



Synthesis, Crystal Structure of One-Dimensional Chains $\{[\text{Zn}(\text{ip})(\text{py})_2]\cdot\text{NMP}\}_n$ (py = Pyridine, NMP = N-methyl-pyrrolidone, H₂ip = Isophthalic acid)

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Hot-solution reactions of $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, pyridine (py) with isophthalic acid (H₂ip) in N-methyl-pyrrolidone (NMP) yields one-dimensional (1D) coordination polymer. Single crystal analysis show that compound **1**, $\{[\text{Zn}(\text{ip})(\text{py})_2]\cdot\text{NMP}\}_n$ with 1D zigzag chains and every two chains face to face to form the slide fastener. Crystal data of **1** are, orthorhombic, space group P, a = 8.5960(3), b = 10.1091(4), c = 26.2070(10), Z = 4. The results indicate that the geometry of ligands play the important roles in the frameworks of products.

Keywords: 1D Zigzag Chains, Pyridine, Crystal structure.

INTRODUCTION

Design and assembly of coordination polymers based on crystal engineering has received extensive attentions because of their excellent properties and applications¹⁻⁵. In the syntheses of coordination polymers, there are many factors such as synthesis temperature^{6,7}, solvent^{8,9}, ligand^{10,11}, pH value^{12,13} and auxiliary ligands¹⁴⁻¹⁶ produce important influences on their crystal structures and functionality. In term of flexible ligands^{17,18}, the geometry of ligand in general could permissive distort when they located in different coordination environment induced by metal ions and other factors. In other hand, the geometry of rigid ligand⁹ commonly couldn't change with different reaction condition and coordination environment and the angle between functional groups of ligand directly impact on the space stretch of coordinate polymerization, further engender different frameworks manipulated by the steric configuration of ligands. Therefore, the ligand geometry plays an important role in determine the structure of the coordination polymers. Moreover, the auxiliary ligands also exhibit an important effect on the structures of coordination polymers, such as N-donor polyamine ligands pyridine, pyrazine, bipyridine¹⁹⁻²² and they could change the coordinate mode of carboxylic and hold the coordinate site of metal ions. We have studied the influence of synthesis temperature, solvent and ligand substituent on the structure of coordination polymers previously²³⁻²⁵. Herein, we report a coordination polymers $\{[\text{Zn}(\text{ip})(\text{py})_2]\cdot\text{NMP}\}_n$ **1** (H₂ip = isophthalic acid, pyridine = pyridine, NMP = N-methyl-

pyrrolidone). This study shows that the auxiliary ligands can bring the obvious influence on the structure of coordination polymers.

EXPERIMENTAL

All chemicals and solvents used in the syntheses were of analytical grade and used without further purification. IR performed on Nicolet 740 FTIR Spectrophotometer, the range of λ is 4000-400 cm^{-1} , the sample platelet with KBr. Elemental analysis was carried out on a CE instruments EA 1110 elemental analyzer. X-ray powder diffractions were measured on a Panalytical X-Pert pro diffractometer with $\text{CuK}\alpha$ radiation.

$\{[\text{Zn}(\text{ip})(\text{py})_2]\cdot\text{NMP}\}_n$ (1): H₂ip (0.166 g, 1 mmol) and $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.298 g, 1 mmol) were dissolved in N-methyl pyrrolidone (8 mL), then pyridine (0.5 mL) was slowly added to the solution. The mixture was placed in a 25 mL conical flask, heated to 90 °C at the rate of 0.2 °C/min and kept at 90 °C for 4 days, then slowly cool down to room temperature at the rate of 0.1 °C/min. Colourless rod crystals (0.173 g, yield 35.54 %) suitable for X-ray diffraction was separated by filtration, washed with deionized water and dried in air. Elemental analysis $[\text{ZnC}_{23}\text{H}_{21}\text{N}_3\text{O}_5]_n$: found (Calcd.) C 56.18 (56.74), H 4.31 (4.36), N 8.34 (8.63) %. FTIR (KBr, ν_{max} , cm^{-1}): 3431 (s), 2972 (w), 1610 (vs), 1568 (m), 1450 (m), 1371 (s), 1268 (w) 1220 (w), 1158 (w), 1071 (w), 1046 (m), 747 (s), 722 (m), 700 (s), 661 (m).

X-ray crystallography: Data collection for **1** were performed on a Bruker SMART Apex CCD diffractometer at 293 K

with graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Absorption correction was applied by using the multi-scan program SADABS²⁶. The structure was solved by direct methods and non-hydrogen atoms were refined anisotropically by least-squares on F^2 using the SHELXTL program^{27,28}. Crystal data as well as details of data collection and refinement for the complexes are summarized in Table-1 and selected bond lengths and angles for **1** show in Table-2.

TABLE-1
CRYSTAL DATA AND DETAILS OF THE DATA
COLLECTION AND REFINEMENT FOR COMPOUND **1**

Complexes	1
Empirical formula	$\text{C}_{23}\text{H}_{23}\text{N}_5\text{O}_5\text{Zn}$
Formula weight	486.81
Temperature(K)	293(2)
Crystal size (mm)	$0.32 \times 0.28 \times 0.26$
Crystal system	Orthorhombic
Space group	P
a (Å)	8.5960(3)
b (Å)	10.1091(4)
c (Å)	26.2070(10)
α (°)	90
β (°)	90
γ (°)	90
V(Å ³)	2277.33(15)
Z	4
D _{calcd} (Mg/m ³)	1.420
μ (mm ⁻¹)	1.117
F(000)	1008
Ref. unique	5449
Ref. ($I > 2\sigma(I)$)	26100
R _{int}	0.0385
Data/restraints/parameters	5449/7/291
R ₁ ($I > 2\sigma(I)$)	0.1011
wR ₂ (all data)	0.2412
Goodness-of-fit on F ²	1.336
Max./min., $\Delta\rho$ (e·Å ⁻³)	1.588/-1.163
Completeness	100

RESULTS AND DISCUSSION

$\{[\text{Zn}(\text{ip})(\text{py})_2]\cdot\text{NMP}\}_n$ (**1**): Compound **1** was synthesized as colourless rod crystals by the reaction of $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and isophthalic acid through hot solution method and comprise one zinc(II) ions, one deprotonated isophthalic acid, two pyridine and a guest molecule N-methyl pyrrolidone. Zn1 is four-coordinated by two pyridine molecules and two monodentate carboxylates respectively from two deprotonated isophthalic acid in distorted tetrahedral geometry. Both two carboxylates from deprotonated isophthalic acid connected one zinc by monodentate mode and adjacent zinc ions linked by deprotonated isophthalic acid to form 1D chains (Fig. 1). All phenyl rings of deprotonated isophthalic acid in every chain situated in the

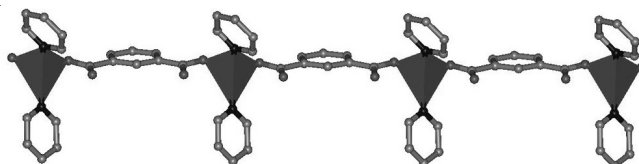


Fig. 1. 1D chain consists of zinc ions, deprotonated isophthalic acid and pyridine in compound **1**. Hydrogen atoms and guest molecules (NMP) are omitted for clarity

same side and the two pyridine coordinated with zinc ion lie in both sides of phenyl plane, the angle of N1-Zn1-N1 is 116.4° . Every two chains integrate by face to face to form the slide fastener and every slide fastener further parallel arrange along *a* axis (Fig. 2). In the slide fastener, the pyridine in a chain dead against the direction of the V shape from the deprotonated isophthalic acid in another chain and the N-methyl pyrrolidone guest molecules located in the void come into being among three pyridine ring from two chains.

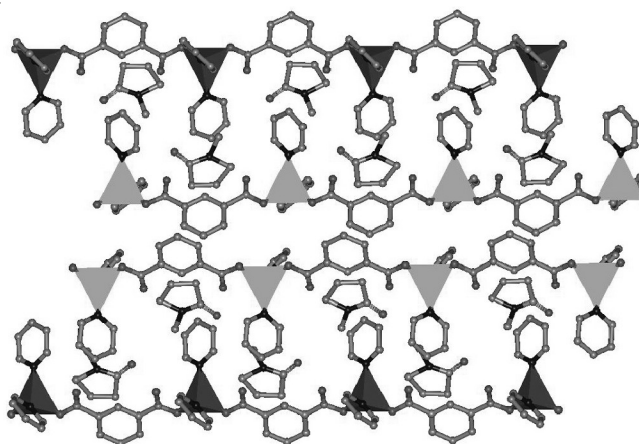


Fig. 2. View of 1D chain piled by AB...mode along a axis in compound **1**. Hydrogen atoms are omitted for clarity

In X-ray powder diffraction pattern (Fig. 3), all of peaks among experimental result are almost consistent with simulated curve and the contents of C, H, N from elemental analysis measurement on the whole coincides with theoretical calculation. Both they are shown that the pure phase of **1** was obtained through hot solution method in N-methyl pyrrolidone. Based on the above result, we can deduce that the V-type of ligand geometry result in 1D structure. In this structure, pyridine can show stronger coordination ability than deprotonated isophthalic acid ligand. There is obvious characteristic in the structure (Table-3), the coordination number of zinc ions is 4 and connection number of carboxylates is 1, while the number of pyridine coordinated with zinc ions is 2 and guest number of pyridine is 1. The compound **1** has higher ratio of void as 33.8 % because of guest molecules N-methyl pyrrolidone inhabited the holes. We also discover the constitutional unit

TABLE-2
SELECTED BOND LENGTHS AND ANGLES FOR THE Zn(II) COMPLEX (Å AND DEG)

Zn1-O1	1.976(5)	O1-Zn1-N1	111.6(3)	O3a-Zn1-N1	114.5(3)
Zn1-O3a	1.972(5)	O1-Zn1-N2	113.2(2)	O3a-Zn1-N2	107.3(3)
Zn1-N1	2.037(6)	O3a-Zn1-O1	98.41(19)	N1-Zn1-N2	116.4(2)
Zn1-N2	2.044(6)				

Symmetry codes: a x, y + 1, z; b x, y-1, z

TABLE-3
STRUCTURAL CHARACTER OF COORDINATION POLYMER **1**

Coordination polymer	$\{[\text{Zn}(\text{ip})(\text{py})_2]\cdot\text{NMP}\}_n$, 1
Coordination number of Zn^{2+}	4
$\text{Zn}^{2+}/\text{COO}^-$	1
PY/Zn^{2+}	2
Guest nmp number	1
Void (%)	33.8

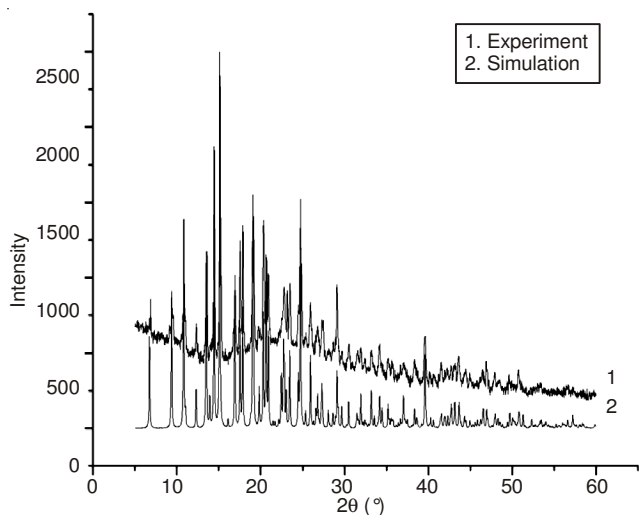


Fig. 3. Simulated and experimental X-ray powder diffraction pattern for **1**

of **1** is a mononuclear zinc chains linked by deprotonated isophthalic acid, Therefore, we can conclude that the geometry of ligands play the important roles in assemble of coordination polymers.

Conclusion

In summary, we have successfully synthesized the coordination polymers $\{[\text{Zn}(\text{ip})(\text{py})_2]\cdot\text{NMP}\}_n$ **1** with mononuclear zigzag zinc chains linked by deprotonated isophthalic acid and guest molecules N-methyl pyrrolidone were molecules located in the void come into being among three pyridine ring from two chains. The X-ray powder diffraction pattern and elemental analysis result show the pure phase was obtained by hot solution method.

CCDC No. 969394 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* (please use the link below) by e-mailing data_request@ccdc.cam.ac.uk, or by contacting: The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(0)1223-336033. www.ccdc.cam.ac.uk/data_request/cif

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