



Research Article

Synthesis, Crystal Structure and Catalytic Activity of Tri-Nuclear Zn(II) Complex Based on 6-Phenylpyridine-2-carboxylic Acid and Bis(4-pyridyl)amine Ligands

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Abstract

A new trinuclear Zn (II) complex, $[Zn_3(L_1)_4(L_2)_2(CH_3COO)_2]$ (**1**) (HL_1 = 6-phenylpyridine-2-carboxylic acid, L_2 = bis(4-pyridyl)amine) has been synthesized by 6-phenylpyridine-2-carboxylic acid, NaOH, bis(4-pyridyl)amine and $Zn(CH_3COO)_2 \cdot 2H_2O$. The complex **1** has also been structural characterized by elemental analysis and single crystal X-ray diffraction. The results reveals that complex **1** is made up of three Zn(II) ions, four L_1 ligands, two L_2 ligands and two CH_3COO^- anions. In **1**, both Zn1 ion and Zn1a ion are five-coordinated with two O atoms from two different L_1 ligands, two N atoms from two different L_1 ligands, and one N atoms from bis(4-pyridyl)amine ligand, respectively, and forms a distorted trigonal bipyramid geometry. And Zn2 ion is four-coordinated with two O atoms from two different CH_3COO^- anions and two N atoms from two different L_2 ligands, forming a distorted tetrahedral geometry. Complex **1** displays a 3D network structure by the intermolecular N-H...O hydrogen bonds. The catalytic performance for oxidation of benzyl alcohol with O_2 was studied under mild reaction conditions using complex **1** as catalyst. The results demonstrated that the catalysts were very active, and the yield of benzaldehyde was 50.8% at 90 °C with THF as solvent under 0.5 MPa O_2 within 3 h.

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Keywords: Trinuclear Zn (II) complex; Synthesis; Structural characterization; Catalytic activity

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1. Introduction

Metal complexes have attracted wide attention from scientists due to their structural diversity and potential applications [1]. Recent studies on Zn(II) complexes have mainly focused on the antibacterial activities [2–4], antitumor activities [5–8], electrochemical properties [9,10], fluorescence properties [11–15], antioxidant activity [16], magnetic properties [17], fluorescent detection [18,19]. Comparing to the above properties of zinc complexes, their catalytic properties have been less studied, however,

they also show potential applications in catalytic activities such as transformation of CO_2 into cyclic carbonates [20], cyanosilylation of aldehydes [21], decomposition reaction of H_2O_2 [22], ring-opening polymerization (ROP) of rac-lactide [23], ketone-amine-alkyne (KA^2) coupling reaction [24] and A^3 coupling reaction [25]. In our previous work, we have also performed the catalytic oxidation of benzyl alcohol with zinc complex as a catalyst [26]. However, there are relatively few studies on oxidation of benzyl alcohol using Zn(II) complexes as catalyst [27]. Our research group has been working on the synthesis, structural characterization and properties of metal complexes [28–33], and has also investigated the catalytic activity of some metal

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complexes [34–38]. To further expand the studies of the structure and catalytic activity of the zinc metal complexes, in this work, a new trinuclear Zn(II) complex has been synthesized by 6-phenylpyridine-2-carboxylic acid, NaOH, bis(4-pyridyl)amine and $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$. The trinuclear Zn(II) complex has been struc-

tural characterized by elemental analysis and single crystal X-ray diffraction. The catalytic activities of Zn(II) complex was studied for the oxidation of benzyl alcohol to benzaldehyde using O_2 as the green oxidant. The chemical diagram of $[\text{Zn}_3(\text{L}_1)_4(\text{L}_2)_2(\text{CH}_3\text{COO})_2]$ (**1**) is given in Figure 1.

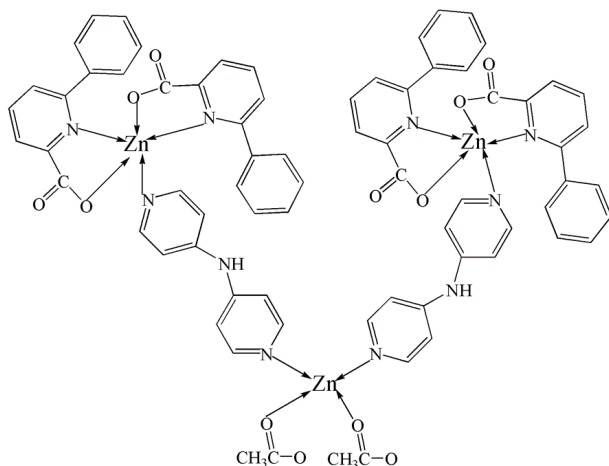


Figure 1. The chemical diagram of $[\text{Zn}_3(\text{L}_1)_4(\text{L}_2)_2(\text{CH}_3\text{COO})_2]$ (**1**).

2. Materials and Methods

2.1 Materials and Measurements

6-Phenylpyridine-2-carboxylic acid (A. R.), NaOH (A. R.), bis(4-pyridyl)amine (A. R.), and $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (A. R.) were purchased from Jilin Chinese Academy of Sciences-Yanshen Technology Co., Ltd.. The C, H and N contents were determined with an Elementar Vario III EL elemental analyzer (Hanau, Germany). The crystal data of complex **1** were collected on a Bruker Smart CCD diffractometer (Bruker, Billerica, MA, USA). The liquid products were analyzed using a gas chromatography spectrometer (GC-6890, Purkinje General Instrument Co., Ltd., China) equipped with a flame ionization detector (FID) and a

Table 1. Crystal data and structure refinement for $[\text{Zn}_3(\text{L}_1)_4(\text{L}_2)_2(\text{CH}_3\text{COO})_2]$ (**1**).

Empirical formula	$\text{C}_{72}\text{H}_{56}\text{N}_{10}\text{O}_{12}\text{Zn}_3$
Formula weight	1449.37
Temperature/K	250.00(10)
Crystal size/mm ³	0.14 × 0.13 × 0.12
Crystal system	Orthorhombic
Space group	$P2_12_12$
$a/\text{Å}$	35.189(3)
$b/\text{Å}$	10.6040(7)
$c/\text{Å}$	10.3295(9)
$a/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/Å ³	3854.4(5)
Z	2
ρ_{calc} , mg/mm ³	1.249
μ/mm^{-1}	0.987
S	1.034
$F(000)$	1488
Index ranges	$-48 \leq h \leq 31$, $-12 \leq k \leq 13$, $-11 \leq l \leq 13$
Reflections collected	14749
$\theta/^\circ$	1.972–29.492
Independent reflections	8054 [$R(\text{int}) = 0.0452$]
Data/restraints/parameters	8054/0/439
Goodness-of-fit on F^2	1.034
Refinement method	Full-matrix least-squares on F^2
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0579$, $wR_2 = 0.1184$
Final R indexes [all data]	$R_1 = 0.0927$, $wR_2 = 0.1332$
Largest diff. peak/hole / e Å ⁻³	0.34 / -0.35

SE-54 capillary column, to determine the conversion and yield.

2.2 Synthesis of $[\text{Zn}_3(\text{L}_1)_4(\text{L}_2)_2(\text{CH}_3\text{COO})_2]$ (1)

The mixture of 6-phenylpyridine-2-carboxylic acid (0.1992 g, 1.0 mmol), NaOH (0.040 g, 1.0 mmol), bis(4-pyridyl)amine (0.1712 g, 1.0 mmol), $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.2195 g, 1.0 mmol), and 20 mL ethanol/ H_2O solution (v:v = 1:1) were added to a 100 mL round bottom flask with stirring. Then the mixture was heated at *ca.* 75 °C with stirring for 6 h. After the reactants cooled to room temperature, filtered and the filtrate was transferred to a small conical vial and volatile slowly. The block crystals of $[\text{Zn}_3(\text{L}_1)_4(\text{L}_2)_2(\text{CH}_3\text{COO})_2]$ (1) were obtained from the filtrate in three weeks. Elemental analysis (%) calcd. for $\text{C}_{72}\text{H}_{56}\text{N}_{10}\text{O}_{12}\text{Zn}_3$: C, 59.61; H, 3.86; N, 9.66. Found (%): C, 59.36; H, 4.16; N, 9.39.

2.3 Crystal Structure Determination

A single crystal of $[\text{Zn}_3(\text{L}_1)_4(\text{L}_2)_2(\text{CH}_3\text{COO})_2]$ (1) (0.14 mm × 0.13 mm × 0.12 mm) suitable for X-ray diffraction was used to collect data on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer with graphite-monochromated Mo *K* α radiation ($\lambda = 0.71073$ Å) at 250.00(10) K. The crystal structure of 1 was solved by direct method using SHELXT 2018/2 [39] and refined with SHELXL 2018/3 [40] by full-matrix least squares on F^2 . The crystal data and structure refinement for 1 are summarized in Table 1.

The crystallographic data for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 2151259. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-

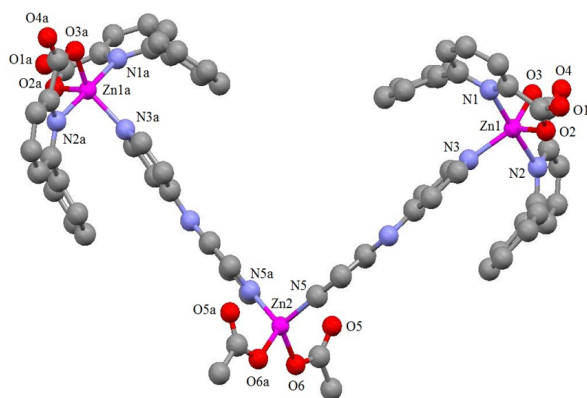


Figure 2. The asymmetric unit of $[\text{Zn}_3(\text{L}_1)_4(\text{L}_2)_2(\text{CH}_3\text{COO})_2]$ (1).

1 2 2 3 - 3 3 6 - 0 3 3; E-Mail: deposit@ccdc.cam.ac.uk).

2.4 General Procedure for the Oxidation of Benzyl Alcohol

The oxidation of benzyl alcohol was performed in a stainless-steel high-pressure reactor under oxygen (0.5 MPa). In a typical reaction, a 20 mL stainless-steel high-pressure reactor containing benzyl alcohol (1 mmol), complex 1 (catalyst, 40 mg), and tetrahydrofuran (THF, 7 mL) was kept at 90 °C, with a magnetic stirring (1000 r/min). The condensed liquid products were analyzed using a gas chromatography.

3. Results and Discussion

3.1 Structural Description of $[\text{Zn}_3(\text{L}_1)_4(\text{L}_2)_2(\text{CH}_3\text{COO})_2]$ (1)

Single-crystal X-ray diffraction shows that the $[\text{Zn}_3(\text{L}_1)_4(\text{L}_2)_2(\text{CH}_3\text{COO})_2]$ (1) crystallizes in the orthorhombic system with the $P2_12_12$ space group. The asymmetric unit of $[\text{Zn}_3(\text{L}_1)_4(\text{L}_2)_2(\text{CH}_3\text{COO})_2]$ (1) is shown in Figure 2. Selected bond lengths and angles of $[\text{Zn}_3(\text{L}_1)_4(\text{L}_2)_2(\text{CH}_3\text{COO})_2]$ (1) are given in Table 2. The results reveals that complex 1 is made up of three Zn(II) ions, four L_1 ligands, two L_2 ligands and two CH_3COO^- anions. In 1, both Zn1 ion and Zn1a ion are five-coordinated with two O atoms (O2, O3 or O2a, O3a) from two different L_1 ligands, two N atoms (N1, N2 or N1a, N2a) from two different L_1 ligands, and one N (N3 or N3a) atoms from bis(4-pyridyl)amine ligand, respectively, and forms a distorted trigonal bipyramid geometry. The sum of the bond angles around both Zn1 and Zn1a are 359.98° (N3–Zn1–O2, 120.65(19)°; O3–Zn1–O2, 107.93(18)°, O3–Zn1–N3, 131.4(2)°, O1–Mn1–N2 (90.57(9)°) and the bond angle of N1–Zn1–N2 is 178.55(19)°, showing that the O2, O3 and N3 construct the basal plane of the trigonal bipyramid and the N1 and N2 occupy the axial position. The Zn2 ion is four-coordinated with two O atoms (O6, O6a) from two different CH_3COO^- anions and two N atoms (N5 or N5a) from two different L_2 ligands, forming a distorted tetrahedral geometry (O6–Zn2–O6a, 97.0(3)°; O6a–Zn2–N5a, 119.5(2)°; O6a–Zn2–N5, 107.1(2)°; O6–Zn2–N5, 119.5(2)°; O6–Zn2–N5a, 107.1(2)°; N5–Zn2–N5a, 107.1(3)°). The Zn–O bond distances are 1.998(4) Å (Zn1–O2), 1.969(5) Å (Zn1–O3), 1.989(5) Å (Zn2–O6) and 1.989(5) Å (Zn2–O6a), and the Zn–N bond distances are 2.153(5) Å (Zn1–N1), 2.191(5) Å

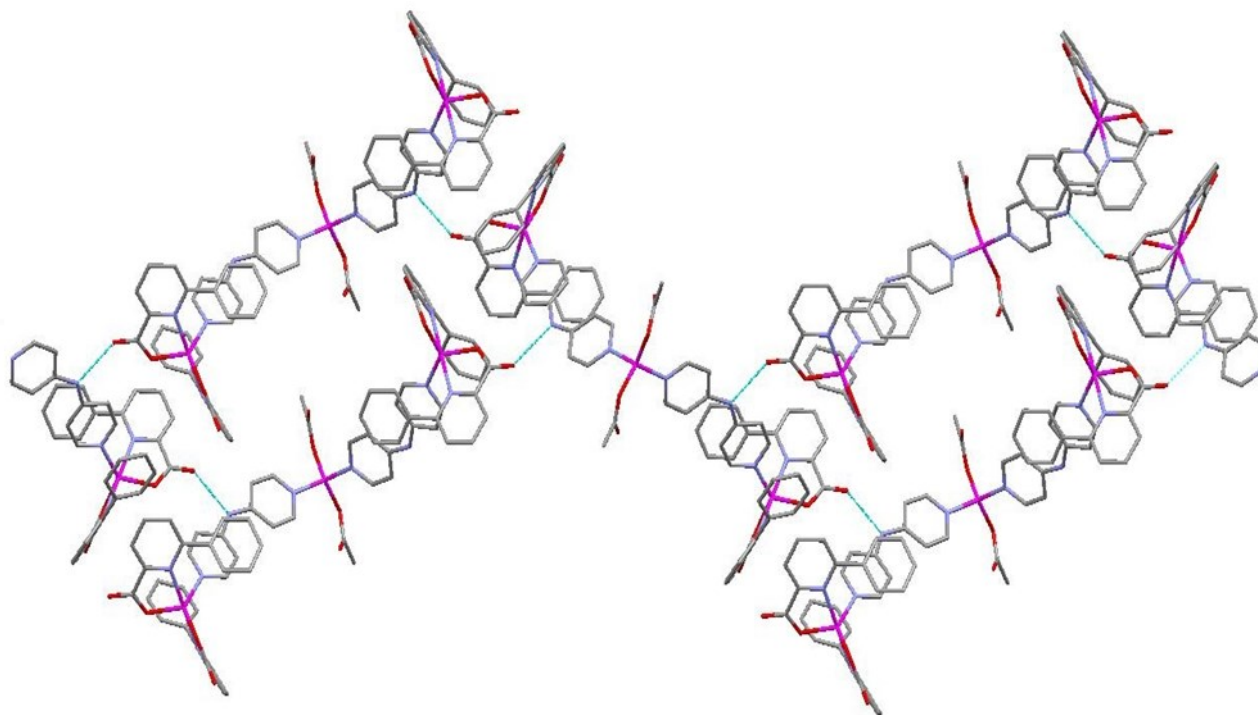


Figure 3. 1D ring-like structure of $[Zn_3(L_1)_4(L_2)_2(CH_3COO)_2]$ (1).

Table 2. Selected bond lengths (Å) and bond angles (°) of $[Zn_3(L_1)_4(L_2)_2(CH_3COO)_2]$ (1).

Bond	<i>d</i>	Angle	(°)
Zn1–O2	1.998(4)	O2–Zn1–N1	78.64(17)
Zn1–O3	1.969(5)	O3–Zn1–N3	131.4(2)
Zn1–N1	2.153(5)	N2–Zn1–N1	178.55(19)
Zn1–N2	2.191(5)	N3–Zn1–N1	92.07(19)
Zn1–N3	2.038(5)	N2–Zn1–N3	89.36(19)
Zn2–O6a	1.989(5)	O2–Zn1–N2	100.41(18)
Zn2–O6	1.989(5)	O2–Zn1–N3	120.65(19)
Zn2–N5	2.030(5)	O2–Zn1–O3	107.93(18)
Zn2–N5a	2.030(5)	O3–Zn1–N1	99.63(19)
C12–O1	1.250(6)	O3–Zn1–N2	79.6(2)
C12–O2	1.291(7)	O6–Zn2–O6a	97.0(3)
C13–O3	1.272(8)	O6a–Zn2–N5a	119.5(2)
C13–O4	1.237(10)	O6a–Zn2–N5	107.1(2)
C36–O5	1.219(10)	O6–Zn2–N5	119.5(2)
C36–O6	1.278(11)	O6–Zn2–N5a	107.1(2)
C7–N1	1.374(8)	N5–Zn2–N5a	107.1(3)
C11–N1	1.343(8)		
C14–N2	1.332(9)		
C18–N2	1.350(9)		
C25–N3	1.343(8)		
C30–N3	1.339(8)		
C27–N4	1.384(8)		
C31–N4	1.407(7)		
C33–N5	1.340(7)		
C34–N5	1.305(8)		

Symmetric code: a: 1-x, 2-y, +z

(Zn1–N2), 2.038(5) Å (Zn1–N3), 2.030(5) Å (Zn2–N5), and 2.030(5) Å (Zn2–N5a), respectively, which are consistent with other Zn(II) complexes [41,42]. The dihedral angle of two pyridine rings of bis(4-pyridyl)amine ligand is 6.31°, indicating that two pyridine rings are almost coplanar. While the dihedral angles of the pyridine ring 1 (C7–C8–C9–C10–C11–N1) and the benzene ring 1 (C1–C2–C3–C4–C5–C6), the pyridine ring 2 (C14–C15–C16–C17–C18–N2) and the benzene ring 2 (C19–C20–C21–C22–C28–C24) of L₁ ligand are 55.91° and 45.25°, respectively, indicating that the pyridine rings and benzene rings are not coplanar. The intermolecular N–H···O hydrogen bond (H4···O1 = 1.94 Å, N4···O1 = 2.795(7) Å and N4–H4···O1 = 171°) interactions lead the complex 1 to form 1D ring-like structure (Figure 3), further forming a 3D network structure (Figure 4). Besides the hydrogen bonds, the π–π interactions also play an important role in forming the 3D network of the complex. The Olex2 [43] and CrystalExplorer software [44] were used to analyze the π–π interactions that are present in the crystal structure. According to the calculation result of Olex2, there are four groups of valid π–π inter-

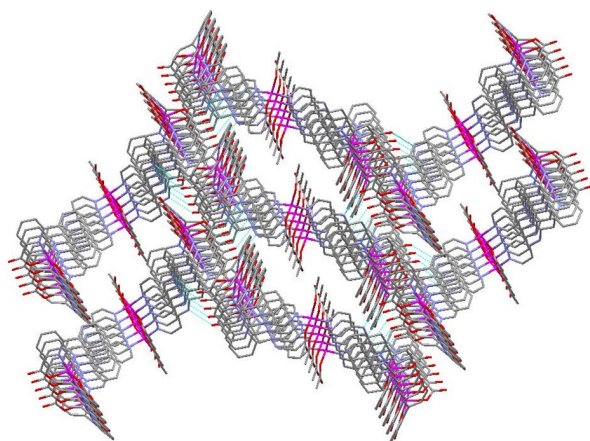


Figure 4. 3D network structure of [Zn₃(L₁)₄(L₂)₂(CH₃COO)₂] (1).

actions involving the stacking of aromatic rings belonging to the ligands and the centroid-centroid distance of plane #1 with #3@1_556(+X,+Y,1+Z), plane #1 with #4@1_555(+X,+Y,+Z), plane #2 with #4@1_555(+X,+Y,+Z), plane #2 with #5@4_546 (1/2-X, -1/2+Y,1-Z) are 3.871, 3.992, 3.590 and 3.915 (Ang.), respectively. The shift distance of the above plane pairs are 0.789, 1.454, 1.253 and 0.475 (Ang.). (plane #1: C1-C6-C5-C4-C3-C2; plane #2: C19-C24-C28-C22-C21-C20; plane #3: N5-C34-C35-C31-C32-C33; plane #4: N3-C30-C29-C27-C26-C25; plane #5: N1-C11-C10-C9-C8-C7). In order to better understand the non-covalent intermolecular interactions and contacts present in the complex 1, a hirshfeld surface analysis was performed by using the CrystalExplorer software (Figure 5).

3.2 Catalytic Studies of Benzyl Alcohol

In order to evaluate the performance of the [Zn₃(L₁)₄(L₂)₂(CH₃COO)₂] (1), the catalytic oxidation of benzyl alcohol to benzaldehyde was investigated (Table 3). The results showed that increasing the reaction time from 0.5 h to 4 h can improve the conversion of benzyl alcohol. A blank experiment (without complex 1) exhibit-

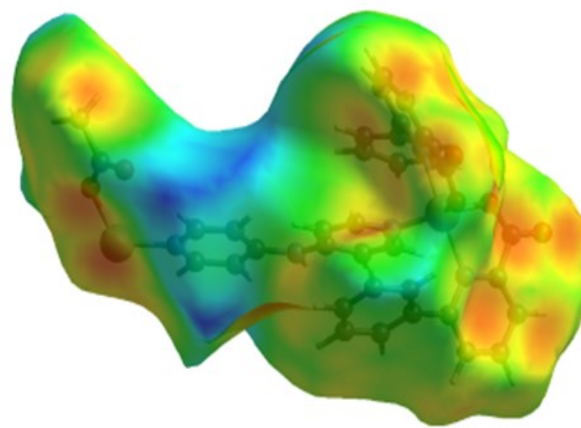


Figure 5. Hirshfeld surface for [Zn₃(L₁)₄(L₂)₂(CH₃COO)₂] (1).

Table 3. The benzyl alcohol conversion and benzaldehyde yield for complex 1 in the selective oxidation of benzyl alcohol at 90 °C under 0.5 MPa O₂.

Sample	Reaction time (h)	Conversion (%)	Yield (%)
Blank	4	12.5	2.5
Complex 1	0.5	7.7	7.6
Complex 1	1	20.4	20.2
Complex 1	2	42.2	41.8
Complex 1	3	78.2	50.8
Complex 1	4	96.3	19.3

Reaction condition: benzyl alcohol 1 mmol, THF 7 mL, complex 1 40 mg, 90 °C, 0.5 MPa

ed a low benzyl alcohol conversion (12.5%) and benzaldehyde yield (2.5%) at 90 °C with THF as solvent under 0.5 MPa O₂ for 4 h. For complex **1**, the conversion of benzyl alcohol was 7.7% at 90 °C within 0.5 h. Then the benzyl alcohol conversion was increased by prolonging reaction time, and the conversions were 20.4%, 42.2%, 78.2%, and 96.3% within 1 h, 2 h, 3 h, and 4 h, respectively. However, the yield of benzaldehyde displayed the different trend with prolonging reaction time. The benzaldehyde yield were 7.6%, 20.2%, 41.8%, 50.8%, and 19.3% within 0.5 h, 1 h, 2 h, 3 h, and 4 h at 90 °C, respectively. The highest yield of benzaldehyde (50.8%) of the reaction was gained at 90 °C within 3 h. The benzyl alcohol conversion and benzaldehyde yield over ZnL₄(Phen)₂ were 37.1% and 1.9% at 90 °C within 4 h under 0.5 MPa of O₂ [26]. Asgharnejad *et al.* reported that the three-dimensional copper-based coordination polymers [Cu(1,4-BDC-Br)(DABCO)_{0.5}]·xDMF·yH₂O exhibited good catalytic activity for the benzyl alcohol oxidation reaction using tert-butyl hydroperoxide as oxidant, the conversion of benzyl alcohol and yield of benzaldehyde were 38% and 29.6% in DMF at 40 °C within 4 h, respectively [45]. Shahamat *et al.* reported that Fe₃O₄-PANI-I(OAc)₂ nanocomposite displayed superior catalytic activity, the yield of benzaldehyde reached 92% at 70 °C for 3 h using 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as oxidant in acetonitrile [46]. Based on the above results, our complex **1** catalyst presents much higher yields (50.8%) than ZnL₄(Phen)₂ and [Cu(1,4-BDC-Br)(DABCO)_{0.5}]·xDMF·yH₂O. Although the benzaldehyde yield is lower than Fe₃O₄-PANI-I(OAc)₂, the complex **1** could oxidized benzyl alcohol with high activity using inexpensive and green oxidant (O₂).

As shown in Figure 1, the chemical diagram of complex **1** contains two coordinated CH₃COO⁻ anions, which can be easily removed by heating before catalyzing. And coordinatively unsaturated zinc could act as catalytic site of benzyl alcohol oxidation. We speculate that the reaction mechanism of complex **1** for the selective oxidation benzyl alcohol to the benzaldehyde is initiated by oxidative dehydrogenation of alcohol taking place on unsaturated zinc [37]. First, the hydroxyl group in benzyl alcohol absorbs on the unsaturated zinc to obtain the intermediate zinc-alcoholate species. Subsequently, the portion in the hydroxyl group is abstracted to complex **1** to form surface adsorbed H species and alkoide intermediates. Then the alkoide intermediates undergo a β-hydrate elimination to give the target product

benzaldehyde. At the same time, zinc-hydride species are formed and reacted with O₂ to give water and to regenerate the complex **1** for further reaction.

5. Conclusions

In summary, a new trinuclear Zn(II) complex has been synthesized by 6-phenylpyridine-2-carboxylic acid, NaOH, bis(4-pyridyl)amine and Zn(CH₃COO)₂·2H₂O. The complex **1** has also been structural characterized by elemental analysis and single crystal X-ray diffraction. Complex **1** displays a 3D network structure by the intermolecular N–H···O hydrogen bonds. The Zn(II) complex exhibited a good catalytic activity for the oxidation reaction of benzyl alcohol with O₂.

Acknowledgments

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