研究简报

一维链状配位聚合物[Cu(CH₃COO)(C₅H₅N)₂]ₙ 的合成与晶体结构

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Synthesis and Crystal Structure of 1D Coordination Polymer [Cu(CH₃COO)(C₅H₅N)₂]ₙ

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Abstract: The coordination polymer $[Cu(CH_3COO)(C_5H_5N)_2]_n$ was synthesized and its crystal structure has been determined by X-ray diffraction technique. The crystal belongs to monoclinic, space group $C2/c$ with a=1.183 2(1) nm, b=1.512 1(2) nm, c=1.391 1(1) nm, β=97.137(3)°, V=2.469 6(4) nm³, $C_{12}H_{13}CuN_2O_2$, M_r=280.78, Z=8, D_c=1.510 g·cm⁻³, μ=1.759 mm⁻¹, $F(000)$=1 152, R_1=0.048 2 and wR_2=0.122 5 for 1 515 observed reflections [$I>2\sigma(I)$]. In the crystal the copper(Ⅱ) atom is tetra-coordinated primarily by two oxygen atoms of two symmetry-related carboxyl groups of acetate anions and two nitrogen atoms of two pyridine ligands in a parallelogram fashion. All of the pyridine rings linked to Cu(1) and Cu(2) are arranged centrosymmetrically on Cu(1). The neighboring copper complex molecules are linked together by the carboxylate oxygen atom of acetate anions to form an infinite one-dimensional linear chain structure. Moreover, π-π stacking interactions between intrachain pyridine molecules play the crucial role in constructing of the supramolecular structure. CCDC: 709977.

Key words: copper(Ⅱ) coordination polymer; crystal structure; one-dimensional chain; stacking interaction

0 Intrduction

Investigations of the coordination chemistry of copper (Ⅱ) continue to be stimulated by interest in developing models for copper proteins and in understanding the factors which give rise to the seemingly infinite variety of distortions from regular stereochemistry observed in Cu^{2+} complexes[1]. The biological functions of metallic enzymes and metalloproteins, such as oxygen-carrying catalysis, are realized mainly via the synergism interaction of metallic active positions[2]. Thus, the preparation on some simple copper complexes is benefit to promote in understanding copper proteins active sites[3~5]. Meanwhile, the copper complexes with pyridine derivatives ligands have been extensively studied due to their excellent magnetic properties, especially in bridge group copper complexes[6]. The investigation on their structures is favorable to understand magnetic exchange interaction in Cu-Cu atoms and demonstrate the relationship between

structure and magnetic property[7,8]. In addition, due to the presence of hetero rings of pyridine ligands in the assembled system, the delicate π-π stacking interactions are available to play a decisive role in regulating the resulting supramolecular networks, which are also crucial in constructing and stabilizing the biological systems[9~13]. As part of our ongoing investigation, a complex $[Cu(CH_3COO)(C_5H_5N)_2]_n$ has been prepared. In its crystal structure the carboxylate oxygen atom acts as the bridging ligand to coordinate to the metal atom, forming a novel copper(II) complex with an infinite one-dimensional chain polymer. Moreover, π-π stacking interactions in the coordination polymer are discovered.

1 Experimental

1.1 Reagents and measurements

Pyridine and other chemicals were of analytical grade and used without further purification except $Cu(OAc)_2 \cdot H_2O$. Elemental analyses for C, H and N were executed with Elementar Vario III element analyzer. The metal ion analysis was measured with HITACHI 180-80 polarized zeeman atomic absorption spectrophotometer. IR spectra were recorded on a FTIR-Tensor27 spectrophotometer using KBr pellets in the 4 000~400 cm^{-1} region. Crystal structure determination was carried out on a Bruker Smart Apex CCD X-ray diffractometer.

1.2 Synthesis of the title complex

The title complex was synthesized by the addition of excess ligand to copper(II) acetate. In a typical experiment, about 0.03 mol pyridine is added to an absolute ethanol solution of $Cu(OAc)_2 \cdot H_2O$ (0.01 mol) slowly[14]. The reaction mixture was refluxed for 3 h and then filtered. Green single crystal of the title complex suitable for X-ray analysis was obtained in the solution of pyridine and triethylamine (V/V, 1:2) by slowly evaporating at room temperature. Yield: 73%. Anal. Calcd. for $C_{12}H_{13}CuN_2O_2$(%): C, 51.33; H, 4.67; N, 9.98; Cu, 22.63. Found (%): C, 51.39; H, 4.58; N, 9.88; Cu, 22.52. IR absorption bands (KBr, cm^{-1}): 3 446, 3 050, 3 002, 2 929, 1 615, 1 489, 1 449, 1 426, 1 346, 1 225, 1 155, 1 082, 1 071, 1 037, 1 011, 757, 707, 682, 627, 418.

1.3 Structure determination

A suitable green single crystal with dimensions of 0.22 mm ×0.24 mm ×0.26 mm was selected for data collection at 291 K, using a Bruker Smart Apex CCD diffractometer equipped with a Mo $K\alpha$ radiation (λ = 0.071 073 nm). A total of 6 644 reflections were collected in the range of 2.2°<θ<26.00° with 2 430 unique ones (R_{int}=0.030), of which 1 515 were observed with I>2σ(I) and used in the structure solution and refinement. The structure was solved by direct methods and refined by full-matrix least-squares techniques (SHELX-97). The crystal structure was solved by direct methods with SHELXS-97 program[15] and refined by full-matrix least-squares technique on F^2 with SHELXL-97 program[16]. All non-hydrogen atoms were refined anisotropically. The positions of the H-atoms were generated geometrically, and refined using a riding model.

The crystal belongs to monoclinic, space group $C2/c$ with a=1.183 2(1) nm, b=1.512 1(2) nm, c=1.391 1(1) nm, β=97.137(3)°, V=2.469 6(4) nm^3, $C_{12}H_{13}CuN_2O_2$, M_r=280.78, Z=8, D_c=1.510 g·cm^{-3}, μ=1.759 mm^{-1}, $F(000)$=1 152, R_1=0.048 2, wR_2=0.122 5 (w=1/[$\sigma^2(F_o^2)$+ (0.06P)^2+1.99P], where P=(F_o^2+2F_c^2)/3), S=1.05, (Δ/σ)$_{max}$ =0.000, ($\Delta\rho$)$_{max}$=380 and ($\Delta\rho$)$_{min}$=−610 e·nm^{-3}.

CCDC: 709977.

2 Results and discussion

2.1 IR spectrum

In the IR spectrum, the conspicuous carboxylate stretching at 1 615 and 1 426 cm^{-1} is assigned to the antisymmetric ν_a(COO) and symmetric stretching frequency ν_s (COO)[17,18], respectively. The calculated Δ value is 189 cm^{-1}, which is compared with that (157 cm^{-1}) of free CH_3COO^- and suggests that the CH_3COO^- group in the title complex behaves as the monodentate ligand[19]. The strong adsorption band of π(COO) around 558 cm^{-1} disappears, so conclusion can be drawn that the carboxyl group adopts bridge coordination mode[2], which is in agreement with the crystal structure of $[Cu(CH_3COO)(C_5H_5N)_2]_n$.

2.2 Crystal structure description

The molecular structure of the title complex is shown in Fig.1. The selected bond lengths and bond
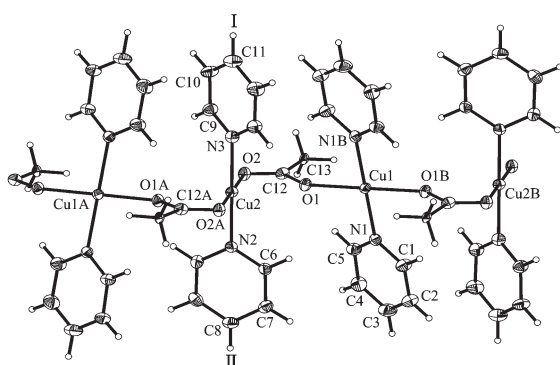
Symmetry codes: A: 1−x, y, 1/2−z; B: 3/2−x, 3/2−y, 1−z

Fig.1　Chain view of the molecule structure of the
tile compound

angles are shown in Table 1. The Cu(Ⅱ) atom is located at a crystallographic inversion center and tetra-coordinated primarily by two oxygen atoms of two symmetry-related carboxyl groups of acetate anions and two nitrogen atoms of two pyridine ligands. Cu(1) and Cu(2) locate in the different coordination environment and all of the pyridine rings linked to Cu(1) and Cu(2) are centrosymmetric on Cu(1). The bond distances of Cu(1)-O(1) and Cu(2)-O(2) are 0.196 4(2) and 0.198 1(2) nm respectively, which are shorter than those of Cu(1)-N(1) [0.205 2(3) nm] and Cu(2)-N(2) [0.200 5(5) nm], suggesting the coordination ability of Cu(Ⅱ) with oxygen is stronger than that with nitrogen[20]. This might be ascribed to the stronger Jahn-Teller effect of d^9 electronic configuration in Cu^{2+} [2]. The similar phenomenon were observed in complexes $[Cu_2(OAc)_4(C_5H_5ClN_2)_2]$ [3] and $[(C_8H_9NO_2)_2Cu_2(CH_3COO)_4]$ [2]. The plane α [defined by O(1), O(1B), Cu(1), N(1) and N(1B), with non deviation] is well coplanar, the bond angles of O(1)-Cu(1)-N(1) and O(1B)-Cu(1)-N(1) are 95.50(12) ° and 84.50(12)° respectively, it is interesting that this plane is a parallelogram plane with Cu(1) as its centre, the same structure is observed in the plane β [defined by O(2), O(2A), Cu(2), N(2) and N(3), with non deviation] which is almost perpendicular to the plane α with the dihedral angle of 87.511(5)°. The Cu(2) atom is linked to two carboxylate groups to form a chain zigzag structure in which the bond angle O(2)-Cu(2)-O(2A) is 179.76(12)° and approaches to 180°. Moreover, this zigzag structure plane is also coplanar well with the largest and mean deviations of 0.002 67 and 0.000 25 nm, respectively.

Each acetate anion coordinates to two copper(Ⅱ) atoms through the oxygen atoms of the carboxyl group, acting as a bridging ligand to form an infinite one-dimensional chain polymer. In the acetate group, the bond distances of C(12)-O(1) and C(12)-O(2) are 0.128 0(4) and 0.121 3(5) nm, respectively, indicating some double-bond character and demonstrating that a three-centered conjugated π bond is formed. Similar distances were also found in the complexes of $[C_{14}H_9CuNO_3 \cdot CH_3OH]$ [21] and $[Cr(salen)(NCS)_2K \cdot H_2O]$ [salen^{2-}=N,N′-ethylenebis(salicyldiminato)] [22]. The bond angle of O(1)-C(12)-O(2) is 124.6(4)° which indicates that this plane has distorted slightly but hasnt deviated from the triangular plane geometry arisen from sp^2 hybrid for the oxygen atom has participated in

Table 1　Selected bond distances (nm) and bond angles (°) for the title complex

Cu(1)-O(1)	0.196 4(2)	Cu(2)-N(3)	0.201 3(5)	N(2)-C(6)	0.132 7(5)
Cu(1)-N(1)	0.205 2(3)	Cu(2)-O(2)^i	0.198 1(2)	N(3)-C(9)	0.132 1(5)
Cu(1)-O(1)^{ii}	0.196 4(2)	O(1)-C(12)	0.128 0(4)	C(1)-C(2)	0.137 0(6)
Cu(1)-N(1)^{ii}	0.205 2(3)	O(2)-C(12)	0.121 3(5)	C(2)-C(3)	0.138 1(8)
Cu(2)-O(2)	0.198 1(2)	N(1)-C(1)	0.134 3(4)	C(3)-C(4)	0.136 7(7)
Cu(2)-N(2)	0.200 5(5)	N(1)-C(5)	0.133 5(6)	C(4)-C(5)	0.137 3(6)
O(1)-Cu(1)-O(1)^{ii}	180.00	N(1)-Cu(1)-N(1)^{ii}	180.00	O(1)-Cu(1)-N(1)	95.50(12)
O(1)-Cu(1)-N(1)^{ii}	84.50(12)	O(1)^{ii}-Cu(1)-N(1)	84.50(12)	O(1)^{ii}-Cu(1)-N(1)^{ii}	95.50(12)
O(2)-Cu(2)-O(2)^i	179.76(12)	N(2)-Cu(2)-N(3)	180.00(2)	O(2)-Cu(2)-N(2)	90.12(8)
O(2)-Cu(2)-N(3)	89.88(8)	O(2)^i-Cu(2)-N(2)	90.12(8)	O(2)^i-Cu(2)-N(3)	89.88(8)
O(1)-C(12)-O(2)	124.6(4)	Cu(1)-N(1)-C(1)	121.0(3)	Cu(1)-N(1)-C(5)	121.5(3)

Symmetry codes: ^{i} 1−x, y, 1/2−z; ^{ii} 3/2−x, 3/2−y, 1−z.

coordination[4]. The Cu···Cu separation across the bridging acetate group is 0.427 66(3) nm, significantly longer than that for the similar complex [Cu(ClCH₂CO₂)₂ (INA)₂]₂[23] with a Cu···Cu separation of 0.394 63(2) nm and shorter than that of [Cu(2-MeSnic)₂(py)₂]₂[24] [Cu···Cu 0.445 4(3) nm]. All of the copper(II) atoms in one infinite chain are almost in a line, in which the bond angles of Cu(1A)-Cu(2)-Cu(1) and Cu(2)-Cu(1)-Cu(2B) are 179.352(1)° and 180°, respectively. The two pyridine rings linked to Cu(1) is parallel, while there are a dihedral angle of 33.121(1)° between the two pyridine ring planes linked to Cu(2). Moreover, the dihedral angles between the two pyridine ring planes I or II and the plane β are 50.435(1)° and 83.556(9)° respectively, by comparison with the dihedral angle of 32.222(1)° between the pyridine rings linked to Cu(1) and the plane α.

In the packing arrangement of the title complex, π-π stacking interactions[25] exsit in intrachain molecules. As illustrated in Fig.2, π-π stacking occurs between the pyridine ring I linked to Cu(2) and adjacent pyridine rings linked to Cu(1). The centroid-to-centroid and centroid-to-plane distances between the pyridine rings [dihedral angle: 12.846(1)°] are 0.371 33(2) nm and 0.255 14/0.282 74 nm. These stacking interactions in intrachain molecules are believed to be largely responsible for the stability of this infinite one-dimensional chain polymer.
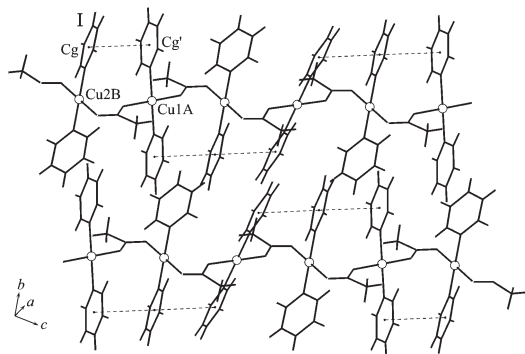
Symmetry codes: A: 1−x, y, 1/2−z; B: 1/2−x, 3/2−y, −z

Fig.2　π-π stacking interactions in intrachain molecules

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