



Construction of a $[\text{Co}_3(\text{IP})(4,4'\text{-obb})_3]_n$ with 4,4'-Oxybisbenzoic Acid and Imidazo[4,5-f][1,10]phenanthroline

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A new coordination polymer $[\text{Co}_3(\text{IP})(4,4'\text{-obb})_3]_n$ (**1**) (4,4'-obb = 4,4'-oxybisbenzoic acid, IP = 1*H*-imidazo[4,5-*f*][1,10]phenanthroline) was synthesized and characterized by single-crystal X-ray diffraction, elemental analysis, IR, PXRD. Single-crystal X-ray analyses revealed that $[\text{Co}_3(\text{IP})(4,4'\text{-obb})_3]_n$ was bridged by 4,4'-obb ligands to form a 1D infinite chain, was further extended to 2D supramolecular structure by hydrogen bonding interactions and $\pi\cdots\pi$ interactions.

Key Words: Coordination polymer, Crystal structure, Cobalt(II).

INTRODUCTION

The field of the novel functional metal-organic frameworks (MOFs) continues to expand at a remarkable pace due to their diverse topologies and potential applications in gas storage, magnetism, catalysis and luminescence¹⁻⁵. It is still a great challenge to rationally prepare and control the structures and composition of target products because of the difficult prediction of either the composition or the structure of the reaction product⁶. Many ligands with carboxyl and N-containing were used due to their various coordination modes and structural features⁷.

EXPERIMENTAL

The elemental analyses for C, H and N were performed on an Elementar Vario Micro Cube analyzer. The IR spectra were recorded on a Thermo Nicolet IR200 FT-IR spectrometer as KBr pellets (4000-400 cm^{-1}). Powder X-ray diffraction (PXRD) analysis was performed on a MiniFlex2 X-ray diffractometer.

Synthesis of $[\text{Co}_3(\text{IP})(4,4'\text{-obb})_3]_n$ (1**):** A mixture of $\text{Co}(\text{NO}_3)_2$ (0.0291 g, 0.1 mmol), 4,4'-oxybisbenzoic acid (4,4'-obb) (0.0258 g, 0.1 mmol), 1*H*-imidazo[4,5-*f*][1,10]phenanthroline (IP) (0.022 g, 0.1 mmol), NaOH (0.008 g, 0.2 mmol) and deionized water (10 mL) was sealed in a 25 mL Teflon-lined stainless steel vessel and heated at 160 °C for 72 h. After cooling to room temperature, the red block crystals were obtained and washed with alcohol for several times (Yield:

52 % based on Co). Experimental PXRD data matches well with simulated powder pattern (Fig. 1). Elemental anal. calcd. (%) for $\text{C}_{82}\text{H}_{50}\text{N}_8\text{O}_{20}\text{Co}_3$: C, 59.85; H, 3.04; N, 6.81. Found: C, 59.78; H, 2.93; N, 6.65. IR: 1618 s, 1384 s, 1241 m, 1159 m, 879 m, 780 w, 619 m.

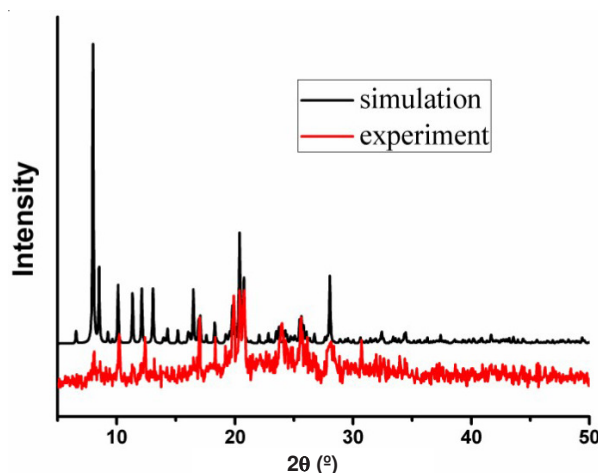


Fig. 1. Powder X-ray diffraction of $[\text{Co}_3(\text{IP})(4,4'\text{-obb})_3]_n$

X-ray crystallography: 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 ($\lambda = 0.71073 \text{ \AA}$) at 293(2) K. The hydrogen atoms bound to carbon

TABLE-1
CRYSTALLOGRAPHIC DATA AND STRUCTURE REFINEMENT SUMMARY FOR COMPLEX 1

Empirical formula	C ₃₂ H ₅₀ N ₈ O ₂₀ Co ₃	Z, Calculated density (mg/m ³)	1, 1.572
Formula weight	1644.09	F(000)	839
Crystal system, space group	Triclinic, P-1	Absorption coefficient (mm ⁻¹)	0.795
Unit cell dimensions	a = 11.439(5) (Å) b = 11.940(5) (Å) c = 14.660(5) (Å)	Limiting indices	-13 ≤ h ≤ 13 -12 ≤ k ≤ 14 -17 ≤ l ≤ 17
Volume (Å ³)	1736.3(12)	θ range for data collection (°)	1.51 to 25.00
Reflections collected / unique	8974 / 6042	Largest diff. peak and hole (e/Å ³)	0.600 and -0.356
Final R indices [I > 2σ(I)]	R1 = 0.0359, wR2 = 0.1034	R indices (all data)	R1 = 0.0486, wR2 = 0.1126

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

Bond (Å)	Co(1)-O(1)	2.0740(18)	Co(1)-O(3A)#1	2.043(2)
	Co(1)-O(1A)#1	2.0740(18)	Co(1)-O(8B)#2	2.1403(18)
	Co(1)-O(3)	2.043(2)	Co(1)-O(8C)#3	2.1403(18)
Bond angles (°)	O(3)-Co(1)-O(1)	95.86(9)	O(1)-Co(1)-O(8B)#2	89.32(7)
	O(3)-Co(1)-O(1A)#1	84.14(9)	O(1)-Co(1)-O(8C)#3	90.68(7)
	O(3A)#1-Co(1)-O(1A)#1	95.86(9)	O(1A)#1-Co(1)-O(8C)#3	89.32(7)
Symmetry code: #1 -x+1,-y+1,-z+1; #2 x+1,y-1,z; #3 -x,-y+2,-z+1.				

were located by geometrically calculations. All non-hydrogen atoms were refined by full-matrix least-squares techniques. All calculations were performed by the SHELXTL97 program⁸. 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: 869418.

RESULTS AND DISCUSSION

Description of crystal structure: Single crystal X - ray diffraction reveals that [Co₃(IP)(4,4'-obb)₃]_n crystallizes in triclinic system, P-1 space group. The asymmetric unit contains three Co cations, four obb anions, two imidazo [4,5-f][1,10]-phenanthroline molecules. As shown in Fig. 2, the Co1 is coordinated by six O atoms from six 4,4'-obb ligands [Co1-O, ranging from 2.043(2)-2.140(18) Å] to form an octahedral geometry, the Co2 is coordinated by three O atoms from three 4,4'-obb ligands and two N atoms from one IP ligand. The Co(II) atoms were linked with obb which lead to form three nuclear molecule and 1D chain was obtained *via* the 4,4'-obb anions (Fig. 3). The centroid distance of parallel benzene rings of IP ligands between neighbouring chains is *ca.* 3.705 Å, which means there are weak π...π interactions between them⁹. As a result, the 1-D chains were built into 2-D supramolecular structure *via* interchain N- H...O hydrogen bonds and π...π interactions (Fig. 4).

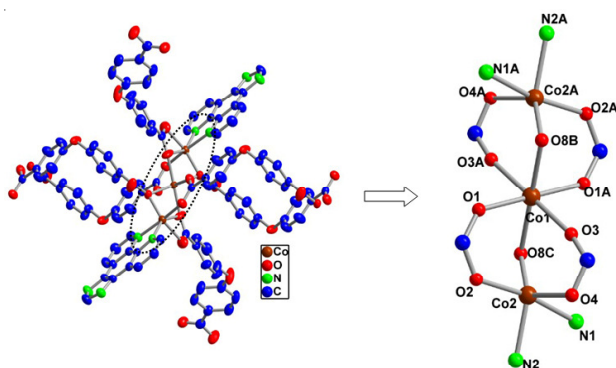


Fig. 2. View of the coordination environment of Co^{II} ions

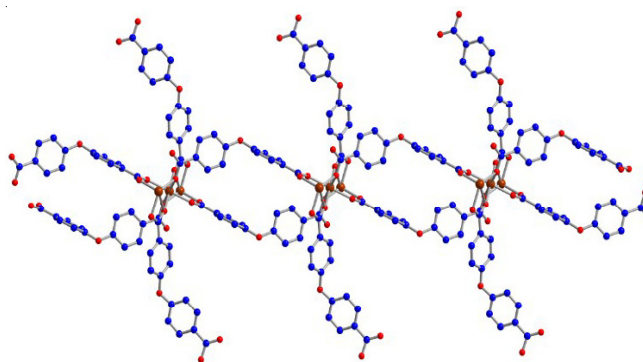


Fig. 3. Perspective views of the 1D chain structure

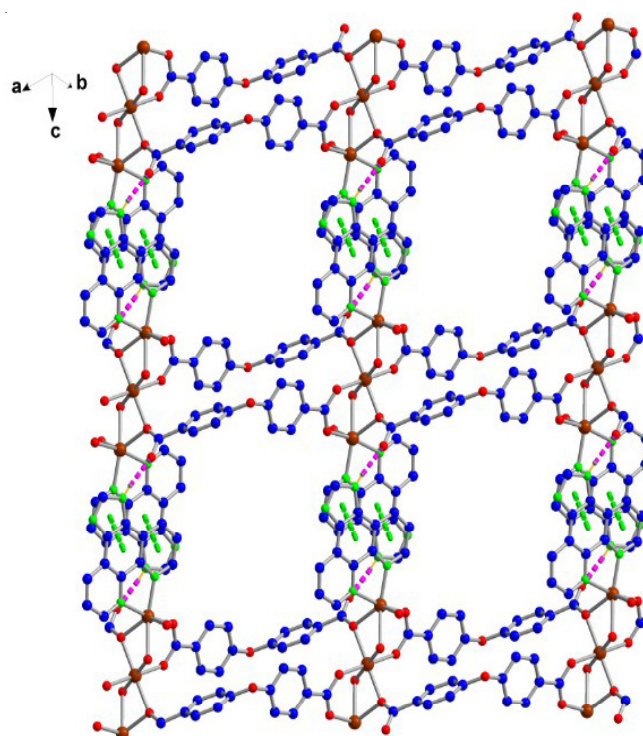


Fig. 4. 2D supramolecular structure showing hydrogen bonding interactions (pink dashed line) and π...π interactions (green dashed line)

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