

Research Article

<http://dx.doi.org/10.21060/cis.2013.116>

Synthesis and Structural Characterization of $[\text{Co}(\text{pbb})_2(\text{H}_2\text{O})_4](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$

Chun-Yan Guo*

Department of Applied Chemistry and Environmental Engineering, Institute of Chemical Application Technology Development, Bengbu College, Bengbu, P. R. China. *E-mail: chyflgg@163.com

Received: December 24, 2012; accepted January 13, 2013

Abstract: A coordination polymer, namely $[\text{Co}(\text{pbb})_2(\text{H}_2\text{O})_4](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (pbb = pyridine-3,5-bis(benzeimidazole-2-yl)), has been obtained and characterized by X-ray diffraction, elemental analyses, and X-ray powder diffraction pattern analysis (PXRD). Single-crystal X-ray analysis reveals the crystal presents 3D supramolecular structure that is connected through hydrogen bonds and aromatic π - π interactions.

Supporting information: FT-IR, X-Ray, Cif file.

Keywords: synthesis; crystal structure; cobalt complex; supramolecular structure

1. INTRODUCTION

The synthesis and study of benzimidazolyl compounds have made increasingly progress in recent years owing to their special biological activities and potential applications [1-3]. On the other hand, benzimidazolyl complexes have been investigated since they may be important for providing potential supramolecular recognition sites for hydrogen-bonding and π - π aromatic stacking interactions [4-6]. According these, we have large interests in the design and syntheses of pyridine-3,5-bis(benzeimidazole-2-yl) (pbb) and its complexes [7]. Herein, we report the synthesis of $[\text{Co}(\text{pbb})_2(\text{H}_2\text{O})_4](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, whose structure have been explored through X-ray single crystal diffraction and powder diffraction pattern analysis.

2. EXPERIMENTAL

The ligand pyridine-3,5-bis(benzeimidazole-2-yl) (pbb) has been obtained according to the literature method [7]. All other reagents and solvents employed were commercially available and used as received without further purification. Elemental analyses (C, H, N) were determined with a Perkin-Elmer model 240C automatic instrument. Infrared spectra on KBr pellets were performed in a Bruker equinox-55 spectrometer in the range of 4000–400 cm^{-1} . The X-ray powder diffraction pattern was recorded with a Rigaku D/Max 3C diffractometer.

2.1. Preparation of $[\text{Co}(\text{pbb})_2(\text{H}_2\text{O})_4](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$

A mixture of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.1 mmol), pbb (0.2 mmol) and N,N'-dimethylformamide (DMF) (2 mL) in water (15 mL) was

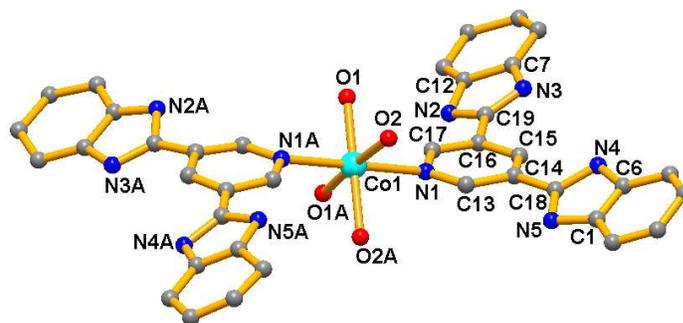


Figure 1: View of the coordination environment of Co(II) in the titled complex

stirred for 15 min in air, then sealed in a 25 mL Teflon-lined stainless steel container, which was heated to 150°C for 72 h. After cooling, pink block crystals were obtained. Anal. calcd for $\text{C}_{38}\text{H}_{37}\text{CoN}_{12}\text{O}_{12}$ (912.73): C, 50.01; H, 4.09; N, 18.42. Found: C, 50.08; H, 4.13; N, 18.36%. IR (cm^{-1} , KBr): 3391 (s), 3194 (m), 2928 (s), 1680 (m), 1625 (m), 1477 (m), 1430 (s), 1381 (s), 1327 (s), 1225 (m), 1125 (w), 1050 (w), 962 (w), 907 (w), 850 (w), 826 (w), 741 (s), 703 (m).

2.2. Crystallography

Single-crystal diffraction data of the title complex were collected on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. The structure was solved by direct methods and refined with the full-matrix least-squares technique on F^2 using the SHELXS-97 [8] and SHELXL-97 [9] program. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms of water were located in successive different Fourier maps and the other hydrogen atoms were treated as riding method. The structure of the complex contains one disordered NO_3^- , which adopt two positions and lie on inversion centers with equal occupancy. The crystal belongs to monoclinic crystal system, $C2$ space group with $a=14.061(5)$, $b=18.020(7)$, $c=9.037(4) \text{ \AA}$, and $\beta=102.968(7)^\circ$. Selected bond lengths and angles of the complex are listed in Table 1.

RESULTS AND DISCUSSION

The single-crystal X-ray analysis reveals that the coordination style between pbb and Co(II) is similar to the one in literature

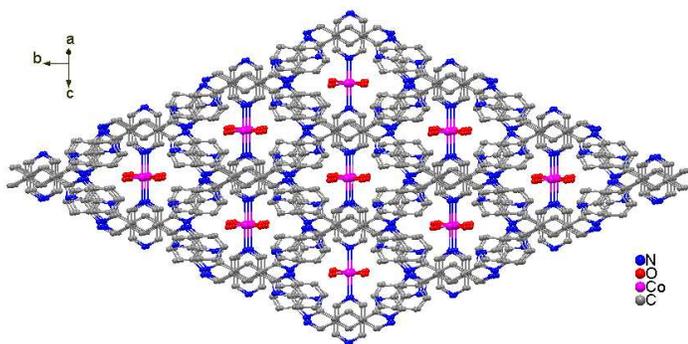
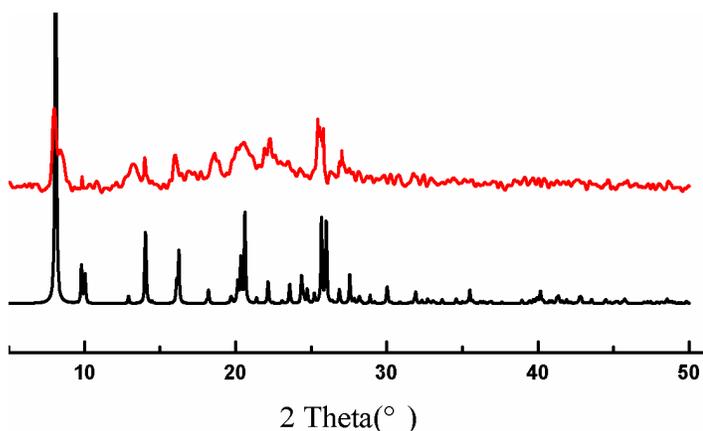
Table 1. Selected bond lengths [Å] and angles [°] for the title complex.

Co(1)-N(1)	2.203(13)	Co(1)-O(2)	2.122(14)
Co(1)-O(1)	1.963(13)	O(2)#1-Co(1)-N(1)	90.4(6)
O(1)#1-Co(1)-O(1)	94.2(4)	O(2)-Co(1)-N(1)	89.2(7)
O(1)-Co(1)-O(2)#1	176.7(4)	O(1)-Co(1)-N(1)#1	89.3(5)
O(1)-Co(1)-N(1)	91.1(5)	O(1)-Co(1)-O(2)	88.7(4)
O(2)#1-Co(1)-O(2)	88.5(7)	N(1)-Co(1)-N(1)#1	179.5(11)

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

[7]. As shown in Figure 1, the Co1 center presents a slightly distorted octahedron, defined by two axial nitrogen atoms from two pbb ligands and four oxygen atoms of four water molecules in the basal plane. Each pbb in complex adopts a malformed geometry with large dihedral angles 25.52° and 25.73°, respectively, between the pyridine-ring and the imidazole-rings.

As expected, strong hydrogen-bonding and extensive π - π interaction play important roles in extended structure of the complex and the 3D supramolecular framework is shown in Figure 2. Interestingly, the metal centers are arranged regularly in 3D architecture. In *ab* plane, all cobalt atoms perch on the same plane. The shortest distance of Co...Co between sheets is 9.037 Å.

**Figure 2:** View of the 3D framework of the title complex**Figure 3:** PXRD analysis of the title complex: bottom-simulated, top-experimental

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. 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 [10-11].

Acknowledgments

This work was supported by the Natural Science Research Foundation for Universities of Anhui Province (No. KJ2012A193) and the Natural Science Foundation of Bengbu College (No. 2011ZR08), China.

REFERENCES

- [1] Geratz, J. D.; Tidwell, R. R.; Lombardy, R. J.; Schwab, J. H. *Am. J. Pathol.*, 139, **1991**, 921.
- [2] Carcanague, D.; Shue, Y.; Wuonola, M.; Uria-Nickelsen, M. *J. Med. Chem.* 45, **2002**, 4300. doi: 10.1021/jm020868v
- [3] Tebbe, M. J.; Spitzer, W. A.; Victor, F.; Miller, S.C.; Lee, C.C.; Sattelberg, T.R.; McKinney, E.; Tang, J.C. *J. Med. Chem.* 40, **1997**, 3937. doi: 10.1021/jm970423k
- [4] Liu, S.; Zuo, J.; Li, Y.; You, X. *J. Mol. Struct.* 705, **2004**, 153.
- [5] Tong, L. *Chem. Rev.* 102, **2002**, 4609. doi: 10.1021/cr010184f
- [6] Yeung, K.; Meanwell, N.; Qiu, Z.; Hernandez, D.; Zhang, S.; McPhee, F.; Weinheimer, S.; Clark, J.M.; Janc, J.W.; *Bioorg. Med. Chem. Lett.* 11, **2001**, 2355. doi:10.1016/S0960-894X(01)00457-7
- [7] Guo, C.; Wang, Y.; Xu, K.; Zhu, H. *Polyhedron*, 27, **2008**, 3529. doi:10.1016/j.poly.2008.08.018
- [8] G.M. Sheldrick, SHELXS 97, Program for Crystal Structure Solution, University of Go-ttingen, Germany, **1997**.
- [9] G.M. Sheldrick, SHELXL 97, Program for Crystal Structure Refinement, University of Go-ttingen, Germany, **1997**.
- [10] Gilbert, A.; Baggott, J. *Essentials of Molecular Photochemistry*, CRC Press, Boca Raton, FL, **1991**.
- [11] Han, Z.; He, Y.; Ge, C.; Ribas.; Xu, L. *Dalton Trans.*, **2007**, 3020. doi: 10.1039/B704327A



This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.