Synthesis, Crystal Structure and Property of a 3D Octamolybdate Coordination Polymer Based on Nickel(II)-bis(triazole) System

WANG Xiu-Li*, ZHAO Dan, TIAN Ai-Xiang*, LIU Guo-Cheng
(Department of Chemistry, Bohai University, Jinzhou, Liaoning 121000, China)

Abstract: A new 3D coordination polymer \( \text{[Ni}_2\text{(bte)}_3(\gamma\text{-MoO}_3\text{S}_6)\text{]}\cdot5\text{H}_2\text{O}(\text{I}) \) \( \text{(bte}=1,2\text{-bis(1,2,4-triazol-1-yl)ethane}) \), has been synthesized under hydrothermal conditions and characterized by elemental analyses, thermogravimetric analysis (TGA) and single crystal X-ray diffraction. The crystal structure analysis indicates that in compound I, the bte ligands link the Ni(II) ions and construct a unique 2D metal-organic layer. The \( \gamma\text{-MoO}_3\text{S}_6\text{]}^{2-} \) anions show two different functions: (i) it acts as a structural directing agent embedding in the 2D metal-organic layer; (ii) it is functionalized by the bte ligands through Mo-N bonds for bridging this 2D metal-organic layer and finally inducing a 3D framework of I with the Schlüff symbol of \( \{3^2\cdot4^1\cdot5^4\cdot6^7\cdot7\} \{3^2\cdot4^1\cdot5^4\cdot6^7\} \). In addition, the electrochemical and fluorescence properties of the title compound have been studied. CCDC: 881771.

Key words: \( \gamma\text{-octamolybdate; metal-organic layer; fluorescence property; bis(triazole)-based ligand} \)

0 Introduction

Polyoxometalates (POMs)-based inorganic-organic hybrid materials have attracted extensive attention in the recent years owing to their versatile architectures and potential applications in catalysis, electrochemistry, biochemistry, photochemistry and magnetism[1-8]. As a remarkable member of POM family, octamolybdates are good candidates to generate various high dimensional frameworks with novel topologies[9-13]. Up to now, eight isomeric forms of octamolybdates (\( \alpha, \beta, \gamma, \delta, \varepsilon, \zeta, \eta \) and \( \theta \) isomers) have
been reported\cite{14-17}, which can be easily captured under hydrothermal conditions. Therefore, octamolybdates have been mostly employed as structural units to construct POM-supported metal-organic frameworks (MOFs) through linking transition metals and organic ligands. Especially, some of these isometric forms can connect with the pure N-containing organic ligands through Mo-N bonds. For example, the $\gamma$-Mo$_6$O$_{24}$$^-$ anion contains six MoO$_3$ units (six coordination sites) and two MoO$_3$ units (five coordination sites). The MoO$_3$ unit exposes the Mo ion with low coordination number and easily coordinates with pure N-containing organic ligands through Mo-N bonds, satisfying its steady six-coordinated mode. Currently, the reports on MOFs containing Mo-N bond are very limited. So it is worth for further studying.

As is known, the organic moiety plays an important role in constructing POM-based hybrid compounds. In previous reports, the exible N-containing ligands become the preferred candidates for the construction of novel intriguing structures and topologies due to their various coordination sites and flexibility, and some POM-based novel topological structures constructed by this kind of ligands have been obtained as expected\cite{18-20}. In the earlier work, we introduced the exible bis (triazole) ligands to the Mo$_6$O$_{24}$-Cu system and successfully obtained a series of organomolybdenum compounds containing Mo-N bonds\cite{25}.

In this work, we employed the metal Ni$^2+$ instead of Cu$^1$/Cu$^+$ for investigating whether the Mo$_6$O$_{24}$$^-$-Ni compounds also containing Mo-N bond can be obtained as expected. In addition, flexible 1, 2-bis (1,2,4-triazole-1-yl)-ethane (bte) (Scheme 1) was selected as exible ligand in this Mo$_6$O$_{24}$-Ni$^2+$ system. It contains four potential coordination sites and a shorter -(CH$_2$)$_2$ spacer, which may induce novel coordination forms. Fortunately, a new octamolybdate-based compound containing relatively rare Mo-N bond, [Ni$_2$(bte)$_2$($\gamma$-Mo$_6$O$_{24}$)] · 5H$_2$O (1), has been synthesized under hydrothermal conditions. The title compound exhibits a novel topology structure and good electrochemical and fluorescence properties.

![Scheme 1](image)

**Scheme 1** The 1, 2-bis(1, 2, 4-triazol-1-yl)-ethane (bte) molecule used in compound 1

### 1 Experimental

#### 1.1 General procedures

All chemicals were of reagent grade and used without further purification. Organic ligand bte was synthesized according to the literature method\cite{25}. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 240C elemental analyzer. Thermogravimetric analysis (TGA) was carried out in N$_2$ on a Pyris Diamond instrument with a heating rate of 10 °C · min$^{-1}$. A CHI 440 electrochemical workstation connected to a Digital-586 personal computer was used for the control of electrochemical measurement and data collection. A conventional three-electrode system was used. A saturated calomel electrode (SCE) was used as the reference electrode and a platinum wire as the counter electrode. The title compound chemically bulk-modified carbon paste electrode (1-CPE) was used as the working electrode. Fluorescence spectra were performed on a Hitachi F-4500 fluorescence/phosphorescence spectrophotometer at room temperature.

#### 1.2 Synthesis of [Ni$_2$(bte)$_2$($\gamma$-Mo$_6$O$_{24}$)] · 5H$_2$O (1)

A mixture of Na$_3$MoO$_4$·2H$_2$O (0.124 g, 0.51 mmol), NiCl$_2$·6H$_2$O (0.12 g, 0.50 mmol), bte (0.03 g, 0.19 mmol) and H$_2$O (10 mL) was stirred for 30 min and then sealed into a 20 mL Teflon-lined autoclave, kept at 160 °C for 3 d. After the autoclave cooled to room temperature over 12 h, light blue block-shape crystals of 1 were filtered off and washed with distilled water (36% yield based on Mo). Elemental analyses calcd. for C$_9$H$_{20}$Mo$_8$N$_8$Ni$_2$O$_{38}$: (\%): C: 16.28, H: 2.26, N: 18.99. Found (\%): C: 16.51, H: 2.08, N: 19.24. IR (solid KBr pellet, cm$^{-1}$): 1: 633.6(m), 1: 533.3(s), 1: 1433.0(m), 1: 1377.1(m), 1: 1288.4(s), 1: 1215.1(s), 1: 1134.1(s), 1: 1058.8(w), 1: 997.1(w), 1: 941.2(w), 1: 889.1(w), 1: 852.5(w), 1: 669.3(s).

#### 1.3 Preparation of 1-CPE

The bulk-modified carbon paste electrode of
compound 1 (1-CPE) was fabricated as follows[27]: 0.03 g of compound 1 and 0.5 g of graphite powder were mixed and grounded together by an agate mortar and pestle to achieve a uniform mixture, and then 0.18 mL of Nujol was added with stirring. The homogenized mixture was packed into a glass tube with a 3 mm inner diameter, and the tube surface was wiped with weighing paper. Electrical contact was established with a copper rod through the back of the electrode.

1.3 X-ray Crystallography

Crystallographic data for compound 1 was collected on a Bruker Smart 1000 CCD diffractometer with Mo Kα (λ = 0.071 073 nm) by ω and θ scan mode at 296 K. The structure of compound 1 was solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL [28]. Metal atoms were located from the E-maps, and other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F². Positions of the hydrogen atoms on carbon atoms were calculated theoretically. The H atoms of the water molecules were not included in the model because of the weak high-angle diffractions and the disorder of the water molecules[25-28]. A summary of the crystallographic data and structure refinements for compound 1 are given in Table 1. Selected bond lengths and angles are given in Table 2.

CCDC: 881771.

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<tr>
<th>Table 1</th>
<th>Crystal data and structure refinement for title complex</th>
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<tr>
<td>Empirical formula</td>
<td>C₃H₅Mn₂N₈O₂₈</td>
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<th>Table 2</th>
<th>Selected bond lengths (nm) and angles (°) for title complex</th>
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<tr>
<td>Ni(1)-O(7)</td>
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<td>Ni(2)-O(6)</td>
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<td>Mo(2)-N(15)</td>
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<td>Mo(2)-O(9)</td>
<td>0.188 0(6)</td>
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<td>O(7)-Ni(1)-N(13)</td>
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<td>N(13)-Ni(1)-N(13)</td>
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<td>N(13)-Ni(1)-N(4)</td>
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<td>O(6)-Ni(2)-N(12)</td>
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<td>N(11)-Ni(2)-N(11)</td>
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<td>N(11)-Ni(2)-N(12)</td>
<td>93.3(3)</td>
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<td>O(13)-Mo(2)-N(15)</td>
<td>95.1(3)</td>
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</table>

Symmetry codes: * -x+1, -y+1, -z+1; ** x-1, y, z; *** -x, -y+1, -z+1; **** -x+2, -y, -z; ***** x+1, y, z-1; ****** -x+1, -y, -z+1
2 Results and discussion

2.1 Description of the structure

Single crystal X-ray structural analysis reveals that the asymmetric structure unit contains a γ-[Mo₆O₃S₆]⁺ anion (abbreviated to γ-Mo₆), two Ni²⁺ ions and two types of bte ligands with different coordination modes (bte⁺ and bte⁻), as shown in Fig.1. The bte⁻ ligands exhibit “Z”-type conformation, linking two Ni²⁺ atoms through two apical N donors, while the bte⁺ ligands show “U”-type conformation. Moreover, the “U”-type bte⁺ ligands own two connection forms: i) linking two Ni²⁺ atoms through two apical N donors similar to that of “Z”-type bte⁻; ii) linking one Ni²⁺ atom and one Mo³⁺ atom of the γ-Mo₆ anion.

There are two crystallographically independent Ni²⁺ ions in compound 1. The NiI ion shows an octahedral coordination geometry {NiN₆O₆}, which is completed by four nitrogen atoms of four bte⁻ ligands, two terminal oxygen atoms of two γ-Mo₆ anions (Ni1-O7⁺=0.204 8(6) nm; Ni1-N4⁺=0.211 6(7) nm; Ni1-N13=0.208 1(7) nm). The Ni2 ion is also six-coordinated in an octahedron geometry {NiN₆O₆} by four nitrogen atoms of two bte⁺ ligands and two bte⁻ ligands, two terminal oxygen atoms of two γ-Mo₆ anions (Ni2-O6=0.207 8 (5) nm; Ni2-N11⁺=0.209 6(7) nm; Ni2-N12=0.213 0(8) nm). These bond distances are comparable to those in the six-coordinated Ni²⁺ compounds²⁸⁻²⁹

In compound 1, two “Z”-type bte⁻ ligands and four “U”-type bte⁺ ligands link six Ni²⁺ ions, inducing a special circle. These special circles link each other by sharing the Ni2 ions and construct a unique 2D metal-organic layer, as shown in Fig.2. The γ-Mo₆ anions embedded in these special circles through the Ni-O bonds, acting as a structural directing agent. In addition, the γ-Mo₆ anions are extended into an

H atoms were omitted for clarity. Symmetry codes: ⁺ −x+1, −y+1, −z+1; ² x−1, y, z; ³ −x, −y+1, −z+1; ⁴ −x+2, −y, −z; ⁵ x+1, y, z−1; ⁶ −x+1, −y, −z+1

Fig.1 (a) The ball-and-stick representation with 50% probability thermal ellipsoids of the structural unit in compound 1 and (b) coordination mode of γ-Mo₆O₃S₆ anion functionalized by bte⁺ ligand through Mo2-N15 bond
infinite 2D inorganic layer bridged by Ni1 and Ni2 atoms along the a axis.

Moreover, the γ-Mo₆ anions are functionalized by another “U”-type bte⁺ ligands through Mo-N bonds, which connect the adjacent 2D metal-organic layer into a 3D framework. In this compound, the γ-Mo₆ anion can be regarded as a six-connected inorganic node, which is coordinated by two pairs of crystallographically independent Ni1 and Ni2 ions through O7 and O6 atoms and a pair of bte⁺ ligands directly through N15 atoms. In order to simplify this framework, we consider the metal Ni1, Ni2 and γ-Mo₆ anions as nodes and a total topology of (6, 6, 6)-connected 3D MOF with the Schlafli symbol of \( \{3^2 \cdot 4^5 \cdot 5^3 \cdot 6^7\}\{3^2 \cdot 4^6 \cdot 5^5 \cdot 6\}_2 \) analyzed by OLEX program \(^{[3]}\) is constructed as shown in Fig.3. The 6-connected Ni1 node and the 6-connected γ-Mo₆ node possesses the same vertex symbols of \( 3^2 \cdot 4^6 \cdot 5^5 \cdot 6 \), while the 6-connected Ni2 node is \( 3^2 \cdot 4^8 \cdot 5^3 \cdot 6^2 \cdot 7 \).

2.2 Thermogravimetric analysis

The thermogravimetric analysis (TGA) of I was performed under N₂ atmosphere with a heating rate of 10 °C · min⁻¹ in the temperature range of 25–800 °C (Fig.4). The TG curve of compound I shows two distinct weight loss steps: The first weight loss step occurs below
250 °C, corresponding to the loss of water molecules. The second weight loss step in the range of 250–800 °C can be attributed to the decomposition of the ligands 37.12% (Calcld. 37.07%).

2.3 Electrochemical properties

The voltammetric behaviours of compound 1 bulk-modified carbon paste electrode (1-CPE) were carried out in the 0.1 mol·L⁻¹ H₂SO₄ aqueous solution at different scan rates. The cyclic voltammetry for 1-CPE at different scan rates is presented in the potential range of +800 to −210 mV (Fig. 5a). There exhibit three reversible redox peaks I-I', II-II' and III-III' with the mean peak potentials \(E_{1/2}=(E_{pa}+E_{pc})/2\) of approximate +295, +156, and −82 mV, respectively, which can be attributed to the redox of the [Mo₆O₃₆]⁴⁻ anion[9]. With increasing of scan rates, the cathodic peak potentials shift to the negative direction and the corresponding anodic peak potentials shift to the positive direction. It can be seen that the peak currents are proportional to the scan rates up to 500 mV·s⁻¹, which indicates that the redox process of the 1-CPE is surface-controlled (Fig.5b).

It’s well known that direct electroreduction of nitrite requires a large overpotential[32] at most electrode surfaces and no obvious response was observed for nitrite at the bare CPE in the potential range of +800 to −210 mV in 0.1 mol·L⁻¹ H₂SO₄ aqueous solution. In this work, the 1-CPE (scan rate: 200 mV·s⁻¹) displayed good electrocatalytic activity toward the reduction of nitrite. At the 1-CPE, with addition of nitrite, all three reduction peak currents gradually increase, while the corresponding oxidation peak currents decrease, indicating that 1-CPE shows good electrocatalytic activity toward the reduction of nitrite.

2.4 Fluorescence property

The fluorescence properties of compound 1 and the free ligand bte were investigated in the solid state at room temperature (Fig.6). The maximal emission peak of compound 1 was observed at about 403 nm \((\lambda_{ex}=270\) nm), whereas the bte at 387 nm \((\lambda_{ex}=300\) nm). The significant red shift of the emission observed in 1 might be attributed to a change in the highest occupied molecular orbital and lowest unoccupied molecular orbital energy levels of γ-Mo₆ anions and neutral ligands coordinating to metal centers, or assigned to the ligand-to-metal charge-transfer (LMCT) band[30].
3 Conclusions

In summary, a new 3D MOF with the Schl"afli symbol of $[3^2 \cdot 4^4 \cdot 5^4 \cdot 6^2 \cdot 7]$ $[3^2 \cdot 4^4 \cdot 5^4 \cdot 6]$ has been isolated successfully under hydrothermal conditions. In the title compound, the $\gamma$-Mo$_6$ anion not only acts as a structural directing agent embedding in the 2D metal-organic layer, but also acts as the bridging unit functionalized by the bte ligands through Mo-N bonds. The electrochemical and fluorescence properties indicate that the title compound is an excellent electrocatalytic and luminescent material.

References: