

NOTE**Cu(II) Coordination Polymer With 1D Chain Structure Based on Pyridine-Carboxylate**

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The pyridine carboxylato-bridged coordination polymers [Cu(pbc)₂] (Hpbc = 3-pyrid-3-ylbenzoic acid) has been synthesized by the hydrothermal method and characterized by X-ray single crystal diffraction. The compound [Cu(pbc)₂] exhibits a 1D chain structure.

Key Words: Copper(II), Coordination polymer, Hydrothermal synthesis, Crystal structure.

The current interests in polymeric coordination networks are rapidly expanding not only for their potential applications in catalysis, molecular adsorption, magnetism, non-linear optics and molecular sensing, but also for their intriguing variety of topologies¹⁻⁵. The suitable linker must have the quality to afford a wide variety of linking sites. One of the common strategies to construct these polymeric transition metal complexes is to select suitable multidentate ligands to integrate the metal ions to a desired framework. So the multidentate ligands with suitable spacers between the linking groups are good choices to get the infinite architectures. Besides covalent bonds, hydrogen bonds are frequently used as powerful crystal engineering tools to form frameworks⁶⁻⁸. Accordingly, the pyridine-carboxylic ligands have been used in many synthetic systems, resulting in great variety of new complexes.

Elemental analysis was carried out on a Carlo Erba 1106 full-automatic trace organic elemental analyzer. FT-IR spectra were recorded with a Bruker Equinox 55 FT-IR spectrometer in dry KBr pullet in the range of 4000-400 cm⁻¹.

Preparation of compounds [Cu(pbc)₂]: The mixture of Cu(OAc)₂·H₂O (0.5 mmol, 0.099 g), Hpbc (1 mmol, 0.199 g), NaOH (1 mmol, 0.040 g) and H₂O (12 mL) was heated in a 20 mL stainless steel reactor with a Teflon liner at 160 °C for 120 h and then was cooled to room temperature at 2 °C/h. Blue black crystals were obtained. Yield: 46 % (based on Cu). Anal. calcd. (%) for C₂₄H₁₆CuN₂O₄: C, 62.62; H, 3.50; N, 6.09. Found. (%): C, 62.51; H, 3.53; N, 6.07. IR (KBr, ν_{max}, cm⁻¹): 1648 s; 1437 s; 869 m; 735; 457 m.

Structure determination: Suitable single crystals were selected under a polarizing microscope and fixed with epoxy cement on fine glass fiber which was mounted on a Bruker Smart 1000 CCD diffractometer with a MoK_α radiation (λ = 0.71073 Å) at 293(2) K. The hydrogen atoms bound to carbon were located by

geometrically calculations. All non-hydrogen atoms were refined by full-matrix least-squares techniques. All calculations were performed by the SHELXTL97 program⁹. Crystal data, intensity collection and structure refinement details are summarized in Table-1. Selected bond lengths and bond angles are given in Table-2. CCDC:710871.

TABLE-1
CRYSTALLOGRAPHIC DATA AND STRUCTURE REFINEMENT
SUMMARY FOR COMPLEX [Cu(pbc)₂]

Empirical formula	C ₂₄ H ₁₆ N ₂ O ₄ Cu	Z, Calculated density (mg/m ³)	4, 1.529
Formula weight	459.92	F(000)	470
Crystal system space group	Monoclinic P2 ₁ /c	Absorption coefficient (mm ⁻¹)	1.128
Unit cell dimensions (Å)	a = 9.029 (5)	Limiting indices	-11 ≤ h ≤ 11
	b = 10.454 (5)		-13 ≤ k ≤ 9
	c = 10.770 (5)		-9 ≤ l ≤ 14
Volume (Å ³)	999.0(9)	θ range for data collection (°)	2.30-23.22
Reflections collected/unique	2401/1659	Largest diff. peak and hole (e/Å ³)	0.315 and -0.278
Final R indices [I > 2σ(I)]	R ₁ = 0.0394, wR ₂ = 0.0863	R indices (all data)	R ₁ = 0.0705, wR ₂ = 0.0992

TABLE-2
SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR COMPLEX [Cu(pbc)₂]

Compound 1			
Cu(1)-O(2)	1.949(1)	Cu(1)-O(2A) ^{#1}	1.949(1)
Cu(1)-N(1A) ^{#3}	2.017(2)	Cu(1)-N(1) ^{#2}	2.017(2)
O(2)-Cu(1)-O(2A) ^{#1}	180.00 (1)	O(2A) ^{#1} -Cu(1)-N(1) ^{#2}	90.19(9)
O(2)-Cu-N(1A) ^{#3}	89.81(9)	N(1) ^{#2} -Cu-N(1A) ^{#3}	180.00

Symmetry codes: (1) -x + 3, -y, -z + 1; (2) -x + 2, -y, -z + 1; (3) x + 1, y, z.

Structure description: The single crystal X-ray diffraction analysis reveals that compound [Cu(pbc)₂] crystallizes in the monoclinic system, space group P2₁/c. The local coordination geometry of polymer [Cu(pbc)₂] with the atom-numbering scheme is shown in Fig. 1a, which is shown that each Cu(II) center is coordinated by two oxygen atoms [Cu-O = 1.949 (18) Å] and two N atoms [Cu-N = 2.017(2) Å]. Each pbc⁻ anion is coordinated to the central atom in monodentate mode: μ₂-N, O and uses its pyridyl N atom and the carboxylate group to link two Cu(II) centers along the a-axis, which lead to two Cu ions and two ligand construct a metallic cycle as the based building block of the 1D chain in the ab-plane (Fig. 1b). The dihedral angle between pyridine ring and phenyl ring is 52.19°.

Crystal packing analysis of compound [Cu(pbc)₂] shows the formation of inter-chain (C-H...O) hydrogen bonds (Fig. 2). In the formation of the 3D supramolecular

structure the inter-chain C-H...O group is linked through the coordinated oxygen atoms of the adjacent chain at a D...A distance of 3.208 Å and a C-H-O angle of 138° (symmetry code: 1 + x, 3/2 - y, -1/2 + z).

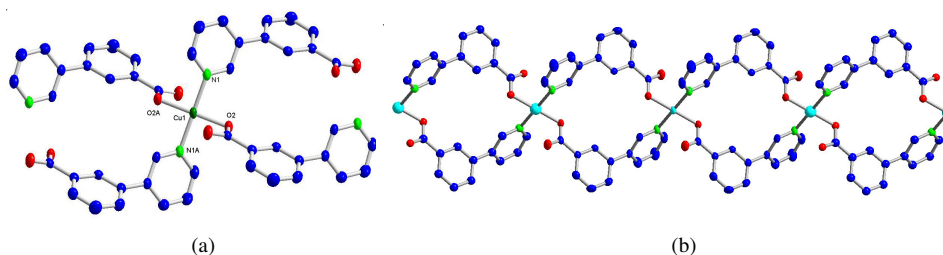


Fig. 1. (a) View of the coordination environment of Cu(II) ion; (b) perspective views of the 1D chain structure view along c axis

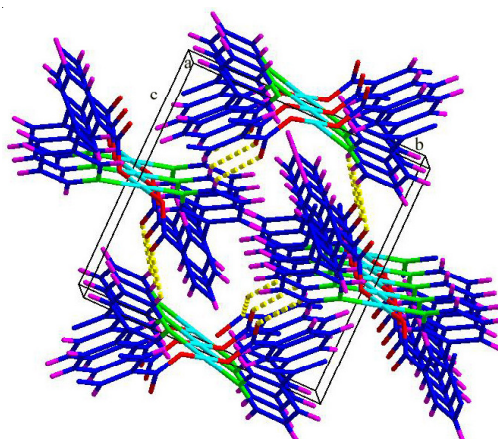


Fig. 2. 3D Supramolecular structure formed by hydrogen bonds indicated by light dashed lines

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