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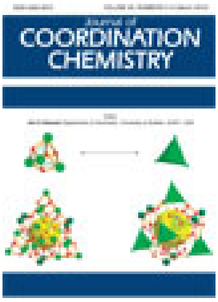

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In situ synthesis of an inorganic–organic hybrid based on a molybdenum-oxo chain: $[Cu_2(pz)(Mo_3O_{10})]_n$

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A polyoxomolybdate, $[Cu_2(pz)(Mo_3O_{10})]_n$ (pz = pyrazine) (**1**), has been synthesized hydrothermally and characterized by elemental analysis, IR, X-ray photoelectron spectra, and thermogravimetric analysis. Single-crystal X-ray diffraction demonstrates that **1** has a 3-D architecture constructed by combination of $\{Mo_3O_{10}\}$ units and $[Cu_2(pz)]^{2+}$. All the terminal oxygen atoms of the polyoxomolybdate are coordinated by univalent copper. Pyrazine came from *in situ* decarboxylation of 2-pyrazinecarboxylic acid and Cu^+ from the *in situ* reduction of Cu^{2+} during the hydrothermal synthesis.

Keywords: Polyoxomolybdate; *In situ* reaction; Decarboxylation; Deoxidization

1. Introduction

Polyoxomolybdates have attracted particular interest because of their robust clusters of different sizes, topologies, and oxidation states [1–3]. Progress has been made in understanding molybdenum polyoxoanion clusters, organic components, and appropriate secondary metals [4–12]. In molybdenum-oxo clusters, Mo adopts a distorted $\{MoO_6\}$ octahedral geometry and infinite chains of $\{MoO_6\}$ octahedra linked through corner-, edge-, and/or face-sharing octahedra construct different molybdenum polyoxoanions, e.g., $\{Mo_2O_7\}$ [13], $\{Mo_3O_{10}\}$ [14], $\{Mo_5O_{18}\}$ [15], $\{Mo_6O_{20}\}$ [16], $\{Mo_7O_{24}\}$ [17], $\{Mo_8O_{26}\}$ [14] are common asymmetric units in low nuclear polyoxomolybdenum building blocks. However, in most cases few terminal oxygen atoms bond with other metalloligand units. Therefore, most compounds of these building blocks are low-dimensional (1-D, 2-D) or supramolecules instead of 3-D networks. For example, Zhang *et al.* reported a series of molybdenum polyoxometalate compounds containing M–L units $[M^{II}(HL)_2(Mo_3O_{10})]$ ($M = Mn, Co, Ni$; L = [3-(2-pyridyl)pyrazole]) which have an isostructural wavelike chain structure [14].

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Kong's $[Cu(4,4'\text{-bipy})(H_2O)(Mo_3O_{10})]\cdot H_2O$ showed a 3-D framework with only one terminal oxygen of each $\{Mo_3O_{10}\}$ bound with metalloligand [18].

In this article, we report a 3-D organic–inorganic hybrid $[Cu_2(pz)(Mo_3O_{10})]_n$ (**1**) based on a molybdenum-oxo chain *via* self-assembly of {Cu–pz} and $\{Mo_3O_{10}\}$ cluster under hydrothermal conditions. This structure has six terminal oxygen atoms of each $\{Mo_3O_{10}\}$ all coordinated with {Cu–pz} groups to form a 3-D framework. *In situ* decarboxylation of 2-pyrazinecarboxylic acid and *in situ* reduction of Cu^{2+} occurred during hydrothermal synthesis.

2. Experimental

2.1. *Materials and methods*

All reagents were purchased from commercial sources and used without purification. C, H, and N analyses were performed on a Perkin-Elmer 2400 C elemental analyzer. Infrared (IR) spectra were recorded on a Nicolet Nexus 870 FT-IR spectrometer using KBr pellets from 4000 to 400 cm^{-1}. Thermogravimetric (TG) analysis was performed on a TGA Q50 instrument under nitrogen with a heating rate of 10°C min^{-1}. X-ray photoelectron spectra (XPS) were performed on a VG Escalabmkll spectrometer (UK) with an Al-Kα ($h\nu = 1486.7$ eV) achromatic X-ray source.

2.2. *Synthesis of* $[Cu_2(pz)(Mo_3O_{10})]_n$ *(1)*

A solution of $Cu(CH_3COO)_2\cdot 3H_2O$ (0.2 mmol, 39.9 mg), 2-pyrazinecarboxylic acid (0.1 mmol, 12.4 mg), $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.1 mmol, 123.6 mg), and H_2O (8 mL) was stirred for 30 min in air and the pH was adjusted to 4 with 1 $molL^{-1}$ HCl. The resulting solution was sealed in a 15-mL Teflon-lined reactor, heated at 160°C for 3 days, and then cooled to room temperature. Dark needle crystals of **1** were obtained by filtration, washed with distilled water, and dried in air. Yield: 20% (based on $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$). Anal. Calcd (%): C, 7.32; H, 0.61; N, 4.27. Found (%): C, 7.46; H, 0.64; N, 4.4.

2.3. *X-ray crystallography*

The structure of **1** was determined by single-crystal X-ray diffraction with data collected on a Bruker APEX-II CCD detector with Mo-Kα radiation ($\lambda = 0.71073$ Å) at 298(2) K in the range $2.29° < \theta < 25.50°$. The structure was solved by direct methods and refined using full-matrix least-squares calculations with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were geometrically fixed to allow riding on the parent atoms to which they are attached. All calculations were performed with SHELXTL-97 program package [19]. Further details for structural analysis are summarized in table 1. Selected bond lengths and angles are listed in table 2.

Table 1. Crystallographic data and structure refinement for **1**.

Empirical formula	$C_4H_4Cu_2Mo_3N_2O10$
Formula weight	654.99
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	*Pnma*
Unit cell dimensions (Å, °)	
a	12.3934(1)
b	7.6160(9)
c	12.7958(15)
Volume (Å^3), *Z*	1207.8(2), 4
Calculated density (Mg m^{-3})	3.602
Absorption coefficient (mm^{-1})	6.548
F(000)	1224
θ range for data collection (°)	2.29–25.50
Limiting indices	$-14 \le h \le 13$; $-9 \le k \le 9$; $-15 \le l \le 6$
Reflections collected	4737
Independent reflections	1143 [*R*(int) = 0.0613]
Completeness to $\theta = 25.50$ (%)	99.8
Refinement method	Full-matrix least-squares on F^2
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0247$, $wR_2 = 0.0600$
Largest difference peak and hole (e Å^{-3})	1.073 and −0.970

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Cu(1)–N(1)	1.988(5)	Mo(1)–O(2)#5	1.935(3)
Cu(1)–O(4)	2.026(4)	Mo(1)–O(2)	1.935(3)
Cu(1)–O(6)#1	2.087(3)	Mo(1)–O(3)	2.200(4)
Cu(1)–O(6)#2	2.087(3)	Mo(1)–O(1)	2.209(4)
Cu(2)–O(5)#3	1.975(4)	Mo(2)–O(6)	1.720(3)
Cu(2)–O(7)	1.999(3)	Mo(2)–O(7)	1.727(3)
Cu(2)–O(7)#4	1.999(3)	Mo(2)–O(3)#6	1.9558(9)
Cu(2)–N(2)	2.080(5)	Mo(2)–O(1)	1.9654(9)
Mo(1)–O(5)	1.726(4)	Mo(2)–O(2)#6	2.188(3)
Mo(1)–O(4)	1.729(4)	Mo(2)–O(2)	2.203(3)
N(1)–Cu(1)–O(4)	131.25(17)	O(4)–Cu(1)–O(6)#1	97.96(11)
N(1)–Cu(1)–O(6)#1	113.59(12)	N(1)–Cu(1)–O(6)#2	113.59(12)

Symmetry codes for **1**: #1 $x - 1/2, y, -z + 1/2$; #2 $x - 1/2, -y + 3/2, -z + 1/2$; #3 $-x + 1/2, -y + 1, z - 1/2$; #4 $x, -y + 1/2, z$; #5 $x, -y + 3/2, z$; #6 $-x + 1, -y + 1, -z + 1$.

3. Results and discussion

3.1. *Description of structure*

Dark needle crystals of **1** were obtained by hydrothermal reaction of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, $Cu(CH_3COO)_2 \cdot 3H_2O$, and 2-pyrazinecarboxylic acid in water at 160°C for 3 days. X-ray single-crystal diffraction measurement show that **1** crystallizes in the orthorhombic system, space group *Pnma*. As shown in figure S1, the asymmetric unit consists of two crystallographically unique Cu^+ ions, one pyrazine, and one $(Mo_3O_{10}^{2-})$ polyoxoanion.

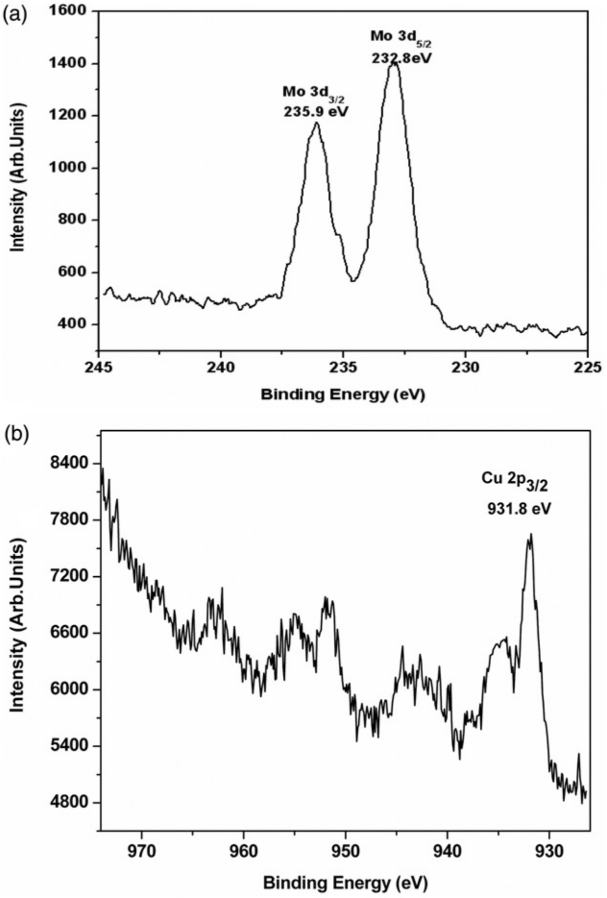


Figure 1. (a) The XPS spectra for Mo in **1**; (b) the XPS spectra for Cu in **1**.

Three distorted $\{MoO_6\}$ octahedra form a $(Mo_3O_{10})^{2-}$ building block further connected *via* corner/edge-sharing oxygen atoms to give an infinite zigzag inorganic chain $[(Mo_3O_{10})^{2-}]_n$ along the *ab*-direction (figure S2). The oxygen atoms can be divided into two groups: O_a (the terminal oxygen atoms connecting the Cu and Mo) and O_b (the bridging oxygen atoms between neighboring Mo's). Relevant Mo–O bond lengths are 1.720(3)–1.729(4) Å for Mo–O_a and 1.935(3)–2.188(3) Å for Mo–O_b, respectively. The O–Mo–O bond angles are in the range 73.60(13)–160.12(13)°.

The two crystallographically independent copper centers exhibit the same coordination (figure S1). The distance between copper ions is 4.268 Å. Three oxygen atoms from $(Mo_3O_{10})^{2-}$ and one N from pyrazine construct a four-coordinate "tetrahedral" geometry (N1, O4, O6A, and O6B for Cu1; N2, O5A, O7A, and O7 for Cu2) with Cu–N = 1.988(5)–2.080(5) Å and Cu–O = 1.975(4)–2.087(5) Å. The L–Cu–L (L = N, O) angles are in the range 96.13(16)–131.25(3)°. The coordination symmetry of copper ions in the title compound indicates that the oxidation state of Cu is monovalent, Cu^+ with d^{10} configuration tending to form tetrahedral coordination complexes. This is also confirmed by bond-valence calculations (table S1) and XPS analysis (figure 1).

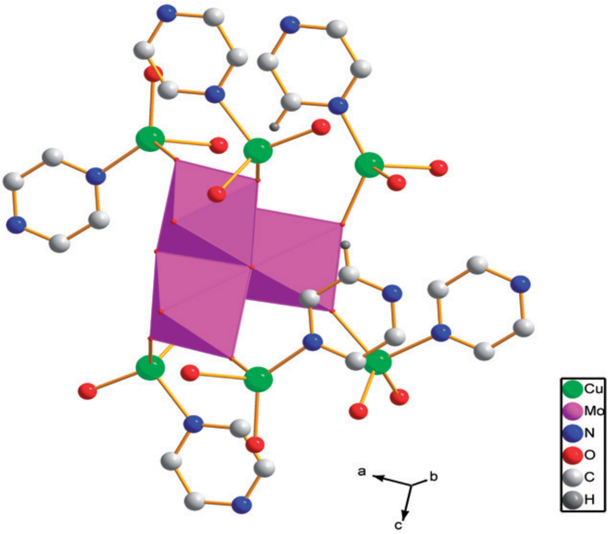


Figure 2. Coordination of $(Mo_3O_{10})^{2-}$ and {Cu–pz}.

Each $(Mo_3O_{10})^{2-}$ functions as a μ_6-ligand to coordinate to six {Cu–pz} units through its terminal oxygen atoms (figure 2), while {Cu–pz} units can be viewed as a μ_2-metalloligand to further link neighboring $[(Mo_3O_{10})^{2-}]_n$ chains. As a result, a 3-D inorganic–organic hybrid architecture is formed (figure 3). Here all six terminal oxygen atoms attached to Mo in $(Mo_3O_{10})^{2-}$ are coordinated with Cu, different from that observed in $[Cu(4,4'\text{-bipy})(H_2O)(Mo_3O_{10})] \cdot H_2O$ [18]. Further investigation shows that close C2–H2 $\cdots \pi$ interactions exist between neighboring pyrazine ring with the distance of 3.891 Å, which might consolidate the structure (figure S3).

Since the starting material we used is 2-pyrazinedicarboxylic acid, not the resultant pyrazine, the *in situ* decarboxylation reaction occurred in our experiment. Decarboxylation cannot easily happen under routine synthetic conditions except for some special aryl carboxylic acid or the presence of certain catalysts [20]. However, it seems not so difficult under hydrothermal conditions. For example, the *in situ* decarboxylation of the 3,4-pyridinedicarboxylic acid could generate isonicotinic acid [20]; the decarboxylation of 2,3-pyrazinedicarboxylic acid or 2,5-pyrazinedicarboxylic acid gave nicotinic acid [21], and the 2,3-pyrazinedicarboxylic acid lost all its carboxyl groups to turn into pyrazine [22]. Here in this work, the *in situ* decarboxylation of 2-pyrazinedicarboxylic acid loses its carboxyl groups and produces pyrazine under hydrothermal conditions. We surmise that the resulting pyrazine is an effective reducing agent for Cu^{2+} to Cu^{+} (scheme 1). Though we have replaced copper salt with other transition metal ions, we failed to harvest similar compounds. These results indicate that Cu(II) plays a unique role in this reaction system to stimulate the decarboxylation, also reported in other literature [23–25]. A previous report states that high oxidation-state metals are reduced by organic amines under hydrothermal conditions [26].

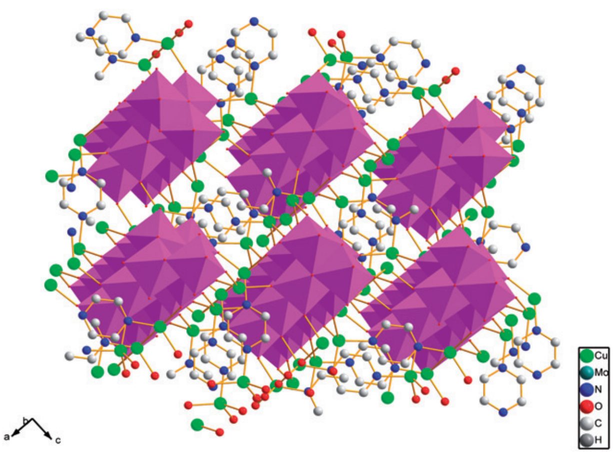
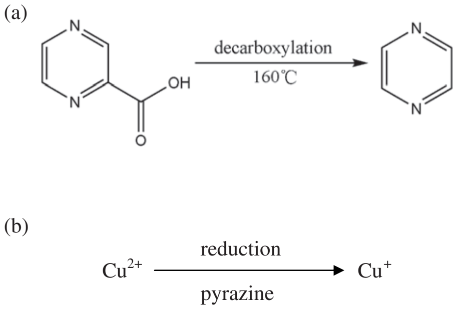


Figure 3. The 3-D structure of **1** along the *ac*-plane, and the polyhedra represent $\{MoO_6\}$ units.



Scheme 1. (a) Pyrazine, formed *via* decarboxylation of 2-pyrazinecarboxylic acid; (b) Cu^+, formed *via* reduction of Cu^{2+}.

3.2. *IR, XPS, and TG analysis*

IR spectrum of **1** using KBr pellet exhibits intense bands at 503, 668 cm^{-1} and 791, 848, 864, 906 cm^{-1} assigned to ν-(Mo–O–Mo) and ν-(Mo=O), respectively [27], and bands at 1156, 1419, and 2360 cm^{-1} assigned to vibration modes of pyrazine [28] (figure S4).

The assignment of formal charges on the metal ions was made by charge balance considerations for the entire compound, combining with bond valence sum. The results indicate that the average oxidation states of Mo and Cu are 5.961 and 1.495 in **1** (table S1) [29, 30]. As shown in figure 1, the XPS spectrum of **1** exhibits two overlapped peaks at 232.8 eV and 235.9 eV, attributable to Mo^{6+} ($3d_{5/2}$) and Mo^{6+} ($3d_{3/2}$) (figure 1a) [31], and one peak at 931.8 eV, attributed to Cu^+ ($2p_{3/2}$) (figure 1b) [32], respectively. So the oxidation states of all Mo and Cu atoms are +6 and +1, respectively, in agreement with the results of the structure determination.

TG analyses of **1** were performed in flowing N_2 with a heating rate of 10°C min^{-1} from 25°C to 800°C (figure S5). The TG curve indicates that **1** shows one continuous weight loss between 25°C and 410°C giving a total loss of 12.98%, which is equivalent to the loss of one pyrazine (Calcd: 12.23%) [33].

4. Conclusions

We have *in situ* synthesized polyoxomolybdate $[Cu_2(pz)(Mo_3O_{10})]_n$ under hydrothermal conditions. It represents an example in polyoxomolybdate chemistry where all terminal oxygen atoms attached to Mo in $\{Mo_3O_{10}\}_n$ are coordinated with Cu(I) constructing a 3-D structure, rare in polyoxomolybdate chemistry for such high connectivity. In addition, **1** is interesting for its unusual self-assembly synthesis. The *in situ* decarboxylation and the *in situ* reduction occurred simultaneously in the same synthesis process. Further work to clarify the factors leading to such high connectivity is ongoing in our group.

Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center with the CCDC reference number 806726. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. Electronic Supplementary Information (ESI) available: IR, Bond valence sum calculation, etc.

Acknowledgments

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