



NOTE

Hydrothermal Synthesis and Crystal Structure of Novel Mn(II) Coordination Polymer Based on 4,4'-Bis(imidazolyl)biphenyl and Trimesic Acid

GUANGLONG ZOU^{1,*}, XUELIN WANG², TINGTING LI¹, ZHIQING FANG¹ and BING XIE^{1,*}

¹School of Chemistry and Environmental Science, Guizhou Minzu University, Guiyang 550025, P.R. China

²School of Science, Guizhou Minzu University, Guiyang 550025, P.R. China

*Corresponding authors: E-mail: scszgm@126.com

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In this paper, a new Mn(II) coordination polymer with 4,4'-bis(imidazolyl)biphenyl (bib) and trimesic acid (H₃btc) has been prepared by hydrothermal synthesis and characterized by single-crystal X-ray diffraction, IR and EA. Complex, [Mn(Hbta)(bib)]_n (**1**), is monoclinic, space group P2₁/c with a = 9.380 (5), b = 10.226 (5), c = 12.590 (5) Å, β = 86.079 (5)°, V = 1169.3 (10) Å³, Z = 2, M_r = 549.39, D_c = 1.560 g/cm³ and F(000) = 562. The final refinement gave R = 0.0333 and wR = 0.0875 for 4708 reflections with I > 2σ(I). X-ray diffraction analysis reveals that the complex **1** displays a two-dimensional layer structure.

Keywords: Hydrothermal synthesis, Crystal structure, Mn(II) coordination polymer.

Due to the intriguing variety of architecture and potential applications in luminescence, gas storage, molecular magnetism and ion exchange, the construction of metal-organic frameworks (MOFs) have attracted widespread interest in recent years¹⁻⁴. Carboxylate ligands have been employed most often in the design and synthesis for metal-organic frameworks because of their versatile linking capability in virtue of both covalent bonding and supramolecular interaction⁵⁻⁸. In the meantime, imidazole-containing ligands, in particular, have proven to be good candidates for the construction of novel metal-organic frameworks due to their flexible and diverse coordination modes⁹⁻¹¹.

Based on above mention, we used the 4,4'-bis(imidazolyl)biphenyl and trimesic acid to construct a new Mn(II) coordination polymer with 2D *sql* topological net.

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

Preparation of [Mn(Hbta)(bib)]_n: The mixtures of MnCl₂·4H₂O (0.099 g, 0.5 mmol), trimesic acid (H₃btc) (0.105 g, 0.5 mmol), 4,4'-bis(imidazolyl)biphenyl (bib) (0.143 g, 0.5 mmol) and H₂O (12 mL) were sealed in a 25 mL Teflon-lined

stainless steel vessel. The mixtures were heated at 140 °C for 72 h and then cooled to room temperature. The colorless block crystals were obtained and washed with alcohol for several times (Yield: 38 % based on Mn). Anal. calcd. for C₂₇H₁₈N₄O₆Mn: C, 59.03; H, 3.30; N, 10.20. Found: C, 59.05; H, 3.31; N, 10.18. IR/cm⁻¹ (KBr): 1682 s, 1633 s, 1574 s, 1419 m, 1302 m, 1237 m, 1174 m, 1030 m, 955 m, 831 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 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 SHELXL 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.

[Mn(Hbta)(bib)]_n: The X-ray crystallographic study reveals that complex **1** crystallized in the system, space group. Each independent Mn(II) is located at the inversion center and coordinated by two nitrogen atoms [Mn(1)-N(1) = 2.2478 (17) and Mn(1)-N(3) = 2.2486 (18)] and four carboxylate oxygen atoms [Mn-O, ranging from 2.1149 (14) Å to 2.3309 (16) Å] to furnish an octahedral geometry. The partial deprotonated H²btc- ligands connect the Mn(II) to form a one-dimensional

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

Compound 1			
Mn(1)-O(1)	2.1149 (14)	Mn(1)-N(1)	2.2478 (17)
Mn(1)-O(2) ⁱ	2.1343 (14)	Mn(1)-O(4) ⁱⁱ	2.2930 (13)
Mn(1)-N(3)	2.2486 (18)	Mn(1)-O(3) ⁱⁱ	2.3309 (16)
O(1)-Mn(1)-O(2) ⁱ	116.51 (5)	O(1)-Mn(1)-O(4) ⁱⁱ	149.26 (5)
O(1)-Mn(1)-N(3)	85.60 (6)	O(2) ⁱ -Mn(1)-O(4) ⁱⁱ	93.53 (5)
O(2) ⁱ -Mn(1)-N(3)	88.08 (6)	N(3)-Mn(1)-O(4) ⁱⁱ	89.25 (5)
O(1)-Mn(1)-N(1)	90.94 (6)	N(1)-Mn(1)-O(4) ⁱⁱ	94.56 (6)
O(2) ⁱ -Mn(1)-N(1)	92.02 (6)	O(1)-Mn(1)-O(3) ⁱⁱ	94.29 (5)
N(3)-Mn(1)-N(1)	176.17 (5)	O(2) ⁱ -Mn(1)-O(3) ⁱⁱ	148.80 (5)
N(3)-Mn(1)-O(3) ⁱⁱ	99.77 (6)	O(4) ⁱⁱ -Mn(1)-O(3) ⁱⁱ	56.77 (4)
N(1)-Mn(1)-O(3) ⁱⁱ	82.10 (5)		

Symmetry code for complex: (i) $-x + 2, -y + 1, -z + 1$; (ii) $-x + 2, -y, -z + 1$.

chain. In 1D chain, the μ_2 - η^1 : η^1 carboxylate group link two Mn(II) atoms to construct a dinuclear Mn(II) unit with the Mn...Mn distance of 4.298 Å. The 1D chains are further connected by bib ligands to construct a two-dimensional layer structure (Figs. 1-3).

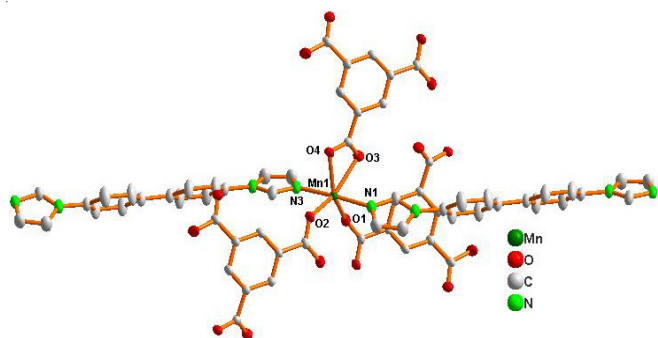


Fig. 1. Coordination environment of Mn(II) ion

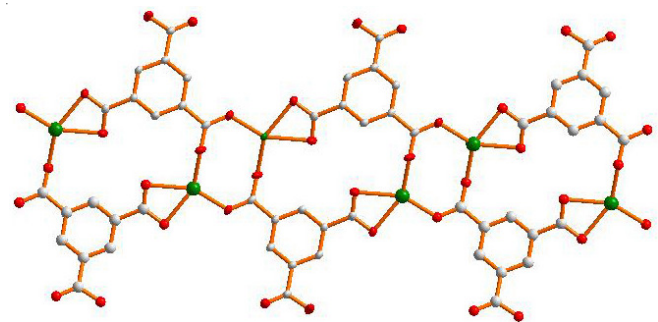


Fig. 2. 1D chain constructed by Mn(II) ions and carboxylate ligands

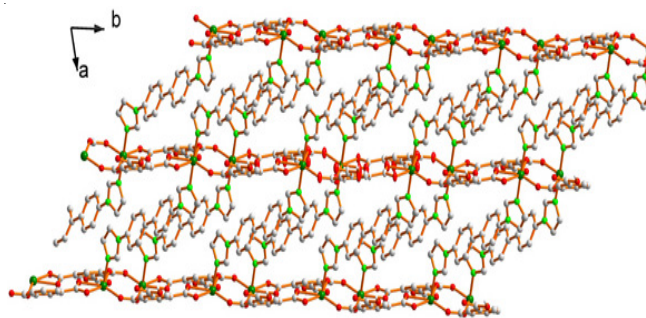


Fig. 3. 2D layer structure for complex 1

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