

Synthesis, Characterization and Crystal Structure of a Supramolecular Compound Diaquabis(1,10-phenanthroline- κ^2 N,N')cobalt(II) 4,4'-Methylenebis(3-hydroxy-2-naphthoate) Tetrahydrate

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In present study, the metal-organic coordinated polymers from pamononic acid, 4,4'-methylenebis(3-hydroxy-2-naphthoic acid) (L), a supramolecular compound $\text{Co}(\text{phen})_2(\text{H}_2\text{O})_2\text{L}\cdot(\text{H}_2\text{O})_4$ (**1**) was synthesized. Its structure was determined by single crystal X-ray diffraction experiment. The compound crystallizes in the monoclinic system and adopts a centrosymmetric space group of C2/c. In $\text{Co}(\text{phen})_2(\text{H}_2\text{O})_2\text{L}\cdot(\text{H}_2\text{O})_4$, two phen ligands coordinate to Co(II) through two N atoms, respectively. And the other two coordinated sites in the octahedron geometry of Co(II) are completed by four H_2O through O atoms. Pamononic acid only acts as a counter anion. There are several hydrogen bonds between coordinated water of coordination cation, pamononic acid anion and solvent water molecules. These hydrogen bonding interactions assemble three components of this compound firmly and from a supramolecular chain along c-axis.

Key Words: Pamononic acid, Supramolecular compound, Hydrogen bond.

INTRODUCTION

Self-assembled supramolecular systems and metal-organic coordinated polymers have received considerable attention, not only for their potential applications as optoelectronic, magnetic materials and sensors, or in gas storage and catalysis but also exhibiting structural and topological novelty¹⁻⁵. When supramolecular framework is regarded as the synthetic target, some noncovalent interactions must be cared for construction, such as hydrogen bonding, π - π stacking, anion- π and C-H... π interactions. These interactions have also been emphasized repeatedly by other literatures⁴⁻⁸. Here, we adopt pamononic acid as a multiple linkage to construct metal-organic coordination polymers and supramolecular systems, because pamononic acid could coordinate to metal centre by its two carboxyl groups and also could form firmly hydrogen bonds profit from its two hydroxyl groups⁹⁻¹⁷. Here we report a supramolecular compound $\text{Co}(\text{phen})_2(\text{H}_2\text{O})_2\text{L}\cdot(\text{H}_2\text{O})_4$ (**1**) constructed by hydrogen bonds, which is obtained in our attempt to synthesis metal-organic coordinated polymer utilizing of pamononic acid.

EXPERIMENTAL

All chemicals were obtained from commercial sources and used as received. Elemental analysis for C, H, N and O were performed on an Elementar Vario MICRO analytic instrument.

Synthesis of $\text{Co}(\text{phen})_2(\text{H}_2\text{O})_2\text{L}\cdot(\text{H}_2\text{O})_4$ (1**):** The compound was synthesized by a solution reaction from pamononic acid. Phen (20 mg, 0.1 mmol) and $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ (12 mg, 0.05 mmol) was dissolved in 5 mL EtOH and 5 mL H_2O to produced a yellow solution. To this solution a 5 mL DMF solution of pamononic acid (20 mg, 0.05 mmol) and NaOH (4 mg, 0.1 mmol) was added at room temperature. Consequently, a yellow solution was formed and filtrated. After evaporating the filtration at room temperature for 2 days, amount of yellow crystals were obtained. (yield 29 mg, 63.5 % based on $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$). Anal. calcd. (%) for $\text{C}_{47}\text{H}_{42}\text{CoN}_4\text{O}_{12}$: C, 61.78; H, 4.63; N, 6.13; O, 21.01. Found (%): C, 61.23; H, 4.91; N, 6.62; O, 21.87.

Single crystal structure determination: X-Ray intensity data of $\text{Co}(\text{phen})_2(\text{H}_2\text{O})_2\text{L}\cdot(\text{H}_2\text{O})_4$ were collected on a black prism crystal (0.48 mm \times 0.20 mm \times 0.12 mm) at 293(2) K on a Rigaku RAXIS-RAPID CCD area detector diffractometer using graphite monoc-hromated MoK_α radiation ($\lambda = 0.071075$ nm). The structure was solved using direct methods and refined by full-matrix least-squares techniques. All non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement. All hydrogen atoms were added at calculated positions and refined using a riding model. The structure was refined on F^2 using SHELXTL-97 software package without any unusual events¹⁸. The crystal and refinement details for

compound **1** are listed in Table-1. The selected bond lengths and bond angles are presented in Table-2.

TABLE-1
CRYSTAL DATA, COLLECTION AND STRUCTURE
REFINEMENT PARAMETERS FOR COMPOUND **1**

C ₂₄ H ₂₀ CoN ₄ O ₂ ·C ₂₃ H ₁₄ O ₆ ·4(H ₂ O) (1)	
Empirical formula	C ₄₇ H ₄₂ N ₄ O ₁₂ Co
Formula weight	913.78
Temperature (K)	293(2)
Crystal system	monoclinic
Space group	C2/c
Crystal size (mm ³)	0.48 × 0.20 × 0.12
Crystal description	Platelet, yellow
a (Å)	17.7125(12)
b (Å)	20.5263(10)
c (Å)	12.5863(7)
β (°)	114.744(7)
volume V (Å ³)	4155.9(4)
Z	4
D _{calc} (Mg m ⁻³)	1.460
μ (mm ⁻¹)	0.49
F ₍₀₀₀₎	1900
2θ _{max} (°)	54.00
Final R indices [I>2σ(I)] [#]	R ₁ = 0.0360, wR ₂ = 0.0557
R indices (all data) [#]	R ₁ = 0.0989, wR ₂ = 0.0640
Goodness-of-fit on F ²	1.024

$$^{\#} R_1 = \frac{(\|Fo|Fc\|)}{\sum |Fo|}; \quad wR_2 = \left\{ \frac{\sum w[(Fo^2 - Fc^2)]^{0.5}}{\sum w[Fo^2]} \right\}$$

TABLE-2
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°) FOR **1**

Co1-O1	2.0847(17)	Co1-O1i	2.0847(17)
Co1-N1	2.1420(18)	Co1-N1i	2.1420(18)
Co1-N2	2.1150(14)	Co1-N2i	2.1150(14)
O1-Co1-O1 ⁱ	93.46(11)	O1-Co1-N1	87.67(7)
O1-Co1-N2	90.26(7)	O1-Co1-N1 ⁱ	173.62(7)
O1-Co1-N2 ⁱ	95.38(7)	O1 ⁱ -Co1-N1	173.62(7)
O1 ⁱ -Co1-N2	95.38(7)	O1 ⁱ -Co1-N1 ⁱ	87.67(7)
O1 ⁱ -Co1-N2 ⁱ	90.26(7)	N1-Co1-N2	78.33(6)
N1-Co1-N1 ⁱ	91.89(9)	N1-Co1-N2 ⁱ	95.89(6)
N2-Co1-N1 ⁱ	95.89(6)	N2-Co1-N2 ⁱ	171.78(9)
N2 ⁱ -Co1-N1 ⁱ	78.33(6)	—	—

Symmetry codes: (i) -x + 1, y, -z + 1/2.

RESULTS AND DISCUSSION

We have synthesized the supramolecular compound Co(phen)₂(H₂O)₂L·(H₂O)₄ (**1**). The compound crystallizes in a monoclinic system and adopts a centrosymmetric space group of C2/c. As shown in Fig. 1, the cation is a Co(II) complex, in which the Co(II) adopt a octahedral coordinated sphere make up of four N atoms from two phen ligands and two O atoms from coordinated water¹⁹⁻²³. Corresponding to the Co(II) complex, the pamonic acid acts as the counter anion. Nearby the cation and anion, there are four solvent water molecules. And there are seven types of O-H...O hydrogen bonds between these three components. These hydrogen bonds have also been examined by the PLATON program^{24,25} and through these interactions, a supramolecular hydrogen bonding chain are present along c-axis (Fig. 2). Fig. 3 showed the packing diagram along the c-direction. The details of hydrogen bonding interactions are shown in Table-3.

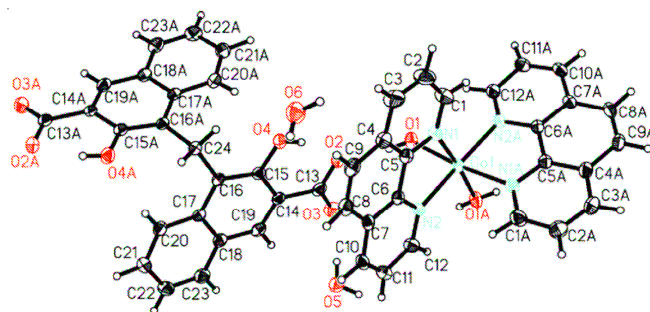


Fig. 1. Structure and labeling of the compound **1**, with displacement ellipsoids drawn at the 30 % probability level and H atoms shown as small spheres of arbitrary radii

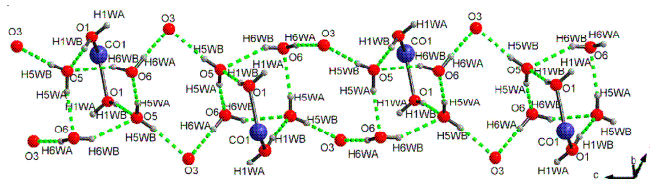


Fig. 2. Hydrogen bonding chain along c axis

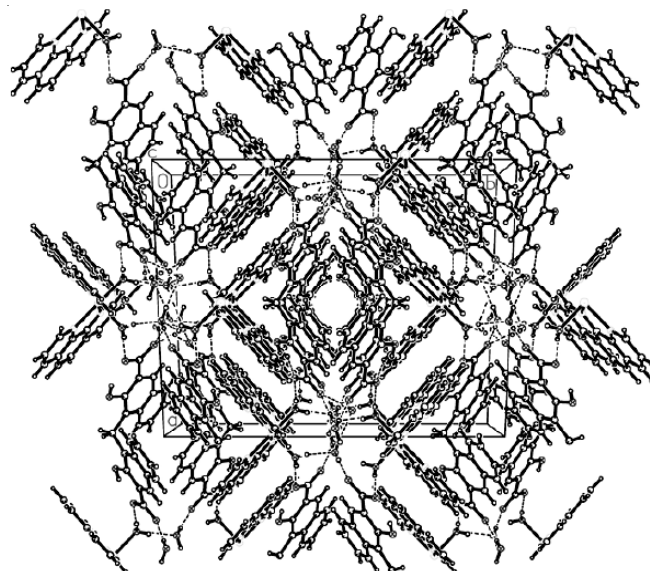


Fig. 3. Packing diagram viewed along the c-direction

TABLE-3
HYDROGEN-BOND GEOMETRY (Å, °) FOR **1**

D-H...A	D-H	H...A	D...A	D-H...A
O1-H1WA...O2	0.83(3)	1.89(3)	2.720(2)	171(3)
O1-H1WB...O5 ⁱⁱ	0.82(3)	1.91(3)	2.732(3)	171(3)
O4-H4...O2	0.78(2)	1.80(3)	2.537(2)	156(3)
O5-H5WA...O6 ⁱⁱⁱ	0.84(3)	2.00(3)	2.828(3)	170(3)
O5-H5WB...O3	0.80(3)	1.89(3)	2.692(2)	173(3)
O6-H6WA...O3 ^{iv}	0.84(3)	1.88(3)	2.717(3)	171(3)
O6-H6WB...O5 ^v	0.79(3)	2.13(3)	2.856(3)	153(3)

Symmetry codes: (ii) x, -y, z-1/2; (iii) x + 1/2, -y + 1/2, z + 1/2; (iv) -x + 1/2, y + 1/2, -z + 1/2; (v) -x + 1/2, -y + 1/2, -z + 1.

Conclusion

We have synthesized the supramolecular compound Co(phen)₂(H₂O)₂L·(H₂O)₄ (**1**). And it is characterized as a chain-like supramolecular structure constructed by seven types of O-H...O hydrogen bonds between cation(anion) and four solvent water molecules.

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