由 α-萘乙酸构筑的一维铜(Ⅱ)配位聚合物的合成、结构和性质研究

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摘要： 合成了一维聚合物$[Cu(NAA)_2]_n$(HNAA=α-萘乙酸)，采用单晶 X-射线、FTIR 和元素分析对生成的晶体进行了结构表征。该聚合物属于正交晶系，$Pbcn$ 空间群，a=3.077 2(3) nm，b=1.272 56(11) nm，c=1.023 51(9) nm，V=4.008 0(6) nm^3，Z=8。Cu(Ⅱ)的配位几何构型是五配位的扭曲四方锥，配体的羧基采用 μ_2-η^1:η^1 和 μ_3-η^2:η^1 两种不同的桥联配位模式，连结 Cu(Ⅱ)离子形成 1D 链，1D 链又被 C-H-π 作用力进一步连结形成 2D 层和 3D 固态超分子结构。磁性研究表明：在该聚合物中，相邻铜离子间存在反铁磁偶合作用。还对其热稳定性进行了研究。

关键词： α-萘乙酸；Cu(Ⅱ)聚合物；磁性；热重
中图分类号： O614.121　　**文献标识码：** A　　**文章编号：** 1001-4861(2012)08-1700-05

Synthesis, Structure and Properties of a 1D Copper(Ⅱ) Coordination Polymer Constructed by α-Naphthylacetic Acid

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Abstract: A copper(Ⅱ) coordination polymer, $[Cu(NAA)_2]_n$ (HNAA=α-naphthylacetic acid) was synthesized and structurally characterized by means of X-ray single-crystal diffraction, IR spectrum and elemental analysis. It crystallizes in orthorhombic space group $Pbcn$ with a=3.077 2(3), b=1.272 56(11), c=1.023 51(9) nm, V=4.008 0(6) nm^3, Z=8. The coordination geometry of Cu(Ⅱ) is a distorted square-pyramid. Carboxylate groups take two kinds of bridging coordination modes: μ_2-η^1:η^1 and μ_3-η^2:η^1, resulting in infinite zigzag 1D chains. These 1D chains are connected together to form layer and 3D stacking framework by C-H-π interactions between naphthyl rings. Magnetic measurement of the polymer shows that a strong antiferromagnetic coupling can be observed. The thermal stable property of the polymer was also investigated. CCDC: 835977.

Key words: α-naphthylacetic acid; copper(Ⅱ) complex; synthesis; magnetic; thermal properties

0　Introduction

The design and construction of metal-organic coordination polymers (MOCPs) have attracted conside-

rable attention due to their interesting structural chemistry and potential applications in gas storage, separation, catalysis, magnetism, luminescence, drug

delivery[1-6], and nonlinear optics (NLO), and optical limiting capability[7-8]. The structures of coordination polymers rely on several factors, but to select suitable bi- or multi-dentate bridging ligands is no doubt the key factor because it has an obvious influence on the topologies of coordination polymers. The behaviors of carboxylate ligands have been adopted to construct various structural coordination frameworks, because they can exhibit a variety of bonding modes to metals, including (i) terminal monodentate, (ii) chelating to a single metal, (iii) bridging bidentate to two metals in a *syn-syn-*, *syn-anti-*, an *anti-anti*-fashion, and (iv) bridging tridentate to two metal centers[9-10]. These interesting findings have prompted us to seek this kind of carboxylate ligands to synthesize desired complexes. Thus, we chose carboxylic acid ligand, α-naphthylacetic acid (HNAA) with a bulky aromatic group, because it may introduce additional π-π and $C-H\cdots\pi$ interactions in stabling the structures of metal-organic frameworks. By doing so, we hope to obtain interesting coordination polymers. Among our attempts, a new polymer, namely $[Cu(NAA)2]_n$ (**1**), was obtained as crystals suitable for single-crystal X-ray analysis. The magnetic and thermal properties of the polymer **1** were investigated as well.

1　Experimental

1.1　Instruments and materials

All chemicals were of reagent grade obtained from commercial sources and used without further purification. IR Spectrum was recorded on a Nicolet NEXUS 470-FTIR spectrophotometer as KBr pellets in the 400~4 000 cm^{-1} region. Elemental analyses (C, H) were carried out on a FLASH EA1112 Elemental Analyzer. TG-DSC measurements were performed by heating the sample from 20 to 800 ℃ at a rate of 10 ℃·min^{-1} on a NETZSCH STA 409PC differential thermal analyzer. Variable temperature magnetic susceptibility data were obtained on polycrystalline Samples from 2 to 300 K in a magnetic field of 2 kOe, using a Quantum Design MPMS-XL7 SQUID magnetometer. All magnetic data have been corrected for diamagnetism by using Pascals constants[11].

1.2　Synthesis of the title complex

0.093 g (0.5 mmol) HNAA and 0.05 g (0.25 mmol) copper (II) acetate was dissolved in 20 mL deionized water, and the pH value of the solution was adjusted to about 8 with sodium hydroxide solution (0.1 mol·L^{-1}).The mixture was heated to reflux for 1 h in a water bath and then cooled to room temperature with green precipitate. The precipitation was redissolved in 30 mL tetrahydrofuran and left to stand at room temperature for several days, green block crystals of **1** were obtained.Yield:79% (based on Cu). Crystals of **1** are stable in the air. Anal. Calcd. for $C_{24}H_{18}CuO_4$ (%): C: 66.35, H: 4.14. Found (%): C: 66.04, H: 4.30. IR (cm^{-1}, KBr): 3 442 (s), 3 045 (w), 2 921 (w), 1 592 (s), 1 511 (m), 1 409 (s), 1 299 (w), 1 260 (m), 1 047 (w), 1 017 (w), 781 (s), 719 (m), 647 (m), 580 (w), 547 (m).

1.3　Crystal structure determination

A green block single crystal of the title complex (0.10 mm ×0.10 mm ×0.10 mm) was selected and mounted on a glass fiber. All measurements were made on a Bruker Smart 1000 diffractometer with a graphite-monochromated Mo $K\alpha$ radiation (λ=0.071 073 nm). All data were collected at 298 (2) K using the ω-2θ scan mode and corrected for Lorenz-polarization effects. A total of 19 795 reflections in the range of 2.55° to 25.02° ($-31 \leqslant h \leqslant 36$, $-13 \leqslant k \leqslant 15$, $-12 \leqslant l \leqslant 11$) and 3 535 unique ones (R_{int}=0.090 9) were collected. The empirical absorption corrections by SADABS were carried out.

The structure was solved by direct methods and expanded by Fourier technique. The non-hydrogen atoms were refined with anisotropic thermal parameters. The maximum peak in the final difference Fourier map is 471 e·nm^{-3} and the minimum -301 e·nm^{-3}. In the final circle of refinement the largest parameter shift $(\Delta/\sigma)_{max}$ is 0.000. All calculations were performed with SHELX-97 crystallographic software package[12]. The crystal data and refinement details for the compound **1** are listed in Table 1, and the selected bond lengths (nm) and bond angles (°) are given in Table 2.

CCDC: 835977.

Table 1　Crystallographic data for complex 1

Empirical formula	$C_{24}H_{18}CuO_4$	μ / mm^{-1}	0.608
Formula weight	433.92	Crystal dimension / mm	0.10×0.10×0.10
Crystal system	Orthorhombic	θ range / (°)	2.55~25.02
Space group	*Pbcn*	$F(000)$	17 848
a / nm	3.077 2(3)	Goodness of fit	0.91
b / nm	1.272 56(11)	Reflections collected	19 795
c / nm	1.023 51(9)	Independent reflns. (R_{int})	3 535
V / nm^3	4.008 0(6)	Obsd. Reflns. ($I>2\sigma(I)$)	1745
Z	8	Parameters refined	262
Temperature / K	298(2)	R, wR ($I>2\sigma(I)$)	0.046 2, 0.079 8
Crystal color	Green	R, wR (all reflections)	0.115 0, 0.098 2
D_c / (g·cm^{-3})	1.396		

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

Cu1-O1	1.935(3)	Cu1-O3	1.954(2)	Cu1-O4^{ii}	2.192(2)
Cu1-O2^{i}	1.935(3)	Cu1-O4^{i}	2.017(2)	Cu1-Cu1^{i}	2.586 8(8)
O1-Cu1-O2^{i}	169.44(11)	O2^{i}-Cu1-O4^{ii}	95.07(12)	O3-Cu1-O4^{i}	169.23(10)
O1-Cu1-O3	87.53(13)	O3-Cu1-O4^{ii}	111.55(10)	O1-Cu1-O4^{ii}	95.25(12)
O2^{i}-Cu1-O3	90.76(13)	O4^{i}-Cu1-O4^{ii}	79.00(10)		
O1-Cu1-O4^{i}	89.39(12)	O2^{i}-Cu1-O4^{i}	90.37(12)		

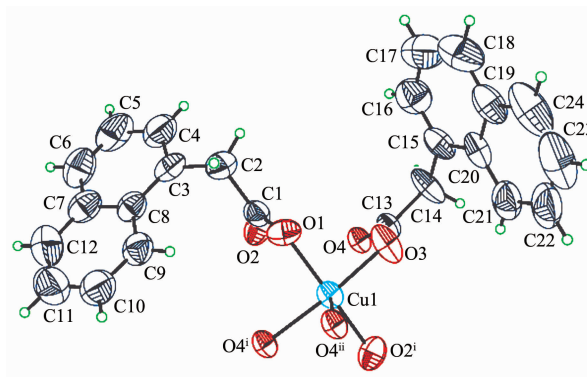Symmetry codes: ^{i} $-x+1$, $-y+1$, $-z+1$; ^{ii} x, $-y+1$, $z+1/2$.

2　Results and discussion

2.1　Crystal structure of 1

The asymmetric unit of **1** and the coordinated environment of copper(II) ion showed in Fig.1. The crystal data and structure refinement for the title complex listed in Table 1. The asymmetric unit of the title polymeric compound (Fig.1) contains one Cu(II) cation and two NAA$^-$ anion ligands. The Cu(II) cation is coordinated by four O atoms (O1, O3, O2^{i}, O4^{i}, symmetry code: ^{i} $-x+1$, $-y+1$, $-z+1$) from four NAA$^-$ anions in the basal plane and the apical position is occupied by O4^{ii} (symmetry code: ^{ii} x, $-y+1$, $z+1/2$) from a fifth NAA$^-$ anion to complete the slightly distorted square-pyramidal coordination geometry. Cu1 atom is displaced by 0.018 09(4) nm from this plane in the direction of the apical O4^{ii} atom. The corresponding equatorial Cu-O bonds are in the range 0.193 5(3) to 0.201 7(2) nm. The apical Cu1-O4^{ii} bond is 0.219 2 (2) nm, it is longer than other Cu-O bonds in the basal plane, showing the typical Jahn-Teller distortion. The distance of Cu-Cu is 0.258 68(8) nm,

which is shorter than the separation reported, indicating a Cu-Cu interaction in this complex[13]. The max bond angles around central Cu1 ion are 169.44(11)° and 169.23(10)°, others range from 87.53(13)° to 95.25(12)° close to 90°, the distorted index τCu1= 0.004(4)[14]. The selected bond lengths and bond angles are listed in Table 2.

In NAA$^-$ anions, carboxylate groups take two

Symmetric code: ^{i} $-x+1$, $-y+1$, $-z+1$; ^{ii} x, $-y+1$, $z+1/2$

Fig.1　Asymmetric unit of **1** and coordination environment with displacement ellipsoids drawn at 30% probability level

different coordination modes. One carboxylate group takes a μ_2-η^1:η^1 chelating coordinate mode with Cu(Ⅱ) ion, the other one take a μ_3-η^2:η^1 bridging coordination mode, which connects the adjacent Cu(Ⅱ) ion to form a infinite extension zigzag polymeric chain (Fig.2).
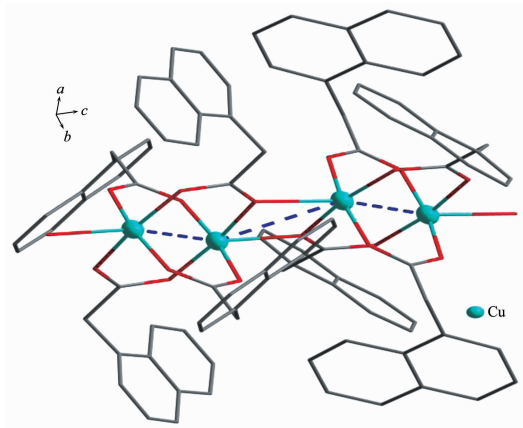

Fig.2　1D chain structure of the complex **1**

There are C-H-π interactions between naphthyl rings from neighbor chains since the separation of centroid-to-C is 0.354 3 nm. These one-dimensional chains are first extended into a 2D layer through this interaction. And then 2D layers further are linked together to give rise to 3D solid-state structure by C-H-π with a distance of 0.441 0 nm[15].
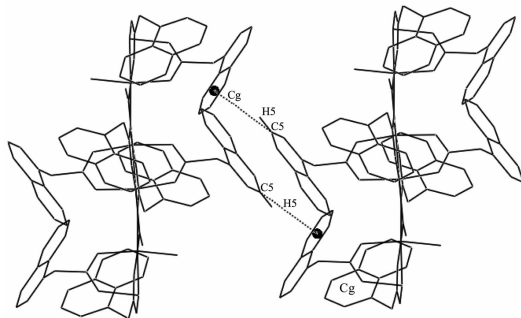

Fig.3　Two-dimensional layer structure of **1** stabilized by C-H-π interactions

2.2　Magnetic properties

Magnetic susceptibility measurements of complex **1** were made in the temperature range 2~300 K. Fig.4 gives the plots of χ_M versus temperature (T). The χ_M value decreases as the temperature is lowered, which indicates the presence of antiferromagnetic interactions between the Cu(Ⅱ) centers bridged by the carboxylate groups. Although the expression for a simple dinuclear structure also reproduces correctly

the temperature dependence of χ_M of the chain compound, a better fit is obtained by using the expression developed by Hatfield and co-workers[16] for alternating chain compounds, which gives g =2.08, $2J$=−254 cm^{-1}, an alternating factor α=0.016 and p = 1.23% (the TIP was here fixed to 3.12×10^{-4} cm$^3 \cdot$ mol^{-1}. These results are in agreement with the many reports of coupling of Cu(Ⅱ) ions through a tetracarboxylate bridge[17]. In the case of the tetranuclear and chain compounds, the additional bridge corresponds to the apical coordination sites of the Cu(Ⅱ) ions, where the spin density is expected to be negligible in any case, since the structure indicates that the magnetic orbital is $d_{x^2-y^2}$. On the contrary, the carboxylate bridges are coordinated in equatorial positions, in a *syn-syn* fashion, yielding a strong overlap and therefore a strong antiferromagnetic coupling.
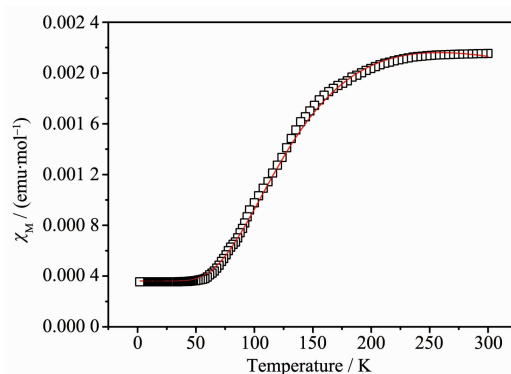

Solid line represents the best-fit curve from 300 to 2 K

Fig.4　Temperature dependence of the magnetic susceptibility in the form of χ_M vs T

2.3　Thermogravimetric analysis (TGA)

From the thermal analysis curve (TG/DTG) of the title complex **1** (Fig.5), we can see that there are two weight loss steps in the temperature range of 25~*ca.* 570 ℃, corresponding to the decomposition of the organic ligand NAA. It firstly loses weight from room temperature to *ca.* 470 ℃ (obsd. 57.25%, calcd. 59.07%), corresponding to the loss of two naphthalene molecules. The residue is copper acetate. The second weight loss of 28.96% from 470 to 560 ℃ results from the release of CO_2 and CH_4 molecules, corresponding to the decomposition of the copper acetate (calcd. 27.72%). The residue is black CuO.
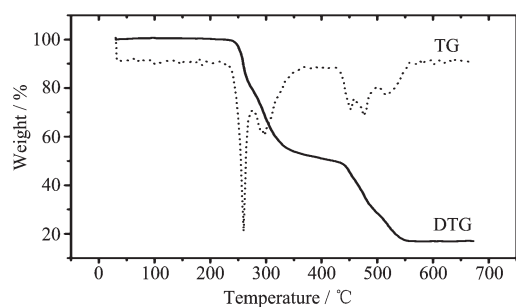
Fig.5　TG curve of **1**

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