

一维螺旋链状过渡金属-苹果酸配合物的合成、晶体结构及表征

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摘要: 本文用铜、邻菲咯啉、钼酸铵和苹果酸合成了 1 种新型配合物 $\text{Cu}_2(\text{phen})_2(\mu\text{-O})_2\text{Mo}(\text{C}_4\text{H}_3\text{O}_5)_2 \cdot 7\text{H}_2\text{O}$ (**1**, phen=1,10-邻菲咯啉, $\text{C}_4\text{H}_3\text{O}_5^{3-}$ =苹果酸根阴离子),并对它进行了单晶 X 射线衍射,红外光谱,元素分析等表征。X 射线衍射分析表明配合物为苹果酸和邻菲咯啉桥联形成的三核铜及钼中心的一维螺旋链状结构,并通过氢键自组装成三维超分子化合物。另外,对配合物的固态的固体荧光性能也进行了研究。

关键词: 铜配合物; 晶体结构; *L*-苹果酸; 超分子; 钼

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1D Spiral-Shaped Chains of Transition Metal-Malate Complex: Synthesis, Crystal Structure and Characterization

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Abstract: A novel complex $\text{Cu}_2(\text{phen})_2(\mu\text{-O})_2\text{Mo}(\text{C}_4\text{H}_3\text{O}_5)_2 \cdot 7\text{H}_2\text{O}$ (**1**, phen=1,10-phenanthroline, $\text{C}_4\text{H}_3\text{O}_5^{3-}$ =malate dianion) has been prepared by reaction of copper, phen, ammonium molybdate and *L*-malic acid in solution and characterized by single-crystal X-ray diffraction analysis, FTIR spectroscopy and elemental analysis. X-ray diffraction reveals that complex **1** consists of molybdenum centers bridged by malate and Cu-phen ligands, which are linked into 1D spiral-shaped chains and self-assembled to form 3D supramolecular architectures via hydrogen bonds. In addition, the photoluminescent properties in solid state were investigated. CCDC: 809924.

Key words: copper complex; crystal structure; *L*-malic acid; supramolecular; molybdenum

0 Introduction

Research on metal-organic frameworks has become a rapid growing area in recent years, not only because they can be designed to create cavities or channel structures with various sizes and shapes, but also due to their potential applications in many fields^[1-5]. Apart from the covalent interactions, hydrogen bonds and π - π stacking interactions are also available tools to design various supramolecular contacts compo-

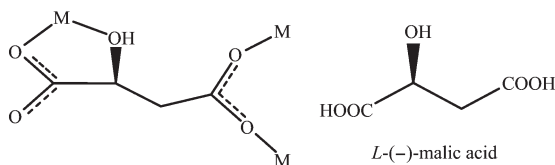
unds^[6]. Owing to their flexible coordination versatility, carboxylic acids ligands have been successfully used to design and construct numerous open frameworks^[7-9]. Hydroxypolycarboxylic acids as polycarboxylate ligands have been aroused particular attention due to their unique features. For example, hydroxypolycarboxylic acids possess terminal carboxylic acid and hydroxyl groups, which may be completely or partially deprotonated leading to a versatile coordination behaviors towards metal cations such as nonchelating, chelating,

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and bridging modes. In addition, hydroxycarboxylic acids can act not only as hydrogen-bond acceptors, but also as hydrogen-bond donors to form novel extended structures^[10]. The malic acid as a hydroxycarboxylic acid with bifunctional ligand, which can be widely found in fruits and living things. Meanwhile, the malic ligand is a suitable candidate for assembling various types of functional supramolecular systems by utilizing intramolecular or intermolecular hydrogen bonds^[11]. To date, a great number of supramolecular complex systems based on malate ligands and transition metal building blocks have been designed and synthesized, which exhibit a wide variety of structures and different magnetic behaviors^[12-16]. In this work, a novel malate complex was successfully synthesized by using phen and malic acid. The complex was constructed from 1D spiralshaped chains first and then extended into 3D supra-molecular network. To the best of our knowledge, the coordination mode (Scheme 1) in complex **1** is unusual for malate, which is only found in $[\text{Mn}(\text{C}_4\text{H}_4\text{O}_5)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ ^[17]. Except the spectra and the crystal structures, the luminescent properties have also been investigated.



Scheme 1 Type of coordination for the *L*-malic ligand found in complex **1**

1 Experimental

1.1 General procedures

All chemicals were used as purchased without further purification. The FTIR spectra were obtained using a Nicolet 5700 FTIR spectrometer using KBr pellets. Elemental analyses for C, H and N were performed on a Perkin-Elmer 2400 Elemental Analyzer. Fluorescence spectra were obtained on VARIAN Cary Eclipse fluorescence spectrometer.

1.2 Synthesis

The complex **1** was obtained by a two-step solution method. Firstly, $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2 mmol), *L*-malic acid (2 mmol) was dissolved in 20 mL H_2O , then was added

phen (1 mmol, dissolved in 10 mL methanol), the pH value was adjusted to about 3 by NaOH and HCl. The resulting mixture was stirred for 30 min and then filtered. After several days, blue crystals were harvested, washed with cooled water and dried on filter paper. Secondly, the crystals (0.3 g) were allowed to react with ammonium molybdate (1 mmol) in 25 mL DMF-water mixture (1:1 V/V) at 50 °C for 2 h with continuous stirring. Meanwhile, the pH value was adjusted to 3.5 by sparse HCl. The filtrate was left unperturbed for the slow evaporation of the solvent. Block deep blue, single crystals suitable for X-ray diffraction analysis appeared after 13 days, and dried at ambient temperature. The elemental analysis results of the title compound $\text{C}_{32}\text{H}_{36}\text{N}_4\text{Cu}_2\text{MoO}_{19}$. Calcd.(%): C 40.92, H 3.86, N 5.97. Found (%): C 40.85, H 3.92, N 5.93. All the experimental results are consistent with the calculated values based on the formula given by X-ray single crystal diffraction. IR spectra (KBr pellet, cm^{-1}): ν 3441, 3061, 1630, 1579, 1519, 1432, 1388, 1308, 1092, 873, 721, 702, 559.

1.3 X-ray crystallography

A suitable crystal with dimension of 0.18 mm × 0.14 mm × 0.11 mm was selected for X-ray diffraction study. Diffraction data were collected on a Bruker SMART APEX-II CCD diffractometer equipped with a graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.071\,073\text{ nm}$) at 296 (2) K using an ω/θ scan mode in the range of $2.18^\circ \leq \theta \leq 27.87^\circ$ with $-30 \leq h \leq 29$, $-9 \leq k \leq 14$, $-20 \leq l \leq 20$. Data reductions and absorption corrections were performed using the SAINT and SADABS software packages, respectively. The intensity data were corrected by L_p factors and empirical absorption. The structure was solved by direct methods and subsequent successive difference Fourier maps, and refined by full-matrix least-squares techniques on F^2 . All calculations were carried out with SHELXTL-97 program^[18-19]. The selected bond lengths, bond angles and hydrogen bonding geometry are given in Table 1, Table 2 and Table 3, respectively. All of the non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were generated geometrically.

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Table 1 Crystal data and structure refinement of 1

Empirical formula	C ₃₂ H ₃₆ N ₄ O ₁₉ Cu ₂ Mo	<i>V</i> / nm ³	3.915(2)
Formula weight	1 003.67	<i>Z</i>	4
Crystal system	Orthorhombic	<i>D_c</i> / (g·cm ⁻¹)	1.476
Space group	<i>C</i> 222 ₁	Reflections collected / unique (<i>R_{int}</i>)	12 321 / 4 711 (0.035 4)
<i>a</i> / nm	2.327 5(8)	Goodness-of-fit on <i>F</i> ²	1.035
<i>b</i> / nm	1.073 7(3)	Flack	0.005(12)
<i>c</i> / nm	1.566 4(5)	Final <i>R</i> indices [<i>I</i> >2σ(<i>I</i>)]	<i>R</i> ₁ =0.033 7, <i>wR</i> ₂ =0.080 6
β / (°)	90	<i>R</i> indices (all data)	<i>R</i> ₁ =0.029 8, <i>wR</i> ₂ =0.078 5

Table 2 Selected bond lengths (nm) and angles (°) of 1

Cu(1)-O(4)	0.193 6(2)	Mo(1)-O(6)	0.172 7(2)	Cu(1)-N(1)	0.197 4(3)
Cu(1)-O(3 ⁱ)	0.202 4(2)	Mo(1)-O(5)	0.192 17(19)	Cu(1)-N(2)	0.203 6(3)
Cu(1 ⁱⁱ)-O(6)	0.215 4(2)	Mo(1)-O(1)	0.219 7(2)		
O(6)-Mo(1)-O(6)	102.74(15)	O(5)-Mo(1)-O(1 ⁱ)	83.47(8)	O(3 ⁱⁱ)-Cu(1)-N(2)	156.78(10)
O(6)-Mo(1)-O(5)	92.47(9)	O(5)-Mo(1)-O(1 ⁱ)	75.67(8)	N(1)-Cu(1)-O(6 ⁱⁱ)	98.01(11)
O(6)-Mo(1)-O(5)	104.4(9)	O(1 ⁱ)-Mo(1)-O(1)	78.77(12)	O(4)-Cu(1)-O(6 ⁱⁱ)	87.30(9)
O(6)-Mo(1)-O(5)	92.46(9)	O(4)-Cu(1)-O(3 ⁱⁱ)	92.59(9)	O(3 ⁱⁱ)-Cu(1)-O(6 ⁱⁱ)	86.00(8)
O(5)-Mo(1)-O(5)	152.98(12)	O(4)-Cu(1)-N(1)	174.39(11)	N(2)-Cu(1)-O(6 ⁱⁱ)	116.56(10)
O(6i)-Mo(1)-O(1 ⁱ)	90.09(10)	N(1)-Cu(1)-O(3 ⁱⁱ)	89.60(11)		
O(6)-Mo(1)-O(1 ⁱ)	164.47(9)	O(4)-Cu(1)-N(2)	93.86(11)		

Symmetry transformations used to generate equivalent atoms: ⁱ *x*, 1-*y*, -*z*; ⁱⁱ -*x*, *y*, 0.5-*z*.

Table 3 Hydrogen bonding geometry

D-H···A	<i>d</i> (D···H) / nm	<i>d</i> (D···A) / nm	<i>d</i> (H···A) / nm	∠D-H···A / (°)
O(1W)-H(1B)···O(1)	0.082	0.284 4(5)	0.208	154
O(1W)-H(1C)···O(7 ⁱ)	0.082	0.285 1(14)	0.211	150
O(1W)-H(1C)···O(7 ⁱⁱ)	0.082	0.275 9(16)	0.198	159
O(2W)-H(2C)···O(6)	0.082	0.327 5(5)	0.256	147
O(2W)-H(2C)···O(4)	0.082	0.293 6(3)	0.236	128
O(3W)-H(3B)···O(1W)	0.082	0.273 2(7)	0.191	180
O(3W)-H(3C)···O(2)	0.082	0.277 0(6)	0.219	128
O(7A)-H(7A)···O(2)	0.082	0.272 8(12)	0.214	128
O(7A)-H(7B)···O(3W)	0.082	0.281 2(12)	0.199	179
O(7B)-H(7D)···O(3W)	0.082	0.292 8(18)	0.234	130
C(1)-H(1A)···O(3)	0.093	0.300 4(5)	0.256	110
C(2)-H(2A)···O(3W)	0.093	0.339 8(7)	0.252	157
C(3)-H(3A)···O(5)	0.093	0.330 0(5)	0.244	155
C(5)-H(5A)···O(6)	0.093	0.322 7(5)	0.256	129
C(15)-H(15B)···O(3W)	0.097	0.345 7(6)	0.256	154

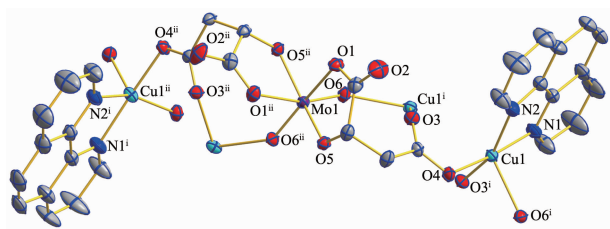
2 Results and discussion

2.1 Structure descriptions

A single-crystal X-ray diffraction reveals that the complex **1** crystallizes in the chiral space group *C*222₁,

with two copper (II) cations, one Mo (VI), two malate ligands, two phen ligands, and seven lattice water molecules in each crystallographic unit, as shown in Fig.1.

The type of copper coordination environment in



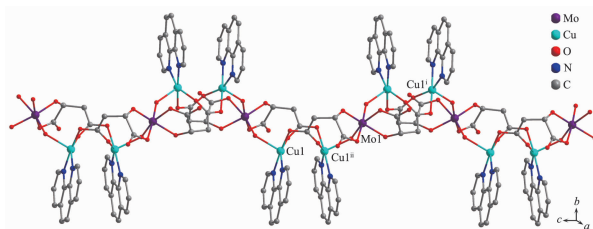
H atoms are omitted, Symmetry codes used to generate the equivalent atoms: ⁱ $x, 1-y, -z$; ⁱⁱ $-x, y, 0.5-z$

Fig.1 Part of crystal structure of the complex

complex **1** is five. In the $\{\text{CuN}_2\text{O}_3\}$ units, there are of two nitrogen atoms belonging to one phen ligand with $\text{Cu}_1\text{-N}$ distance of $0.197\,4(3)\sim 0.203\,6(3)$ nm and $\text{N-Cu}_1\text{-N}$ angle of $82.17(12)^\circ$, and two oxygen atoms belonging to the carboxylate group of two bridging malic ligands, another oxygen atoms from the bridging $\mu\text{-O}$ of water molecule to finish its distorted square-pyramidal coordination environment. The $\text{Cu}_1\text{-O}_4$ (malic) and $\text{Cu}_1\text{-O}_3$ (malic) bond distances are $0.193\,6(2)$ and $0.202\,4(2)$ nm whereas $\text{Cu}_1\text{-O}_6$ ($\mu\text{-O}$) distance is $0.215\,4(2)$ nm. In the $\{\text{MoO}_6\}$ units, the Mo^{6+} is surrounded by six oxygen atoms, four oxygen atoms from the carboxylate and hydroxycarboxylate group of two malic ligands with $\text{Mo}_1\text{-O}$ distance of $0.172\,7(2)\sim 0.219\,7(2)$ nm. Interestingly, the other two oxygen atoms are from $\mu\text{-O}$, resulting in a distorted octahedral coordination environment. In addition, the fact that the bond distance of $\text{Mo}_1\text{-O}_{\text{carboxyl}}$ ($0.219\,7(2)$ nm) is significantly longer than that of $\text{Mo}_1\text{-O}_{\text{hydroxyl}}$ ($0.192\,17(19)$ nm) indicates that the hydroxyl group of **1** dehydrogenates, which is different from many other α -hydroxycarboxylate complexes^[20-25].

It is worthwhile to note that the malate dianions bridge molybdenum and copper centers to form 1D polymeric chains running along the crystallographic c axis (Fig.2) with adjacent $\text{Cu}\cdots\text{Cu}$ distance of $0.331\,8(11)$ nm. Interestingly, a pair of 1D chains selfassemble to generate molecular double chains (Fig.3).

To the best of our knowledge, the double-stranded chains bridging mode of the malate ligand has been only previously reported for the compounds $[\{\text{Cu}(\text{Hhbd})\}(\text{bpy})]\cdot 3\text{H}_2\text{O}$ ^[10], and $[\text{Cu}(\text{mal})(\text{bpy})]\cdot 3\text{H}_2\text{O}$ ^[16], where the malic is coordinated, like in this case. In contrast, the



Symmetry codes used to generate the equivalent atoms: ⁱ $x, 1-y, -z$; ⁱⁱ $-x, y, 0.5-z$

Fig.2 1D chain of the complex

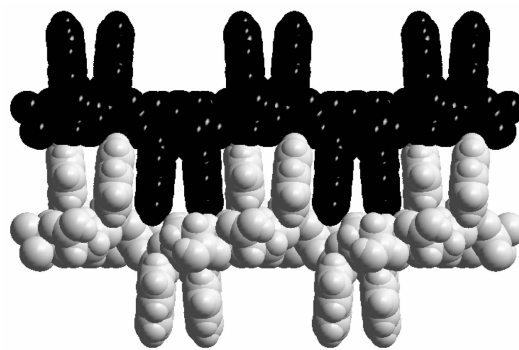
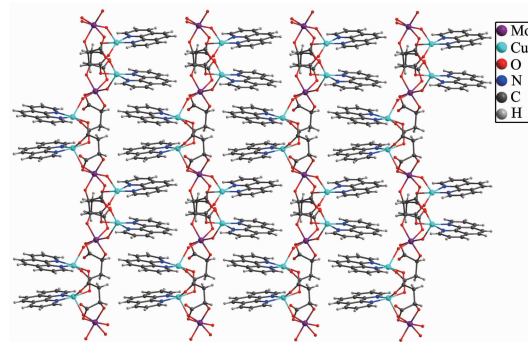


Fig.3 1D single-stranded and ladder-like, double-stranded chains

complex **1** is chiral as expected from the space group, which attributes to the bridging *L*-malic ligand^[26].

Furthermore, neighboring pairs of double chains interact with each other through $\text{O-H}\cdots\text{O}$ and $\text{C-H}\cdots\text{O}$ hydrogen bonds with $\text{O}\cdots\text{O}$ distance of $0.272\,8(12)\sim 0.327\,5(5)$ nm and $\text{C}\cdots\text{O}$ distances in the range of $0.300\,4(5)\sim 0.345\,7(6)$ nm (Table 3), which are arranged to generate 2D sheets (Fig.4).



H_2O are omitted for clarity

Fig.4 View of the 2D layer via hydrogen-bonding of the complex

Adjacent layers are linked by the lattice water molecules to form a 3D supramolecular network via hydrogen bonds. Undoubtedly, hydrogen bond interactions are usually playing an important role in the

stabilization of supramolecular architectures^[27-29]. It is instructive to note that the difference in mode of the Mo-O-Cu of bridging (Fig.2) displays an interesting 1D spiral-shaped chain with the phen ligands arranged uniquely at two sides of the chain. Unlike the other related work on undulating chains extended into 3D network via supramolecular interactions such as hydrogen bonds and π - π stacking interactions^[30-35], the complex **1** is formed only by the parallel stacking of the adjacent double-stranded chains via the hydrogen bonds interactions, without obvious π - π stacking interactions.

2.2 Luminescent property

As shown in Fig.5, the free ligand phen displays photoluminescent emission peaks at 362 and 379 nm upon excitation at 230 nm. In contrast, the complex **1** exhibits an emission maximum at 528 nm upon excitation at 234 nm. Compared to the free phen ligand, the complex **1** has a remarkable energy emission shift, which may be attributed to a π - π^* transition of the ligand.

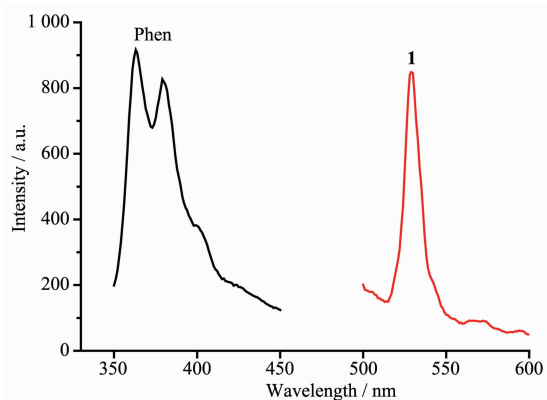


Fig.5 Emission spectra of the phen ligand and the complex **1**

3 Conclusions

In summary, a 3D supramolecular network $\text{Cu}_2(\text{phen})_2(\mu\text{-O})_2\text{Mo}(\text{C}_4\text{H}_3\text{O}_3)_2 \cdot 7\text{H}_2\text{O}$ was constructed from malate-bridged chains of copper (II) and Mo (VI) units and chelating aromatic ligands. More significantly, in the complex **1** the malate bridges the copper and molybdenum centers to form spiral-shaped chains via hydroxyl and carboxylate groups in an unusual coordination mode. Furthermore, the complex **1**

exhibits a 3D supramolecular network with 1D spiral-shaped chain formed by various supramolecular interactions. This work implies that new structures with unique structural features may be isolated in metal-malic acid system by varying the synthetic conditions.

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