Inorg. Chem. **2007**, *46*, 6233–6235

Inorganic Chemistry
Communication

Porous Nonlinear-Optical Material Based on a Twin-Nest-Shaped Heterothiometallic Cluster: $\{[NH_4][W_2O_2S_6Cu_6I_3(4,4'\text{-bipy})_4]\cdot 5H_2O\}_n$

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Received April 26, 2007

A novel 3D porous coordination complex based on a twin-nest-shaped heterothiometallic cluster has been synthesized and characterized. The complex shows an unprecedented structure type and interesting nonlinear-optical properties. Its gas sorption property was studied and shown to be comparable to that of previously reported metal–organic frameworks.

In recent years, porous coordination polymers have received much attention for their potential use in gas storage,[1] catalysis,[2] and other properties such as magnetism[3] and optical features.[4] Further functionalization of porous architectures remains challenging,[5] and generally there are at least two synthetic strategies. One is the incorporation of a secondary functional group such as OH,[6] NH_2,[7] COOH,[8] and pyridine[9] into the organic linkers to afford secondary binding sites for guest recognition or catalysis. Another is to use metal clusters as building blocks instead of single metal ions in the construction of porous networks. So far, several preformed metal clusters have been incorporated into infinite frameworks to afford materials with fascinating properties, including octahedral zinc carboxylate clusters,[10] metal−metal-bonded dimeric clusters,[11] $[W_6(\mu_3\text{-S})_8(CN)_6]$,[6−12] and hexarhenium chalcogenide clusters.[13]

Mo(W)/Cu(Ag)/S heterothiometallic clusters have long been explored for their potential applications in catalysis and biological processes.[14] Our group in the past decade has systematically studied their nonlinear-optical (NLO) properties.[15] Results from previous studies suggest improvements of NLO properties including the optical-limiting effect when converting monomeric thiometallic clusters into cluster−organic polymers.[16] In addition, the coordination modes of

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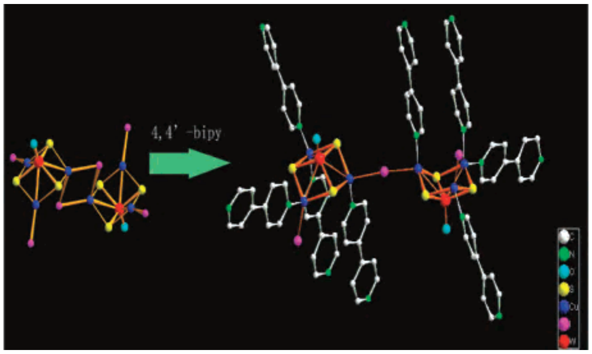
Scheme 1



the heterothiometallic clusters can differ from single metal ions so that the cluster−organic frameworks would give rise to remarkable structures and topologies. We have previously reported an unprecedented 3D porous cluster coordination polymer containing both interpenetrating cationic and anionic 3D diamondoid nets by using tetrathiometalate $[WS_4Cu_4]^{2+}$ building blocks.[17]

We now focus on a twin-nest-shaped cluster $[W_2O_2S_6Cu_6I_6]^{2-}$.[18] The cluster ion consists of two nest-shaped $[WOS_3Cu_3I_3]^{2-}$ fragments interconnected through a four-membered CuI_2Cu ring. We believe that full or partial substitution of the coordinated iodides with organic linkers could afford novel frameworks. We report here the synthesis, structure, and NLO properties of a new cluster coordination polymer, $\{[NH_4][W_2O_2S_6Cu_6I_3(4,4'\text{-bipy})_4]\cdot 5H_2O\}_n$ (**1**), by the self-assembly reaction of the cluster block $[W_2O_2S_6Cu_6I_6]^{2-}$ with 4,4′-bipy (bipy = bipyridine) as the bridging ligand (Scheme 1).

Compound **1** was obtained from the reaction of $[NH_4]_2[W_2O_2S_6Cu_6I_6]$ and 4,4′-bipy in *N*,*N*-dimethylformamide (DMF)/CH_3CN. Single crystals for X-ray diffraction (XRD) analysis were grown by slow diffusion of diethyl ether into the filtrate.[19] As shown in Scheme 1 (or see Figure S3 in the Supporting Information), the oxidation states of the W and Cu centers remain unchanged (6+ and 1+, respectively). The cluster unit consists of two nest-shaped $[WOS_3Cu_3I_3]^{2-}$ fragments connected through iodides [Cu−I distance: 2.632(1) Å]. In each of the fragments, one terminal O atom is attached to the W center [W−O distance: 1.718(5) Å] of the WS_3Cu_3 nest-shaped core, with W−S bond lengths of 2.244(2) Å and O−W−S angles ranging from 108.6(2) to 110.8(2)°. Each Cu atom has an approximately tetrahedral geometry in **1**, compared to the trigonal-planar or distorted tetrahedral coordination modes in the $[W_2O_2S_6Cu_6I_6]^{2-}$ cluster. However, the coordination environments are quite different. With the full substitution of the terminal I atoms by the 4,4′-bipy ligand, Cu1 is coordinated by two μ_3-S atoms and two N atoms, with Cu1−S2, Cu1−S3, Cu1−N1, and Cu1−N4 bond lengths of 2.286(2), 2.269(2), 2.102(7), and 2.011(7) Å, respectively. As for Cu2, the 4,4′-bipy ligands simply change the coordination geometry of the Cu atoms from trigonal-planar to tetrahedral, with Cu2−S1, Cu2−S2, Cu2−N3, and Cu2−I1 bond lengths of 2.303(2), 2.307(2), 2.066(8), and 2.5559(13) Å, respectively. The 4,4′-bipy ligands also partially substitute one of the bridging iodides of the four-membered $Cu^I{}_2Cu$ ring in the $[W_2O_2S_6Cu_6I_6]^{2-}$ cluster [Cu3−N2, 2.052(7) Å; Cu3−I2, 2.6325(11) Å]. As a result, the dihedral angle between the two nest-shaped $[WOS_3Cu_3I_3]^{2-}$ fragments changes from 180° to about 147°.

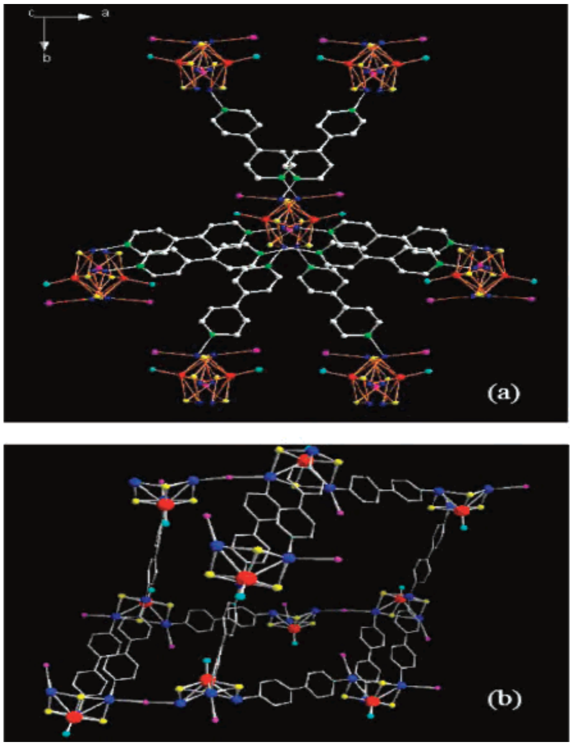


Figure 1. (a) View of the twin-nest-shaped cluster as a star-shaped six-connecting center. Color code: W, red; S, yellow; Cu, blue; I, pink; N, bright green; O, turquoise; C, white. (b) Diamondoid-like network units of compound **1**.

As indicated in Figure 1a, the twin-nest-shaped cluster is coordinated by eight 4,4′-bipy linkers, including two pairs of parallel ones, with a separation of 3.6 Å, implying weak $\pi-\pi$ interactions. From a topological perspective, each cluster serves as a star-shaped six-connecting center in a 3D infinite network, with the large dimension of 24.6 × 21.1 Å. There is a diamondoid threefold interpenetrating network in the framework of the cluster polymer, with a cluster fragment $[WOS_3Cu_3I_3]^{2-}$ as the node (Figures 1b and 2a,b). The three independent diamondoid networks stack parallel to the *c* axis to afford large hexagonal channels with a cross section of approximately 13.2 × 13.2 Å (Figure 2c).

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(19) Synthesis of compound **1**: A well-ground mixture of $[NH_4]_2[WO_2S_2]$ (0.174 g, 0.5 mmol) and CuI (0.382 g, 2.0 mmol) was added to a mixture of DMF and CH_3CN (15 mL; 2:1, v/v) under a purified nitrogen atmosphere. After stirring for 10 h, 4,4′-bipy (0.312 g, 2 mmol) was added and the mixture was stirred for another 2 h. The filtrate was layered with diethyl ether. Red block-shaped single crystals suitable for XRD were obtained several days later in 12% yield. Crystal data for **1**: $C_{40}H_{46}Cu_6I_3N_9O_7S_6W_2$, $M_r = 2086.96$, monoclinic, space group $C2/c$, $a = 17.927(4)$ Å, $b = 24.839(5)$ Å, $c = 16.881(3)$ Å, $\beta = 103.615(3)°$, $V = 7306(2)$ Å^3, $Z = 4$, $\mu = 6.327$ mm^{-1}, $\rho_{calcd} = 1.897$ g cm^{-3}, GOF = 1.041, R1 (wR2) = 0.0479 (0.0973) [5253 observed ($I > 2\sigma(I)$ for 7177 ($R_{int} = 0.042$) independent reflections out of a total of 19 658 reflections with 353 parameters)].

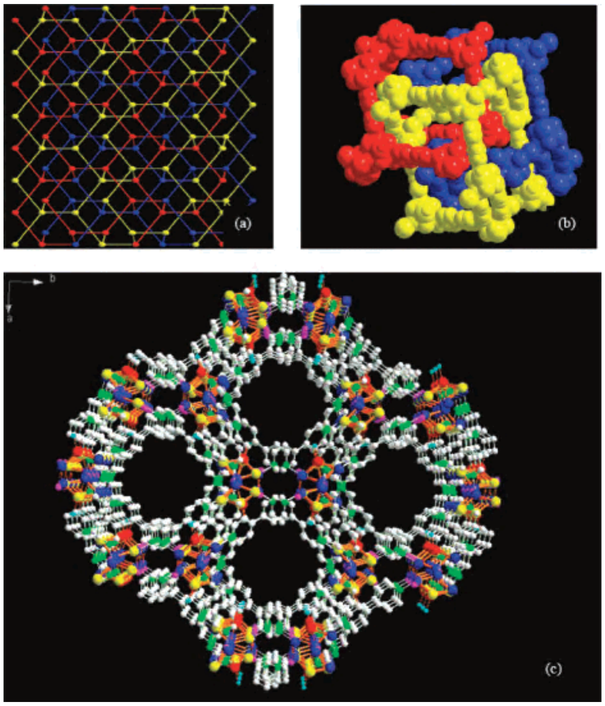

Figure 2. (a) Schematic view of the threefold interpenetration network. Each node and rod represents a cluster fragment $[WOS_3Cu_3I_3]^{2-}$ and 4,4′-bipy ligands, respectively. (b) Space-filling picture showing the threefold interpenetrating framework. (c) Hexagonal channels formed from the interpenetration of the threefold diamondoid networks along the *c* axis.

The total void value of the channels without water guests is estimated (by Platon[20]) to be 2546.2 Å^3, approximately 34.9% of the total crystal volume 7306(3) Å^3. All of the solvent water molecules are accommodated in a disordered fashion in the channels. Thermogravimetric analysis (TGA) of compound **1** reveals a weight loss of 2.1% in the region of 18−80 °C, consistent with the loss of lattice water molecules from the channels of compound **1**. (The crystals of compound **1** could lose some of the solvent molecules when exposed to the atmosphere.) A plateau region in the temperature range of 90−200 °C indicates that the molecular architecture of the compound is stable up to 200 °C in the absence of guests. The purity of compound **1** is confirmed by power XRD analyses, in which the experimental spectra of **1** are almost consistent with its simulated spectrum (Figure S2 in the Supporting Information). As depicted in Figure S2 in the Supporting Information, the diffraction profiles after removal of water are almost the same as those of the as-synthesized compound, which supports the fact that **1** remains intact after removal of the water molecules.

To evaluate the permanent porosity of the framework of compound **1**, dinitrogen sorption isotherm measurements (Figure 3) were performed on a desolvated crystalline sample at 77 K. Indeed, it shows a typical type I gas sorption behavior and a dinitrogen uptake of approximately 256 cm^3 (STP)/g, with a Langmuir surface area of 1172 m^2/g, a Brunauer−Emmett−Teller surface area of 844 m^2/g, and a pore volume of 0.39 cm^3/g (the Dubinin−Radushkevitch model). To our knowledge, compound **1** is the first heterothiometallic cluster based porous solid to be characterized by gas sorption that exhibits a porosity quite comparable to that of previously reported metal−organic frameworks (MOFs; $S_{\mathrm{Langmuir}} = 1100$ m^2/g for MOP-28).[21]

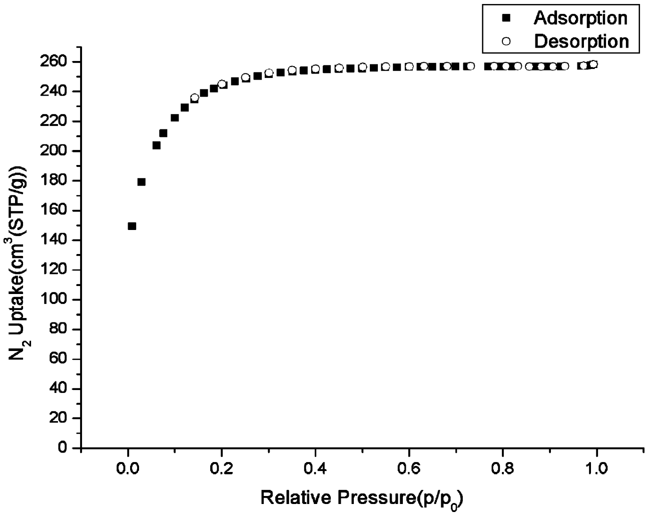

Figure 3. Dinitrogen sorption isotherm (77 K) for compound **1**.

The UV−vis absorption spectrum of compound **1** shows that it has very weak linear absorption at wavelengths ranging from 532 to 800 nm. The third-order NLO property of **1** was determined by using a Z-scan technique.[22] The effective NLO absorptive index α_2 and refractive index n_2 values were 1.62×10^{-10} mW^{-1} and 5.49×10^{-11} esu, respectively; this shows that polymer **1** exhibits optical self-focusing behavior and reverse saturable absorption (RSA) effects (Figure S4 in the Supporting Information).

In summary, we have synthesized a unique 3D porous cluster coordination polymer based on a twin-nest-shaped heterothiometallic cluster. Its gas sorption property was studied and shown to be comparable to that of previously reported MOFs. It was also found to show optical self-focusing behavior and RSA effects. Further work is in progress.

Acknowledgment. This work was supported by the National Natural Science Fund (Grants 20571039 and 20171020), the Ministry of Education of China (Grant 20050284031), and the Nature Science Foundation of Jiangsu province (Grant BK2006124).

Supporting Information Available: Experimental procedure, TGA, XRD patterns, and X-ray crystallographic files in CIF format for the structure determination of compounds **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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