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NOTE

Hydrothermal Synthesis and Crystal Structure of Ni(II) Coordination Polymer of 4,4'-Benzophenonedicarboxylic Acid and *bis*(4-pyridyl)amine

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A new coordination polymer of nickel(II) with the formula {[Ni (bda)(bpa)]·(H_2O)$_n$}(**1**) (H_2bda = 4,4'-benzophenonedicarboxylic acid and bpa = *bis*(4-pyridyl)amine), has been prepared by hydrothermal synthesis. Complex {[Ni (bda)(bpa)]·(H_2O)n}(**1**), monoclinic, space group C2/c with a = 23.735 (5)Å, b = 12.146 (5) Å, c = 16.789 (5) Å, β = 106.731 (5)° V = 4635 (3) Å^3, Z = 8, M_r = 516.14, D_c = 1.479 g/cm^3, F(000) = 2128 and μ = 0.88 mm^{-1}. The final refinement gave R = 0.0402 and wR = 0.1242 for 4735 reflections with I > 2σ(I). X-ray diffraction analysis reveals that complex 1 shows a two-dimensional structure with 1D helical chains.

Keywords: Nickel(II), Coordination polymer, 4,4'-Benzophenonedicarboxylic acid, *Bis*(4-pyridyl)amine).

The rational design and synthesis of coordination polymers based on organic ligands remains an area of recent interest not only for their intriguing and variety of structures, but also for their potential application as optical materials[1-4]. It is still a great challenge to rationally design and realize the target crystalline materials. In the self-assembly processes of coordination polymers, many factor should be considered, such as organic ligands, temperature, pH values, solvents, *etc.*[5-8]. The most effective and facile method to construct novel coordination polymers is the appropriate choice of the well-designed organic ligands containing modifiable backbones. In this paper, we select the *bis*(4-pyridyl)amine which can freely rotate around its central kink to meet to the requirement of coordination geometries of metal ion in the assembly process since the orientation of this diimine's nitrogen donor atoms promoted by its central N-H group act synergistically as important structure-directing agents during self-assembly.

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.

Synthesis of {[Ni (bda)(bpa)]·(H_2O)$_n$}(1): The mixtures of *bis*(4-pyridyl)amine) (bpa) (0.5 mmol), $Ni(NO_3)_2·6H_2O$ (0.5 mmol), 4,4'-benzophenonedicarboxylic acid (H_2bda) (0.5 mmol), NaOH (1 mmol, 0.04 g) and 12 mL of water were heated to 120 °C for 3 days and then cooled to room-temperature. The red crystals were obtained in pure phase, washed with water and ethanol and dried at room temperature (Yield: 40 % based on Ni). Elemental Anal. Calcd. (%) for $C_{25}H_{19}$Ni-N_3O_6: C, 58.18; H, 3.71; N, 8.14. Found: C, 58.19; H, 3.71; N, 8.15.

X-ray crystallography: Single crystal X-ray diffraction analyses of present Ni(II) complex was carried out on a Bruker SMART APEXII CCD diffractometer equipped with a graphite monochromated MoK_α radiation (λ = 0.71073 Å) by using a ω-scan mode. Empirical absorption correction was applied using the SADABS programs[9]. All the structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 using the program SHEXL 97[10]. 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.

Description of structure {[Ni(bda)(bpa)]·(H_2O)$_n$}(1): Single crystal X-ray analysis reveals that the present complex crystallized in the monoclinic C2/c space group. Crystal structure analysis shows that asymmetric unit of 1 consists of one Ni(II) atom, one bda^{2-}, one bpa ligand and one lattice water molecule. Ni(II) is six-coordinated by four carboxylate oxygen atoms [Ni-O, ranging from 2.0541(17) Å to 2.2210(18) Å] and two nitrogen atoms [Ni(1)-N(1) = 2.0508(19)Å and Ni(1)-N(3) = 2.0390(19) Å] , displaying an octahedral geometry (Fig. 1). The carboxylate groups adopt chelating coordination mode which connect Ni(II) to form a one-dimensional helical chain with the pitch of 24.292 Å (Fig. 2). The 1D helical chains

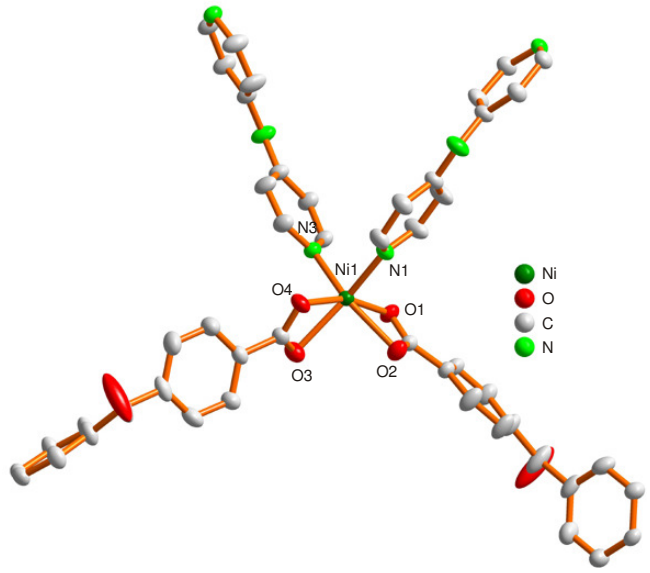

Fig. 1. Coordination environment of Ni(II) atom

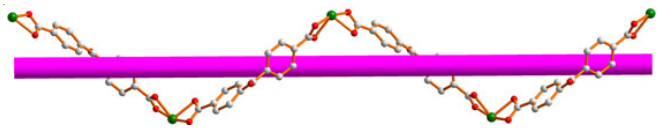

Fig. 2. One-dimensional chain constructed by Ni(II) atoms and bda 2-ligands

are connected by bpa ligand to construct a 2D-layer structure (Fig. 3). If the Ni(II) ions and organic ligands are regarded as nodes and linkers, respectively, the 2D layer structure can be simplified as 4-connected sql topology.

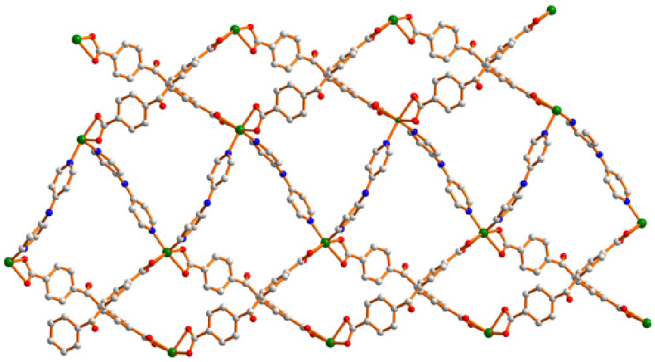

Fig. 3. Two-dimensional layer structure for complex 1

REFERENCES

1. C.-S. Liu, J.-J. Wang, Z. Chang, L.-F. Yan and X.-H. Bu, *CrystEngComm*, **12**, 1833 (2010).
2. L. Zhang, Y. Ling, D.J. Li, J. Li and M. Du, *Inorg. Chim. Acta*, **363**, 2010 (2010).
3. F. Guo, B.Y. Zhu, G.L. Xu, M.M. Zhang, X.L. Zhang and J. Zhang, *J. Solid State Chem.*, **199**, 42 (2013).
4. D.S. Liu, Y. Sui, C.C. Huang, T.H. Pan, X.H. Huang, J.Z. Chen and X.Z. You, *Inorg. Chem. Commun.*, **13**, 762 (2010).
5. J.Q. Liu, Z.B. Jia and Y.Y. Wang, *J. Mol. Struct.*, **987**, 126 (2011).
6. Z.L. Xie, M.L. Feng, J.R. Li and X.Y. Huang, *Inorg. Chem. Commun.*, **11**, 1143 (2008).
7. R. Prajapati, L. Mishra, K. Kimura and P. Raghavaiah, *Polyhedron*, **28**, 600 (2009).
8. A. Thirumurugan and C.N.R. Rao, *J. Mater. Chem.*, **15**, 3852 (2005).
9. AXS Bruker, SAINT Software Reference Manual, Madison, WI (1998).
10. G.M. Sheldrick, SHELXTL NT Version 5.1. Program for Solution and Refinement of Crystal Structures, University of Göttingen, Germany (1997).