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Research Article

Synthesis, Crystal Structure of Tetra-Nuclear Macrocyclic Zn (II) Complex and Its Application as Catalyst for Oxidation of Benzyl Alcohol

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Abstract

A new six coordinated tetra-nuclear macrocyclic Zn(II) complex, $ZnL_4(Phen)_2$ (**1**) (HL= 3-bromo-2-hydroxybenzaldehyde-pyridine-2-carbohydrazone, Phen = 1,10-phenanthroline) has been synthesized by the self-assembly of 3-bromo-2-hydroxybenzaldehyde-pyridine-2-carbohydrazone, $Zn(CH_3COO)_2 \cdot 2H_2O$, NaOH and 1,10-phenanthroline in water/ethanol (v:v = 1:3) solution. Complex **1** was characterized by elemental analysis, infra red (IR), and single-crystal X-ray diffraction (XRD) analysis. The results show that Zn1 and Zn1b ions are six-coordinated with a distorted octahedral geometric configuration by four O atoms of two different L ligands and two N atoms of two different L ligands, Zn1a and Zn1c ions are also six-coordinated with a distorted octahedral geometric configuration by two N atoms of two different L ligands, two N atoms of Phen ligands and two O atoms of two different L ligands. Complex (**1**) forms 3D network structure by the π-π interaction. The selective oxidation reactions of benzyl alcohols catalyzed by complex (**1**) was investigated. The highest benzyl alcohol conversion and benzaldehyde selectivity were obtained at 100 °C for 4 h under 5 bar of O_2.

Keywords: Hydrazone; Tetra-nuclear macrocyclic Zn(II) complex; Synthesis; Structural characterization; Oxidation of benzyl alcohol

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1. Introduction

Macrocyclic metal complexes exhibit widespread potential applications in cytotoxicity, antioxidant and antibacterial activities [1–4], photoluminescent property [5-7], catalytic properties, such as: hydrosilylation of diphenyl acetylenes [8], electrocatalytic oxygen reduction [9,10], ring opening reaction [11], electrocatalytic CO_2 reduction [12], hydrogen evolution reaction [13], water oxidation catalysis [14], gas adsorption [15], magnetic property [16], and so on. According to the literatures report [17–22], precious metal oxide, hydrogen peroxide, precious metal nanomaterials and MOFs are used as a catalyst to produce benzaldehyde by oxidation of

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benzyl alcohol. However, there are few studies on catalytic oxidation of benzyl alcohol to benzaldehyde by macrocyclic metal complexes. In our previous works, some macrocyclic metal complexes have been synthesized and their structures and properties have also been investigated [23–28]. In order to further investigate the structure and property of macrocyclic metal complexes, in this work, a new tetra-nuclear macrocyclic Zn(II) complex, $ZnL_4(Phen)_2$ (**1**) (HL = 3-bromo-2-hydroxybenzaldehyde-pyridine-2-carbohydrazone, Phen = 1,10-phenanthroline) has been synthesized by the self-assembly of 3-bromo-2-hydroxybenzaldehyde-pyridine-2-carbohydrazone, $Zn(CH_3COO)_2\cdot 2H_2O$, NaOH and 1,10-phenanthroline in water/ethanol (v:v = 1:3) solution. The structure of complex (**1**) was characterized by elemental analysis, IR and single-crystal X-ray diffraction analysis. The selective oxidation reactions of benzyl alcohols catalyzed by complex **1** was investigated. The highest benzyl alcohol conversion and benzaldehyde selectivity were obtained at 100 °C for 4 h under 5 bar of O_2.

2. Materials and Method

2.1 Materials and Measurements

The ligand of 3-bromo-2-hydroxybenzaldehyde-pyridine-2-carbohydrazone was synthesized by our research group itself and confirmed by element analysis and infrared spectroscopy. Other reagents of NaOH (A. R.), 1,10-phenanthroline (A. R.), and $Zn(CH_3COO)_2\cdot 2H_2O$ (A. R.) were purchased from Sinopharm Chemical Reagent Co., Ltd.. Using an Elementar Vario III EL elemental analyzer (Hanau, Germany) to analyze C, H and N. The crystal data of $ZnL_4(Phen)_2$ (**1**) were collected on a Bruker Smart CCD diffractometer (Bruker, Billerica, MA, USA). The se-

Table 1. Crystallographic data of tetra-nuclear macrocyclic Zn(II) complex (1).

Empirical formula	$C_{19}H_{12}BrN_4O_2Zn$
Formula weight	473.61
Temperature/K	100.00(10)
Crystal system	Orthorhombic
Space group	*F*ddd
a/Å	18.8920(5)
b/Å	38.6707(10)
c/Å	26.7016(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	19507.3(8)
Z	32
ρ_{calc}, mg/mm^3	1.290
μ/mm^{-1}	3.462
S	1.130
F(000)	7520
Index ranges	$-23 \le h \le 13$, $-47 \le k \le 35$, $-22 \le l \le 32$
Reflections collected	11111
θ/°	3.253-73.313
Independent reflections	4816 [R(int) = 0.0261]
Data/restraints/parameters	4816/0/245
Goodness-of-fit on F^2	1.130
Refinement method	Full-matrix least-squares on F^2
Final R indexes [I>=2σ (I)]	R_1 = 0.0555, wR_2 = 0.1247
Final R indexes [all data]	R_1 = 0.0586, wR_2 = 0.1266
Largest diff. peak/hole / e Å^{-3}	0.78/-0.51

lective oxidation reactions of benzyl alcohols catalyzed by complex 3 was carried out in a 20 mL stainless steel high pressure reactor. The conversion of benzyl alcohol and the selectivity of benzaldehyde were determined by gas chromatography spectrometer equipped with a SE-54 column (GC-1100, Beijing Purkay General Instrument Co. Ltd).

2.2 Synthesis of Tetra-nuclear Macrocyclic Zn(II) Complex

3-Bromo-2-hydroxybenzaldehyde-pyridine-2-carbohydrazone (0.5 mmol, 0.11601 g) and NaOH (0.5 mmol, 0.020 g) were dissolved into 20 mL ethanol/H_2O solution (v:v = 1:1) with stirring at room temperature. After 0.5 h, $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.5 mmol, 0.0865 g) was added to the above solution. After reaction at *ca.* 75 °C for 3 hours, 1,10-phenanthroline (0.5 mmol, 0.0901 g) was added to the above solution. The reaction mixture was stirred for 4 h at *ca.* 75 °C. The white precipitate formed and filtered. Slowing volatilization of filtrate at room temperature, the crystals of tetra-nuclear macrocyclic Zn(II) complex (**1**) were obtained in 30 days. Elemental analysis (%) calcd. for $C_{19}H_{12}BrN_4O_2Zn$: C, 48.14; H, 2.53; N, 11.82. Found (%): C, 47.96; H, 2.76; N, 11.59.

2.4 Crystal Structure Determination

A suitable (0.12 mm × 0.11 mm × 0.09 mm) single crystal of tetra-nuclear macrocyclic Zn(II) complex (**1**) was selected to collect data on a Super Nova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 100.00(10) K during data collection. *SHELXL* program [29] was used to solve the structure by direct method, and refined by the *OLEX2* program [30]. The crystallographic data of tetra-nuclear macrocyclic Zn(II) complex (**1**) are given in Table 1.

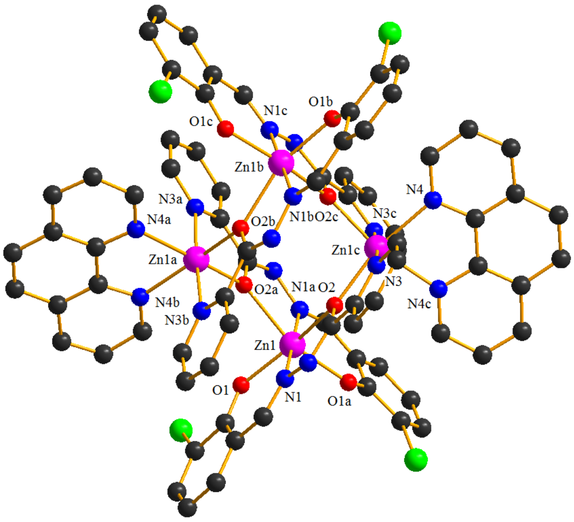

Figure 1. The molecular structure of tetra-nuclear macrocyclic Zn(II) complex (1).

2.5 The Procedure for The Oxidation of Benzyl Alcohol

The selective oxidation reactions of benzyl alcohols catalyzed by tetra-nuclear macrocyclic Zn(II) complex (**1**) was carried out in a 20 mL stainless steel high pressure reactor. 0.050 g tetra-nuclear macrocyclic Zn(II) complex (1) catalyst, benzyl alcohol (1.0 mmol) and 1,4-dioxane (7 mL) were added into the reactor, and then pure O_2 was purged into the reactor. The suspension was stirred magnetically at 90 °C or 100 °C for 4 h under 3–5 bar O_2 pressure. The conversion of benzyl alcohol and the selectivity of benzaldehyde were determined by gas chromatography spectrometer equipped with a SE-54 column. The products were identified by comparison with known authentic standards, and an external standard method was used for the qualitative analysis.

3. Results and Discussion

3.1. Structural Description of Tetra-nuclear Macrocyclic Zn(II) Complex (1)

The structural analysis of tetra-nuclear macrocyclic Zn(II) complex (**1**) shows that it crystallizes in the orthorhombic system with the *F*ddd (no. 70) space group. The molecular structure of tetra-nuclear macrocyclic Zn(II) complex (**1**) is shown in Figure 1. The selected bond lengths (Å) and angles (°) for tetra-nuclear macrocyclic Zn(II) complex (1) are given in Table 2. As shown in Figure 1, the tetra-nuclear macrocyclic Zn(II) complex (**1**) is made up of four Zn(II) ions, four 3-bromo-2-

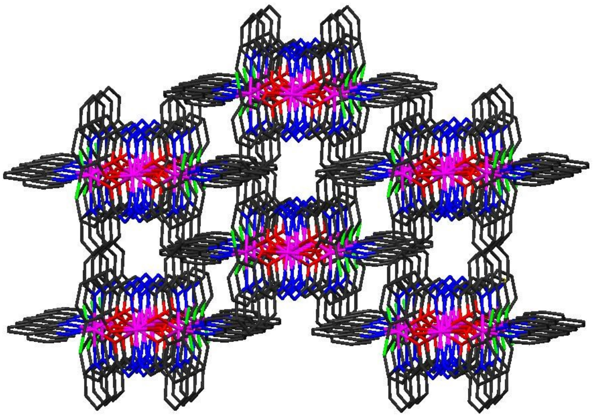

Figure 2. 3D network structure of tetra-nuclear macrocyclic Zn(II) complex (1).

hydroxybenzaldehyde-pyridine-2-carbohydrazone ligands and two 1,10-phenanthroline ligands. In **1**, four Zn(II) atoms adopt different coordination mode: Zn1 and Zn1b ions are six-coordinated with a distorted octahedral geometric configuration by four O atoms (Zn1: O1, O1a, O2, O2a; Zn1b: O1b, O1c, O2b, O2c) of two different L ligands and two N atoms (Zn1: N1, N1a; Zn1b: N1b, N1c) of two different L ligands, Zn1a and Zn1c ions are also six-coordinated with a distorted octahedral geometric configuration by two N atoms (Zn1a: N3a, N3b; Zn1c: N3, N3c) of two different L ligands, two N atoms (Zn1a: N4a, N4b; Zn1c: N4, N4c) of Phen ligands and two O atoms (Zn1a: O2a, O2b; Zn1c: O2, O2c) of two different L ligands. Four Zn(II) atoms form tetra-nuclear macrocyclic structure by the bridge effect of four carbonyl oxygen atoms. The Zn-O and Zn-N distances are in the range of 2.046(3)-2.259(2) Å (Zn-O), 2.052(3)-2.182(3) Å (Zn-N), respectively, which are comparable to other Zn(II) complexes [31-33]. The tetra-nuclear macrocyclic Zn(II) complex (**1**) assemble an extended 3D supramolecular network structure via π-π stacking interactions of aromatic rings of ligands (Figure 2).

Table 2. Selected bond lengths (Å) and bond angles (°) for tetra-nuclear macrocyclic Zn(II) complex (1).

Bond	d	Angle	(°)
Zn1-O1	2.046(3)	O1-Zn1-O1a	100.83(17)
Zn1-O1a	2.046(3)	O1-Zn1-O2a	90.26(10)
Zn1-O2	2.259(2)	O2a-Zn1-O1a	159.04(11)
Zn1-O2a	2.259(2)	O1a-Zn1-O2	90.26(10)
Zn1-N1	2.052(3)	O1-Zn1-O2	159.04(11)
Zn1-N1a	2.052(3)	O1-Zn1-N1	87.57(12)
C6-Br1	1.895(5)	O1a-Zn1-N1	93.15(12)
Zn1c-O2	2.090(2)	O1-Zn1-N1a	93.15(12)
Zn1c-O2c	2.090(2)	O1a-Zn1-N1a	87.57(12)
Zn1c-N3	2.143(3)	O2-Zn1-O2a	85.16(13)
Zn1c-N3c	2.143(3)	N1a-Zn1-O2	105.14(11)
Zn1c-N4	2.182(3)	O2a-Zn1-N1a	73.99(11)
Zn1c-N4c	2.182(3)	N1-Zn1-O2a	105.14(11)
C1-O1	1.293(5)	N1-Zn1-O2	73.99(11)
C8-O2	1.288(4)	N1a-Zn1-N1	178.87(18)
N1-N2	1.397(4)	O2c-Zn2-O2	99.56(14)
C7-N1	1.297(5)	O2c-Zn2-N3	99.57(11)
C8-N2	1.308(5)	O2-Zn2-N3c	99.57(11)
		O2-Zn2-N3	78.31(11)
		O2c-Zn2-N3c	78.31(11)
		O2c-Zn2-N4c	163.92(11)
		O2-Zn2-N4c	93.09(11)
		O2c-Zn2-N4	93.08(11)
		O2-Zn2-N4	163.92(11)
		N3c-Zn2-N3	176.77(17)
		N3-Zn2-N4	89.88(12)
		N3c-Zn2-N4	92.66(12)
		N3-Zn2-N4c	92.66(12)
		N3c-Zn2-N4c	89.88(12)

Symmetry transformations: a: 5/4-*x*, 5/4-*y*, +*z*; c: 5/4-*x*, +*y*, 5/4-*z*.

3.2 Activity of Benzyl Alcohol Oxidation

After preparation and characterization of tetra-nuclear macrocyclic Zn(II) complex (**1**), its catalytic activity was investigated in the selective oxidation of benzyl alcohol with molecular oxygen as the sole oxidant. O_2 is inexpensive and only produces water as its byproduct. The reaction temperature and pressure were optimized in the selective oxidation of benzyl alcohol in the presence of tetra-nuclear macrocyclic Zn(II) complex (**1**). The results are summarized in Table 3. A blank experiment showed a low benzyl alcohol conversion (9.6%) at 100 °C under 5 bar of O_2 with 1,4-dioxane as solvent for 4 h. By contrast, good benzyl alcohol conversions were observed tetra-nuclear macrocyclic Zn(II) complex (1), suggesting that complex (1) could catalyse the oxidation of benzyl alcohol. For tetra-nuclear macrocyclic Zn(II) complex (**1**), the benzyl alcohol conversion and benzaldehyde selectivity were 37.1% and 5.2% at 90 °C for 4 h under 5 bar O_2. When the reaction temperature increase to 100 °C, the benzyl alcohol conversion and benzaldehyde selectivity greatly enhanced to 78.1% and 29.2%. The conversion of benzyl alcohol and selectivity of benzaldehyde were 49.0% and 10.8% at 100 °C for 4 h under 3 bar O_2. The observed main by-product is benzoic acid, together with amounts of benzyl benzoate. The selectivities of benzoic acid are 55.3%, 45.4%, 47.3% for complex (**1**) on oxidation reactions under 90 °C 5 bar, 100 °C 5 bar, and 100 °C 3 bar, respectively. The highest benzyl alcohol conversion (78.1%) and benzaldehyde selectivity (29.2%) were obtained at 100 °C for 4 h under 5 bar of O_2. Nabae *et al.* found that HBPI (hyperbranched polyimide) functionalized with TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) could works as a heterogenous catalyst for the benzyl alcohol oxidation in the presence of a catalytic amount of HNO_3 [34].

The benzyl alcohol conversion and benzaldehyde selectivity are 11% and 100% on TEMPO/HBPI, respectively [34]. Li *et al* [35]. reported that conjugated metalloporphyrin polymers (MnP-AMPs) with BET surface area of 345 m^2/g had good catalytic performance for the oxidation of benzyl alcohol, achieving complete conversion within 2 h and benzaldehyde selectivity of 98%. Asgharnejad *et al.* [36] synthesized three-dimensional copper-based coordination polymers $[Cu(1,4\text{-}BDC\text{-}Br)(DABCO)_{0.5}]\cdot xDMF\cdot yH_2O$ using $Cu(NO_3)_2\cdot 3H_2O$, triethylenediamine (DABCO), 2-bromoterephthalate (1,4-BDC-Br), CH_3COOH, and DMF. The copper-based coordination polymers exhibited good activity (conversion: 38%) and selectivity to benzaldehyde (78%) in the benzyl alcohol oxidation using tert-butyl hydroperoxide as an oxidant in DMF at 40 °C for 4 h [36]. Based on the above results, the catalytic activity and selectivity of complex (**1**) in the oxidation of benzyl alcohol was lower than MnP-AMPs catalyst. Although the selectivity of benzaldehyde is less than those of TEMPO/HBPI and $[Cu(1,4\text{-}BDC\text{-}Br)(DABCO)_{0.5}]\cdot xDMF\cdot yH_2O$, the complex (**1**) could oxidized benzyl alcohol with high activity using O_2 as sole oxidant without adding any other substances.

To examine the scope of substrate of the oxidation reaction, we extended our studies to different combinations of alcohols. The results are

Table 3. Oxidation of benzyl alcohol to benzaldehyde on tetra-nuclear macrocyclic Zn(II) complex (1) in 1,4-dioxane.

Entry	Catalysts	Temperature (°C)	Pressure (bar)	Reaction time (h)	Conversion (%)	Benzylaldehyde Selectivity (%)	Benzoic acid Selectivity(%)
1	Complex (1)	90	5	4	37.1	5.2	52.3
2	Complex (1)	100	5	4	78.1	29.2	45.4
3	Complex (1)	100	3	4	49	10.8	47.3

Table 4. Catalytic activities of complex (1) for the oxidation of various alcohols.

Entry	Substrates	Conversion (%)	Aldehyde Selectivity (%)	Acid Selectivity (%)
1	4-chlorobenzyl alcohol	82.1	27.2	50.3
2	4-methylbenzyl alcohol	81.6	28.9	27.0
3	4-methoxybenzyl alcohol	86.4	7.7	60.7
4	n-butanol	86.2	24.9	51.9

Note: reaction condition: complex (1) (0.05 g),100 °C, 5 bar, 4 h.

summarized in Table 4. Aromatic alcohols including those bearing functional groups, such as: alkoxy, alkyl, and chloro, were able to undergo the corresponding oxidation reaction, and afforded good conversions of alcohols in the selective oxidation reaction. The conversions are 82.1%, 81.6%, and 86.4% for 4-chlorobenzyl alcohol, 4-methylbenzyl alcohol, and 4-methoxybenzyl alcohol, respectively. The nature of substituents (electron with drawing or electron-donating) has an ignore influence on the catalytic activity. Moreover, n-butanol also displayed a high catalytic activity with conversion of 86.2%. The selectivities of aldehydes are 27.2%, 28.9%, 7.7%, and 24.9% for 4-chlorobenzyl alcohol, 4-methylbenzyl alcohol, 4-methoxybenzyl alcohol, and n-butanol, respectively. It gives high selectivity of by-product acids, and the selectivities of acids are 50.3%, 27.0%, 60.7%, and 51.9% for 4-chlorobenzyl alcohol, 4-methylbenzyl alcohol, and 4-methoxybenzyl alcohol, respectively.

4. Conclusions

In summary, a new tetra-nuclear macrocyclic Zn(II) complex, $ZnL_4(Phen)_2$ (**1**) has been synthesized and structural characterized by elemental analysis, IR, and single-crystal X-ray diffraction analysis. The selective oxidation reactions of benzyl alcohols catalyzed by complex (**1**) have been investigated.

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