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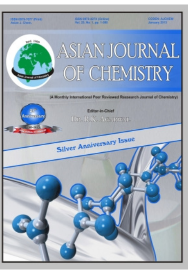

NOTE

Synthesis and Crystal Structure of [μ_2-1,1'-(1,4-Butanediyl)-*bis*-(imidazole)(μ_2-oxalato)Zn(II)]

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Hydrothermal reactions of 1,1'-(1,4-butanediyl)-*bis*-(imidazole) (bbi) and oxalic acid (ox) with zinc nitrate gave rise to one new coordination polymer, namely, $[Zn(bbi)(ox)]_n$. It was characterized by elemental analysis and single-crystal X-ray diffraction methods. This compound has one Zn metal center and shows a 3D three-fold interpenetrating framework, leaving no void to host the solvent molecules.

Key Words: Hydrothermal synthesis, Coordination polymer, Crystal structure.

In the past couple of decades, metal-organic frameworks have been explored extensively duo to their potential applications in gas storage, heterogeneous catalysis, magnetism, luminescence[1-7], *etc*. Multidentate N-donor or O-donor ligands have been often employed in the construction of metal-organic frameworks and remarkable achievements have been attained in this area. Yet accurate structural control and deep understanding of the structure-property relationship remain the fundamental challenges at the current stage. From the viewpoint of self-assembly, proper selection of metal centers and organic ligands with suitable shape, functionality, flexibility and symmetry are a key to achieve the target coordination polymers. Therefore, systematic investigation of an assembling system with the fixed metal centers and coordination organic molecules is crucial for gaining expected target product. Recent studies have further demonstrated that the coordination systems assembled from mixed ligands, will show more diverse and interesting polymeric networks with potential properties[8-12]. Following this strategy, we have made an investigation on metal-organic frameworks with 1,1'-(1,4- butanediyl)-*bis*-(imidazole) (bbi) and oxalic acid (ox) and Zn(II) salt.

All reagents and solvents were commercially available and used as received without purification. The elemental analyses for C, H and N were performed on a Elementar Vario micro cube analyzer.

Preparation of compound $[Zn(bbi)(ox)]_n$: A mixture of bbi (0.021 g, 0.1 mmol), oxalic acid (0.009 g, 0.1 mmol), $Zn(NO_3)_2\cdot 6H_2O$ (0.030 g, 0.1 mmol) and deionized water (7.0 mL) was placed in a 16 mL Teflon-lined stainless steel vessel and heated to 160 ºC for 72 h. After cooling to room temperature, colourless block crystals were obtained, which were washed with water and dried in air. Yield: 0.015 g (43 % based on Zn). Anal. calcd. for $C_{12}H_{14}N_4O_4Zn$ (%): C 41.90, H 4.07, N 16.29. Found: C 42.23, H 3.82, N 16.36.

Structure determination: Single crystal of $[Zn(bbi)(ox)]_n$ suitable for X-ray analysis was selected directly from the above preparations. It was mounted on glass fibers and then the crystallographic data collections was carried out on a Bruker Smart Apex(II) CCD area-detector diffractometer with graphite-monochromated MoK_α radiation (λ = 0.71073 Å) at 296 K using ω and φ-scan technique. The diffraction data was integrated by using the SAINT program[13], which was also used for the intensity corrections for the Lorentz and polarization effects. Semiempirical absorption correction was applied using the SADABS program[14]. The crystal structure was solved by direct method using SIR97 program[15] and refined anisotropically for all non-hydrogen atoms by full-matrix least squares on all F^2 data using SHELXL97[16]. The single suite WINGX was used as an integrated system for all the crystallographic programs[17]. All hydrogen atoms were added according to theoretical models, assigned isotropic displacement parameters and allowed to ride on their respective parent atoms, the $U_{iso}(H) = 1.2\ U_{eq}(C)$. Crystal data and a structure determination summary was listed in Table-1. The selected bond lengths and angles was listed in Table-2.

The complex $[Zn(bbi)(ox)]_n$ crystallizes in the triclinic space group P-1 and the asymmetric unit contains one Zn^{2+} cation, one oxalate anion and one bbi ligand. As shown in Fig. 1, each Zn1 metal center is coordinated by four O atoms from two different oxalate anions, two N atoms from two different bbi ligands to form octahedral coordination geometry. The equatorial position was occupied by three O atoms (O1B, O2, O4) and one N atom (N3) and the apical positons were occupied by N1 and N3, respectively. The Zn-O bond lengths are in the rang of 2.1219(17)-2.1532(16) Å and the Zn-N bond lengths are 2.1355(19) and 2.1005(18) Å.

TABLE-1
CRYSTALLOGRAPHIC DATA AND STRUCTURE REFINEMENT SUMMARY

Empirical formula	$C_{12}H_{14}N_4O_4Zn$
Formula weight	343.64
Crystal system space group	Triclinic P-1
Unit cell dimensions (Å,°)	a = 9.112(1) b = 9.494 (2) c = 9.551(1) α = 68.61(1) β = 64.98(1) γ = 88.21(1)
Volume (Å^3)	689.8(1)
Z, Calculated density (mg/m^3)	2, 1.655
F(000)	352
θ Range for data collection	2.33-27.50
Limiting indices	$-11 \leq h \leq 11$ $-12 \leq k \leq 12$ $-12 \leq l \leq 12$
Goodness-of-fit on F^2	1.007
Final R indices [I > 2 σ(I)]	$R_1 = 0.0259$; $wR_2 = 0.0652$
R indices (all data)	$R_1 = 0.0302$; $wR_2 = 0.0677$
Largest diff. peak and hole (e/Å^3)	0.990 and -0.221

TABLE-2
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°)

Bond	Dist.	Bond	Dist.
Zn(1)-O(1)^i	2.1219(17)	Zn(1)-O(2)	2.1507(16)
Zn(1)-O(3)	2.1532(16)	Zn(1)-O(4)	2.1249(17)
Zn(1)-N(1)	2.1355(19)	Zn(1)-N(3)	2.1005(18)
Angle	(°)	Angle	(°)
N(3)-Zn(1)-O(1)^i	87.43(6)	O(4)-Zn(1)-O(3)	77.76(6)
N(3)-Zn(1)-O(4)	100.20(6)	N(1)-Zn(1)-O(3)	163.52(6)
O(1)^i -Zn(1)-O(4)	170.45(5)	N(3)-Zn(1)-O(2)	165.34(6)
N(3)-Zn(1)-N(1)	93.47(8)	O(1)#1-Zn(1)-O(2)	77.93(5)
O(1)^i -Zn(1)-N(1)	99.53(6)	O(4)-Zn(1)-O(2)	94.29(6)
O(4)-Zn(1)-N(1)	85.83(6)	N(1)-Zn(1)-O(2)	89.72(7)
N(3)-Zn(1)-O(3)	90.96(8)	O(3)-Zn(1)-O(2)	89.98(7)
O(1)^i -Zn(1)-O(3)	96.52(6)		

Symmetry code: (i) -x, -y+1, -z

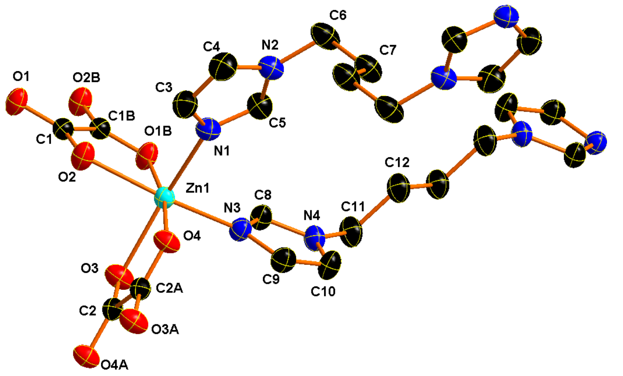


Fig. 1. Coordination environments of the Zn^{2+} ion with the ellipsoid of 50 % probability (symmetry codes: (A) -x, -y, -z; (B) -x, -y+1, -z). All hydrogen atoms are omitted for clarity

In this structure, the oxalate anions connect two Zn cations by a chelating coordination mode to form one dimensional zigzag chains propagating along b axis (Fig. 2). The adjacent chains are further cross-linked by bbi ligands *via* coordinating to the Zn meatl center forming the resultant three-dimensional framework (Fig. 3). Although there exists large channels in one single net, it is mainly penetrated by the other two equivalent nets, leaving no void to host the solvent molecules.

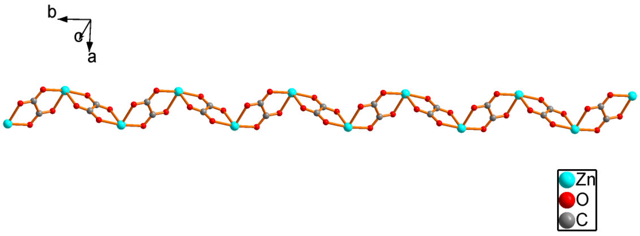
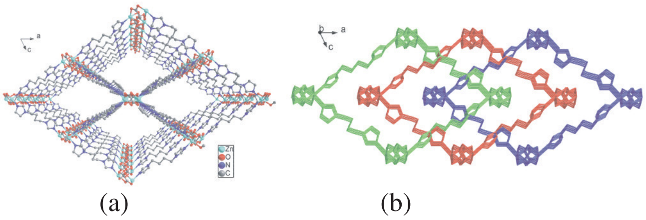


Fig. 2. 1D chain structure assembled from ox anion and Zn^{2+} cation extending along b axis



(a) (b)

Fig. 3. (a) Perspective view of the 3D packing diagram along the b axis. (b) View of the three-fold interpenetration network viewed along the approximate b axis

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