



NOTE

Hydrothermal Synthesis and Crystal Structure of Novel Zn(II) Coordination Polymer Based on 1,3,5-Benzene tricarboxylic Acid and N-Donor Ligands

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In this paper, a new zinc(II) coordination polymer with 4,4'-bis(imidazolyl)biphenyl (bib) and 1,3,5-benzene tricarboxylic acid (H₃bct) has been prepared by hydrothermal synthesis and characterized by single-crystal X-ray diffraction, IR and EA. Complex, ([Zn(H₃bct)(H₂O)₂]_n·(H₃bct)·(bib))_n (**1**), is triclinic, space group P-1 with a = 7.227 (5), b = 12.081 (5), c = 15.562 (5) Å, β = 87.780 (5)°, V = 1280.2 (11) Å³, Z = 1, Mr = 1260.29, Dc = 1.635 g/cm³ and F(000) = 648. The final refinement gave R = 0.0454 and wR = 0.0497 for 5127 reflections with I > 2σ(I). X-ray diffraction analysis reveals that the complex **1** displays a three-dimensional supramolecular structure *via* hydrogen bonds.

Keywords: Zn(II), Coordination polymer, 1,3,5-Benzene tricarboxylic acid.

Self-assembly processes involving metal ions and well-designed organic ligands have attracted considerable attention currently in the field of supramolecular chemistry and crystal engineering from the viewpoints of the development of new materials with unique electronic, magnetic, catalytic and optical properties¹⁻⁴. It is well-known that organocarboxylate exhibit various network topologies and remarkable prospect, therefore the construction of coordination polymers using metal ions and anionic O-donor ligands is one of the hotspot in the crystal engineering field. In addition, the prospect of second organic into a reaction system provides further impetus for research on metal-organic supramolecular frameworks. Among the second organic ligands, the neutral imidazole-containing ligands are often used⁵⁻¹¹.

Based on the above mentions, we used the 1,3,5-benzene tricarboxylic acid and 4,4'-bis(imidazolyl)biphenyl to construct a new Zn(II) coordination polymer. The title complex displays a three-dimensional supramolecular structure *via* hydrogen bonds.

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.

Synthesis

A mixture of Zn(NO₃)₂·6H₂O (0.149 g, 0.5 mmol), bib (0.143 g, 0.5 mmol), H₃bct (0.105 g, 0.5 mmol) and deionized water (12 mL) was sealed in a 25 mL Teflon-lined stainless steel vessel and heated at 120 °C for 48 h and cooled to room temperature. The colorless block crystals were obtained and washed with alcohol for several times (Yield: 41 % based on Zn). Anal. Calc. for C₅₄H₄₂N₄O₂₈Zn: C, 51.46; H, 3.36; N, 4.45. Found: C, 51.45; H, 3.35; N, 4.46. IR: 3314 br, 1604 s, 1507 s, 1421 m, 1336 m, 1217 m, 1112 m, 1008 m, 937 m, 803 m, 798 m.

X-ray crystallography: Single crystal X-ray diffraction analyses of complex **1** were 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 programs¹². All the structures were solved by direct methods and refined by full-matrix least-squares methods on F² using the program SHEXL 97¹³. 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. Selected bond and angle parameters are listed in Table-1.

The structure of complex **1** is determined by X-ray single-crystal diffraction with system space group. The asymmetric

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

| Compound 1 | | | |
|------------------|-------------|----------------|-------------|
| Zn(1)-O(1w) | 2.1334 (18) | Zn(1)-O(1) | 2.0437 (17) |
| Zn(1)-O(2w) | 2.126 (2) | O2w-Zn1-O(1w) | 91.11 (7) |
| O(1)-Zn(1)-O(1w) | 87.06 (7) | O(1)-Zn(1)-O2w | 91.73 (6) |

unit of complex **1** consists of one crystallographically independent Zn(II) center, one coordinated H_2btc^- , two coordinated water molecules, one free H_2btc^- and a half of free bimb molecule. As shown in Fig. 1, the Zn(II) is coordinated by two carboxylate oxygen atoms from two different H_2btc^- ligands and four oxygen atoms from four coordinated water molecules in an octahedral geometry. Fig. 2 shows the 3D supramolecular architecture of complex **1**. There exist abundant hydrogen-bonding interactions between uncoordinated carboxylate oxygen atoms and the coordinated water molecules. The guest molecules distribute in the pore of 3D supramolecular structure.

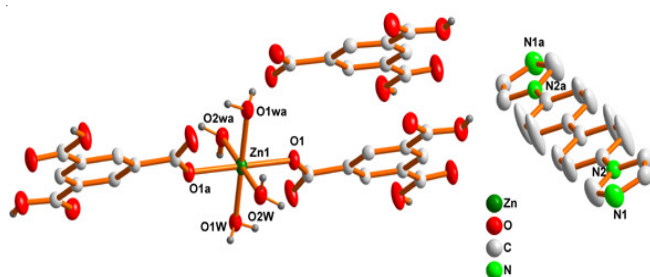


Fig. 1. Coordination environment of Zn(II) ion

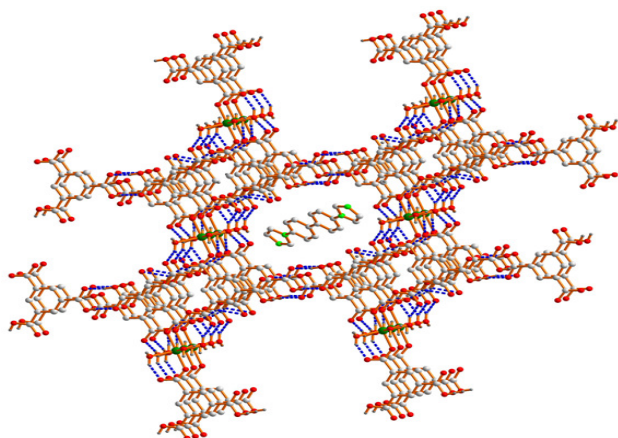


Fig. 2. Packing diagram of complex **1**

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