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A novel selenium–molybdenum oxide chain inserted with copper (II) complex: Synthesis, structure, and magnetic property

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Abstract

A one-dimensional polyoxomolybdate compound inserted with both selenite and copper (II) complex, $[(bipy)CuSeMo_3O_{12}]_n$, has been hydrothermally synthesized and structurally characterized. This is the first example that polyoxomolybdate framework modified by both selenite and transition metal complex. A strong ferromagnetic interaction occurred in this compound due to magnetic coupling between copper (II) centers.

Keywords: Hydrothermal synthesis; Polyoxomolybdate; Copper (II) complex; Selenium; Magnetic property

The polyoxomolybdates system, as an important family of polyoxometalates (POMs), has been receiving extensive attention not only because of structural variety, but also potential applications in many fields such as catalysis, materials science and medicine [1–6]. Recently, different research groups worldwide have employed various approaches to incorporate some tetrahedral groups into molybdenum oxide cluster unit (such as Mo_4O_{13}, Mo_5O_{15} and Mo_6O_{18}) so as to modify molybdenum oxide framework [7–18]. However, the modification of molybdenum-oxide-based compound by coupling $Se^{IV}O_3$ groups are relatively unexplored [19,20]. It can be expected that the nature of Se^{IV} ion containing lone pair will play an important role in the structural modification. In particular, the heterometallic compounds with selenite have shown potential applications in medicines and selenium deposition of wastewater or radioactive waste [21–27]. Therefore, it should be of considerable signification to explore the rational synthesis of molybdenum oxide-based compounds containing selenite. The introduction of copper (II) complex in such synthesis can effectively provide either structure-directing effect or magnetic center. Based on the above consideration, we are interested in rational synthesis of new polyoxomolybdates with selenite group. Herein we report the hydrothermal synthesis, structural characterization and magnetic property of a novel selenium-molybdenum oxide chain inserted with five-coordinative copper (II) complex, $[(bipy)CuSeMo_3O_{12}]_n$. This is the first example that polyoxomolybdate framework modified by both selenite and transition metal complex. Such 1D chains further link to each other through π–π stacking and hydrogen bond interactions. A strong ferromagnetic interaction occurred in this compound due to magnetic coupling between copper (II) centers.

$[(bipy)CuSeMo_3O_{12}]_n$ (**1**): Compound **1** was synthesized by employing the hydrothermal method in the

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presence of organic 2,2′-bipyridine. A mixture of H_2MoO_4 (0.9804 g, 6.0 mmol), H_2SeO_3 (1.4892 g, 12.0 mmol), $Cu(CH_3CO_2)_2$ (0.2142 g, 1 mmol) and 2,2′-bipyridine (0.1398 g, 0.8 mmol) in 10 mL of distilled water was sealed in an autoclave equipped with a Teflon liner (25 mL), and then heated at 160 °C for 166 h. Then the temperature was recovered to room temperature by −9 °C/h. The pH values before and after the reaction were 2.5 and 4.0, respectively. Blue green, block-shaped crystals of **1** were collected in about 38% yield (0.3726 g) (based on Mo). $C_{10}H_8CuSeMo_3N_2O_{12}$ (778.5): Calcd. C, 15.42; H, 1.03; N, 3.60; Cu, 8.16; Mo, 36.97; Se, 10.14. Found: C, 15.80; H, 1.85; N, 3.76; Cu, 8.34; Mo, 36.68; Se, 10.02%.

The IR spectra of compound **1** is characterized by the vibration of ν(Mo–O) around 881–962 cm^{-1} for $\{Mo_6O_{18}\}$ cluster unit, and the bands around 720–773 and 416–439 cm^{-1} can be assigned to the vibrations of the selenite groups. On the other hand, the bands around 1601–1606 and 1451–1492 cm^{-1} are originate from the organic group 2,2′-bipyridine in compound **1** (Fig. S1).

The asymmetric unit of compound **1** [34] crystallizes in the space group $P\bar{1}$ and contains 29 non-hydrogen atoms of which 17 belong to the inorganic framework and 12 to the organic group 2,2′-bipyridine (see Fig. S2). The structural unit consists of a heterometallic octanuclear $Mo_6Cu_2Se_2$ cluster build up from an $\{Mo_6O_{18}\}$ cluster, $\{SeO_3\}$ trigonal pyramids and $\{CuN_2O_3)\}$ square pyramids (Fig. 1). The six Mo atoms arrange them into two groups, which one group is composed of four $\{MoO_6\}$ octahedra and the other group contains two $\{MoO_6\}$ units. The former four Mo atoms are interconnected by edge- and face-sharing to form a planar $\{Mo_4O_{13}\}$ cluster unit. On the other hand, the other two Mo atoms link to each other by sharing edge oxygen atoms to form a $\{Mo_2O_5\}$ unit. The $\{Mo_2O_5\}$ unit shares a corner with the $\{Mo_4O_{13}\}$ unit through two oxygen atoms and then constructs a novel twist $\{Mo_6O_{18}\}$ cluster unit (Fig. S3). This novel structure is very different to the reported $\{Mo_4O_{13}SeO_3\}$ and $\{Mo_5O_{15}SeO_3\}$ units [20], which the four or five $\{MoO_6\}$ octahedra link to each other as a circle shape. As a result, Mo2–Mo3 and Mo1–Mo3 distances are different as 3.701 and 3.373 Å, respectively. Mo–O distances range from 1.687(2) to 2.4158(19) Å shown in Table 2 (see supplementary material), which indicates that $\{MoO_6\}$ octahedron severely distorted. The Se atom is three-coordinate, with Se–O distance ranging from 1.652(2) to 1.759(2) Å. These Mo–O and Se–O distances are little longer than those reported structures [20,21]. The $\{SeO_3\}$ trigonal pyramid connects to the $\{Mo_4O_{13}\}$ and $\{Mo_2O_5\}$ cluster by O3 and O2 oxygen atoms respectively and another oxygen atom covalently bonds to $\{CuN_2O_3\}$ unit. Interestingly, Cu atom is five-coordinate to form a $\{CuN_2O_3\}$ square pyramid with two nitrogen atoms are from the organic group 2,2′-bipyridine. The $\{CuN_2O_3\}$ is attached to the $\{Mo_2O_5\}$

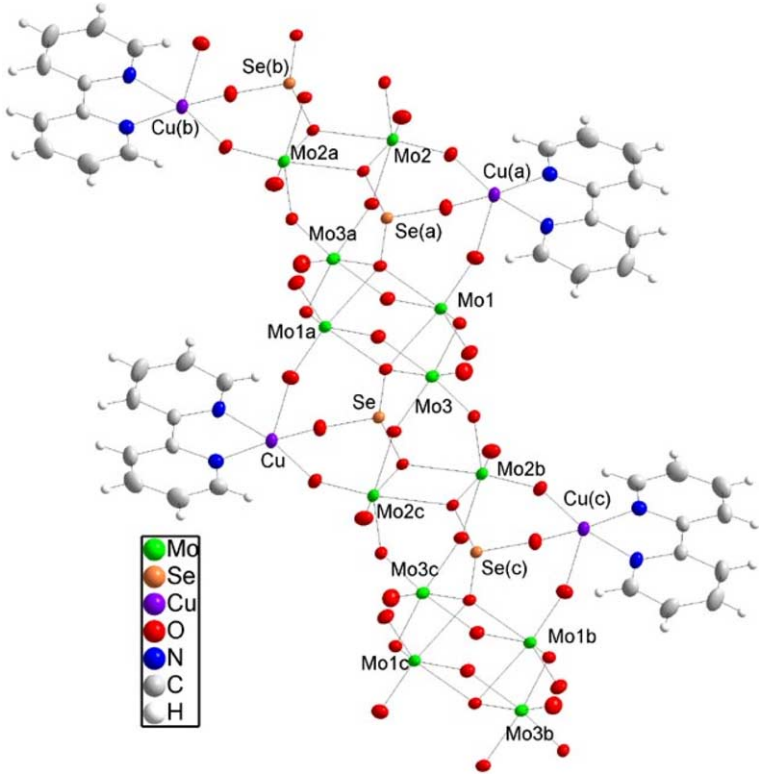

Fig. 1. A view of ORTEP representation of compound **1**.