

Synthesis, Crystal Structure, and Thermal Stability of $[\text{Mo}_2\text{O}_4(\mu_2\text{-O})(\text{C}_6\text{H}_4\text{O}_2)_2(\text{H}_2\text{O})] \cdot (\text{C}_8\text{H}_9\text{N}_2)_2 \cdot 2\text{H}_2\text{O}^1$

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Abstract—From hydrothermal treatment of benzene-1,2-diamine, pyrocatechol, and MoO_3 in acetic acid solution, a new compound, $[\text{Mo}_2(\mu_2\text{-O})_2(\text{C}_6\text{H}_4\text{O}_2)_2(\text{H}_2\text{O})] \cdot (\text{C}_8\text{H}_9\text{N}_2)_2 \cdot 2\text{H}_2\text{O}$ (**I**), constructed from pyrocatechol chelated dinuclear molybdenum units and 2-methylbenzimidazole has been synthesized. Single-crystal structure analysis reveals that the compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 23.365(2)$, $b = 7.2214(5)$, $c = 19.3021(16)$ Å, $\beta = 97.929(4)$, $V = 3225.6(5)$ Å³, $Z = 4$, $M = 808.46$, $\rho_c = 1.665$ g/cm³, $\mu(\text{MoK}\alpha) = 0.84$ mm⁻¹, $F(000) = 1608$, the final $R = 0.0622$ and $wR = 0.1484$ for 7385 independent reflections with $R_{\text{int}} = 0.0393$. Interestingly, an in situ condensation between acetic acid and benzene-1,2-diamine has occurred, and the unexpected 2-methyl-1-H-benzo[d]imidazoles serve as counterions and N–H donors to form stable hydrogen-bond network in the crystal. Furthermore, intermolecular hydrogen bonds are found among the cations, anions and crystalline water molecules. The double nuclear molybdenum units are connected by O–H...O hydrogen bonds with the crystalline water molecules to form one-dimensional chains, and the chains are further joined together by N–H...O to form a quasi-two dimensional structure.

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INTRODUCTION

In the past few years, the research on hybrid molecular materials has grown into an attractive subject in inorganic chemistry for their structural diversity, fascinating properties and potential applications [1–4]. In this research field, catecholate-coordinated molybdenum compounds, a class of molecular materials, have aroused much interests for their structure similarity to the oxo-transfer enzymes and potential applications in catalysis, DNA cleavage and so on [4–8].

As far as the molecular structure of catecholate is concerned, it has several favorable factors in the preparation of hybrid molecular materials. Firstly, the steric geometry and activity of the center metals can be modulated by two hydroxyl groups at the *ortho* position via chelated coordination [9]. Secondly, the catecholate molecules can effectively control the self-condensation of the anions which are tend to form complex structures, such as atomic clusters [7, 10]. Thirdly, the lone pair electrons in the oxygen atoms of the hydroxyl groups make it possible to form large amounts of hydrogen bonds which are favorable for selective catalysis and separation. Besides, the aromatic rings can serve as antenna for photon receiving and emission in the hybrid molecular materials with fascinating optical property.

Here MoO_3 , catecholate, and *o*-phenylenediamine were selected as reaction substrates for the preparation of new molybdenum base hybrid molecular materials in a hydrothermal process. In the reaction system, acetic acid was used to modulate the pH values, while *o*-phenylenediamine was designed to be used as structure directing reagents and counter ions. Interestingly, 2-methylbenzimidazoles, unexpected species coming from in situ condensation of *o*-phenylenediamine with acetic acid were found in the crystal structure. Furthermore, the pyrocatechol controlled the self-condensation of MoO_4^{2-} into clusters and resulted in the formation of di-nuclear molybdenum subunits. Thirdly, there are two kinds of hydrogen bonds as O–H...O and N–H...O make the subunits orderly organized into a quasi-2-dimensional structure.

EXPERIMENTAL

Materials and instruments. All starting materials were purchased commercially and used as received without further purification. IR spectrum (KBr pellets) was recorded on a Magna 750 FT-IR spectrometer in the range of 400–4000 cm⁻¹. Elemental analysis was carried out on an Elementar Vario EL III elemental analyzer. Thermogravimetric analysis (TGA) was performed on a NETSCHZ STA-449C thermoanalyzer from 30 to 1200°C with a heating rate of 10°C/min in flowing air.

¹ The article is published in the original.

Synthesis of $[\text{Mo}_2\text{O}_4(\mu_2\text{-O})(\text{C}_6\text{H}_4\text{O}_2)_2(\text{H}_2\text{O})] \cdot (\text{C}_8\text{H}_9\text{N}_2)_2 \cdot 2\text{H}_2\text{O}$ (I). In a typical synthesis, MoO_3 (0.1 g), benzene-1,2-diamine (0.1 g), pyrocatechol (0.1 g), and H_2O (13 mL) were mixed in a 23 mL Teflon-lined stainless steel autoclave. After stirring for a few minutes, the pH value was modulated to 4.3 with acetic acid, and then the autoclave was sealed, heated to 180°C , and maintained at the temperature for 5 days. After the reactor was cooled down to room temperature at a rate of $5^\circ\text{C}/\text{h}$, red-brown crystals suitable for X-ray structure analysis were separated by filtration and dried naturally (86% yield based on molybdenum).

For $\text{C}_{28}\text{H}_{32}\text{N}_4\text{O}_{12}\text{Mo}_2$ (I)

anal. calcd., %: C, 41.25; H, 4.02; N, 6.77.

Found, %: C, 41.66; H, 3.97; N, 6.94.

IR (ν , cm^{-1}): 3426 m, 3060 w, 1629 m, 1575 m, 1477 s, 1257 s, 1104 w, 1020 w, 905 s, 814 s, 738 s, 624 s.

X-ray structure determination. A red brown single crystal with dimensions of $0.32 \times 0.29 \times 0.06$ mm was selected and mounted on a glass fiber for structure determination. X-ray diffraction data were collected on a Bruker Smart CCD diffractometer equipped with graphite-monochromated MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$) in the range of $3.02^\circ \leq \theta \leq 27.48^\circ$ at 293 K. An empirical absorption correction was applied using the SADABS program [11]. The crystal structure was solved by direct methods with SHELXS-97 program [12], and refined by full-matrix least-squares techniques on F^2 with SHELXL-97 software package [13]. All non-hydrogen atoms were refined anisotropically. The position of the hydrogen atoms were generated geometrically, refined with isotropic thermal parameters, and allowed to ride on their parent atoms before the final cycle of refinement. For I, the final $R = 0.0622$, $wR = 0.1484$ ($w = 1/[\sigma^2(F_o^2) + (0.0697P)^2 + 7.0167P]$, where $P = (F_o^2 + 2F_c^2)/3$) based on 6419 reflections with $I > 2\sigma(I)$, $S = 1.081$ and $(\Delta/\sigma)_{\text{max}} = 0.001$.

A summary of the crystallographic data and structure refinement is shown in Table 1, the selected bond distances and bond angles are listed in Table 2, and the hydrogen bond lengths and bond angles are given in Table 3.

Supplementary material for structure I has been deposited with the Cambridge Crystallographic Data Centre (no. 819677; deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

RESULTS AND DISCUSSION

The crystal structure of I is built up of pyrocatechol coordinated di-nuclear molybdenum anions, protonated 2-methylbenzimidazole cations, and lattice water molecules (Fig. 1). In terms of the anions, both of the metal atoms are in octahedral geometry. The

Table 1. Crystallographic data and experimental details for complex I

| Parameter | Value |
|--|--|
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| a , \AA | 23.365(2) |
| b , \AA | 7.2214(5) |
| c , \AA | 19.3021(16) |
| α , deg | 90.00 |
| β , deg | 97.929(4) |
| γ , deg | 90.00 |
| V , \AA^3 | 3225.6(5) |
| Z | 4 |
| ρ_{calcd} , g cm^{-3} | 1.665 |
| Crystal size, mm | $0.32 \times 0.29 \times 0.06$ |
| $F(000)$ | 1632 |
| $\mu(\text{MoK}_\alpha)$, mm^{-1} | 0.84 |
| θ Range for data collection, deg | 3.02 to 27.48 |
| Index range h, k, l | $-30 \leq h \leq 23, -9 \leq k \leq 9, -25 \leq l \leq 25$ |
| Type of scan | ω scans |
| Reflections collected | 24 100 |
| Independent reflections (R_{int}) | 7385 (0.0393) |
| Reflections with $I > 2\sigma(I)$ | 6419 |
| Number of parameters | 415 |
| Goodness-of-fit on F^2 | 1.081 |
| Final R_1, wR_2 ($I > 2\sigma(I)$)* | $R_1 = 0.0622, wR_2 = 0.1484$ |
| R_1, wR_2 (all data)** | $R_1 = 0.0745, wR_2 = 0.1575$ |
| $\Delta\rho_{\text{max}}$ and $\Delta\rho_{\text{min}}$, $e \text{ \AA}^{-3}$ | 0.889 and -0.658 |

* $R = \Sigma(F_o - F_c)/\Sigma(F_o)$, ** $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma(F_o^2)^2\}^{1/2}$.

Table 2. Selected bond lengths (Å) and bond angles (deg) for complex I

| Bond | <i>d</i> , Å | Bond | <i>d</i> , Å | Bond | <i>d</i> , Å |
|---------------|--------------|---------------|--------------|----------------|--------------|
| Mo(1)–O(4) | 1.694(4) | Mo(1)–O(8) | 2.140(3) | Mo(2)–O(3) | 1.930(3) |
| Mo(1)–O(5) | 1.728(4) | Mo(1)–O(7) | 2.329(3) | Mo(2)–O(6) | 1.961(4) |
| Mo(1)–O(3) | 1.948(3) | Mo(2)–O(2) | 1.705(4) | Mo(2)–O(7) | 2.116(3) |
| Mo(1)–O(9) | 1.975(4) | Mo(2)–O(1) | 1.714(4) | Mo(2)–O(10) | 2.506(4) |
| Angle | ω, deg | Angle | ω, deg | Angle | ω, deg |
| O(4)Mo(1)O(5) | 102.11(18) | O(4)Mo(1)O(7) | 166.16(16) | O(3)Mo(2)O(6) | 148.03(15) |
| O(4)Mo(1)O(3) | 97.61(17) | O(5)Mo(1)O(7) | 86.47(15) | O(2)Mo(2)O(7) | 101.69(17) |
| O(5)Mo(1)O(3) | 102.78(17) | O(3)Mo(1)O(7) | 69.67(12) | O(1)Mo(2)O(7) | 153.97(18) |
| O(4)Mo(1)O(9) | 102.53(18) | O(9)Mo(1)O(7) | 87.74(14) | O(3)Mo(2)O(7) | 74.83(13) |
| O(5)Mo(1)O(9) | 92.51(17) | O(8)Mo(1)O(7) | 79.27(13) | O(6)Mo(2)O(7) | 76.07(14) |
| O(3)Mo(1)O(9) | 151.53(15) | O(2)Mo(2)O(1) | 104.3(2) | O(2)Mo(2)O(10) | 175.15(17) |
| O(4)Mo(1)O(8) | 94.11(17) | O(2)Mo(2)O(3) | 98.60(18) | O(1)Mo(2)O(10) | 80.51(17) |
| O(5)Mo(1)O(8) | 161.86(16) | O(1)Mo(2)O(3) | 102.65(17) | O(3)Mo(2)O(10) | 79.50(13) |
| O(3)Mo(1)O(8) | 82.81(14) | O(2)Mo(2)O(6) | 99.99(18) | O(6)Mo(2)O(10) | 79.82(13) |
| O(9)Mo(1)O(8) | 75.92(15) | O(1)Mo(2)O(6) | 97.67(18) | O(7)Mo(2)O(10) | 73.53(13) |

Table 3. Geometric parameters of hydrogen bonds for I*

| Contact D–H...A | Distance, Å | | | Angle DHA, deg |
|----------------------------------|-------------|-------|----------|----------------------|
| | D–H | H...A | D...A | |
| O(1w)–H(1wA)···O(5) ^a | 0.96 | 1.96 | 2.904(5) | 168 |
| O(1w)–H(1wB)···O(8) ^b | 0.96 | 1.85 | 2.798(5) | 168 |
| O(2w)–H(2wA)···O(1) ^c | 0.96 | 1.83 | 2.789(7) | 179 |
| O(2w)–H(2wB)···O(2) ^d | 0.96 | 1.94 | 2.898(7) | 179 |
| O(10)–H(10B)···O(5) ^e | 0.85 | 2.02 | 2.764(5) | 146 |
| N(1)–H(1B)···O(2w) | 0.86 | 1.92 | 2.746(7) | 161 |
| N(2)–H(2B)···O(3) | 0.86 | 1.90 | 2.751(5) | 169 |
| N(3)–H(3B)···O(1w) | 0.86 | 1.94 | 2.769(6) | 161 |
| N(4)–H(4A)···O(10) | 0.86 | 2.00 | 2.797(6) | 154 |

* Symmetry transformations used to generate the equivalent atoms:
^a $x, -y + 3/2, z + 1/2$; ^b $x, -y + 1/2, z + 1/2$; ^c $-x + 1, -y + 1, -z + 1$; ^d $-x + 1, -y + 2, -z + 1$; ^e $x, y - 1, z$.

Mo(1) atom is coordinated by six oxygen atoms, including two terminal oxygen atoms (O(4), O(5)), O(8) and O(9) atoms provided by a pyrocatechol, O(7) atom from another pyrocatechol, and O(3) sharing with the Mo(2) atom. The Mo(2) atom is also coordinated by six oxygen atoms, including O(1) and O(2) as terminal atoms, O(6) and O(7) from the pyrocatechol, O(3) sharing with the Mo(1) atom, and an oxygen O(10) provided by the coordinated water. The two MoO₆ octahedrons are sharing a common edge constructed by O(7) from a pyrocatechol and μ₂-O(3).

Apart from static electronic interactions among the anions and cations, abundant hydrogen bonds are found to link the subunits from different directions. As listed in Table 2, there are two kinds of hydrogen bonds as O–H...O and N–H...O that make the subunits orderly organized. Typical O–H...O hydrogen bonds are shown in Fig. 2 and the H atoms are omitted for clarity. Firstly, the lattice water molecules marked as O(2w) are serving as double hydrogen donors to form hydrogen bonds with terminal oxygen atoms O(5) and O(8) from neighboring anions. Secondly, another kind of lattice water molecules marked as O(1w) are also serving as double hydrogen donors to form hydrogen bonds with O(3) donated by the catechol molecules

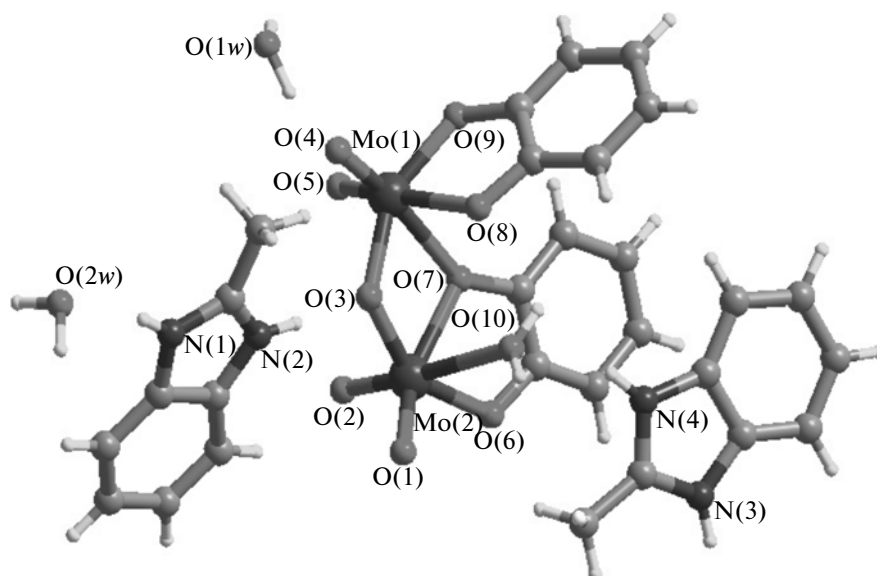


Fig. 1. Molecular structure of compound I.

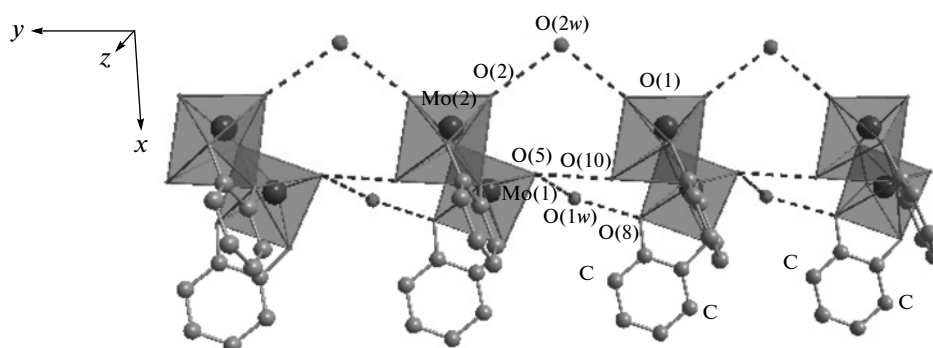


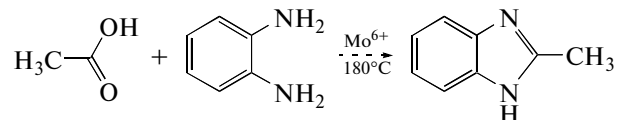
Fig. 2. One-dimensional assembly of the catechol-Mo subunits via O–H...O hydrogen bonds.

and terminal oxygen atoms O(5) from neighboring anions. Furthermore, the H₂O molecules coordinate to the Mo(2) atoms marked as O(10) also donate hydrogen atoms to form O–H...O hydrogen bonds with the terminal oxygen atoms marked as O(5) from neighboring anions. These three types of O–H...O hydrogen bonds make pyrocatechol coordinated dinuclear molybdenum anions orderly aligned along the (010) direction.

In terms of the O–H...O hydrogen bonds, the two protonated 2-methylbenzimidazole cations are both serve as double hydrogen bonds donors in the crystal structure with N...O distances ranging from 2.746(7) to 2.797(6) Å. As show in Fig. 3a, the N(1) atoms of 2-methylbenzimidazoles are connecting with lattice water molecules (marked as O(2w)), while the N(2) atoms are linked with the μ₂-O(3) atoms. However, in Fig. 3b the nitrogen atoms of the 2-methylbenzimidazole are connected with one lattice water (O(1w)) and the coordinated H₂O molecules (O(10)). A quasi-two

dimensional array of the separated subunits connected by N–H...O hydrogen bonds is presented in Fig. 4.

Notably, there are no 2-methylbenzimidazoles but *o*-phenylenediamines were used as substrates in the preparation of compound I. The appearance of 2-methylbenzimidazoles in the products indicates an in situ reaction occurred in the hydrothermal procedure. The unexpected species may originate from the condensation between the *o*-phenylenediamine and the acetic acid under autogenous pressure at 180°C:



Once the reaction was carried out in absent of molybdenum, no crystals can be found. In previous reports, such condensation usually occurred in presence of polyphosphoric acid. The polyphosphoric acid can effectively promote the condensation reaction by re-

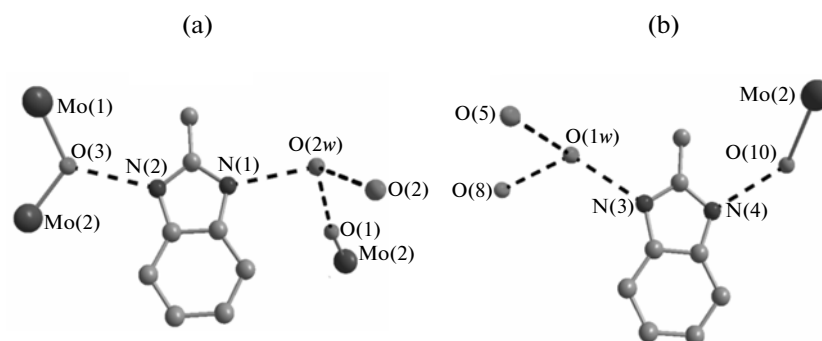


Fig. 3. Typical N–H...O hydrogen bonds in complex I.

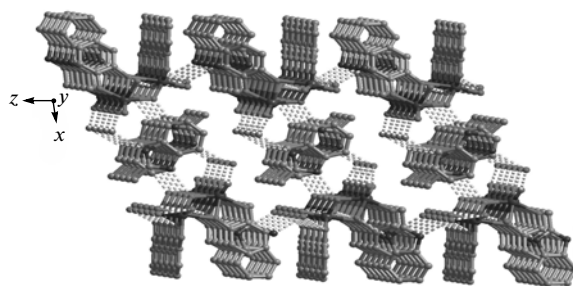


Fig. 4. Projection of compound I along the *y* axis.

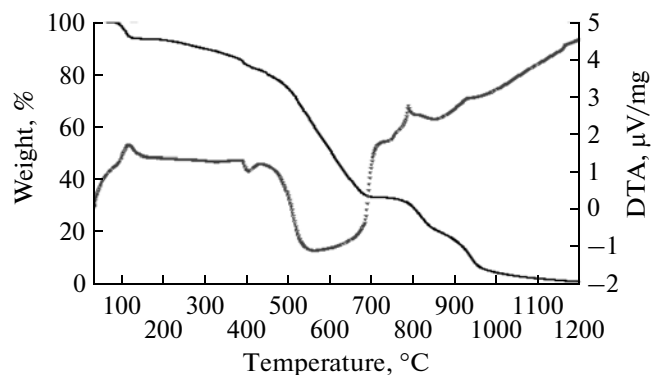


Fig. 5. TG–DTA curve of compound I in flowing air at a rate of 10°C/min.

moving the water molecules yield during the reaction [14, 15]. However, just limited research on the condensation carried out in aqueous solution has been reported [16, 17]. Recently, Liu reported an example on in situ formation of 2-methylbenzimidazoles while preparing zincophosphite [17]. Though these researches have been carried out, just little knowledge on the formation mechanism has been obtained. Here, it is speculated that the protons and molybdenum species in the solution should be responsible for the effective condensation. Although further researches are still demanded to clarify the formation mechanism of the 2-methylbenzimidazoles, this research may provide a new and effective pathway for the

preparation and separation of 2-methylbenzimidazoles in aqueous solution.

TGA of compound I was conducted in flowing air when I was heated to 1200°C at a rate of 10°C/min (Fig. 5). The first-stage weight loss from 95 to 120°C is 4%, which corresponds to the removal of the lattice water (calcd. 4.46%). The weight loss from 200 to 700°C is complicated and can be ascribed to the damage of the organic coordinates and elimination of the coordinated water molecules. The residue at 700°C is 34.5%, which is in consistent with the content of MoO₃ (calcd. 35.4%). The gradual weight loss from 800 to 1200°C may be caused by the evaporation

of MoO₃ for its low melting point (795°C) and sublimation temperature (900–1100°C).

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