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Hybrid Coordination Polymer Constructed from *β*-Octamolybdates Linked by Quinoxaline and Its Oxidized Product Benzimidazole Coordinated to Binuclear Copper(I) Fragments

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The one-dimensional polymer, $[Cu_2(C_8H_6N_2)_2(C_7H_6N_2)]_2[Mo_8O_{26}]$ (**1**), which consists of β-$[Mo_8O_{26}]^{4-}$ anions linked by quinoxaline and its oxidized product benzimidazole ligands coordinated to binuclear copper(I) fragments, provides the first demonstration that the isolated copper(I) complex under hydrothermal conditions "captures" the reduction product of original starting organonitrogen ligand to form a copper(I)–β-octamolybdate complex.

Recently, the synthesis and characterization of polymolybdates linked by coordinated transition metal fragments has attracted great attention. It is not only because of the chemistry itself but also because of their widely promising potential applications in many fields.[1−6] However, although great progress has been made, the understanding of the formation mechanism of such materials is still far behind, although it is described normally as self-assembly.

Recent elaborations have proven that the hydrothermal synthesis, which causes the reaction mechanism to shift from the kinetic to the thermodynamic domain as compared to traditional aqueous reactions, provides a powerful tool for the synthesis of such materials.[7] It has been well-known that the construction of hybrid materials is often realized by utilization of N-donor rigid heteroatom aromatic organic ligands under hydrothermal reaction conditions. To date, great numbers of polyoxometalates bridged by organonitrogen ligands coordinated to copper fragments have been reported. In several cases, the starting reagents are copper(II) salts, while the oxidation states of copper atoms in these complexes are often assigned as +1 on the basis of charge neutrality, crystal color, and coordination environments.[8] Thus, it is noteworthy that, under hydrothermal conditions, organonitrogen species behave typically not only as ligands but also as reducing agents in the presence of Cu(II). This characteristic results obviously from the combination of the reactive oxidation−reduction potencies of the copper atoms and the organonitrogen ligands as well as the specific hydrothermal conditions. However, providing reliable evidence is still a challenge facing chemists.

In the course of our investigation on N-donor rigid heteroatom aromatic ligands in the bridged copper−molybdate system, we obtained a hybrid material, $[Cu_2(C_8H_6N_2)_2(C_7H_6N_2)]_2[Mo_8O_{26}]$ (**1**), which provides powerful evidence for the study of how the quinoxaline ligand was oxidized while the copper(II) atom was reduced.

Brown crystals of **1** were simply synthesized by the hydrothermal reaction of copper(II) acetate, sodium molybdate, and quinoxaline ligand at low pH.[9] The IR spectrum of **1** exhibits broad bands from 1500 to 1038 cm^{-1}, which can be assigned to the absorption of the ligands. The strong

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(9) The pH of a mixture of $Na_2MoO_4 \cdot 2H_2O$ (0.242 g, 1.0 mmol), $Cu(OCOCH_3)_2 \cdot H_2O$ (0.10 g, 0.50 mmol), and quinoxaline (0.10 g, 0.77 mmol) in H_2O (18 mL) was adjusted to 4.0 by concentrated HCl, and then, the mixture was heated at 170 °C for 5 days in a sealed 30 mL Teflon-lined stainless steel vessel under autogenous pressure. After the reaction was slowly cooled to room temperature, brown crystals were produced. Yield: 56.3%, based on Mo. Anal. Calcd for **1**: C, 25.18; H, 1.65; N, 7.66. Found: C, 25.26; H, 1.63; N, 7.61.

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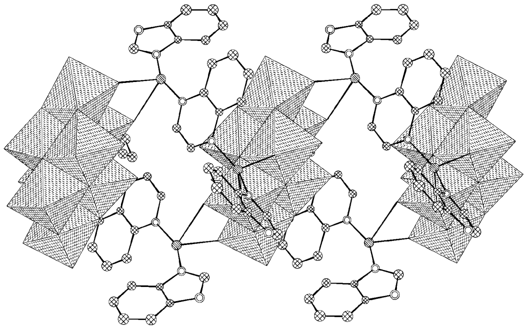

Figure 1. Polyhedral representation of the β-$[Mo_8O_{26}]^{4-}$ anion and ball-and-stick representation of the binuclear copper(I).

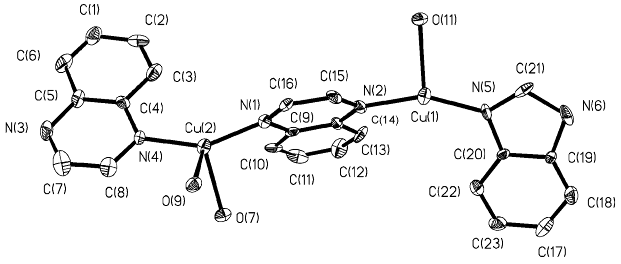

Figure 2. ORTEP representations of the binuclear copper(I) unit in **1** (30% probability ellipsoids).

bands from 955 to 895 cm^{-1} are attributed to the Mo═O stretching, while multiple bands attributed to the bridging (Mo—O—Mo(Cu)) groups' absorptions are found in the 862−449 cm^{-1} region. The X-ray diffraction analysis[10] suggests that the structure of **1** may be described as chains constructed from β-octamolybdates bridged by quinoxaline- and benzimidazole-coordinated binuclear copper(I) fragments (Figure 1). The structure of the centrosymmetric $[Mo_8O_{26}]^{4-}$ anion, which is built up from eight $\{MoO_6\}$ edge-shared octahedra, is a typical β-octamolybdate.[11]

There are four coordinated binuclear copper(I) fragments around each central β-$[Mo_8O_{26}]^{4-}$ anion. Two crystallographically independent copper sites comprise two different distinct environments to form binuclear units (Figure 2). The first one is a distorted tetrahedron, which is defined by two nitrogen atoms from the quinoxaline ligands (Cu−N = 1.92(1)−1.93(1) Å) and two terminal oxygen atoms from β-octamolybdate (Cu−O = 2.14(1)−2.41(1) Å) with angles within 78.1(3)−148.6(5)°. The second Cu(I) site is coordinated by two nitrogen atoms from quinoxaline (Cu−N = 1.92(1) Å) and benzimidazole (Cu−N = 1.87(1) Å), and then by one terminal oxygen atom from a molybdenum atom in another β-octamolybdate (2.25(1) Å) to complete a trigonal environment for the copper(I) atom with angles in the 96.1(3)−155.1(4)° range. These two copper atoms are joined together by one quinoxaline, which acts as a bidentate ligand. The remaining quinoxaline and benzimidazole ligands perform only as monodentate ligands. It is quite interesting that the previously mentioned four coordinated binuclear copper(I) subunits link up two adjacent $[Mo_8O_{26}]^{4-}$ units via six oxo groups of octamolybdate into a beautiful one-dimensional linear chain, which is somehow like meso-chiral double helices (Figure 3).

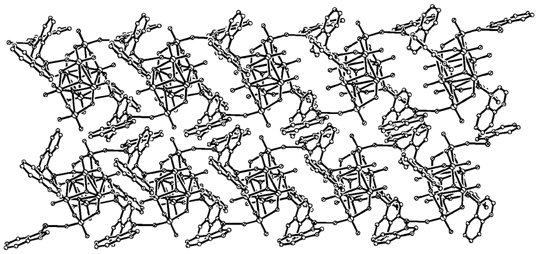

Figure 3. Stereoscopic view of the extended one-dimensional chain of **1**.

It is quite surprising that there is a benzimidazole ligand coordinated to one copper atom directly. As no benzimidazole was added to the starting reaction mixture, the most possible source is that the benzimidazole is the oxidation product of the quinoxaline. However, as the reaction mechanism of hydrothermal synthesis is shifting from the thermodynamic to the kinetic domain as compared to a high temperature solid-state reaction or from the kinetic to the thermodynamic control compared to a conventional solution synthetic approach, the equilibrium phases are replaced by more structurally metastable phases. It is very difficult to follow up the track and predict the true oxidation mechanism of quinoxaline into benzimidazole. The most possible case is that after complicated oxidation−reduction process in the presence of Cu(II), quinoxaline is oxidized into the benzimidazole ligand and acts an effective ligand coordinating to copper atoms directly. Several methods have been proposed to confirm the isolated complex. The EI-MS spectra show peaks at m/z 130 and 118, which demonstrate clearly that the quinoxaline and benzimidazole ligands are both incorporated into **1**. The EI-MS peaks of the original quinoxaline ligand exclude the possibility that the benzimidazole ligand is introduced from the starting regents.

In conclusion, in this communication we show a beautiful one-dimensional polymeric chain of β-octamolybdates linked up by quinoxaline and benzimidazole ligands coordinated to binuclear copper(I) fragments. It is the first complex in which that organonitrogen ligand performs as an effective reduction reagent and its product benzimidazole ligand coordinates to copper(I) atoms directly under hydrothermal conditions.

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Supporting Information Available: Tables, possible mechanism of the oxidation process of quinoxaline, and EI-MS spectra. One X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Crystal data for **1**: $C_{46}H_{36}Cu_4Mo_8N_{12}O_{26}$, M_r = 2194.55, triclinic, space group $P\bar{1}$, a = 9.463(1) Å, b = 12.507(1) Å, c = 13.015(1) Å, α = 80.738(2)°, β = 85.819(3)°, γ = 76.338(2)°, U = 1476.2(1) $Å^3$, Z = 1, D_c = 2.469 g cm^{-3}, μ = 3.140 mm^{-1}, $F(000)$ = 1056. Final R1 = 0.0579, wR2 = 0.0849, and S = 1.045 for 2684 reflections with $F_o > 4\sigma(F_o)$ and 434 parameters.

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