二维网状 Cu(ntp)$_2$(H$_2$O)$_4$ 晶体的直接合成、
晶体结构和热分解机理研究

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摘要：用直接法合成了配合物 Cu(ntp)$_2$(H$_2$O)$_4$, 并测定了其晶体结构。分子式为 C$_{16}$H$_{16}$CuN$_2$O$_{16}$。晶体属单斜晶系, C2/c 空间群, 晶胞参数为 a=2.266 5(7) nm, b=0.706 8(2) nm, c=1.575 5(4) nm, β=126.42(1)°。对晶体进行了 DSC 和 TG-DTG 热分析, 根据结果提出了可能的热分解过程。

关键词：直接合成；晶体结构；热分解
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Direct Synthesis, Crystal Structures and Thermal Analyses of the Two-Dimensional
Cu(ntp)$_2$(H$_2$O)$_4$ Crystal (ntp=2-nitroterephthalate)

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Abstract: The Cu(ntp)$_2$(H$_2$O)$_4$ coordination compound has been synthesized by direct method and its crystal has been cultured and characterized by X-ray single crystal structural analysis. The crystal is formulated as C$_{16}$H$_{16}$CuN$_2$O$_{16}$ and crystallized in monoclinic system, space group C2/c, with a=2.266 5(7) nm, b=0.706 8(2) nm, c=1.575 5(4) nm, β=126.42(1)°, V=2.030 8(13) nm^3, D$_c$=1.818 g·cm^{-3}. Based on DSC and TG-DTG analyses, the thermal decomposition mechanism of Cu(ntp)$_2$(H$_2$O)$_4$ is predicted that it loses its four coordinated water molecules followed by a large weight loss and formation of copper oxide on heating. CCDC: 271680.

Key words: direct synthesis; crystal structure; thermal decomposition

0　Introduction

The interest to find coordination polymers with novel micro-porous structures has expanded greatly in the past few decades due to their topological diversity and potential uses in the fields such as catalysis, optical materials, ion exchange, gas and solution adsorption or separation, and so on [1~7]. Researchers have found that the organic molecules play a very important role in the final structures of the coordination polymers[8~10]. A large amount of coordination polymers using terephthalic acid (TPA) as organic linkers have been synthesized and they behave diverse novel structures when the preparing conditions are different[11~14]. We used 2-nitroterephthalic acid (NTPA) as starting material for the synthesis of our targeting co-

ordination polymers. In the crystal structure, we can find that the Cu(II) center is coordinated by two O atoms from terephthalates and four from water molecules in a distorted octahedral pattern. By means of hydrogen bonds among neighboring molecules, two-dimensional frameworks come into form. In order to deeply investigate its properties, we have performed thermal analyses on the crystal and studied its possible thermodynamic mechanisms.

1 Experimental

1.1 Instruments

Elemental analysis was carried on Flash EA 1112 full-automatic microanalyser. Bruker Equinox 55 infrared spectrometer was used for FTIR analysis, using KBr pellet in the range of 4 000~400 cm^{-1} with the resolution of 8 cm^{-1}. Pyris 1 DSC was used for differential scanning calorimetry analysis using high pure nitrogen as purge gas with flowing rate of 20 mL·min^{-1}. The crystal sample was powdered and sealed in aluminum pan with the heat rate of 10 K·min^{-1}. Pyris 1 TGA was used for TG-DTG analysis using high pure nitrogen as purge gas with flowing rate of 20 mL·min^{-1}. The crystal sample was powdered and put in the platinum sample pan with the heat rate of 10 K·min^{-1}.

1.2 Synthesis of Cu(ntp)$_2$(H$_2$O)$_4$

Dissolved NTPA(0.211 3 g, 1 mmol)in 10 mL water and adjust the pH value to 6~7 by adding 10% NaOH into the solution. At the same time, Cu(NO$_3$)$_2$·3H$_2$O(0.241 6 g, 1 mmol) was dissolved in 10 mL water, and the pH value was adjusted to 3~4 using 5% HNO$_3$. Accompanied by strong stirring, the NTPA solution was heated to about 353 K, then dropwised the Cu (NO$_3$)$_2$·3H$_2$O solution into the above aqueous system slowly. And then, heated the whole system to 373 K and stayed at 373 K for 2 h.

Stopped the reacting system after 2 h, and left the whole system stay in atmosphere to room temperature. Filtrated the solution and cultured the filtrate in ambient atmosphere. 10 d later, pale-blue block crystals suitable for X-ray single crystal diffraction experiment formed (about 43% yield based on Cu). The resulting crystal was collected by filtration, washed with water 2 mL×3, and dried at room temperature. Anal. for Cu(ntp)$_2$(H$_2$O)$_4$, Calcd.(wt%): C, 34.57; H, 2.90; N, 5.04. Found (wt%): C, 34.46; H, 3.03; N, 5.15. FTIR (KBr pellet) spectra (cm^{-1}) of Cu(ntp)$_2$(H$_2$O)$_4$: 3 359s (ν_{O-H}), 2 975w ($\nu_{=C-H}$), 2 927m ($\nu_{=C-H}$), 2 890w ($\nu_{=C-H}$), 1 690s ($\nu_{C=O}$), 1 596w ($\nu_{C=C}$), 1 534s ($\nu_{N=O}$), 1 480m ($\nu_{C=C}$), 1 365s ($\nu_{N=O}$), 825w ($\delta_{=C-H}$).

1.3 Crystal structure determination

A pale-blue single crystal with dimensions of 0.38 mm × 0.34 mm× 0.26 mm was mounted on Siemens P4 X-ray single crystal diffractometer which uses graphite mono-chromatized Mo $K\alpha$ radiation (λ= 0.071 073 nm) and $\omega/2\theta$ scanning mode at 291(2) K. The collected reflections are 2 186, of which 1 889 [R_{int}=0.013 0] are independent. Lp corrections and empirical adsorption corrections were performed on all data. The structure was solved by direct methods using SHELXS-97 program[15] and refined by full-matrix least squares on F^2 using SHELXL-97 program[16]. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were located from the difference Fourier map and refined isotropically. The detailed crystallographic data are listed in Table 1.

CCDC: 271680.

Table 1　Crystal data and structure refinement for Cu(ntp)$_2$(H$_2$O)$_4$

Empirical formula	C$_{16}$H$_{16}$CuN$_2$O$_{16}$	θ range for data collection / (°)	2.23~25.48
Formula weight	555.85	Indices range (h, k, l)	$0 \leqslant h \leqslant 27$, $0 \leqslant k \leqslant 8$, $-19 \leqslant l \leqslant 15$
Crystal system	Monoclinic	μ (Mo $K\alpha$) / mm^{-1}	1.169
Space group	$C2/c$	Reflections collected	2 186
a / nm	2.266 5(7)	Independent reflections	1 889 [R_{int}=0.013 0]
b / nm	0.706 8(2)	Data/restraints/parameters	1 889 / 5 / 181
c / nm	1.575 5(4)	F(000)	1 132
β / (°)	126.42(1)	Goodness-of-fit on F^2	1.005

Contionued Table 1

V / nm³	2.030 8(13)		R indices (all data)	$R_1^a= 0.045\,0$, $wR_2^b = 0.079\,6$
Z	4		Final R indices [$I>2\sigma(I)$]	$R_1=0.031\,8$, $wR_2=0.076\,0$
D_c / (g·cm⁻³)	1.818		Largest difference peak and hole / (e·nm⁻³)	270 and −309

$^{a}R_1=\sum\limits_{h\,k\,l}\left|\,|F_o|-|F_c|\,\right|/\sum\limits_{h\,k\,l}|F_o|$; $^{b}wR_2=[\sum\limits_{h\,k\,l}w(F_o^2-F_c^2)^2/\sum\limits_{h\,k\,l}w(F_o^2)^2]^{1/2}$, $w=1/[s^2(F_o^2)+(0.041\,0P)^2+0.000\,0P]$, where $P=(F_o^2+2F_c^2)/3$

2　Results and discussion

2.1　Synthesis

Direct methods have been used by other researchers in the preparation of coordination polymers using carboxyl group as ligands[12,18]. The preparation conditions are very important for the final obtained materials, especially the temperature and the pH value of the solution. One reason for which we have not obtained the coordination polymers maybe is that the deprotonation reagent(the base used in the reaction) is not sufficient for fully deprotonating the dicarboxyl. Another aspect that influences the final structure of the obtained coordination compounds, according to former researchers′ work, is the type of solvent.
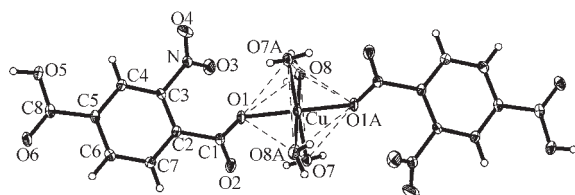
2.2　Crystal structure

From the molecular structure of the title compound in Fig. 1, we can find that the Cu center which is sp^3d^2 hybridized is coordinated to ligands-one NTPA and four H₂O-by means of O atoms in an octahedral geometry. From Fig.1, we can also find that the whole system is centrosymmetric. The O7A, O8A and(ntp)A can be got by the centrosymmetric operations of O7, O8 and ntp. The selected bond distances and bond angles are listed in Table 2. The Cu-O bond distance is 0.191 9(17) nm between Cu and O1, and 0.197 2(2) nm, 0.255 6(2) nm respectively for Cu-O7, Cu-O8. From the bond distances of Cu and O atoms of all the ligands, we can find that Cu is structurally distorted. The large bond distances′ difference between Cu-O7 and Cu-O8 can be explained by their different spatial

Fig.1　Molecular structure of Cu(ntp)₂(H₂O)₄

environments, there is a strong hydrogen bond between O2 and O7(the O2-O7 bond distance is 0.271 3 (3) nm). The Cu-O8 bonds are just the extended coordination bonds in the Jahn-Teller effect of Cu(Ⅱ) center.

From the bond distances, we can also find that Cu-O1$_{ntp}$ bond distance(0.191 9(17) nm) is approximate to the averaged Cu-O$_{tp}$ bond distance in Cu$_{tp}$(OH₂)₂· H₂O(0.192 3 nm) and Cu$_{tp}$(OH₂)₂(0.191 6(2) nm), while the two different Cu-O$_{H_2O}$ bond distances Cu-O7$_{H_2O}$ (0.197 2(2) nm) and Cu-O8$_{H_2O}$(0.255 6(2) nm) are also in consistent with the bond distances between Cu and two kinds of water molecules that exist in the above two compounds. In Cu$_{tp}$(OH₂)₂·H₂O, the averaged Cu-O$_{H_2O}$ bond distance is 0.198 5 nm and the bond distances to the apical water molecules are 0.247 7(3) nm and 0.248 0(24) nm; In Cu$_{tp}$(OH₂)₂, the Cu-O$_{H_2O}$ bond distance is 0.199 2(3) nm and the bond distance to the apical water molecule is 0.242 4(4) nm[19].

The bond angles of O7-Cu-O7A, O8-Cu-O8A, O1-Cu-O1A are all 180°. There is a little deviation from 90° in the angles of O1-Cu-O7(92.57°), O1-Cu-O7A(87.44°), O1-Cu-O8(93.49°), O1-Cu-O8A(86.51°), O7-Cu-O8(91.13°) and O7-Cu-O8A(88.87°). So we can infer that because of the Jahn-Teller effect, the Cu is structurally distorted greatly in bond distances and slightly in bond angles. The coordination octahedron of Cu center is illustrated by the dash lines in Fig.1.

The bond distances of O1-C1 and O2-C1, O5-C8 and O6-C8 are 0.126 4 nm and 0.124 0 nm, 0.132 4 nm and 0.121 1 nm respectively. And the bond angles of O2-C1-O1 and O6-C8-O5 are 126.9 (2)° and 123.9(2)° respectively. From these we can find that the C-O bond distances are averaged and O-C-O bond angles are expanded when the carboxyl group is coor-

Table 2　Selected bond distances (nm), bond angles (°) and dihedral angles for Cu(ntp)$_2$(H$_2$O)$_4$

Cu-O1	0.191 9(2)	Cu-O7	0.197 2(2)	Cu-O8	0.255 6(2)
O1-C1	0.126 4(3)	O2-C1	0.124 0(3)	O5-C8	0.132 4(3)
O6-C8	0.121 1(3)				
O1-Cu-O1A	180.00	O7-Cu-O7A	180.00	O8-Cu-O8A	180.00
O1-Cu-O7	92.57(8)	O1-Cu-O7A	87.43(8)	O1-Cu-O8	93.48(7)
O1-Cu-O8A	86.50(7)	O7-Cu-O8	91.12(8)	O7-Cu-O8A	88.86(8)
O2-C1-O1	126.90(2)	O6-C8-O5	123.90(2)		
O1-C1-C2-C3	52.80	O5-C8-C5-C6	4.52		

Symmetry transformations used to generate equivalent atoms: A = −x+1,−y+2,−z+1

dinated to Cu center.

The hydrogen bond between O2 and O7 also form the 5-member ring of Cu−O1−C1−O2⋯O7. The plane equation of this ring is: −10.096x + 3.564y + 13.545z=5.382 1. The plane equation of benzene ring is:−7.019x + 6.669y + 4.386z=3.735 1. From the angle between the ring and benzene plane (45.50°) we can find that the carboxyl deviate from the benzene plane when it is coordinated to metal centers. This can also be demonstrated by the angle between benzene plane and uncoordinated carboxyl plane(5.50°). The uncoordinated carboxyl plane equation is:−8.032x + 6.461y + 5.810z=4.074 0. Besides this, the nitro plane also deviated from the benzene plane by 47.70°. The nitro plane equation is:8.207x+5.418y+3.338z=7.218 8. The deviation of the nitro plane can be assigned to the stereoscopic effect.

The packing diagram of Cu(ntp)$_2$(H$_2$O)$_4$ along (101) crystal plane is illustrated in Fig.2. From the illustration in Fig.2, we can find that in virtue of hydrogen bonds, the molecules-as illustrated in Fig.1 are linked together along b axis to form a two-dimensional crystal network. The hydrogen bonds those link the molecules together are mainly O7−H⋯O2, O7−H⋯O6, O8−H⋯O2 and O8−H⋯O5. The hydrogen bonds are not the same. For O7−H⋯O2, it′s the intramolecular hydrogen bond in which the O2 atom is from the same molecule as O7. This kind of hydrogen bond has been discussed above. The O7−H⋯O6 hydrogen bond is intermolecular bond that acts as space linker to link the molecule with neighboring molecule together. The

O6 atom in the intermolecular O7−H⋯O6 hydrogen bond comes from 2-nitroterephthalate of another molecule. O8−H⋯O2 and O8−H⋯O5 are both intermolecular hydrogen bonds, in which O2 and O5 come from 2-nitroterephthalates of another two different molecules.

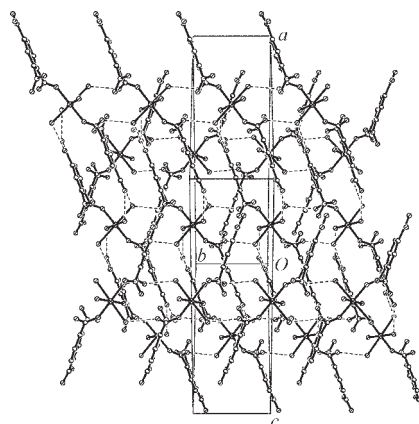Fig.2　Packing diagram of Cu(ntp)$_2$(H$_2$O)$_4$ along (101) crystal plane (Hydrogen atoms are omitted for clarity)

2.3　Thermal analyses

From the DSC curve (Fig.3), we can find that there is one endothermic peak at 394 K and one exothermic peak at 621 K. The first peak can be assigned to the removal of water from the crystal and the second peak is assigned to decomposition of the compound as demonstrated in TG-DTG analysis following.

From the TG-DTG results (Fig.4), we can find that there are two main weight loss stages. The first is 11.32%, the second is 76.44% and the total weight loss is 87.76%. From the DTG curve, we find that the
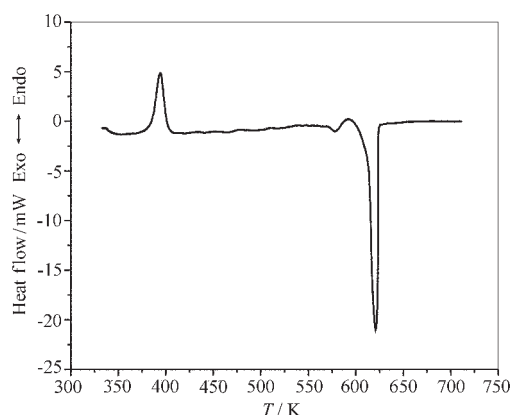
Fig.3　DSC curve of Cu(ntp)$_2$(H$_2$O)$_4$
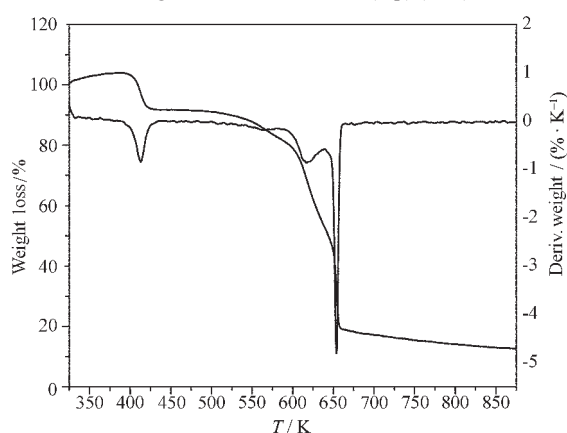
Fig.4　TG-DTG curves of Cu(ntp)$_2$(H$_2$O)$_4$

$$Cu(ntp)_2(H_2O)_4 \xrightarrow[-4H_2O]{413\ K} Cu(ntp)_2 \xrightarrow{653\ K} CuO$$

first weight loss step reaches its largest rate at 413 K and may be assigned to the loss of 4H$_2$O (Calcd. 12.96 %), the second weight loss step reaches its largest rate at 653 K and can be assigned to the loss of 5-nitroterephthalate and formation of some kind of materials. The loss of water molecules in the first stage can be demonstrated in the FTIR spectra of the residues got at 450 K there is no wide water bonds at about 340 0 cm^{-1}. The final residue is 12.24% and we assign it to be CuO (Calcd. 14.31%). The composition of final residue can also be demonstrated by the FTIR spectra of the final residues from the above thermal decompositions. The bands at 779 cm^{-1} and 531 cm^{-1} are the characteristic bands of CuO[20]. So the decomposition mechanism of Cu(ntp)$_2$(H$_2$O)$_4$ is predicted that:
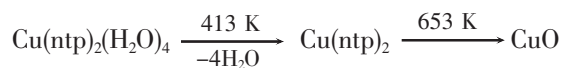
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