

Synthesis and Structural Characterization of $[\text{Co}_{0.5}(\text{bimb})_{1.5}]_n \cdot n\text{ClO}_4$ (bimb = 1,4-bis(imidazol-1-yl)-butane)

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Abstract: A new cobalt(II) coordination polymer, namely $[\text{Co}_{0.5}(\text{bimb})_{1.5}]_n \cdot n\text{ClO}_4$ (bimb = 1,4-bis(imidazol-1-yl)-butane) (**1**), has been prepared and fully characterized by single-crystal X-ray diffraction, elemental analyses, IR spectroscopy and X-ray powder diffraction pattern analysis (PXRD). Of the compound, the Co(II) center is octahedral coordinated with bimb serving as a bridging ligand by employing six N-donor to coordinate with the Co(II) center. It exhibits three-dimensional network structure *via* bimb ligands.

Supporting information: CIF file.

Keywords: hydrothermal synthesis, crystal structure, coordination polymer.

1. INTRODUCTION

Researches on the metal-directed extended networks have drawn great attention owing not only to their intriguing structural motifs but also to their potential applications in catalysis, medicine, hostguest chemistry and molecular-based magnetic materials [1-5]. In this field, the metals often have different valences, making a number of building blocks to fulfill special needs. Many important properties of coordination polymers depend largely on their structures and topology. Therefore, the selection of special inorganic and organic building blocks is the key to the construction of a desired framework [6]. In this respect, bis(imidazol-1-yl) complexes have been investigated since they may be important for providing potential supramolecular recognition sites for hydrogen-bonding and π - π aromatic stacking interactions [7-10]. According these, we have large interests in the design and syntheses of 1,4-bis(imidazol-1-ylmethyl)-benzene and its complexes [11-13]. Herein, we report the synthesis of $[\text{Co}_{0.5}(\text{bimb})_{1.5}]_n \cdot n\text{ClO}_4$, whose structure have been explored through X-ray single crystal diffraction and characterized by elemental analyses, IR spectroscopy and X-ray powder diffraction pattern analysis (PXRD).

2. EXPERIMENTAL

2.1. General Procedures

All reagents were purchased commercially and used without further purification. Elemental analyses (C, H and N) were

measured on a Perkin-Elmer 2400 CHN Elemental Analyzer. IR spectrum was recorded in the range of 4000 ~ 400 cm^{-1} on an Alpha Centaur FT/IR Spectrophotometer using a KBr pellet. The X-ray powder diffraction pattern was recorded with a Rigaku D/Max 3C diffractometer.

2.2. Synthesis of $[\text{Co}_{0.5}(\text{bimb})_{1.5}]_n \cdot n\text{ClO}_4$

The title compound was prepared from a mixture of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.073 g, 0.2 mmol), 5-nitroisophthalic acid (0.042 g, 0.2 mmol), bimb (0.038 g, 0.2 mmol) and H_2O (18 mL) in a 30 mL Teflon-lined autoclave under autogenous pressure at 150 $^\circ\text{C}$ for five days. After cooling to room temperature, pink block crystals were collected by filtration and washed with distilled water in 45% yield (based on Co). Anal. Calcd. (%) for $\text{C}_{30}\text{H}_{42}\text{Cl}_2\text{CoN}_{12}\text{O}_8$: C, 43.49; H, 5.11; N, 20.29. Found (%): C, 42.95; H, 4.92; N, 19.87. IR (KBr, cm^{-1}): 3125(w), 2952(w), 1637(w), 1521(m), 1464(w), 1443(w), 1405(w), 1373(w), 1303(w), 1280(w), 1236(m), 1095(s), 936(m), 870(w), 834(w), 772(w), 742(w), 728(w), 667(m), 637(w), 450(w).

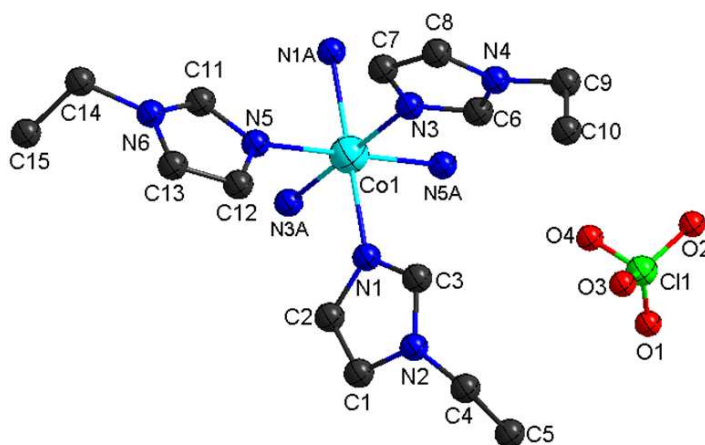


Figure 1: View of the coordination environment of Co(II) in the titled complex

2.3 X-ray Crystallography

Single-crystal X-ray diffraction data for compound **1** was recorded on a Bruker Smart Apex II CCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. The structure was solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using a full-matrix least-

squares procedure based on F^2 [14,15]. The hydrogen atom positions on carbon atoms were fixed geometrically at calculated distances and allowed them to ride on the parent atoms. The detailed crystallographic data and structure refinement parameters for **1** are summarized in Table 1.

Table 1: Crystallographic data for compound **1**

Empirical formula	$C_{30}H_{42}Cl_2CoN_{12}O_8$
Fw	828.59
Crystal system	Triclinic
Space group	P-1
a [Å]	9.8378(11)
b [Å]	9.8481(11)
c [Å]	9.8963(11)
α [°]	88.495(2)
β [°]	89.000(2)
γ [°]	88.792(2)
Volume [Å ³]	958.11(19)
Z	1
D_c (g/cm ³)	1.436
GOF	1.032
Reflns collected/unique	5173 / 3690
R_{int}	0.0205
$R1$ [$I > 2\sigma(I)$]	0.0883

3. RESULTS AND DISCUSSION

3.1. IR analysis

In the IR spectrum, the C–H stretching mode for the imidazole ring is relatively weak and observed at about 3125 cm⁻¹. Peaks at 1637, 1521 and 1464 cm⁻¹ could be attributed to $\nu(C=C)$ vibration of imidazole ring. The peak at 1373 cm⁻¹ is ascribed to the $\nu(C=N)$ vibration of bimb.

3.2. Description of the crystal structure

Selected bond lengths and angles for **1** are listed in Table 2. A single-crystal X-ray diffraction study reveals that compound **1** crystallizes in triclinic system with space group *P-1* and the molecular structure contains half unique Co(II) atom, one and half bimb ligands and one free ClO_4^- , as shown in Figure 1. Co (1) is six coordinated with slightly distorted octahedral coordination geometry defined by six nitrogen donors (N1, N1A, N3, N3A, N5, N5A) from six different bimb ligands. Four nitrogen atoms (N1, N1A, N3, N3A) define an equatorial plane, while the axial coordination sites are occupied by two nitrogen atoms (N5, N5A) too. The bond distances of Co–N in compound **1** fall in the 2.168(5)~2.171(4) Å range, which are in the normal

range and the coordination angles around Co(II) atom are in the range 89.27(19)~180.00(16)°. The bix ligand adopts *trans*-conformation bridging mode with a dihedral angle between the two imidazole rings of 0°.

The Co(II) center forms a type of 6N mixed neutrality complex, and are interconnected by the bridging bimb ligands to generate an infinite $\{Co_2(bimb)_2\}_\infty$ chain. The similar Co(II) complex of a type of 6N is reported [16]. The Co...Co separation through the bimb ligands bridges is 9.838~14.144 Å, the neighboring 1D $\{Co_2(bimb)_2\}_\infty$ infinite chains are linked *via* bimb ligands to develop into 3D framework again, which is different from the reported paper with bimb [17]. More interestingly, the cavities with thirty-six numbered rings were formed among the structures through coordinate-covalent interactions (Figure 2).

To investigate whether the analyzed crystal structure is truly representative of the bulk materials, X-ray powder diffraction (PXRD) technology has been performed for the complex at room temperature (Figure 3). The main peak positions observed are in good agreement with the simulated ones.

Table 2: Selected bond distances (Å) and angles (deg) for **1**

Co(1)-N(1)	2.168(5)
Co(1)-N(1A)	2.168(5)
Co(1)-N(3)	2.171(4)
Co(1)-N(3A)	2.171(4)
Co(1)-N(5)	2.168(6)
Co(1)-N(5A)	2.168(6)
N(1)-Co(1)-N(1A)	180.000(1)
N(1)-Co(1)-N(3)	90.49(19)
N(1A)-Co(1)-N(3)	89.51(19)
N(1)-Co(1)-N(3A)	89.51(19)
N(1A)-Co(1)-N(3A)	90.49(19)
N(3)-Co(1)-N(3A)	180.000(1)
N(5A)-Co(1)-N(5)	180.00(16)
N(5A)-Co(1)-N(1)	90.6(2)
N(5)-Co(1)-N(1)	89.4(2)
N(5A)-Co(1)-N(1A)	89.4(2)
N(5)-Co(1)-N(1A)	90.6(2)
N(5A)-Co(1)-N(3)	90.73(19)
N(5)-Co(1)-N(3)	89.27(19)
N(5A)-Co(1)-N(3A)	89.27(19)
N(5)-Co(1)-N(3A)	90.73(19)

Symmetry transformations used to generate equivalent atoms:
A: -x+1,-y+1,-z+2

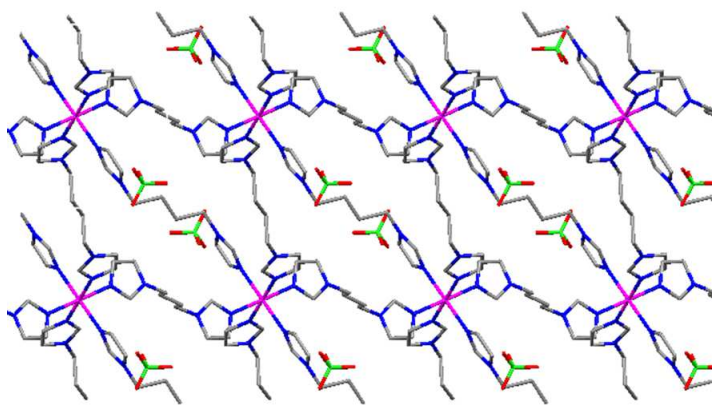


Figure 2: View of the 3D framework of the title complex

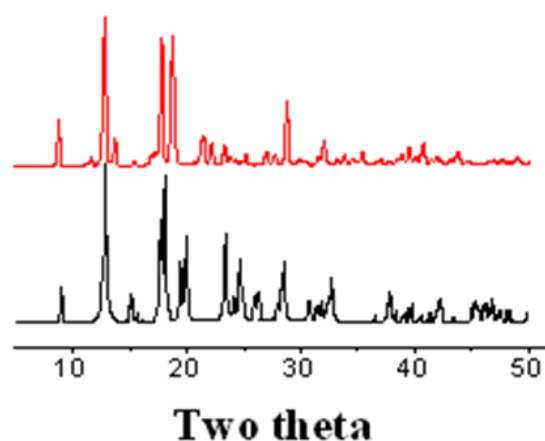


Figure 3: PXRD analysis of the title complex: bottom-simulated, top-experimental.

Although minor differences can be found in the positions, widths, and intensities of some peaks, it still can be considered that the bulk synthesized materials and the analyzed crystal are homogeneous. The differences may be due to the preferred orientation of the powder samples [18-19].

Supplementary materials

CCDC 931880 contains the supplementary crystallographic data. The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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