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New Skeletal 3D Polymeric Inorganic Cluster $[W_4S_{16}Cu_{16}Cl_{16}]_n$ with Cu in Mixed-Valence States: Solid-State Synthesis, Crystal Structure, and Third-Order Nonlinear Optical Properties

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A new 3D polymeric inorganic cluster with Cu in mixed-valence states was synthesized by the solid-state reaction of $(NH_4)_2WS_4$, S_8, CuCl, and Et_4NCl; S_8 may be regarded as the oxidizing agent converting Cu(I) to Cu(II) and causing the polymerization of $[WS_4]^{2-}$. The third-order nonlinear optical (NLO) properties are determined, and the results show that the cluster exhibits both large NLO absorptive and strong refractive behaviors.

The crystal engineering of 1D to 3D coordination molecules and supramolecules is one of the most active research topics of current chemistry and molecular materials science, giving rise to novel structures and geometries related to topology and supramolecular chemistry but also providing useful properties such as catalytic activity, conductivity, and nonlinear optical (NLO) properties.[1−7] Tetrathiometalates $[MS_4]^{2-}$ (M = Mo, W) are versatile reactants, which have been used extensively for the syntheses of a variety of heterothiometallic cluster compounds, including some polymeric complexes.[8] Examples are the 1D zigzag-chain polymeric cluster $[W_4S_{16}Ag_4{\cdot}2Ca(DMSO)_6]_n$,[9] the 2D square-planar polymeric cluster $[Cu_2WS_4]_n$,[10] and the 3D polymeric cluster $\{[NEt_4]_2[Cu_4(NC)_4WSe_4]\}_n$.[11] In the quest for new polymeric clusters with interesting structures and useful properties, we used a solid-state reaction to synthesize Mo(W)/Cu(Ag)/S polymeric clusters. In earlier work, clusters were generally prepared from $[MS_4]^{2-}$, CuX (AgX), and $[NR_4]X$.[11] We now introduce S_8 as a starting material,[1] with the expectation that S_8 might function as an oxidizing agent to obtain Cu^{II} clusters and cause $[MS_4]^{2-}$ polymerization. The solid-state synthesis and structural characterization of a new skeletal 3D heterothiometallic polymeric cluster $[W_4S_{16}Cu_{16}Cl_{16}]_n$ (**1**), with Cu in mixed-valence states and $[MS_4]^{2-}{}_m$ polymer units, are now reported.

The new polymeric cluster **1** was generated from the solid-state reaction of $[NH_4]_2[WS_4]$, CuCl, S_8, and $[NEt_4]Cl$ followed by extraction with dimethylformamide. The extract was layered by MeCN to furnish dark-red crystals of the title compounds in modest yield. Such a solid-state reaction has previously been shown to be an effective and powerful method for producing other polynuclear mixed-metal sulfide clusters.[12−15]

As illustrated in Figure 1,[16] the 3D framework of **1** has a very high degree of symmetry in the *I*4/*mmm* space group. Polymer **1** consists of two repeating cluster fragments, $[W_4S_{16}Cu_8]$ and $[Cu_4Cl_8]$. The structure of the fragment $[W_4S_{16}Cu_8]_n$ (Figure 2, left) is intriguing, with each W atom

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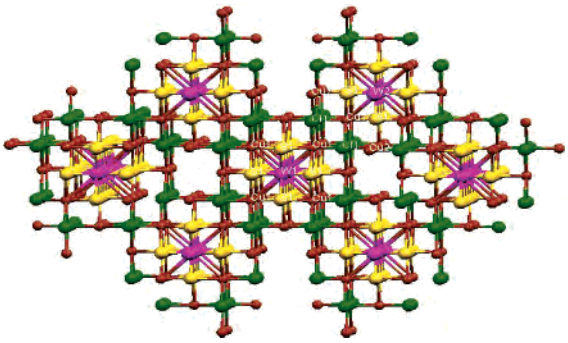

Figure 1. Perspective view along the *c* axis of the 3D network in $[W_4S_{16}Cu_{16}Cl_{16}]_n$ showing the cavities.

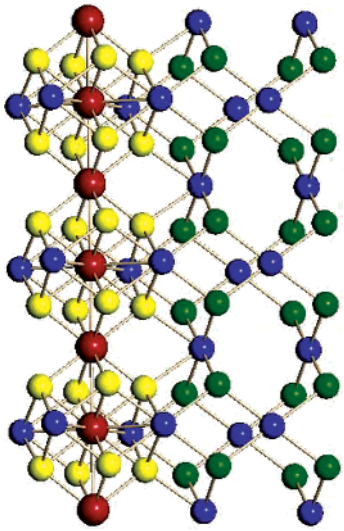

Figure 2. Sections of the crystal structures along the *a* axis of $[W_4S_{16}Cu_8]_n$ (left) and $[Cu_8Cl_{16}]_n$ (right) with parallel, 1D infinite chains. The green balls represent Cl atoms, the purple balls represent W atoms, the yellow balls represent S atoms, and the blue balls represent Cu atoms.

being connected to eight S atoms, and the W_4S_{16} moiety may be considered as four WS_4 units fused by S atoms. The four S atoms of each WS_4 unit are twisted by 90° relative to those of its neighbors. Two S atoms of each WS_4 unit are bound to the W atom of the neighboring WS_4 unit. Therefore, each W atom is coordinated by eight S atoms to form a 1D $(WS_4)_n$ polymer. To the best of our knowledge, this connecting mode is unprecedented. Within this 1D polymer, the W−S bond lengths of 2.295(5) Å are longer than those of the W−S bonds (2.165 Å) in $(NH_4)_2WS_4$.[17] The W···W separation is about 2.7654(8) Å, which may indicate some bonding interaction. The four Cu atoms are symmetrically connected by eight S atoms around each W atom. Thus, the W and the four Cu atoms are coplanar. The W−Cu bond length of 2.715(5) Å is normal and unexceptional for a W/Cu/S cluster.

(16) Crystal data for **1**: $W_4S_{16}Cu_{16}Cl_{16}$, tetragonal, space group *I*4/*mmm*. $a = b = 11.526(2)$ Å, $c = 5.531(2)$ Å, $\alpha = \beta = \gamma = 90.00°$, $V = 734.8(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 6.400$ mg·cm^{-3}, $\lambda = 0.710\,73$ Å, μ(Mo Kα) = 1.470 mm^{-1}, $F(000) = 1288$. A total of 1923 reflections were collected in the range of $2.50° \le \theta \le 25.43°$, of which 226 were unique reflections and 166 with $I \ge 2\sigma(I)$ were collected for the analysis. The structure was solved and refined by full-matrix least squares on F^2 values (SHELXL-97). Non-hydrogen atoms were refined anisotropically. The final indices were R1 = 0.0534 and wR2 = 0.1245 with GOF = 1.031.

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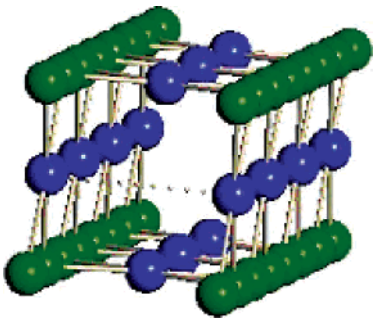

Figure 3. Sections of the crystal structures along the *c* axis of $[Cu_8Cl_{16}]_n$ with a 3.675-Å-diameter channel. The blue balls represent Cu atoms, and the green balls represent Cl atoms.

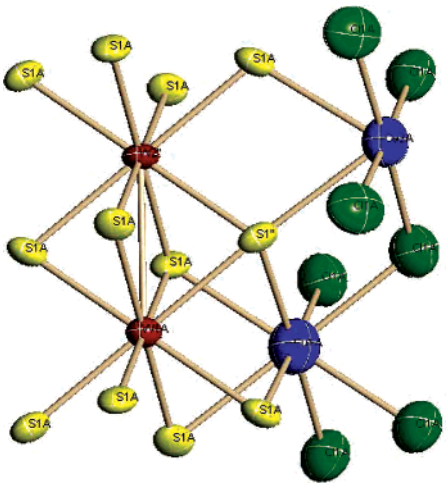

Figure 4. Perspective view of part of the polymeric cluster showing the whole bond surroundings for Cu1 (below) and Cu2 (above).

Alternatively, the structure of the fragment $[W_4S_{16}Cu_8]$ may be described as a linear stacking of the two planes (S_4 and WCu_4) along the ...W−W... vector. The fragment $[Cu_8Cl_{16}]_n$ (Figure 2, right) is also interesting, with each Cu atom being coordinated by four Cl atoms and two S atoms and each Cl atom being coordinated by two Cu atoms. Figure 3 shows that the Cu_8Cl_{16} moiety comprises sets of Cl_4 squares with central Cu atoms and a 3.675-Å-diameter channel formed in the *c* axis. There exist weak S···S and Cl···Cl interactions between adjacent S atoms and Cl atoms with a S···S distance of 2.765 Å and a Cl···Cl distance of 2.765 Å along the *a* axis. As shown in Figure 4, the two repeating cluster fragments $[W_4S_{16}Cu_8]$ and $[Cu_8Cl_{16}]$, connected by Cu1−Cl and Cu2−S bonds, are interwoven into a 3D polymer. The Cu1−S bond length of 2.368(4) Å is 0.104 Å shorter than that of Cu2−S, which indicates that the Cu2 atoms are pulled outward in order to release the strain of the whole framework.

As testified by an X-ray photoelectron spectroscopy (XPS) experiment (Figure 5), the Cu atoms in this polymeric cluster appear to show different oxidation states: Cu^+ and Cu^{2+}. The Cu $2p_{3/2}$ peaks are broad, and two Cu $2p_{3/2}$ peaks (marked as a and b) are resolved using a curve-fitting procedure. Peak a at the lower energy of 931.7 eV is in agreement with Cu^+ reported in earlier literature.[18] Peak b at the higher energy of 933.8 eV is very close to that of the Cu^{2+} ion;[18] meanwhile, the weak satellite peaks at 949.1 and

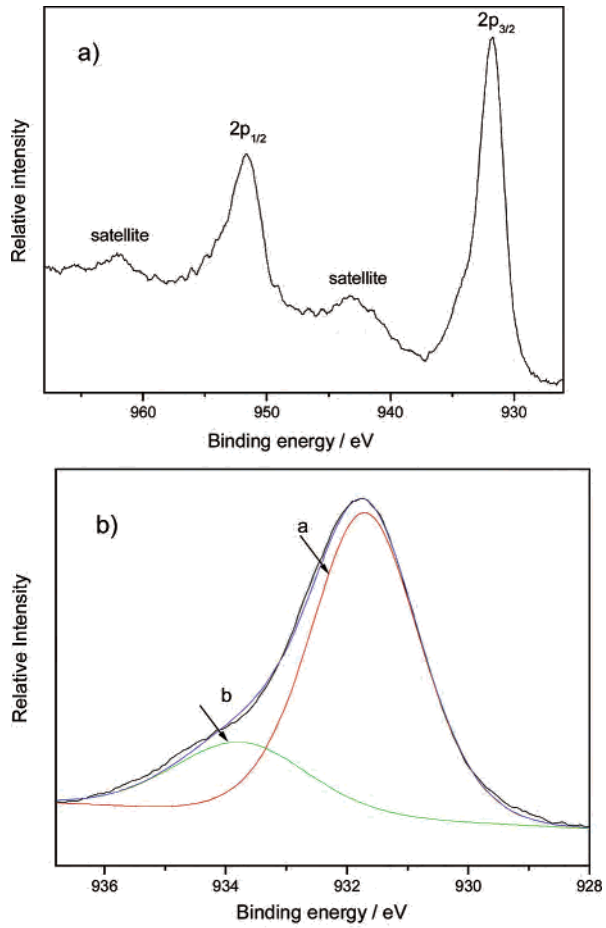

Figure 5. XPS spectra of Cu atoms in the polymeric complex.

962.1 eV also indicate that the complex may contain Cu^{2+} ions. Because early W/Cu/S cluster compounds have implicated Cu^{+}, the oxidation state of the Cu atoms in the fragment $[W_4S_{16}Cu_8]$ is assigned as 1+ while that of $[Cu_8Cl_{16}]$ is 2+. The presence of Cu^{2+} is attributed to the oxidation of some Cu^{+} atoms to Cu^{2+} under the reaction conditions.

The polymeric cluster shows large NLO absorptive and strong refractive behaviors. The nonlinear absorptive index α_2 and refractive index n_2 are calculated to be 1.6×10^{-9} m W^{-1} and 2.9×10^{-16} m^2 W^{-1}, respectively. They are obviously better than that of the 1D zigzag clusters $\{[MOS_3Cu_3(CN)(py)_3]\cdot 0.5C_6H_6\}_n$ (M = Mo or W)[19] and are comparable to those of the 1D helical cluster $\{[La(Me_2SO)_8][(\mu\text{-}WSe_4)_3Ag_3]\}_n$[11] and 2D network polymeric cluster $[MoS_4Cu_6I_4(py)_4]_n$.[14]

In conclusion, we have synthesized the 3D polymeric cluster $[W_4S_{16}Cu_{16}Cl_{16}]_n$ by the reaction of $[NH_4]_2[WS_4]$, CuCl, S_8, and $[NEt_4]Cl$ in the solid state. The cluster contains two cluster fragments: $[W_4S_{16}Cu_8]$ and $[Cu_8Cl_{16}]$. The former shows an intriguing unprecedented polymeric structure. The role of S_8 is, in part, as an oxidizing agent resulting in the formation of the Cu^{II} cluster and also as an agent for the $[MS_4]^{2-}$ polymerization. We are now investigating the possible mechanism of this reaction, as well as the NLO properties and conductivity properties of the polymeric cluster.

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Supporting Information Available: Experimental details for synthesis, IR data, and X-ray data for **1** (CIF and PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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