Coordination Polymers

Self-Assembly of Interpenetrating Coordination Nets Formed from Interpenetrating Cationic and Anionic Three-Dimensional Diamondoid Cluster Coordination Polymers**

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The design and synthesis of metal–organic coordination polymers has become an exciting field in the past decade, and numerous interesting coordination polymers based on metal ions and organic bridging ligands have been synthesized by many research groups.[1] Many of these compounds contain channels or voids that are similar to those in porous materials such as zeolites and clays.[2] Tetrathiometalate clusters $[MS_4]^{2-}$ (M = W, Mo) have long been explored for their diverse coordination modes and potential applications in catalysis, biological processes, and nonlinear optical (NLO) materials.[3] Rather few polymeric heterothiometallic cluster coordination polymers based on the thiometalates have been synthesized.[4] Such coordination polymers have invariably contained polymer aggregates that were: 1) anionic, such as $[NH_4]_n[AgWS_4]_n$,[5] $\{[N(CH_2C_6H_5)(C_2H_5)_3][MoAgS_4]\}_n$,[6] $\{[NEt_4][Mo_2O_2S_6Cu_6I_3(4,4'\text{-bipy})_5]\cdot MeOH\cdot H_2O\}_n$ (4,4'-bipy = 4,4'-bipyridine),[7] or $\{[Et_4N]_2[MoS_4Cu_4(CN)_4]\}_n$,[8] 2) cationic, as in the transition metal coordination polymers, or 3) neutral, as in $[MoS_4Cu_6I_4(py)_4]_n$ (py = pyridine),[9] $\{[MoOS_3(CN)(py)_3]\cdot 0.5\,C_6H_6\}_n$,[10] or $[Cu(4,4'\text{-bipy})Cl]_n$.[11] Structures containing interpenetrating nets that have different topologies and/or chemical compositions are known,[1] although no example has previously been reported of a coordination polymer containing both cationic and anionic coordination polymer aggregates.

We report here such an unprecedented cluster coordination polymer, namely compound **1**, which contains interpenetrating cationic and anionic 3D diamondoid cluster coordination polymers.

$\{[WS_4Cu_4(4,4'\text{-bipy})_4][WS_4Cu_4I_4(4,4'\text{-bipy})_2]\cdot 4\,H_2O\}_n$ **1**

Compound **1** was obtained from the reaction between $[NH_4]_2[WS_4]$, CuI, $[n\mathrm{Bu}_4\mathrm{N}]\mathrm{I}$, and 4,4'-bipy, in a ratio of 1:2:2:2, in DMF/CH_2Cl_2 solution, followed by filtration and slow diffusion of diethyl ether into the filtrate to give single crystals suitable for an X-ray diffraction study. The crystallographic analysis of compound **1**[12] revealed that the 3D cationic cluster coordination polymer can be considered as comprising square, pentanuclear $[WS_4Cu_4]^{2+}$ building blocks, each linked by four pairs of parallel 4,4'-bipy ligands (Figure 1). The W and the four Cu atoms are coplanar in each $[WS_4Cu_4]^{2+}$ building block, and the $\{WS_4\}^{2-}$ unit has a tetrahedral structure with W2–S2 bond lengths of 2.235(2) Å, and S2-W2-S2 angles ranging from 108.60(11)° to 110.50(12)°. Each of the four Cu atoms is also tetrahedrally coordinated by two N atoms from two 4,4'-bipy ligands and two μ_3-S atoms, with Cu2–N2, Cu3–N3, Cu2–S2, and Cu3–S2 bond lengths of 2.023(7) Å, 2.043(7) Å, 2.272(2) Å, and 2.280 Å, respectively.

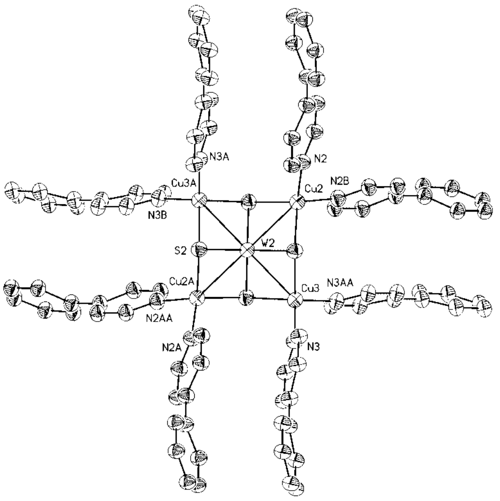

Figure 1. The cationic cluster coordination polymer unit $[WS_4Cu_4(4,4'\text{-bipy})_4]^{2+}$.

The angles N2-Cu2-N2B and N3-Cu3-N3AA are 106.1(4)° and 112.3(4)°, respectively, hence the four 4,4'-bipy molecules are almost tetrahedrally disposed, which results in a diamondoid network with a large channel dimension of 24.482 Å × 21.009 Å (Figure 2a). Each six-membered ring contains six $[WS_4Cu_4]^{2+}$ nodes and six pairs of 4,4'-bipy connecting rods. The separation between each pair of 4,4'-bipy units is nearly 3.7 Å, thus implying weak π–π interactions.

In fact, there is a twofold interpenetrating 3D network in the cationic coordination polymer (Figure 3a and 3b). Similar interpenetrating diamondoid frameworks have also been

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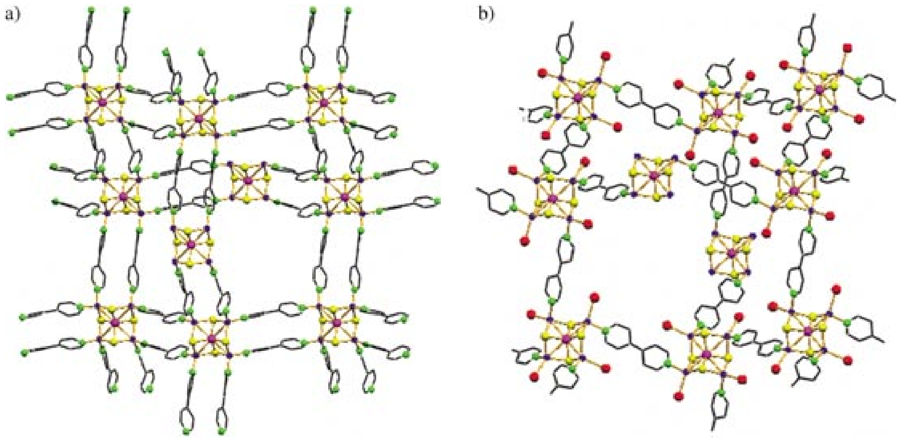

Figure 2. a) The diamondoid structure of the cationic cluster coordination polymer $\{[WS_4Cu_4(4,4'\text{-bipy})_4]^{2+}\}_n$. b) The diamondoid structure of the anionic cluster coordination polymer $\{[WS_4Cu_4I_4(4,4'\text{-bipy})_2]^{2-}\}_n$. Hydrogen atoms have been omitted for clarity. W violet, S yellow, Cu blue, N green, C black line.

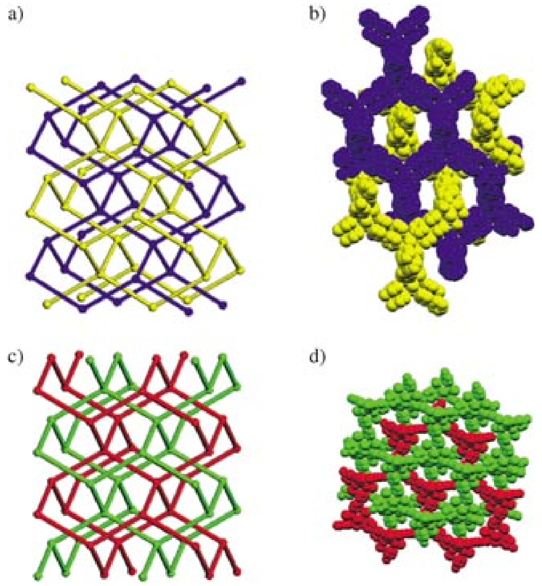

Figure 3. a) View of the cationic cluster coordination polymer. Each node and rod represents a cluster cation $[WS_4Cu_4]^{2+}$ and a pair of 4,4′-bipy ligands, respectively; b) space-filling picture showing the twofold interpenetrating cationic cluster coordination polymer $\{[WS_4Cu_4(4,4'\text{-bipy})_4]^{2+}\}_n$; c) view of the anionic cluster coordination polymer. Each node and rod represents a cluster anion $[WS_4Cu_4I_4]^{2-}$ and a single 4,4′-bipy ligand, respectively; d) space-filling picture showing the twofold interpenetrating anionic cluster coordination polymer $\{[WS_4Cu_4I_4(4,4'\text{-bipy})_2]^{2-}\}_n$.

found in some other coordination polymers containing transition metal ions.[13] The 3D anionic cluster coordination polymer is almost exactly analogous to the cationic cluster coordination polymer, except that the building block is the $[WS_4Cu_4I_4]^{2-}$ ion, which is nearly tetrahedrally coordinated by four N atoms of four 4,4′-bipy molecules (Figure 4). Each Cu atom is tetrahedrally coordinated by two μ$_3$-S atoms, one I atom, and one N atom from one of the 4,4′-bipy ligands, with Cu1–N1 and Cu1–I1 bond lengths of 2.090(7) Å and 2.5516(13) Å, respectively, which leads to another diamondoid network with a larger channel dimension of 24.828 Å × 24.217 Å (Figure 2b). Each six-membered ring contains six $[WS_4Cu_4I_4]^{2-}$ nodes and six 4,4′-bipy connecting rods. The anionic cluster coordination polymer also exists as a twofold interpenetrating framework (Figure 3c and 3d).

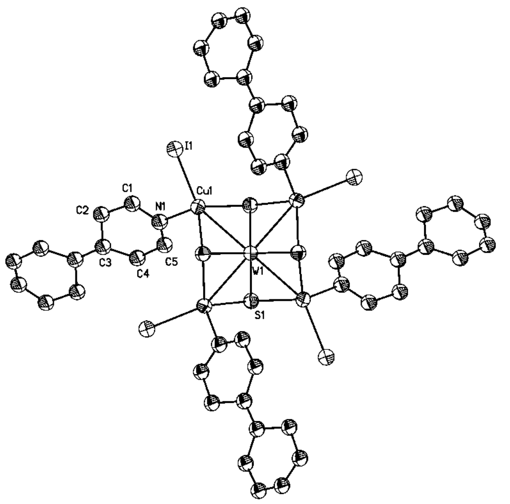

Figure 4. The anionic cluster coordination polymer unit $[WS_4Cu_4I_4(4,4'\text{-bipy})_2]^{2-}$.

It is noteworthy that the two pyridine rings of each 4,4′-bipy ligand are coplanar, except that two C atoms, C_1 and C_2, are disordered and were refined to an occupancy ratio of 0.5 in the anionic cluster coordination polymer; in the cationic cluster coordination polymer the pyridine rings of each 4,4′-bipy ligand are not coplanar, with the pyridine rings twisted by 25.8°, 46.4°, and 63.9°, respectively. The whole molecule has an intricate, fourfold interpenetrating diamondoid structure (Figure 5), containing large 11.124 Å × 11.129 Å channels; all the solvent water molecules are disordered along the *c* axis (Figure 6). The channel volume is about 293 Å^3,[14] and the water molecules interact with the frameworks through hydrogen bonds.

Thermogravimetric analysis (TGA) of compound **1** under a nitrogen flow showed that the frameworks are rigid, with no weight change observed up to 203 °C. The solvent water and some of the organic ligands were lost between 203 °C and 268 °C (residue 68.1 %), then most of the remaining ligands were gradually removed from 268 °C to 337 °C (residue 54.4 %) and from 337 °C to 571 °C (residue 41.4 %). No further weight change was observed above 700 °C. The unit-cell parameters of a single crystal are nearly identical up to 180 °C, which is consistent with the TGA results. However,

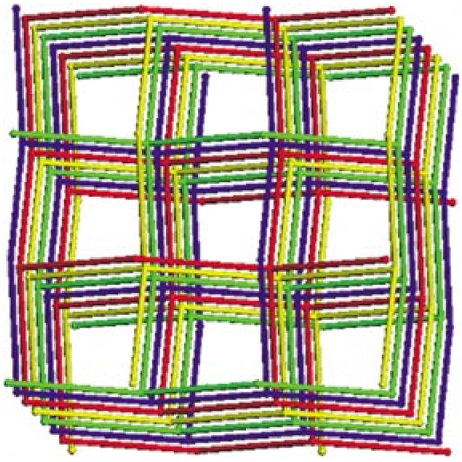

Figure 5. Schematic view of the cluster coordination polymer **1**. The cationic and anionic cluster coordination polymers are shown in blue/yellow and red/green, respectively. (The blue/yellow node and rod represent the cluster cation and the double 4,4′-bipy ligand, respectively; the red/green node and rod represent the cluster anion and the single 4,4′-bipy ligand, respectively.)

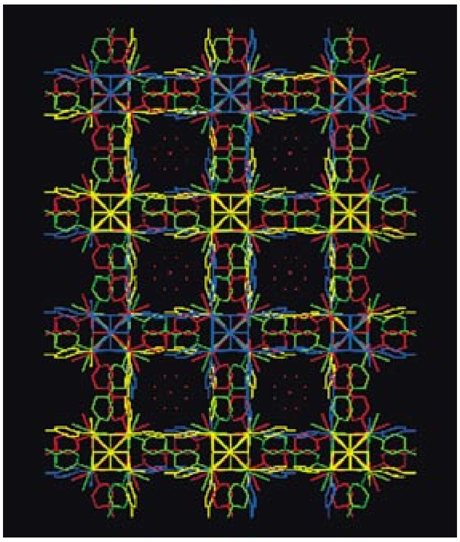

Figure 6. Packing diagram of compound **1**, viewed along the *c* axis. Hydrogen atoms have been omitted for clarity. Blue/yellow and red/green represent the cationic and anionic cluster coordination polymers, respectively. The red balls are the O atoms of the water molecules.

heating compound **1** to 230 °C and then cooling again causes a change in the X-ray powder diffraction (XRPD) pattern compared to that of **1** at room temperature, which indicates that the frameworks are only partially retained.

Two peaks at $\lambda_{max} = 292$ and 411 nm, observed in the UV/Vis spectrum of **1**, showed that the polymer has a relatively low linear absorption in the visible and near-IR region. We therefore performed a *Z*-scan experiment to investigate its nonlinear optical properties.[15] The compound was dissolved in DMSO at a concentration of 5.8×10^{-5} mol dm^{-3}. This solution was then placed in a 2-mm-thick cuvette. The linear transmittance of the sample was 76 %. The results of the open-aperture and the normalized transmittance are shown in Figure 7 a.

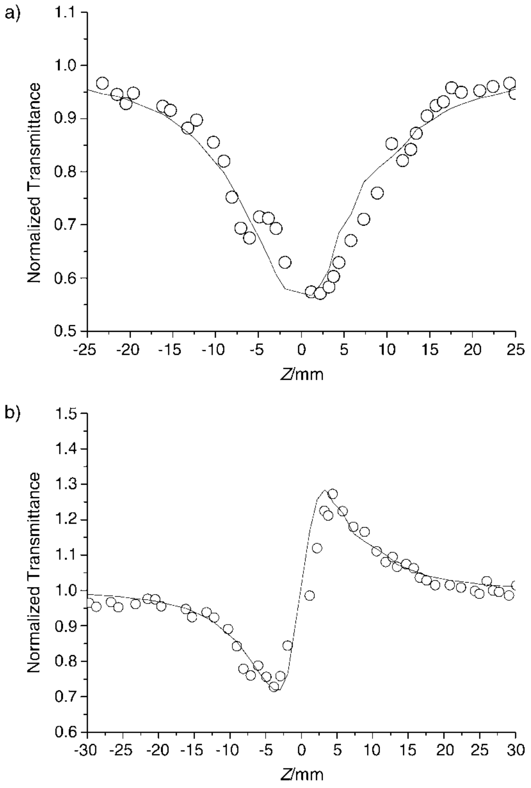

Figure 7. *Z*-scan data of cluster **1**: a) NLO absorption; b) NLO refraction.

The open circles are the experimental data, and the solid curves are the fit given by the *Z*-scan theory described in ref. [15]. The open-aperture *Z*-scan curve of the compound has a deep valley, and the transmittance drops to the lower value of 57 %. This result suggests that the compound has a strong nonlinear absorption; it may therefore be a promising candidate for use in optical limiting. It should be pointed out that both the excited-state population (and absorption) and the two-photon absorption could be responsible for the measured NLO effect. It is evident that the theoretical curves qualitatively reproduce the general pattern of the observed experimental data. This suggests an effectively third-order behavior for the experimentally detected NLO effects. The *Z*-scan data measured with the aperture are depicted in Figure 7 b. The normalized curve has a sharp peak and a valley, which identifies compound **1** as a self-focusing material. A reasonably good fit between the experimental data and the theoretical curves, as described in ref. [15], was obtained. The effective third-order NLO absorptive index β and refractive index n_2 value were 1.6×10^{-10} mW^{-1} and 6.4×10^{-11} esu, respectively; this shows that polymer **1** exhibits optical self-focusing behavior and reverse saturable absorption (RSA) effects.

In summary, a new kind of interpenetrating 3D cluster coordination polymer based on the tetrathiometalates has been obtained. Its NLO properties show that **1** exhibits optical self-focusing behavior and reverse saturable absorption effects. Further work is in progress.

Experimental Section

A well-ground mixture of $[NH_4]_2[WS_4]$ (0.5 mmol), CuI (1.0 mmol), $[n\mathrm{Bu}_4\mathrm{N}]\mathrm{I}$ (1.0 mmol), and 4,4′-bipy (1 mmol) was added to a mixture of DMF and CH_2Cl_2 (15 mL; v/v 2:1) under a purified nitrogen atmosphere. After stirring for 10 h, the filtrate was layered with diethyl ether. A few red crystals were separated several days later. A red prismatic single crystal (0.02 g, 15 %) suitable for X-ray diffraction was obtained when the filtrate was allowed to slowly evaporate in air. Elemental analysis calcd (%) for **1**: C 27.20, H 2.13, N 6.34; found: C 27.84, H 1.89, N 6.71. IR (KBr): $\tilde{\nu} = 3448$ (w), 3043 (w), 1672 (s), 1601 (s), 1530 (m), 1483 (m), 1409 (s), 1213 (m), 1068 (m), 807 (s), 626 (m), 567 (w), 499 (w), 438 cm^{-1} (s).

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[12] Single-crystal X-ray structure determination of **1**: The data were collected at $T = 123$ K on a Rigaku mercury CCD diffractometer with graphite-monochromated MoK_α radiation ($\lambda = 0.7107$ Å). All calculations were performed by using SHELXTL version 6.10 package on a Dell-4550 computer.[16] The structure was solved by direct methods and refined by full-matrix least-squares methods. Crystal data: red prism, $0.35 \times 0.30 \times 0.25$ mm, $C_{60}H_{56}Cu_8I_4N_{12}O_4S_8W_2$, $M_r = 2649.27$, tetragonal, space group $I4(1)/acd$, $a = b = 24.780(4)$, $c = 28.159(7)$ Å, $V = 17291(6)$ Å^3, $Z = 8$, $\mu = 6.242\ \mathrm{mm}^{-1}$, $\rho_{\mathrm{calcd}} = 2.036\ \mathrm{g\,cm}^{-3}$, GOF = 1.051, $R1$ ($wR2$) = 0.0515 (0.1369) [4259 observed ($I > 2\sigma(I)$ for 3390 independent reflections (with $R_{\mathrm{int}} = 0.036$)) out of a total of 55837 reflections with 252 parameters]. CCDC-231994 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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