



NOTE

Synthesis and Crystal Structure of New (3,5)-Connected Ni(II) Coordination Polymer

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In this paper, a new Ni(II) coordination polymer with 3,4-pyridine dicarboxylic acid(3, 4-PDB) and 1,4-*bis* (1-imidazol-yl)-2,5-dimethyl benzene (bimb) has been prepared by hydrothermal synthesis and characterized by single-crystal X-ray diffraction, IR and EA. Complex, $[\text{Ni}(3, 4\text{-PDB})(\text{bimb})(\text{H}_2\text{O})]_n$ (**1**), is monoclinic, space group $P2_{1/c}$ with $a = 10.254(5)$, $b = 14.219(5)$, $c = 14.288(5)\text{\AA}$, $\beta = 100.816(5)^\circ$, $V = 2046.2(14)\text{\AA}^3$, $Z = 4$, $M_r = 480.12$, $D_c = 1.559\text{ g/cm}^3$ and $F(000) = 992$. The final refinement gave $R = 0.0285$ and $wR = 0.0800$ for 4205 reflections with $I > 2\sigma(I)$. X-ray diffraction analysis reveals that the complex **1** displays a new three-dimensional structure with a (3,5)-connected topology.

Keywords: Ni(II), Coordination, Polymer, Synthesis, Crystal structure.

The field of metal-organic frameworks (MOFs) or coordination polymers has continuously evolved since Hoskins and Robson first combined the inorganic and organic molecular units to create infinite networks in the early 1990s^{1,2}. In fact, the driving force for this is that there exist endless possibilities and inexhaustible synthetic options to tailor their structures and properties, which provides a huge source of experimental systems for both fundamental science and potential applications³⁻⁵. As a result, in the realm of coordination polymers, many intriguing topological types and associated interesting properties have been investigated in-depth^{2,3}. However, from the perspective of developing advanced crystalline materials, one of the most attractive targets is to establish a clear relationship between the network structures and properties of coordination polymers, which represents a great challenge, both experimentally and theoretically⁶.

In the paper, we used the 3,4-pyridine dicarboxylic acid (3,4-PDB) and 1,4-*bis* (1-imidazol-yl)-2,5-dimethyl benzene (bimb) to construct a new Ni(II) coordination polymer with a (3,5)-connected topology.

All reagents and solvents employed were commercially available and used without further purification. Elemental analysis was carried out on a Carlo Erba 1106 full-automatic trace organic elemental analyzer. FT-IR spectra were recorded with a Bruker Equinox 55 FT-IR spectrometer as a dry KBr pellet in the 4000-400 cm^{-1} range.

Preparation of $[\text{Ni}(3,4\text{-PDB})(\text{bimb})(\text{H}_2\text{O})]_n$ (1**):** The mixtures of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.5 mmol, 0.145 g), 3,4-PDB (0.5

mmol, 0.084 g), bimb (0.5 mmol, 0.105 g), NaOH (1 mmol, 0.04 g) and 12 mL of water were heated to 160 °C for 4 days and then cooled to room-temperature. The green crystals were obtained in pure phase, washed with water and ethanol and dried at room temperature (Yield: 52 % based on Ni). Anal. Calc. for $\text{C}_{21}\text{H}_{18}\text{N}_4\text{O}_5\text{Ni}$: C, 54.23; H, 3.90; N, 12.05. Found: C, 54.34; H, 3.89; N, 12.07. IR (KBr, ν_{max} , cm^{-1}): 3111 (m), 1610 (m), 1535 (s), 1432 (s), 1309 (m), 1245(m), 1122 (m), 944 (m), 836(m), 785 (m), 722 (m).

X-ray crystallography: Single crystal X-ray diffraction analyses of complex **1** was carried out on a Bruker SMART APEXII CCD diffractometer equipped with a graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073\text{\AA}$) by using a ω -scan mode. Empirical absorption correction was applied using the SADABS programs⁷. All the structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 using the program SHELX 97⁸. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located by geometrically calculations and their positions and thermal parameters were fixed during the structure refinement.

Single X-ray analysis shows that complex **1** crystallizes in the monoclinic $P2_{1/c}$ space group. As shown in Fig. 1, each Ni(II) ion possesses octahedral coordination environment completed by two carboxylate oxygen atoms [$\text{Ni}(1)\text{-O}(1) = 2.0723(13)\text{\AA}$ and $\text{Ni}(1)\text{-O}(3) = 2.0900(12)$], one nitrogen atom of pyridyl ring [$\text{Ni}(1)\text{-N}(1) = 2.1307(14)$], two nitrogen atoms of imidazole rings [$\text{Ni}(1)\text{-N}(2) = 2.0719(16)\text{\AA}$ and $\text{Ni}(1)\text{-N}(4) = 2.0647(16)\text{\AA}$] and a terminal coordinated water molecule

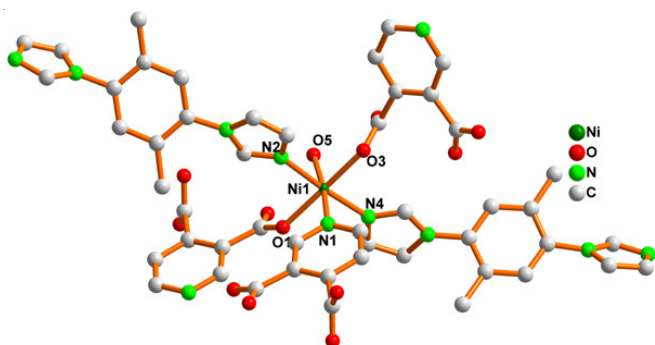


Fig. 1. Coordination environment for Ni(II) ion

[Ni(1)-O(5) = 2.1293(14) Å]. The equatorial plane is defined by O1, O3, N2 and N4. The axial positions are occupied by N(1) and O(5) with the angle N(1)-Ni(1)-O(5) of 174.14(5)°. In complex 1, the carboxylate ligands connect the Ni(II) atoms to form a two-dimensional layer structure. There are two different metalocycles in the two-dimensional network of 1, namely 28-membered ring and 14-membered ring. In 1, two types of rings adopt two arrangements (Fig. 2).

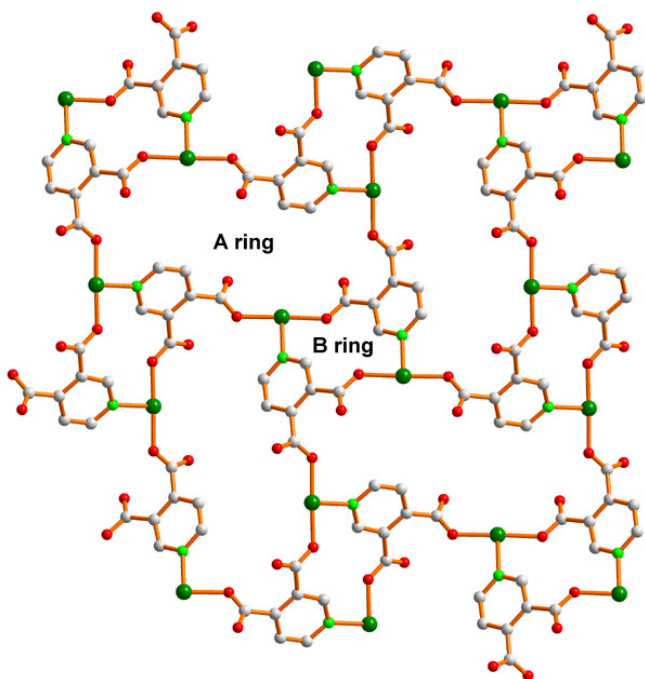


Fig. 2. 2D layer structure constructed by carboxylate ligand and Ni(II) ions

The bimb ligands as connector further connect the 2D layer to a 3D structure. Based on the topological view, the 3D structure can be simplified as a (3, 5)-connected topological net with point symbol (4.6²)-(4.6⁶.8³) (Fig. 3).

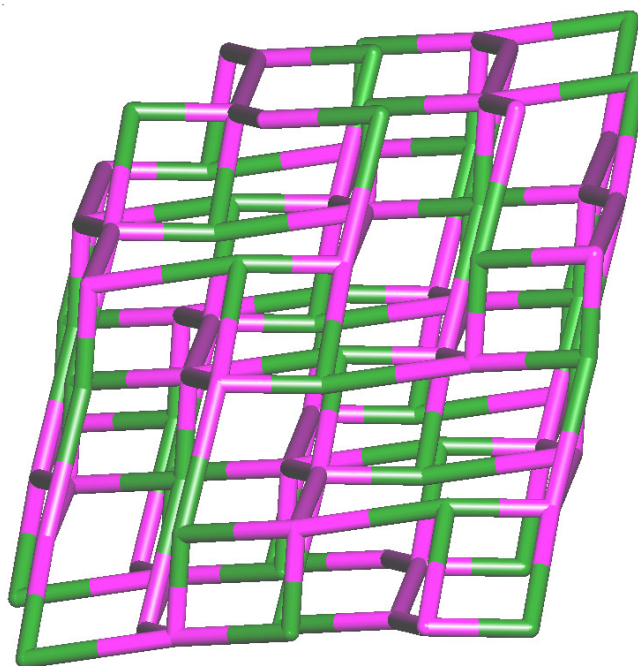


Fig. 3. 3.5-Connected topological net for complex 1 with point symbol (4.6²).(4.6⁶.8³)

REFERENCES

1. B.F. Hoskins and R.J. Robson, *J. Am. Chem. Soc.*, **111**, 5962 (1989).
2. B.F. Hoskins and R.J. Robson, *J. Am. Chem. Soc.*, **112**, 1546 (1990).
3. O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi and J. Kim, *Nature*, **423**, 705 (2003).
4. D.J. Tranchemontagne, J.L. Mendoza-Cortes, M. O'Keeffe and O.M. Yaghi, *Chem. Soc. Rev.*, **38**, 1257 (2009).
5. J.J. Perry IV, J.A. Perman and M.J. Zaworotko, *Chem. Soc. Rev.*, **38**, 1400 (2009).
6. J.J. Morris, B.C. Noll and K.W. Henderson, *Chem. Commun.*, 5191 (2007).
7. SAINT Software Reference Manual; Bruker AXS: Madison, WI (1998).
8. G.M. Sheldrick, SHELXTL NT, version 5.1; Program for Solution and Refinement of Crystal Structures, University of Göttingen, Germany (1997).