer polymer with large inner cavities.

Introduction

The designed syntheses of new coordination polymers have attracted great attention in recent years because of not only their intriguing variety of architectures and topologies but also their potential applications in catalysis, ion exchange, nonlinear optics, and chemical absorption.[1] This type of research began with the use of metal ions and organic bridging ligands to construct numerous one-, two-, and three-dimensional polymeric networks.[2] Recently, there has been increasing interest in applications of metal clusters as fundamental building blocks and polydentate organic ligands as linkers to build polymeric arrays.[3] For example, several multidimensional molecular tubes based on dimetal building units and the extended supramolecular arrays containing hexanuclear rhenium clusters have been reported.[4] Such cluster-based coordination polymers are of particular interest because the clusters normally have larger size and multiple coordination sites which, when combined with suitable organic ligands, may lead to a variety of unusual shapes and novel properties. In effect, by careful choice of cluster subunits and linkers, polymeric frameworks with large voids

---

* To whom correspondence should be addressed. E-mail: swdu@ms.fjirsm.ac.cn.

[†] Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences.

[‡] Graduate School of the Chinese Academy of Sciences.

(1) (a) Eddaoudi, M.; Moler, D. B.; Li, H. L.; Chen, B. L.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319. (b) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. *Nature (London)* **2002**, *404*, 982. (c) Chui, S. S. Y.; Lo, S. M. F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D. *Science* **1999**, *283*, 1148. (d) Lin, W. B.; Wang, Z. Y.; Ma, L. *J. Am. Chem. Soc*. **1999**, *121*, 11249. (e) Zaworotko, M. J. *Angew. Chem, Int. Ed.* **1998**, *37*, 1211. (f) Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc*. **1994**, *116*, 1151.

(2) (a) Fujita, M. *Chem. Soc. Rev.* **1998**, *27*, 417. (b) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853. (c) Holliday, B. J.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 2022.

(3) (a) Cotton, F. A.; Lin, C.; Murillo, C. A. *Acc. Chem. Res.* **2001**, *34*, 759. (b) Chisholm, M. H. *Acc. Chem. Res*. **2000**, *33*, 53.

(4) (a) Selby, H. D.; Orto, P.; Carducci, M. D.; Zheng, Z. P. *Inorg. Chem.* **2002**, *41*, 6175. (b) Selby, H. D.; Orto, P.; Zheng, Z. P. *Polyhedron* **2003**, *22*, 2999.

10.1021/ic061142i CCC: $33.50

or channels can be generated.[5] In addition, the presence of organic linkers in the cluster-supported networks may alter the physical properties of the clusters, providing an opportunity to search for new materials with a variety of potential applications.[6]

The chemistry of Mo(W)/Cu/S complexes remains an active research area because of their importance in biological systems and material science.[7] Many Mo(W)/Cu/S polymeric compounds with fascinating structures have been reported. In these compounds, the Mo(W)/Cu/S cluster subunits are normally connected by bridging ligands such as halide ions, cyanide, thiocyanate, and thiolates.[8] Recently, pyridyl-based ligands, in particular 4,4′-bipyridine, have been used to construct Mo(W)/Cu/S polymeric frameworks such as $\{[NEt_4][Mo_2O_2S_6Cu_6I_3(4,4'\text{-bipy})_5]\cdot MeOH\cdot H_2O\}_n$ and $\{[WS_4Cu_4(4,4'\text{-bipy})_4][WS_4Cu_4I_4(4,4'\text{-bipy})_2]\cdot 4H_2O\}_n$.[9] The former compound is a 2D polymer with incomplete cubanes $\{OMoS_3Cu_3I\}$ as subunits and 4,4′-bipy as linkers while the latter is a 3D polymer containing interpenetrating diamondoid cationic clusters $[WS_4Cu_4(4,4'\text{-bipy})_4]^{2+}$ and anionic clusters $[WS_4Cu_4I_4(4,4'\text{-bipy})_2]^{2-}$. In contrast to the rigid 4,4′-bipy, the bix (bix = 1,4-bis(imidazole-1-ylmethyl)benzene) ligand has been proven to be more flexible and is able to connect various metal ions forming multidimensional infinite networks.[10] However, examples of cluster-based polymers with bix ligands have not been seen in the literature. In this paper, we report the synthesis and crystal structures of novel cluster-based polymers $[S_2W_2S_6Cu_4(bix)_2]_n$ (**1**), $\{[WS_4Cu_4(NCS)_2(bix)_3]\cdot CH_3CN\}_n$ (**2**), $\{[WS_4Cu_2(bix)]\cdot DMF\}_n$ (**3**), $[WS_4Cu_3(CN)(bix)]_n$ (**4**), and $\{[OWS_3Cu_3(bix)_2][I]\cdot DMF\cdot 2H_2O\}_n$ (**5**), in which the bix ligands serve as linkers to connect W/Cu/S cluster subunits giving rise to 2D sheet structures and interpenetrating or noninterpenetrating 3D networks.

Experimental Section

Material and Methods. All operations were carried out in a vacuum, and the reactants were sealed with solvents in glass tubes (15 × 0.8 cm). The starting materials $[X]_2[WES_3]$ (X = NH_4, Et_4N; E = O, S) and $[Et_4N]_3[Cu_4(NCS)_5WS_4]$ and the bix ligand were prepared according to literature procedures.[10a,11,12] Other chemicals were obtained from commercial sources and used as received.

Infrared spectra were recorded on a Nicolet Magna 750 FT-IR spectrophotometer as KBr pellets. UV−vis diffuse reflectance measurements were made at room temperature in the 330−1100 nm range with a Perkin-Elmer Lambda-35 UV/vis spectrophotometer. Powder X-ray diffraction (XRD) patterns were recorded by BDX300 X-ray diffraction with Cu Kα radiation ($\lambda = 0.154$ nm). Elemental analyses were performed on a Vario EL III elemental analyzer. Thermogravimetric analyses were carried out on a NETZSCH STA 449C unit at a heating rate of 15 °C min^{-1} under a nitrogen atmosphere.

Crystal Structure Analyses. The intensity data sets for compounds **1**−**5** were collected on a Rigaku Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) at 293 K (173 K for **2**).[13] The structures were solved by direct methods with the SHELXS-97 program,[14] and heavy atoms were located from *E*-maps. Other non-hydrogen atoms were derived from successive difference Fourier syntheses. The structures were refined on F^2 by full-matrix least squares using SHELXL-97[15] with anisotropical thermal parameters for all non-hydrogen atoms except those of the disordered imidazole ring. The positions of H atoms were generated geometrically (C−H bond fixed at 0.96 Å), assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms before the final cycle of refinement. One of the imidazole rings in **2** is disordered over two sets of positions and was refined with restraints. The CN group of CH_3CN molecule in **2** was disordered and also refined with restraints. Crystallographic data are presented in Table 1.

$[S_2W_2S_6Cu_4(bix)_2]_n$ (1). A mixture of CuNCS (0.33 mmol, 40.14 mg) and $[NH_4]_2[WS_4]$ (0.11 mmol, 38.30 mg) was stirred with 2 mL of DMF for 3 h. The resultant solution was transferred to a glass tube containing bix (0.17 mmol, 40.51 mg) and was evacuated and sealed. The glass tube was then heated to 120 °C for 1 day. After the solution was cooled to room temperature over 2 days, dark-red crystals of **1** were obtained in 21% yield (based on $[NH_4]_2[WS_4]$). Anal. Calcd for $C_{28}H_{28}Cu_4N_8S_8W_2$: C, 24.80; H, 2.07; N, 8.27. Found: C, 25.11; H, 2.24; N, 8.14. IR (KBr pellet, cm^{-1}): 1635 m, 1532 m, 1512 s, 1234 s, 1105 s, 1088 m, 922 m, 834 w, 750 s, 707 m, 656 m, 498 m (W═S), 436 s (W−S).

$\{[WS_4Cu_4(NCS)_2(bix)_3]\cdot CH_3CN\}_n$ (2). Method A. A mixture of $[Et_4N]_2[WS_4]$ (0.11 mmol, 62.99 mg), CuNCS (0.33 mmol, 40.14 mg), and bix (0.17 mmol, 40.51 mg) was placed in a glass tube, and 2 mL of CH_3CN was added. The tube was sealed after evacuation and heated to 120 °C for 1 day. Upon slow cooling of the solution to room temperature over 2 days, red crystals of **2** were obtained in 25% yield (based on CuNCS). Anal. Calcd for $C_{46}H_{45}Cu_4N_{15}S_6W$: C, 38.38; H, 3.13; N, 14.60. Found: C, 37.96; H, 3.17; N, 14.78. IR (KBr pellet, cm^{-1}): 2086 vs (CN), 1638 m, 1518 s, 1508 s, 1235 m, 1108 s, 1086 s, 934 w, 828 w, 741 w, 717 w, 657 m, 430 w (W−S).

Method B. A mixture of $[Et_4N]_3[Cu_4(NCS)_5WS_4]$ (0.10 mmol, 125.00 mg) and bix (0.30 mmol, 71.49 mg) was placed in a glass

---

(5) Bain, R. L.; Shriver, D. F.; Ellis, D. E. *Inorg. Chim. Acta* **2001**, *325*, 171.

(6) Feng, P.; Bu, X.; Zheng, N. *Acc. Chem. Res.* **2005**, *38*, 293.

(7) (a) George, G. N.; Pickering, I. J.; Yu, E. Y.; Prince, R. C.; Bursakov, S. A.; Gavel, O. Y.; Moura, I.; Moura, J. J. G. *J. Am. Chem. Soc.* **2000**, *122*, 8321. (b) Shi, S.; Ji, W.; Tang, S. H.; Lang, J. P.; Xin, X. Q. *J. Am. Chem. Soc.* **1994**, *116*, 3615. (c) Che, C. M.; Xia, B. H.; Huang, J. S.; Chan, C. K.; Zhou, Z. Y.; Cheung, K. K. *Chem.—Eur. J.* **2001**, *7*, 3998.

(8) (a) Hou, H. W.; Wei, Y. L.; Song, Y. L.; Zhu, Y.; Fan, Y. T. *Inorg. Chim. Acta* **2004**, *357*, 421. (b) Lang, J. P.; Jiao, C. M.; Qiao, S. B.; Zhang, W. H.; Abrahams, B. F. *Inorg. Chem.* **2005**, *44*, 3664. (c) Potvin, C.; Manoli, J. M.; Sécheresse, F.; Marzak, S. *Inorg. Chem.* **1987**, *26*, 4370. (d) Li, Z. H.; Du, S. W.; Wu, X. T. *Inorg. Chem.* **2004**, *43*, 4776.

(9) (a) Lang, J. P.; Kawaguchi, H.; Tatsumi, K. *Chem. Commun.* **1999**, 2315. (b) Zhang, Q. F.; Niu, Y. Y.; Leung, W. H.; Song, Y. L.; Williams, I. D.; Xin, X. Q. *Chem. Commun.* **2001**, 1126. (c) Liang, K.; Zheng, H. G.; Song, Y. L.; Lappert, M. F.; Li, Y. Z.; Xin, X. Q.; Huang, Z. X.; Chen, J. T.; Lu, S. F. *Angew. Chem. Int. Ed. Engl.* **2004**, *43*, 5776. (d) Lang, J. P.; Xu, Q. F.; Yuan, R. X.; Abrahams, B. F. *Angew. Chem., Int. Ed.* **2004**, *43*, 4741.

(10) (a) Hoskins, B. F.; Robson, R.; Slizys, D. A. *J. Am. Chem. Soc.* **1997**, *119*, 2952. (b) Carlucci, L.; Ciani, G.; Prosepio, D. M. *Chem. Commun.* **2004**, 380. (c) Carlucci, L.; Ciani, G.; Prosepio, D. M. *Cryst. Growth Des.* **2005**, *5*, 37.

(11) McDonald, J. W.; Friesen, G. D.; Rosenhein, L. D.; Newton, W. *Inorg. Chim. Acta* **1983**, *72*, 205.

(12) Manoli, J. M.; Potvin, C.; Secheresse, F.; Marzar, S. *Inorg. Chim. Acta* **1988**, *150*, 257.

(13) *Crystalclear*, version 1.36; Molecular Structure Corp. Rigaku, MSC/SSI: Orem, UT, 2001.

(14) Sheldrick, G. M. *SHELXS 97*, *Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997.

(15) Sheldrick, G. M. *SHELXL 97*, *Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Geremany, 1997.

Table 1. Summary of Crystallographic Data for Compounds **1**−**5**

param	**1**	**2**	**3**	**4**	**5**
formula	$C_{28}H_{28}Cu_4N_8S_8W_2$	$C_{46}H_{45}Cu_4N_{15}S_6W$	$C_{17}H_{20}Cu_2N_5OS_4W$	$C_{15}H_{14}Cu_3N_5S_4W$	$C_{31}H_{39}Cu_3IN_9O_4S_3W$
fw	1354.92	1438.34	749.55	767.02	1199.23
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	$C2/c$	$P2_1/n$	$P\bar{1}$
a, Å	8.4113(9)	12.2328(5)	25.503(2)	5.5001(5)	10.566(3)
b, Å	15.8194(17)	25.3056(11)	11.0317(6)	22.689(2)	12.616(4)
c, Å	14.5418(14)	17.4975(8)	19.6110(16)	17.2520(15)	17.495(6)
α, deg	90	90	90	90	71.369(6)
β, deg	96.051(4)	92.616(2)	119.076(2)	93.429(5)	87.414(10)
γ, deg	90	90	90	90	77.259(9)
V, Å^3	1924.2(3)	5410.9(4)	4822.0(6)	2149.0(3)	2154.7(12)
Z	2	4	8	4	2
D_{calcd}, g cm^{-3}	2.339	1.766	2.068	2.371	1.842
μ, mm^{-1}	8.593	3.945	6.873	8.664	5.026
F(000)	1288	2848	2888	1456	1156
R^a	0.0445	0.0326	0.0305	0.0556	0.0543
$R_w{}^b$	0.0892	0.0628	0.0721	0.0960	0.1069

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$.

tube, and 2 mL of CH_3CN was added. The tube was sealed after evacuation and heated to 120 °C for 1 day. Upon slow cooling of the solution to room temperature over 2 days, red crystals of **2** were obtained in 32% yield. Microanalyses and infrared and XRD spectra confirm the identity of the product.

{[WS₄Cu₂(bix)]·DMF}*ₙ* (3). A mixture of $[NH_4]_2[WS_4]$ (0.11 mmol, 38.30 mg), CuNCS (0.22 mmol, 26.76 mg), and bix (0.11 mmol, 26.21 mg) was placed in a glass tube, and 2 mL of DMF was added. The tube was sealed after evacuation and heated to 90 °C for 1 day. Upon slow cooling of the solution to room temperature over 3 days, red crystals of **3** were obtained in 27% yield. Anal. Calcd for $C_{17}H_{20}Cu_2N_5OS_4W$: C, 27.22; H, 2.67; N, 9.34. Found: C, 27.13; H, 2.61; N, 9.28. IR (KBr pellet, cm^{-1}): 1654 vs (C═O), 1519 s, 1424 m, 1383 m, 1234 m, 1106 m, 1085 s, 937 w, 816 w, 728 m, 656 m, 464 s, 439 m (W−S).

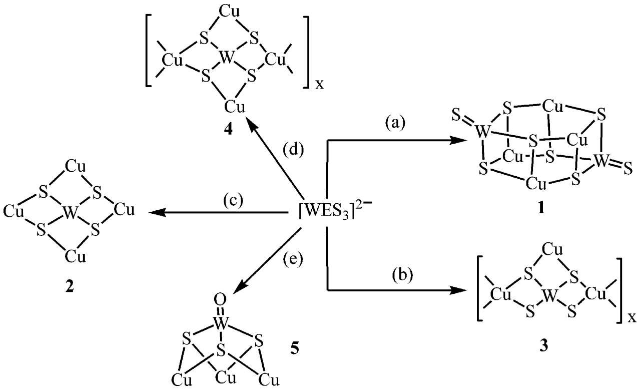
[WS₄Cu₃(CN)(bix)]*ₙ* (4). Compound **4** was prepared under conditions similar to those for **2** (method A) with CuCN (0.33 mmol, 29.56 mg) instead of CuNCS. Yield: 30%. Anal. Calcd for $C_{15}H_{14}Cu_3N_5S_4W$: C, 23.47; H, 1.83; N, 9.13. Found: C, 23.35; H, 2.06; N, 9.35. IR for **3**: 2130 vs (CN), 1630 m, 1517 s, 1385 m, 1238 m, 1106 s, 1086 m, 1076 m, 835 w, 721 m, 656 m, 437 s (W−S).

{[OWS₃Cu₃(bix)₂][I]·DMF·2H₂O}*ₙ* (5). A mixture of $[NH_4]_2WOS_3$ (0.20 mmol, 66.42 mg), CuI (0.60 mmol, 114.27 mg), bix (0.40 mmol, 95.32 mg), CH_2I_2 (0.1 mL), and DMF (2 mL) was sealed in a reaction tube. The mixture was heated to 90 °C for 48 h and was cooled to room temperature over 24 h. Orange crystals of **5** were obtained (yield 34%). Anal. Calcd for $C_{31}H_{39}Cu_3IN_9S_3WO_4$: C, 31.02; H, 3.25; N, 10.51. Found: C, 31.23; H, 3.38; N, 10.71. IR for **5**: 1665 vs (C═O), 1518 s, 1386 m, 1233 m, 1107 s, 1094 s, 924 s (W═O), 823 w, 738 w, 656 m, 431 m (W−S).

Results and Discussion

Synthesis. Reactions of $[WES_3]^{2-}$ (E = S, O) with CuX (X = NCS, CN, I) and bix by the solvothermal method resulted in the formation of compounds **1**−**5**, depending on the reaction temperature, copper sources, and the solvents (DMF or CH_3CN) used (Scheme 1). Treatment of a mixture of $[NH_4]_2WS_4$ and 3 or 2 equiv of CuNCS in DMF with bix at 120 or 90 °C led to the formation of an interpenetrating 3D polymer **1** or a noninterpenetrating 3D polymer **3**. The IR spectra of **1** and **3** displayed no absorptions due to NCS groups, suggesting that they were replaced by bix ligands during the reactions. Although compounds **1** and **3** have similar compositions, they have different structural types of the cluster building blocks. Compound **1** contains a closed structure of $W_2S_6Cu_6$ hexagonal prism as a fundamental building block while **3** features a novel inorganic $(WS_4Cu_2)_n$ chain structure. When using CuI as the copper salt, the reaction with $[WOS_3]^{2-}$ and bix and a small amount of CH_2I_2 in DMF at 90 °C yielded product **5**.

Scheme 1. Formation of W/Cu/S Cluster Building Blocks for **1**−**5** under Different Reaction Conditions[a]



[a] Key: (a) E = S, CuNCS, bix, DMF, 120 °C; (b) E = S, CuNCS, bix, DMF, 90 °C; (c) E = S, CuNCS, bix, CH_3CN, 120 °C; (d) E = S, CuCN, bix, CH_3CN, 120 °C; (e) E = O, CuI, bix, CH_2I_2, DMF, 90 °C.

It is noticed that, in acetonitrile solution, CuNCS can readily react with $[WS_4]^{2-}$ to form cluster units $[WS_4(CuNCS)_4]$ and $[WS_4(CuNCS)_3]$, where $[WS_4]^{2-}$ act as tetradentate ligands to combine with Cu atoms and give a WS_4Cu_4 or WS_4Cu_3 "open structure".[12] It is therefore possible to obtain polymers with WS_4Cu_4 or WS_4Cu_3 as basic building blocks in similar reactions with those for **1** and **3** by using acetonitrile as solvent instead of DMF. The reaction of $[Et_4N]_2[WS_4]$ and bix with CuNCS or CuCN in CH_3CN gave completely different types of coordination polymers, namely compounds **2** and **4**, respectively. The IR spectra of **2** and **4** showed the presence of NCS, CN, and bix ligands, indicating that the NCS and CN groups were partially replaced by bix ligands. The molecular structure of **2** indeed consists of a WS_4Cu_4 cluster core as that observed in $[WS_4(CuNCS)_4]$, while **4** contains a rare inorganic $(WS_4Cu_3)_n$ chain structure.

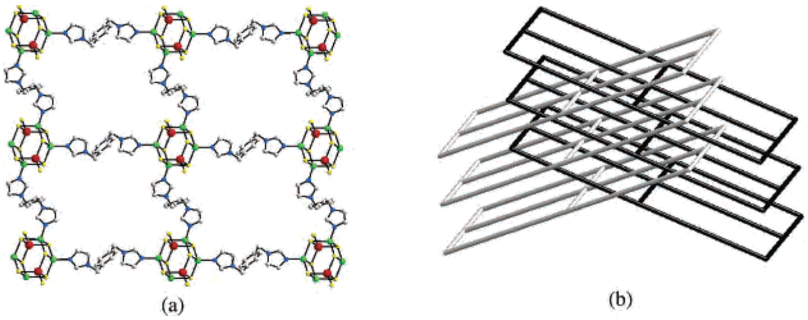


Figure 1. (a) Portions of the sheet derived from a (4,4)-connected net in **1**: red, W; green, Cu; yellow, S; blue, N; gray, C. Hydrogen atoms are omitted for clarity. (b) Schematic representation of **1**, showing the inclined interpenetrating (4,4) networks along the *c* axis.

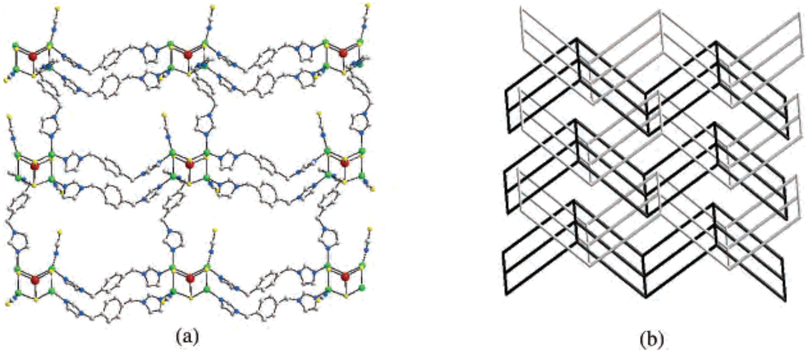


Figure 2. (a) Part of the 2D network within **2**: red, W; green, Cu; yellow, S; blue, N; gray, C. Hydrogen atoms are omitted for charity. (b) Schematic representation of **2**, showing the parallel interpenetrating (4,4) networks along the *c* axis.

Compound **2** can also be prepared in a more reasonable way by the ligand substitution reaction of $[Et_4N]_3[Cu_4(NCS)_5WS_4]$[12] with bix in acetonitrile at 120 °C.

Although the solvothermal method has been widely used in the syntheses of organic−inorganic hybrids to obtain new compounds with novel structures, it has scarcely been used in the preparation of W/Cu/S clusters. In fact, the crystals of compounds **1**−**5** cannot be obtained if the reactions are carried out at room temperature. Besides, the presence of CH_2I_2 is crucial to the preparation of **5**. In the absence of CH_2I_2, no desirable crystals were obtained.

Crystal Structure of 1. The crystal structure of **1** reveals a distorted hexagonal prism of $W_2S_6Cu_4$ that contains a center of symmetry (Figure 1a). The tungsten and sulfur atoms occupy alternate vertexes of the cage. One additional sulfur atom is externally bonded to each tungsten as was inferred from spectroscopic data. The structure of the cage can be regarded in terms of two incomplete cubanelike WS_3Cu_3 units fused together in a way that the sulfide ions from one unit serve as ligands for the Cu atoms in the other. The bond lengths and angles within the cage are unremarkably close to those reported for similar W/Cu/S clusters. However, the cage appears more compact than that of other most related clusters which also contain a similar prismatic $W_2S_6Cu_4$ unit. For example, the mean distances of W−Cu and Cu···Cu in **1** are 2.702 and 2.735 Å, respectively, which are shorter than those of $[W_2Cu_4S_6(PPh_3)_4O_2]$ (2.780 and 2.867 Å) and $\{W_2Cu_4S_6[(C_7H_7)_3P]_4O_2\}$ (2.784 and 2.801 Å).[16] Bix groups are attached to each copper atom, forming an extended 2D sheet with (4,4) grid topology. The macrocyclic ring $\{(S_2W_2S_6Cu_4)_4(bix)_4\}$ can be viewed as the basic building blocks of the structure, in which the apexes are occupied by the $S_2W_2S_6Cu_4$ clusters and the sides by the bix ligands. The grid motif has the dimensions of 17.55 × 17.92 Å (based on the centers of the cage clusters), the diagonals are 21.49 × 28.22 Å, and the interior angles are 74.57 and 105.43°, respectively. Because of the length and flexibility of the bix ligand, the (4,4) networks do not lie in the same plane but represent a chair conformation. In the polymeric structure of **1**, each (4,4) net has an infinite number of identical sheets passing through it, inclined at ca. 38°. Two rods from an inclined sheet pass through every window of the other sheet in a parallel−parallel fashion, producing an interlocked 3D structure (Figure 1b). Thus, the large cavities formed by one stack of parallel nets are blocked due to the interpenetration with the other stack of nets. It should be noted that **1** is the first example of a hexagonal prism cluster being incorporated into an interpenetrating 3D network, though similar cage clusters of $[Cu_6X_6]$ (X = Cl, Br and I) with a tripyridine ligand have recently been reported. The latter complexes are noninterpenetrating 2D-sheet polymers.[17]

Crystal Structure of 2. Single-crystal X-ray diffraction analysis reveals that the fundamental building block of **2** is a pentanuclear cluster $WS_4Cu_4(NCS)_2$ rather than a hexanuclear cluster as in **1** (Figure 2a). In the $WS_4Cu_4(NCS)_2$ cluster unit, both W and Cu atoms are tetrahedrally coordinated. There are two types of Cu atoms; one is coordinated by two bix ligands, and the other is coordinated by a bix and a NCS group. The structural parameters of the WS_4Cu_4-

---

(16) (a) Müller, A.; Bögge, H.; Hwang, T. K. *Inorg. Chim. Acta* **1980**, *39*, 71. (b) Doherty, R.; Hubbard, C. R.; Mighell, A. D.; Siedle, A. R.; Stewart, J. *Inorg. Chem.* **1979**, *18*, 2991.

(17) Ohi, H.; Tachi, Y.; Kunimoto, T.; Itoh, S. *Dalton Trans.* **2005**, *19*, 3146.

$(NCS)_2$ fragment are typical, and those for the thiocyanate groups are within the range usually reported for the N-bonded terminal NCS groups.[12,18] From a topological perspective, each cluster serves as a 4-connecting node in an infinite 2D sheet. The bix ligands link the $WS_4Cu_4(NCS)_2$ units in a trans arrangement resulting in a strongly distorted rectangular macrocyclic ring $\{[WS_4Cu_4(NCS)_2]_4(bix)_6\}$. The size of each ring is ca. 17.50 × 15.02 Å (based on the connections between cluster centers) with the long edge being a pair of bix ligands and the short edge being a single bix unit. Due to the tetrahedral geometry at the W centers and a significant bending of the bix ligands, the rectangular ring in **2** is also nonplanar. The adjacent rings share edges and vertexes to form highly undulating (4,4) 2D layers parallel to the crystallographic *bc* plane. There are two sets of parallel noncatenated "wavy" layers which are displaced in such a way to give a 3D polycatenated array, with each layer catenated by two others ("above" and "below") (Figure 2b). This parallel interpenetration causes blocking of the cavities, leaving room only for small CH_3CN solvent molecules.

Crystal Structure of 3. The structure of **3** features a 3D framework constructed from the 1D inorganic $(WS_4Cu_2)_n$ chains linked by bix ligands (Figure 3a, top). In **3**, the bix ligands display two kinds of molecular configuration (cis and trans) on the basis of the two amidazole groups in the relative orientation respected to the benzene plane. Interestingly, each inorganic $(WS_4Cu_2)_n$ chain is constructed from WS_4Cu_3 cluster units by sharing two bridging Cu atoms (Cu2 and Cu2A) each of which is coordinated by four sulfur atoms from two neighboring WS_4 subunits in chain. The remaining Cu atom (Cu1) has a tetrahedral coordination geometry with two sulfur atoms from WS_4 and two N atoms from the cis and trans bix ligands, respectively. Each cis bix ligand connects two Cu1 atoms from the adjacent $(WS_4Cu_2)_n$ chains forming a undulated bricklike layer (Figure 3b). Furthermore, the trans bix ligands align in a tilted fashion between the adjacent bricklike layers and bridge Cu1 atoms from two layers, forming a noninterpenetrating 3D architecture. As shown in Figure 3c, the 3D architecture of **3** possesses approximately hexagonal channels along the [101] direction with an effective size of ca. 13 × 7 Å^2. In **3**, the DMF molecules are located in the channels and there are a number of C−H···O hydrogen bonds present between the DMF molecules and the bix ligands (Figure S2). Presumably, these weak intermolecular interactions contribute to the stabilization of the noninterpenetrating 3D structure of **3**. Removing the DMF molecules from **3** in a vacuum at ca. 120 °C causes a significant phase change and produces compound **1**, which was confirmed by the XRD (Figures S3 and S4), IR, and element analysis. These observations indicated that the solvated DMF molecules might play an important rule in the stabilization of **3** and prevent the polymeric framework of **3** from forming interpenetration.

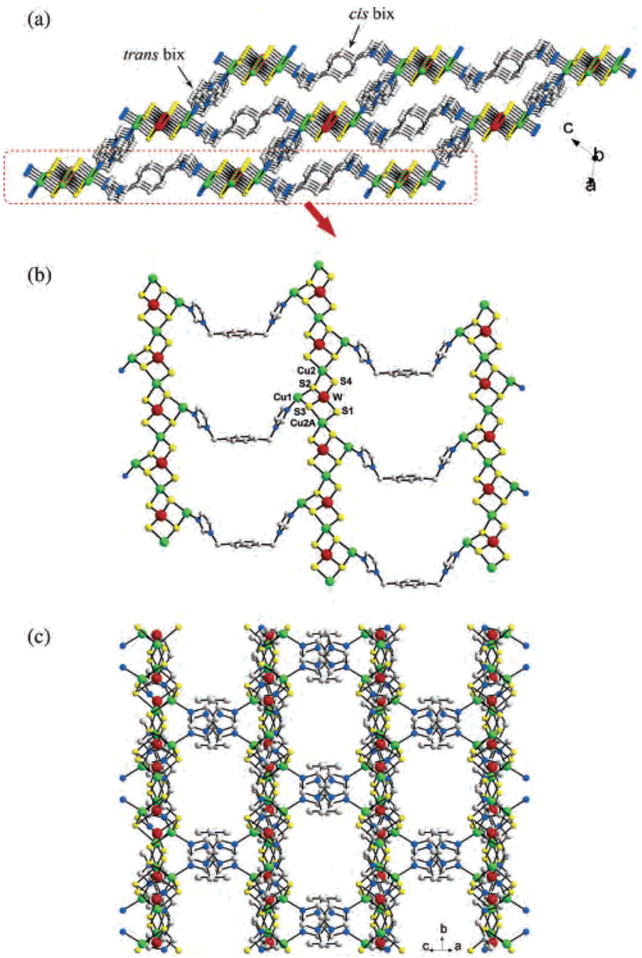


Figure 3. (a) 3D structure of **3** with the bricklike layer linked by trans bix. (b) Portion of the bricklike layer of **3**. (c) Framework structure of **3** viewed along [101] direction, showing the hexagonal channels. Key: red, W; green, Cu; yellow, S; blue, N; gray, C. DMF and Hydrogen atoms have been omitted for clarity.

Crystal Structure of 4. The asymmetric unit of the crystal structure of **4** contains a WS_4Cu_3 unit, a cyanide ligand, and bix ligand (Figure 4a). As illustrated in Figure 4b, compound **4** consists of a 2D polymeric sheet formed by linking inorganic $(WS_4Cu_3)_n$ chains via cyanide bridges and bix ligands. Each $(WS_4Cu_3)_n$ chain is constructed from WS_4Cu_4 cluster units by sharing two bridging Cu atoms. This structural type is unique for the W/Cu/S compounds but similar to that found in $[WAgS_4NH_4{\cdot}NH_3C(CH_2OH)_3{\cdot}2DMF]_n$ and $[W_4Ag_4S_{16}{\cdot}2Ca(DMSO)_6]_n$, where the polymeric chains are formed through the connection of adjacent, nearly perpendicular $[-WS_2Ag-]$ rhomboidal fragments.[19] The Cu atoms in **4** which connect two neighboring WS_4^{2-} anions are tetrahedrally coordinated with four S atoms, while the other Cu atoms also exhibit tetrahedral geometry through coordination to two sulfur atoms, a single bridging cyanide, and a N donor from bix ligand. The Cu−(μ-CN)−Cu portion in **4** is slightly bent, with Cu(1)−C(15)−N(3) and C(15)−N(3)−Cu(2)* angles of 177.5(9) and 172.0(8)°, respectively. The mean W···Cu distance of 2.737 Å is longer than that found in four-coordinate Cu clusters such as $[Et_4N]_2[WS_4Cu_4(NCS)_4]$ (2.691 Å)[12] but shorter than that of $[WS_4Cu_4(dppm)_4]$-

---

(18) Beheshti, A.; Clegg, W.; Fallah, H. *Inorg. Chim. Acta* **2001**, *322*, 1.

(19) (a) Huang, Q.; Wu, X. T.; Wang, Q. M.; Sheng, T. L. *Inorg. Chem.* **1995**, *34*, 4931. (b) Huang, Q.; Wu, W. T.; Lu, J. X. *Inorg. Chem.* **1996**, *35*, 7445.

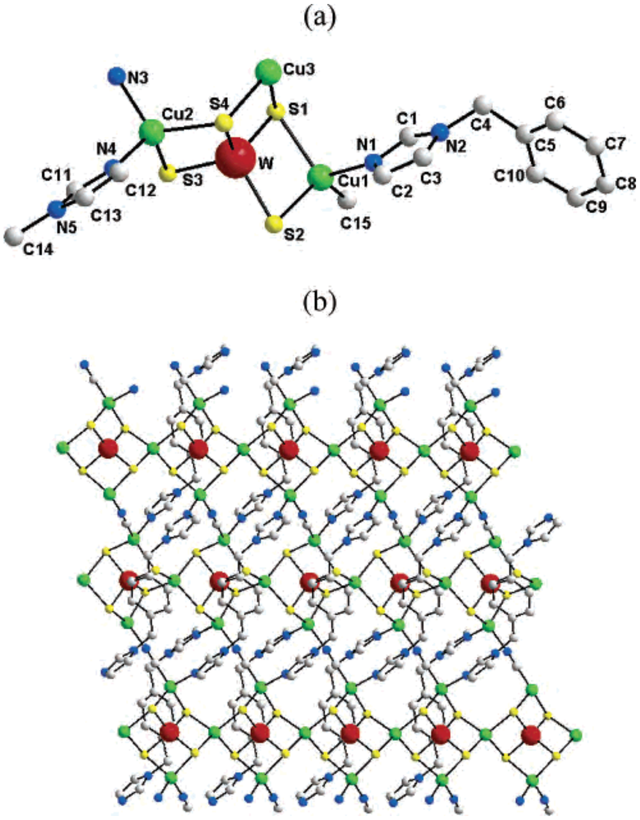


Figure 4. (a) Plot of the asymmetric unit in **4** with atom numbering scheme. (b) View of the 2D-polymer sheet of **4**.

$(PF_6)_2$ (2.760 Å).[20] While the cyanide groups serve as bridges between two neighboring $(WS_4Cu_3)_n$ chains, the bix ligands, which are in a trans conformation, cross-link two $(WS_4Cu_3)_n$ chains. The interchain W···W distance within a layer is ca. 9.5 Å. Compounds **4** and **3** are notable as two-dimensional and three-dimensional polymers composed of rare inorganic $(WS_4Cu_3)_n$ or $(WS_4Cu_2)_n$ chains supported by cyanide and/or bix ligands, respectively. Such structures are unprecedented in Mo(W)/Cu/S coordination polymer system.

Crystal Structure of 5. The basic building block of the polymer **5** is an incomplete cubanelike cluster cation $[OWS_3Cu_3]^+$ which is composed of one W atom, one terminal O atom, three Cu atoms, and three μ_3-S atoms. The Cu centers have different coordination environments. Each of the atoms Cu2 and Cu3 is surrounded by one N atom from bix and two μ_3-S atoms in a distorted trigonal environment while Cu1 is tetrahedrally bound by two N atoms from bix and two μ_3-S atoms. The bix ligands bridge between Cu atoms of adjacent $[OWS_3Cu_3]^+$ cores in a trans conformation forming a large rhombic grid with side lengths 12.62 × 18.07 Å and diagonal distances 12.66 × 28.36 Å on the basis of the cluster−cluster interval (Figure 5). These (4,4) grids are further extended into a 2D wavelike layer by sharing $[OWS_3Cu_3]^+$ joints and bix edges. In contrast to **1** and **2**, the 2D coordination networks of **5** do not interpenetrate each other, which is rare in such large macrometallacycle frameworks. Packing views of the complex **5** are shown in Figure 6. The grid layers are closely stacked with strong interlayer $\pi-\pi$ interactions between parallel aromatic imidazole rings of the bix of nearest neighboring layers (the offset face to face separation is ca. 3.20 Å; the centroid−centroid distance is ca. 3.59 Å). Further inspection of the structure reveals that there exist very large inner cavities (ca. 16.8 × 22.3 Å) along the crystallographic *a* direction, which are filled with DMF and water molecules as well as noncoordinating I^- counteranions. These dimensions are close to those reported in a 2D network complex with $\{OMoS_3Cu_3I\}$ cluster cores and 4,4′-bipy bridges.[9b]

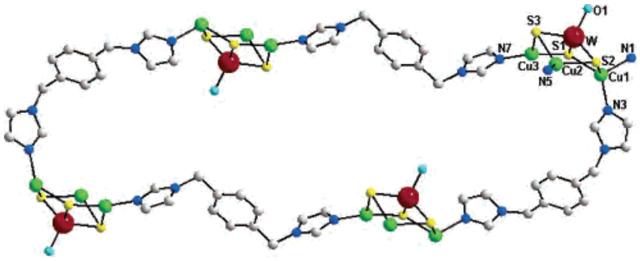


Figure 5. View of the macrometallacycle ring of **5** with partial atom-numbering scheme. Hydrogen atoms have been omitted for clarity.

Infrared Spectra and Optical Absorption Spectra. The infrared spectra for compounds **1**−**5** are similar, showing characteristic bands for bix in the 1638−656 cm^{-1} range. In addition, bands were observed in the spectra of **2** and **4** at 2086 and 2130 cm^{-1}, respectively, assigned to $\nu_{C\equiv N}$ from NCS and CN groups. The $W-S_{br}$ stretching vibrations for compounds **1**−**5** were observed at 436 (**1**), 430 (**2**), 439 (**3**), 437 (**4**), and 431 (**5**) cm^{-1}, respectively. Different from those of compounds **2**−**4**, the spectrum of **1** showed an additional $\nu_{W=S}$ stretching vibration at 498 cm^{-1} while that of **5** displayed a $\nu_{W=O}$ band at 924 cm^{-1}.

Optical absorption spectra of compounds **1**−**5** (Figure 7) have been measured by diffuse-reflectance experiments. The UV−vis absorption data were calculated from the reflectance data using the Kubelka−Munk function:[21] $\alpha/S = (1 - R)^2/2R$, where R is the experimentally observed reflectance, α the absorption coefficient, and S the scattering coefficient. By the use of straightforward extrapolation method, the band gaps for **1**−**5** are about 1.98, 2.09, 2.10, 2.11, and 2.25 eV, respectively.[22] These results show that the present compounds may be classed as semiconductors.

Thermogravimetric Analysis. The TGA curves for compounds **1**−**5** are shown in Figure S1. Compounds **1** and **4** are stable up to 313 and 305 °C, respectively, from which they begin to dramatically lose their organic components. For **2**, the weight loss (ca. 2%) before 316 °C could be assigned to the escape of CH_3CN molecules which is a little smaller than the expected value (2.85%) probably due to the efflorescence of solvent molecules. The second step of weight loss begins at 316 °C, from which the organic components were burnt. In the TGA curve of **3**, the initial weight loss between 165 and 174 °C corresponds to the release of DMF

---

[20] Lang, J. P.; Tatsumi, K. *Inorg. Chem.* **1998**, *37*, 6308.

[21] (a) Kotüm, G. *Reflectance Spectroscopy*; Springer-Verlag: New York, 1969. (b) Wendlandt, W. W. *Reflectance Spectroscopy*; Interscience Publishers: New York, 1966.

[22] Cao, G.; Rabenberg, L. K.; Nunn, C. M.; Mallouk, T. E. *Chem. Mater.* **1991**, *3*, 149.

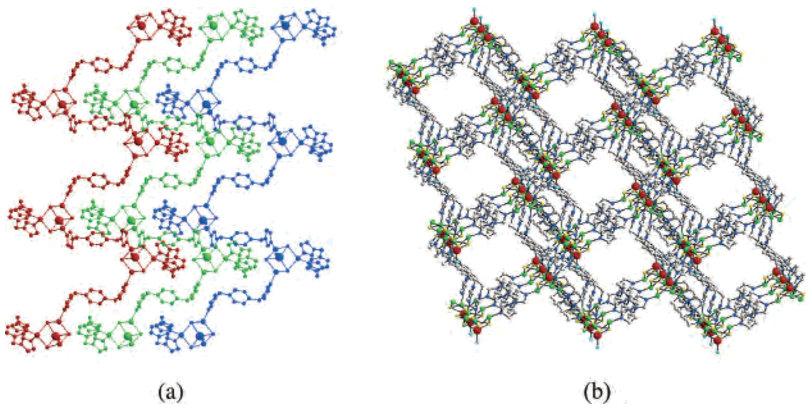


Figure 6. (a) Ball-and-stick packing diagram of **5** in the *ac* plane. (b) Stacked layers in the *bc* plane, showing the inner cavities. Hydrogen atoms, DMF, and water have been omitted for clarity. See Figure 1 for the color code.

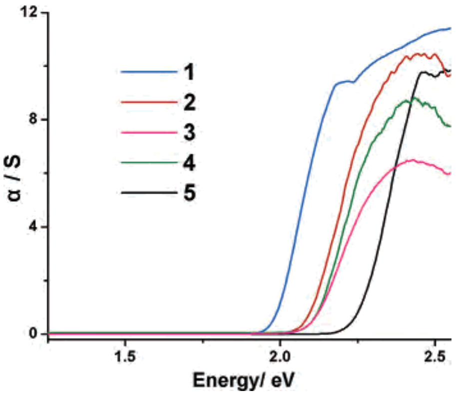


Figure 7. Optical absorption spectra for **1**−**5**.

molecules (observed, 10%; calculated, 9.7%). The second step of weight loss, occurring between 316 and 374 °C is due to the decomposition of organic components. The weight loss of **5** in the range 114−180 °C could be assigned to the escape of H_2O and DMF molecules. The observed weight loss of ca. 8.8% is close to the theoretical value (9.1%). The second step of weight loss begins at 299 °C, from which the organic groups were burnt.

Conclusion

In summary, we have demonstrated herein a facile synthesis of several coordination polymers of W/Cu/S clusters containing inclined (4,4) or parallel (4,4) interpenetrating and noninterpenetrating multidimensional frameworks. Although the (4,4) grid network is one of the most frequently encountered types of coordination polymers with ditopic spacers, the connecting nodes are usually single metal ions rather than cluster compounds.[23] Multidimensional networks with clusters behaving as shared corners and bidentate bix ligands as spacers have not previously been reported. Under similar reaction conditions, the employment of different solvents or copper sources resulted in different structures for the copper thiotungstate cluster building blocks as well as differences in the networks' interpenetration modes. By the choice of appropriate cluster components and connecting elements, other metal−sulfur cluster supported supramolecules with interesting topologic structures and molecular architectures can be obtained. Work is continuing in this area.

Acknowledgment. We thank the State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences (CAS), the Ministry of Science and Technology of China (Grant 001CB108906), and the National Science Foundation of China (Grants 20333070 and 20673117) for financial support.

Supporting Information Available: TGA curves and crystallographic data for **1**−**5** (CIF), a figure of **3** showing the C−H···O interactions, and XRD patterns of **3** before and after the removal of DMF. This material is available free of charge via the Internet at http://pubs.acs.org.

IC061142I

---

(23) (a) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460. (b) Carlucci, L.; Ciani, G.; Proserpio, D. M. *Coord. Chem. Rev.* **2003**, *246*, 247.