



Synthesis and Crystal Structure of Nickel Complex Assembled from Pyridine-Carboxylate Ligand

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The pyridine carboxylato-bridged coordination polymer $[\text{Ni}(\text{3,3-pbc})_2(\text{H}_2\text{O})_2]_n$ (3,3-pbc=3-pyrid-3-ylbenzoic acid) has been synthesized and structurally characterized by elemental analysis, IR and X-ray diffraction. Single crystal X-ray analyses reveal that the carboxylate groups of 3,3-pbc ligand adopt one coordinated mode: *bis*-monodentate ($\mu_2\text{-}\eta^1\text{:}\eta^1$) and bidentate chelating ($\mu\text{-}\eta^1\text{:}\eta^1$) fashion. Hydrogen bonding interactions are found in compound which further extend and stabilize the coordination motifs.

Key Words: Coordination polymer, Hydrothermal synthesis, Crystal structure, Pyridine-carboxylate ligand.

INTRODUCTION

In recent years, coordination polymers and supramolecular complexes have attracted much attention, owing to their potential application as functional materials¹⁻³. It is well-known that the structural and functional information of such target materials were constructed by the metal-ligand coordination bonds or intermolecular weak interactions. In this case, the design of new types of ligands such as pyridyl and/or carboxylate groups have been proven to the most important strategy, due to their potential multiple coordination mode⁴⁻⁷. Hydrogen bonds are suitable for the design of polymeric arrangement and crystal engineering because of their important directional interactions and because they can interlink 1-D or 2-D structures into higher-dimensionality systems.

As a part of our work towards rational design and preparation of functional coordination frameworks, we selected 3-pyrid-3-ylbenzoic acid as assembly ligand considering following reasons: (a) it has carboxylate oxygen atoms and nitrogen atom that provide rich coordination modes; (b) due to deprotonated carboxyl groups and pyridyl nitrogen atom, it can acts as hydrogen bond acceptor and/or hydrogen accept hydrogen bond donor. In this paper, we report a new metal-organic frameworks $\{[\text{Ni}(\text{pbc})_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$.

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

Synthesis of $\{[\text{Ni}(\text{pbc})_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$: A mixture of 3,3-pbc (0.199 g, 1 mmol), $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ (0.119 g, 0.5 mmol), NaOH (1.5 mmol, 0.06 g) and distilled water (18 mL) was heated in a 25 mL stainless-steel reactor with a Teflon liner 160 °C for 120 h, followed by slow cooling to room temperature. Green block crystals were obtained in 70 % yield (based on Ni). Anal. calcd. (%) for $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_6\text{Ni}$: C, 58.69; H, 4.10; N, 5.70. Found (%): C, 58.21; H, 4.12; N, 5.62. IR (KBr, ν_{max} , cm^{-1}): 3420, br; 1618, s; 1530, s; 1390, s; 672, m; 435, m.

X-Crystallography: Suitable single crystals were selected under a polarizing microscope and fixed with epoxy cement on fine glass fibers which were mounted on a Bruker Smart 1000 CCD diffractometer with a $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) 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 SHELXTL 97 program⁸. Crystal data, intensity collection and structure refinement details are summarized in Table-1. Selected interatomic distances and bond angles are given in Table-2 CCDC: 710870.

EXPERIMENTAL

All reagents and solvents employed were commercially available and were used as received without further purification.

RESULTS AND DISCUSSION

Structure description: Compound crystallizes monoclinic system space group $\text{P2}_1/c$. As shown in Fig. 1, it is shown

TABLE-1
CRYSTALLOGRAPHIC DATA AND STRUCTURE
REFINEMENT SUMMARY FOR COMPLEX

Empirical formula	C ₂₄ H ₂₀ N ₂ O ₆ Ni
Formula weight	491.13
Crystal system space group	Monoclinic P2 ₁ /c
Unit cell dimensions	a = 10.490(2) Å b = 12.920(3) Å c = 16.074(3) Å α = 118.085(10) β = 104.421(10) γ = 90.118(10)
Volume (Å ³)	2166.7(8)
Z, calculated density (mg/m ³)	4, 1.506
F(000)	1016
θ range for data collection	1.95-27.73
Limiting indices	-12 ≤ h ≤ 13 -8 ≤ k ≤ 16 -20 ≤ l ≤ 20
Goodness-of-fit on F ²	0.972
Final R indices [I > 2σ(I)]	R ₁ = 0.0410 wR ₂ = 0.1140
R indices (all data)	R ₁ = 0.0519 wR ₂ = 0.1191
Largest diff. peak and hole (e/Å ³)	1.195 and -1.021

that nickel(II) atom is coordinated by three carboxylate oxygen atoms [Ni(1)-O(1) = 2.120 (16) Å, Ni(1)-O(2) = 2.184(17) Å and Ni(1)-O(4) = 2.004(17) Å] and two nitrogen atoms [Ni(1)-N(1) = 2.109 (11) Å and Ni(1)-N(2) = 2.100(11) Å] from four different pbc⁻ ligands and one coordinated water molecule [Ni(1)-O(1W) = 2.062 (17) Å], showing a distorted octahedral geometry. In the complex, all 3,3-pbc⁻ ligands act as diconnectors to link two Ni(II) centers and adopt two coordination modes: μ₂-N, O and μ₂-N, O, O which connect Ni(II) to form zigzag one-dimensional chain structure viewed along the a-axis (Fig. 2). The dihedral angles are 33.05° (μ₂-N, O) and 15.79° (μ₂-N, O, O) between pyridine ring and phenyl ring in pbc⁻ ligand.

In the complex, there exist intermolecular hydrogen bonds (Fig. 3). The inter-chain (O-H...O) hydrogen bonds is formed between the O-H group of the coordinated water molecule and carboxylate oxygen (O2 and O3), with a H1WA...O3 distance of 1.81 Å (symmetry code: -x, 2-y, -z), a H1WB...O2 distance of 1.97 Å (symmetry code: -x, 2-y, -z) and a H2WA...O3 distance of 1.95 Å (symmetry code: -x, -1/2 + y, 1/2-z). It is no doubt that the hydrogen-bonding interactions contribute to the alignment of the complex in the crystalline state.

TABLE-2
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°)

Bond	Dist.	Bond	Dist.	Bond	Dist.
Ni(1)-O(4)#1	2.004 (2)	Ni(1)-O(1)	2.120(2)	Ni(1)-O(2)	2.184(2)
Ni(1)-N(1)#2	2.109 (1)	Ni(1)-N(2)	2.100 (1)	-	-
Angle	(°)	Angle	(°)	Angle	(°)
O(4)#1-Ni(1)-O(1w)	92.88(8)	O(4)#1-Ni(1)-N(2)	90.25(7)	N(2)-Ni(1)-O(1)	99.59(6)
O(1w)-Ni(1)-N(2)	88.44(7)	O(4)#1-Ni(1)-N(1)#2	90.48(7)	O(4)#1-Ni(1)-O(2)	108.91(7)
O(1w)-Ni(1)-N(1)	176.55(6)	N(2)-Ni(1)-N(1)#2	92.35(6)	N(2)-Ni(1)-O(2)	160.77(6)
O(4)#1-Ni(1)-O(1)	170.13(7)	O(1w)-Ni(1)-O(1)	88.20(7)	O(1)-Ni(1)-O(2)	61.28(6)

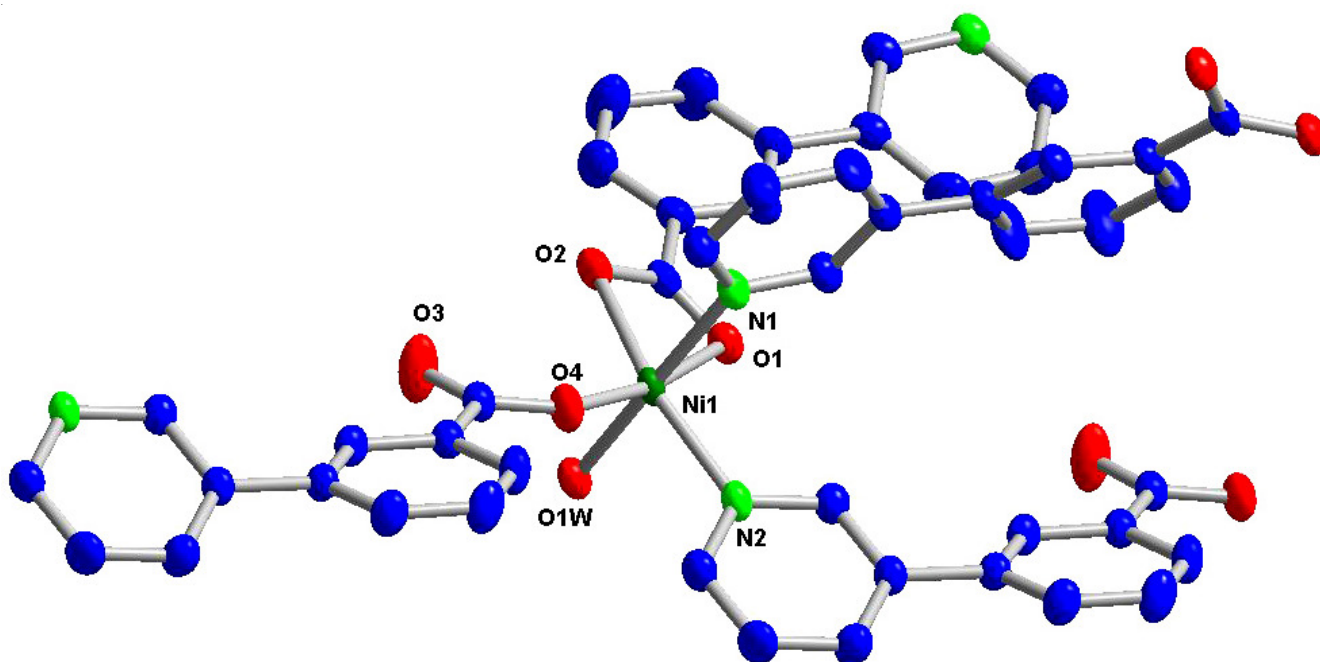


Fig. 1. View of the coordination environment of Ni(II) ion for compound 2. All hydrogen atoms and lattice water molecular are omitted for clarity

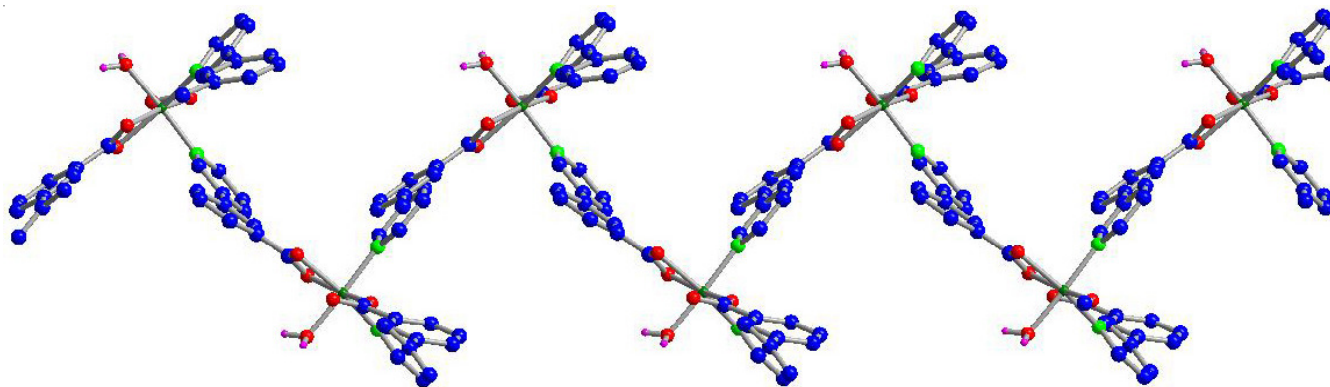


Fig. 2. One-dimensional Zigzag chain along the a axis for compound 2

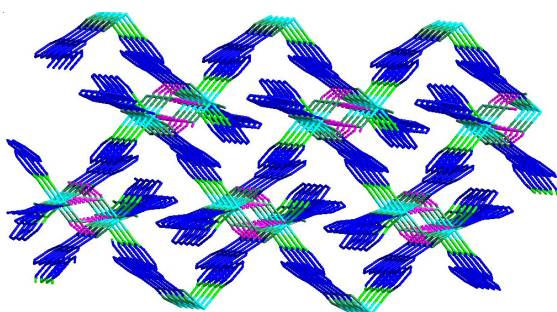


Fig. 3. 3D Supramolecular structure formed by hydrogen bonds indicated by dashed lines for compound 2 viewed along a axis

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