Three new zinc(II) complexes: design, synthesis, characterization and catalytic performance

Gong Li, Qiao Zhang, Shuang Yang, Mengdi Zhu, Yuejiao Fu, Ziheng Liu, Na Xing and Lei Shi

College of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian, P. R. China

ABSTRACT

Three new Zn(II) complexes, [Zn₂L₂(OAc)₂]·2CH₃OH (1), [ZnL(3-NA)₂]·C₁H₂O (2) and [ZnL(2-NA)₂] (3) were synthesized by the reaction of Zn(CH₃COO)₂·2H₂O or Zn(ClO₄)₂·6H₂O with 2-amino-N'-(pyridin-2-ylmethylene)benzohydrazide (HL), 3-nitrobenzoic acid (3-NA) or 2-nitrobenzoic acid (2-NA). The complexes were characterized by elemental analyses, single crystal X-ray diffraction, IR, UV-Vis and ¹H NMR spectroscopy. The single crystal X-ray diffraction analyses revealed that the Zn ions in the complexes are five-coordinate in tetragonal pyramid configuration. The complexes and their starting materials Zn(CH₃COO)₂·2H₂O and Zn(ClO₄)₂·6H₂O were studied for their catalytic performance in the selective oxidation of cyclohexane (Cy) with aqueous H₂O₂ as oxidant. The conditions such as time, the amount of H₂O₂, solvent and HNO₃ additive were optimized. The results showed that 3 has the best activity under mild conditions compared to the starting zinc materials and the referenced zinc complexes.

ARTICLE HISTORY

Received 12 August 2021
Accepted 13 June 2022

KEYWORDS

Hydrazone; zinc complex; crystal structure; catalytic oxidation; cyclohexane

CONTACT Na Xing scarlet_na@163.com; Lei Shi shilei515dl@126.com College of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian, 116029, P. R. China

Supplemental data for this article is available online at https://doi.org/10.1080/00958972.2022.2098472.
1. Introduction

Selective oxidation of cyclohexane (Cy) to cyclohexanone (K, CyO) and cyclohexanol (A, CyOH), generally known as KA-oil, plays a significant role in the chemical industry since KA-oil is an important intermediate material to produce Nylon-6 and Nylon-66 polymers [1–5]. It is vital to find suitable selective oxidation catalysts to improve the yield of KA-oil. In the past decades, research on metal catalysts with high catalytic activity for Cy oxidation has mainly concentrated on precious metal materials for their high efficiency and stability [6–9]. However, the expensive price and toxicity limit the application and development of precious metals. Therefore, non-noble transition elements with low-cost and high catalytic activity have been committed to exploration [10–12]. Among them, zinc compounds have been widely studied for their excellent activity on C-H oxidation [13–18].

Vijayaraj et al. reported enhancement of the stability of aniline oxidation by Cu0.5Zn0.5Fe2O4 at 300 °C [13]. Hao et al. prepared Zn-Al oxide to catalyze carboxylation of 1,2-propylene glycol in the presence of urea [14]. The yield of propylene carbonate was 96.6% at 180 °C. Lachheb et al. found that the conversion of styrene and selectivity of styrene oxides was 60% and 50%, respectively, when ZnO acts as a photocatalytic catalyst under H2O2/UV radiation at 250 °C [15]. Based on the above research results, Zn compounds can be considered to be potential catalysts for catalytic oxidation. However, Zn salts have barely been reported in work for Cy oxidation.

Among zinc compounds, zinc complexes have often been synthesized and discussed as C-H oxidation catalysts. Shixaliyev et al. synthesized Zn[NHC(CCl3)NC–(CCl3)NH]2 with Zn(CH3COO)2·2H2O, NH4OH and trichloroacetoniitriile and applied it in the Henry reaction with H2O2 for 24 h [16]. The product yield reached 98.7% with acetaldehyde as substrate. Zou et al. synthesized [[(CH3)2NH2][Zn2(HCOO)2-(MnIII-TCPP)]-5DMF-2H2O (H6TCPP = tetrakis(4-carboxyphenyl)porphyrin) using MnCl-H4TCPP, Zn(NO3)2·6H2O and DMF/AcOH as starting materials [17]. Jadav et al. synthesized a tetranuclear zinc complex, [Zn4(L)2(LH)2((CH3)2SO)2·2CH3OH·(CH3)2S–O·H2O(LH3=3-(E)-(2-hydroxypheynilimino)methyl-4-hydroxy-5-hydroxymethylphenyl)], and incorporated it into a MCM-48 mesoporous silica material to form a Zn composite modified material [18]. The morpholine conversion can reach up to 95% at 70 °C in 6 h when catalyzed by this complex (20 mg).

In this work, three new zinc(II) complexes, [Zn2L2(OAc)2]2CH3OH (1), [ZnL(3-NA)2]·H2O (2) and [ZnL(2-NA)2] (3), with 2-amino-N’-(pyridin-2-ylmethylene)benzohydrazide (HL) as ligand have been synthesized and structurally characterized. Their catalytic performance for Cy oxidation were compared with their starting materials (zinc salts).

2. Experimental

2.1. Materials and methods

Zinc nitrate (≥99.0%), zinc bromide (≥99.0%) dichloromethane (≥99.8%) and nitric acid (65-68%) were obtained from Tianjin Damao Chemical Reagent Co., Ltd. (China). Cyclohexane (≥99.5%), methanol (≥99.5%), methylbenzene (≥99.5%), acetonitrile
(≥99.5%), ethanol (≥99.7%), diethyl ether (≥99.5%), hydrogen peroxide 30% (≥30%), oxalic acid (≥99.8%), trichloromethane (≥99.5%), carbon tetrachloride (≥99.5%), hydrochloric acid (36-38%), salicylic acid (≥99.5%), hydroxypropanoic acid (85–90%) and phosphoric acid (85%) were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. (China). Cyclohexanol (≥98.5%) and cyclohexanone (≥99.5%) were obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. (China). Sulfuric acid (95–98%) was bought from Shenyang Xinxi Reagent Co., Ltd. (China). Zinc bromide (99.9%), zinc acetate (99.5%), zinc perchlorate hexahydrate, potassium bromide (99.9%), zinc iodide (≥98%), triphenylphosphine (≥99%), sodium 3-nitrobenzoate (≥95%), 2-nitrobenzoic acid (98%) and 2-pyridinecarboxaldehyde (98%) were obtained from Shanghai Macklin Biochemical Co., Ltd. (China). All other reagents and solvents were purchased from China Chemical Reagent Co. Ltd. (China).

Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. IR spectra were recorded on a Jasco FT/IR-4000 spectrometer as KBr pellets from 4000 to 400 cm⁻¹. UV–Vis spectra were recorded on a Perkin-Elmer Lambda 900 spectrometer. ¹H NMR spectra were obtained by a 500 MHz Bruker Advance instrument. Molar conductivities of the complexes were measured in methanol (room temperature) using a DDS-11A conductivity meter. Single crystal structures were determined by a Bruker D8 Venture CCD diffractometer.

2.2. Synthesis of 1–3

Free hydrazine compound 2-amino-N’-(pyridin-2-ylmethylene)benzohydrazide (HL) was prepared following the procedure described in the literature [19].

2.2.1. Preparation of diacetato-di(2-pyridinecarboxyaldehyde 2-aminobenzoylhydrazone)dizinc(II) bismethanol (1)

HL (1.0 mmol, 0.24 g) was dissolved in methanol (20 mL), to which was added dropwise a solution of Zn(CH₃COO)₂·2H₂O (1.0 mmol, 0.22 g) in methanol (30 mL). The mixture was stirred for 10 min at room temperature and filtered. The filtrate was kept in air for a few days to form crystals suitable for single crystal X-ray diffraction. The crystals were isolated by filtration. Yield: 0.22 g (56%). Characteristic IR data (KBr, cm⁻¹): 3453, ν(–OH); 1627, ν(C ≡ N); 553, ν(Zn–O); 436, ν(Zn-N). UV–Vis data (methanol, λ/ nm): 295(π→π*), 310(n→π*), 393(LMCT). Anal. Calcd for C₃₂H₃₆N₈O₈Zn₂: C, 48.6; H, 4.6; N, 14.2. Found: C, 48.5; H, 4.7; N, 14.0%. ¹H NMR (500 MHz, d₆-DMSO) δ 8.69 (s, 1H, NH), 8.50 (d, 1H, PyH), 8.44 (s, 1H, CH ≡ N), 8.06 (t, 1H, PyH), 7.97 (t, 1H, PyH), 7.85 (d, 1H, ArH), 7.71 (t, 1H, PyH), 7.55 (t, 1H, ArH), 7.37 (t, 1H, ArH), 6.67 (s, 1H, NH), 6.53 (d, 1H, ArH), 3.37 (s, 1H, NH), 3.18 (s, 3H, CH₃). 182 (s, 3H, CH₃).

2.2.2. Preparation of di(3-nitrobenzoato)-(2-pyridinecarboxyaldehyde 2-aminobenzoylhydrazone)zinc(II) monohydrate (2)

HL (1.0 mmol, 0.24 g) was dissolved in methanol (20 mL), to which was added dropwise a mixture of Zn(ClO₄)₂·6H₂O (1.0 mmol, 0.37 g) and 3-nitrobenzoic acid (1.0 mmol, 0.17 g) in methanol (30 mL). The mixture was stirred for 10 min at room temperature and filtered. The filtrate was kept in air for a few days to form crystals suitable for
single crystal X-ray diffraction. The crystals were isolated by filtration. Yield: 0.23 g (35%). Characteristic IR data (KBr, cm\(^{-1}\)): 3455, \(\nu(-\text{OH})\); 1631, \(\nu(\text{C} = \text{N})\); 527, \(\nu(\text{Zn-O})\); 427, \(\nu(\text{Zn-N})\). UV–Vis data (methanol, \(\lambda/\text{nm}\)): 251(\(\pi\rightarrow\pi^*\)), 300(n→\(\pi^*\)), 391(LMCT). Anal. Calcd for C\(_{27}\)H\(_{22}\)N\(_6\)O\(_{10}\)Zn: C, 49.4; H, 3.4; N, 12.8. Found: C, 49.6; H, 3.3; N, 13.0%. \(^1\)H NMR (500 MHz, \(d_6\)-DMSO) \(\delta\) 8.65 (s, 1H, NH), 8.64 (m, 2H, ArH), 8.56 (d, 2H, ArH), 8.51 (d, 1H, PyH), 8.40 (s, 1H, CH=C=N), 8.38 (m, 2H, ArH), 8.02 (m, 2H, ArH), 7.88 (d, 1H, PyH), 7.75 (m, 2H, ArH + PyH), 7.47 (t, 1H, PyH), 7.12 (t, 1H, ArH), 6.68 (s, 1H, NH), 6.50 (m, 2H, ArH), 3.34 (s, 1H, NH).

2.2.3. Preparation of di(2-nitrobenzoato)-(2-pyridinecarboxyaldehyde 2-aminobenzoylhydrazone)zinc(II) (3)

HL (1.0 mmol, 0.24 g) was dissolved in methanol (20 mL), to which was added dropwise a mixture of Zn(ClO\(_4\))\(_2\)-6H\(_2\)O (1.0 mmol, 0.37 g) and 2-nitrobenzoic acid (1.0 mmol, 0.17 g) in methanol (30 mL). The mixture was stirred for 10 min at room temperature and filtered. The filtrate was kept in air for a few days to form crystals suitable for single crystal X-ray diffraction. The crystals were isolated by filtration. Yield: 0.23 g (36%). Characteristic IR data (KBr, cm\(^{-1}\)): 3477, \(\nu(-\text{OH})\); 1645, \(\nu(\text{C} = \text{N})\); 556, \(\nu(\text{Zn-O})\); 463, \(\nu(\text{Zn–N})\). UV–Vis data (methanol, \(\lambda/\text{nm}\)): 296(\(\pi\rightarrow\pi^*\)), 308(n→\(\pi^*\)), 395 (LMCT). Anal. Calcd for C\(_{27}\)H\(_{20}\)N\(_6\)O\(_9\)Zn: C, 50.8; H, 3.2; N, 13.2. Found: C, 50.6; H, 3.1; N, 13.0%. \(^1\)H NMR (500 MHz, \(d_6\)-DMSO) \(\delta\) 8.66 (s, 1H, NH), 8.63 (m, 2H, ArH), 8.50 (m, 1H, ArH), 8.47 (m, 4H, ArH), 8.43 (s, 1H, CH=C=N), 8.37 (m, 2H, ArH), 7.88 (d, 1H, PyH), 7.80 (m, 2H, ArH + PyH), 7.53 (t, 1H, PyH), 7.14 (t, 1H, ArH), 6.67 (s, 1H, NH), 6.53 (m, 2H, ArH), 3.38 (s, 1H, NH).

2.3. X-Ray crystallography

Diffraction intensities for 1-3 were collected at 298(2) K using a Bruker D8 Venture CCD diffractometer with MoK\(_x\) radiation (\(\lambda=0.71073\) Å). The collected data were reduced with SAINT [20], and multi-scan absorption correction was performed using SADABS [21]. Structures of the complexes were solved by direct method and refined against \(F^2\) by full-matrix least-squares method using SHELXT and SHELXL [22, 23]. All non-hydrogen atoms were refined anisotropically. The amino and water H atoms in the compounds were located from difference Fourier maps and refined isotropically. The remaining hydrogen atoms were placed in calculated positions and constrained to ride on their parent atoms. In 2, the water molecule is partial occupancy (0.5) and disordered, which leads to O10–H10A bond without a hydrogen bond acceptor. The occupancy of the water molecule fixed at 0.5 can give the thermal factor 0.42, which is similar to other non-hydrogen atoms. In addition, the occupancy (0.5) can give the lowest \(R_1\) and \(wR_2\) values, and the better WGHT scheme. Crystallographic data for 1–3 are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

2.4. Catalytic oxidation reaction

The catalytic oxidation of Cy to KA-oil with H\(_2\)O\(_2\) as oxidant was carried out in a glass flask with a water circulated condenser. In a typical procedure, 0.3 mg of catalysts
Table 1. Crystal data for 1–3.

|     | 1                      | 2                      | 3                      |
|-----|------------------------|------------------------|------------------------|
| **Formula** | C_{32}H_{36}N_{8}O_{8}Zn_{2} | C_{27}H_{22}N_{6}O_{10}Zn | C_{27}H_{20}N_{6}O_{9}Zn |
| **FW** | 791.43 | 655.88 | 637.86 |
| **Crystal shape/color** | Block/yellow | Block/yellow | Block/yellow |
| **Crystal size/mm** | 0.25 × 0.23 × 0.22 | 0.25 × 0.23 × 0.22 | 0.17 × 0.15 × 0.15 |
| **Crystal system** | Triclinic | Monoclinic | Triclinic |
| **Space group** | P-1 | C2/c | P-1 |
| **a (Å)** | 8.6372(11) | 21.6506(17) | 9.8651(11) |
| **b (Å)** | 9.9520(11) | 14.9103(13) | 11.9829(19) |
| **c (Å)** | 10.7327(12) | 17.3318(12) | 12.7603(13) |
| **α (°)** | 83.5530(10) | 90.0000(8) | 89.057(2) |
| **β (°)** | 70.9610(10) | 90.808(10) | 79.28(2) |
| **γ (°)** | 80.5380(10) | 90.0000(8) | 70.425(2) |
| **V (Å³)** | 858.52(17) | 5594.4(8) | 1394.7(3) |
| **Z** | 1 | 2 | 2 |
| **λ (MoKα) (Å)** | 0.71073 | 0.71073 | 0.71073 |
| **T (K)** | 298(2) | 298(2) | 298(2) |
| **μ (MoKα) (cm⁻¹)** | 1.459 | 0.948 | 0.945 |
| **T_{min}** | 0.7118 | 0.7976 | 0.8558 |
| **T_{max}** | 0.7396 | 0.8186 | 0.8712 |
| **Reflections/parameters** | 5110 / 236 | 16331 / 412 | 7968 / 394 |
| **Unique reflections** | 3159 | 5199 | 5056 |
| **Observed reflections [I > 2σ(I)]** | 2660 | 3334 | 4113 |
| **Restrains** | 4 | 9 | 3 |
| **Goodness of fit on F²** | 1.034 | 1.039 | 1.068 |
| **R_I, wR² [I > 2σ(I)]** | 0.0353, 0.0775 | 0.0475, 0.1089 | 0.0441, 0.0851 |
| **R_I, wR² (all data)** | 0.0463, 0.0847 | 0.0904, 0.1294 | 0.0588, 0.0941 |

Table 2. Selected bond lengths (Å) and angles (°) for 1–3.

|     | 1                           | 2                           | 3                           |
|-----|-----------------------------|-----------------------------|-----------------------------|
| **Bond lengths** |                             |                             |                             |
| Zn1–O1 | 2.188(2)                    | 2.244(3)                    | 2.212(2)                    |
| Zn1–O2 | 1.943(2)                    | 1.971(2)                    | 1.954(2)                    |
| Zn1–O4 | 1.946(3)                    |                             |                             |
| Zn1–O6 |                             |                             | 1.964(2)                    |
| Zn1–N1 | 2.275(2)                    | 2.149(3)                    | 2.115(3)                    |
| Zn1–N2 | 2.046(2)                    | 2.082(3)                    | 2.082(2)                    |
| Zn1–N4 | 2.083(2)                    |                             |                             |
| **Bond angles** |                             |                             |                             |
| O2–Zn1–O1 | 96.18(8)                    | 94.93(11)                   | 94.14(8)                    |
| O2–Zn1–N1 | 98.69(9)                    | 105.72(12)                  | 104.92(10)                  |
| O2–Zn1–N2 | 130.66(9)                   | 131.18(11)                  | 125.73(9)                   |
| O2–Zn1–N4 | 125.14(9)                   |                             |                             |
| N1–Zn1–O1 | 148.09(8)                   | 147.91(11)                  | 149.16(8)                   |
| N2–Zn1–O1 | 73.99(8)                    | 72.03(10)                   | 72.89(8)                    |
| N2–Zn1–N1 | 74.89(8)                    | 75.89(12)                   | 76.29(9)                    |
| N2–Zn1–N4 | 104.04(8)                   |                             |                             |
| O4–Zn1–O1 |                             | 92.10(11)                   |                             |
| O4–Zn1–O2 |                             | 101.58(11)                  |                             |
| O4–Zn1–N1 |                             | 107.07(12)                  |                             |
| O4–Zn1–N2 |                             | 125.10(11)                  |                             |
| O6–Zn1–O1 |                             | 96.23(9)                    |                             |
| O6–Zn1–O2 |                             | 99.91(9)                    |                             |
| O6–Zn1–N1 |                             | 103.80(12)                  |                             |
| O6–Zn1–N2 |                             | 133.20(12)                  |                             |
| N4–Zn1–O1 | 94.88(8)                    |                             |                             |
| N4–Zn1–N1 | 99.28(9)                    |                             |                             |
(1–3) were dissolved in 3 mL solvent and a certain amount of Cy, HNO₃ promoter and 30% H₂O₂ added in sequence. The reaction was performed at 60 °C for 4 h.

For the product analyses, 0.03 g of methylbenzene (internal standard) and 1.5 mL of diethyl ether (to extract the substrate and the organic products from the reaction mixture) were added to 1.5 mL samples, respectively. After stirring for 10 min, a sample (0.1 mL) was taken from the organic phase and analyzed by the internal standard method using gas chromatography (GC). The catalytic performance was evaluated in terms of the conversion of Cy and the turnover number (TON), according to the following equations:

\[
\% \text{Cy conversion} = \frac{\text{Cy}_\text{in} - \text{Cy}_\text{out}}{\text{Cy}_\text{in}}
\]

\[
\text{TON of CyOH} = \frac{\text{mols of CyOH produced}}{\text{mols of catalysts}}
\]

\[
\text{TON of CyO} = \frac{\text{mols of CyO produced}}{\text{mols of catalysts}}
\]

3. Results and discussion

3.1. Chemistry

Free hydrazone HL was readily prepared by the condensation reaction of equimolar quantities of 2-pyridinecarboxaldehyde and 2-aminobenzohydrazide in methanol (Scheme 1). Complex 1 was prepared by reaction of equimolar quantities of the hydrazone and zinc acetate in methanol. Notably, it can also be obtained by reaction of HL with zinc perchlorate and sodium acetate. Complexes 2 and 3 were synthesized by reaction of HL and zinc perchlorate with 3-nitrobenzoic acid or 2-nitrobenzoic acid, respectively, in methanol (Scheme 2). Single crystals of the complexes were obtained by slow evaporation of the methanolic solutions of the complexes. Molar conductivities of 1-3 within the normal values 20-30 Ω⁻¹·cm²·mol⁻¹ indicated their non-electrolytic nature [24].

3.2. Structure description of 1-3

The molecular structure of 1 is shown in Figure 1. The compound contains a dinuclear zinc molecule and two methanol molecules. Each Zn ion has a five-coordinate square-pyramidal configuration with the base plane defined by the pyridine nitrogen, imino nitrogen and carbonyl oxygen of the hydrazone ligand and the acetate oxygen, and with the apical position occupied by the amino nitrogen of the other hydrazone ligand. The calculated \( \tau \) value for the Zn units in 1 is 0.29. The cis and trans bond angles
Scheme 2. The synthetic procedure for 1–3.

Figure 1. Molecular structure of 1 with 30% probability thermal ellipsoids.
in the basal plane in 1 are in the ranges of 73.99(8)–98.69(9)° and 130.66(9)–148.09(8)°, respectively. The bond angles among the apical and basal donor atoms are in the ranges of 94.88(8)–125.14(9)°. All these values indicate that the square-pyramidal coordination is distorted. The distortion may arise from the strain created by the five-membered chelate rings N1–Zn1–N2 and O1–Zn1–N2 related to the donor atoms of the hydrazone ligand, with bite angles of 74.89(8) and 73.99(8)° in 1. The Zn–N and Zn–O bond distances are in the ranges of 2.046(2)–2.275(2) Å and 1.9429(19)–2.1879(18) Å, respectively. The analogous Zn complex, [Zn(2FopNO2Ph)Cl(DMSO)], with this type of ligand shows values for these two distances in the ranges 2.059(2)–2.259(2) Å and 2.008(2)–2.098(2) Å [25], and the distances for the [Zn(2BzpNO2Ph)Cl(DMSO)] complex are between 2.073(7)–2.219(7) Å and 2.032(6)–2.080(6) Å, which are similar to 1 [26].

In the crystal structure of 1, the molecules are connected by intermolecular N–H⋯O, O–H⋯O and C–H⋯O hydrogen bonds [N4–H4B = 0.90(1) Å, H4B⋯O3i = 2.09(2) Å, N4⋯O3i = 2.952(3) Å, N4–H4B⋯O3i = 161(3)°; O4–H4C = 0.90(1) Å, H4C⋯O1 = 1.88(1) Å, O4⋯O1 = 2.777(3) Å, O4–H4C⋯O1 = 173(4)°; C3–H3 = 0.93 Å, H3⋯O4ii = 2.57 Å, C3⋯O4ii = 3.3884(4) Å, C3–H3⋯O4ii = 147°; symmetry codes: i): x, y, 1+z; ii): –1+x, 1+y, z] to form a one-dimensional chain structure (Figure 2).

The molecular structures of 2 and 3 are shown in Figures 3 and 4, respectively. The two complexes are isostructural with different nitrobenzoate co-ligands, viz.
3-nitrobenzoate for 2 and 2-nitrobenzoate for 3. The Zn(II) ions display very distorted square-based pyramidal coordination geometry. The calculated τ values for the Zn units in 2 and 3 are 0.27. The Zn ions’ basal plane in both complexes are defined by the pyridine nitrogen (N1 and N2) and carbonyl oxygen (O1) from L and oxygen atoms (O2) from the two nitrobenzoate ligands. The fifth coordination site is occupied by an oxygen atom in another nitrobenzoate ion. The cis and trans bond angles in the basal plane are in the ranges of 72.03(10)–94.93(11)° and 131.18(11)–147.91(11)° for 2, and 72.89(8)–104.92(10)° and 125.73(9)–149.16(8)° for 3. The bond angles among the apical and basal donor atoms are in the ranges of 92.10(11)–125.10(11)° for 2 and 96.23(9)–133.18(9)° for 3. All these values indicate that the square-pyramidal

Figure 3. Molecular structure of 2 with 30% probability thermal ellipsoids.

Figure 4. Molecular structure of 3 with 30% probability thermal ellipsoids.
coordination is highly distorted. The distortion may arise from the strain created by the five-membered chelate rings N–Zn–N and O–Zn–N related to the donor atoms of the hydrazone ligand, with bite angles of 75.89(12)° and 72.03(10)° in 2 and 76.29(9)° and 72.89(8)° in 3. The Zn–N and Zn–O bond distances are in the ranges of 2.082(3)–2.149(3) Å and 1.946(3)–2.244(3) Å, respectively, which are similar to those distances of the corresponding coordinated zinc ion in a similar coordination environment. In mononuclear complex [ZnCl₂(C₁₅H₁₆N₄O)], the Zn cation is five-coordinate in a strongly distorted square pyramidal geometry; the Zn–N distances are between 2.1122(19) Å and 2.2080(18) Å, and the Zn–O distance is 2.2019(15) Å [27]. In [ZnCl₂(η³-N,N,O-dpkbh)] (dpkbh = di-2-pyridyl ketone benzoyl hydrazone), the Zn–N distance is in the range 2.1452(16)–2.1679(16) Å, and the distance Zn–O is 2.2274(14) Å [28].

In the crystal structure of 2 (Figure 5), the molecules are connected by intermolecular N–H···O hydrogen bonds [N₄–H₄A = 0.82(4) Å, H₄A···O₅iii = 2.20(5) Å, N₄···O₅iii = 2.993(5) Å, N₄–H₄A···O₅iii = 162(5)°; N₃–H₃ = 0.96(4) Å, H₃···O₃iv = 1.79(4) Å, N₃···O₃iv = 2.723(4) Å, N₃–H₃···O₃iv = 162(4)°; symmetry codes: iii): x, 1−y, 1/2+z; (iv):1/2−x, 1/2−y, 1−z] to form a two-dimensional network structure. In 2, a 2D network structure (layers parallel with the (100) lattice plane) is observed. In the crystal structure of 3 (Figure 6), molecules form a chain structure through intermolecular N–H···O hydrogen bonds [N₃–H₃ = 0.86Å, H₃···O₃v = 1.91 Å, N₃···O₃v = 2.7194(4) Å, N₃–H₃···O₃v = 156°; symmetry codes: (v): 2−x, 1−y, 1−z]. In the crystals of 3, molecules form hydrogen-bonded dimers through intermolecular N–H···O hydrogen bonds.
3.3. IR spectra analyses

Infrared spectra of 1–3 are given in Figures S1–S3. A typical vibration is observed at 3450–3476 cm\(^{-1}\) in the IR spectrum of 1–3, which belongs to the stretching vibration band of the O–H group. The sharp bands located at 1353–1379 cm\(^{-1}\) indicate the N–H bending vibrations [29]. The intense band observed at 1646 cm\(^{-1}\) is the C—O vibration [30]. The vibrations for CH=N are in the range 1625–1630 cm\(^{-1}\) [31, 32]. The absorption bands in the 427–463 cm\(^{-1}\) region can be attributed to the Zn–N stretching vibration, and the absorption bands in the 527–556 cm\(^{-1}\) region are due to the Zn–O stretching vibration [33, 34].

3.4. UV–Vis spectra analyses

At room temperature, UV–Vis absorption spectra of 1-3 were measured with methanol as solvent, as shown in Figures S4–S6, which are similar. The absorption peaks observed near 400 nm could be attributed to the charge transfer transition (LMCT) [35, 36]. Bands at 300, 308 and 310 nm are due to the \(n\rightarrow\pi^*\) transition of conjugated double bonds in the hydrazone ligand. Absorption peaks at 296, 295, and 296 nm can be attributed to \(\pi\rightarrow\pi^*\) transition in the hydrazone ligand [37].

3.5. Catalytic activity

The catalytic activities of several zinc salts in Cy selective oxidation are compared in Table 3. It can be seen clearly that the TON\(_{\text{CyOH}}\) values are all less than 10, indicating

![Molecular packing of 3 observed along the c axis. Hydrogen bonds are indicated by dashed lines.](image)

Table 3. The catalytic activities of zinc salts.

| Catalysts                     | Con./% | TON\(_{\text{CyOH}}\) |
|-------------------------------|--------|---------------------|
| ZnBr\(_2\)                    | 35     | 4                   |
| ZnI\(_2\)                     | 40     | 5                   |
| Zn(NO\(_3\))\(_2\)\cdot 6\text{H}_2\text{O} | 44     | 5                   |
| Zn(CH\(_3\)COO)\(_2\)\cdot 2\text{H}_2\text{O} | 47     | 6                   |
| Zn(ClO\(_4\))\(_2\)\cdot 6\text{H}_2\text{O} | 51     | 10                  |

Reaction conditions: Cy (6.43 mmol), H\(_2\)O\(_2\) (2 mmol, \(n_{\text{oxidant}}/n_{\text{Cy}}=0.3:1\)), catalyst (0.0003 g), HNO\(_3\) (0.643 mmol, \(n_{\text{acid}}/n_{\text{Cy}}=0.1:1\)), CH\(_3\)CN (3 mL), 60 °C, 4 h.
that only trace amounts of CyOH can be formed in this condition. The TON\textsubscript{CyOH} order was 
\[ \text{Zn(ClO}_4\text{)}_2\cdot6\text{H}_2\text{O} > \text{Zn(CH}_3\text{COO)}_2\cdot2\text{H}_2\text{O} > \text{Zn(ClO}_4\text{)}_2\cdot6\text{H}_2\text{O} > \text{ZnI}_2 > \text{ZnBr}_2. \]
Zn(ClO\textsubscript{4})\textsubscript{2}·6H\textsubscript{2}O has the best catalytic activity, with 51% Cy conversion and 10 TON\textsubscript{CyOH} value. Hence, Zn(ClO\textsubscript{4})\textsubscript{2}·6H\textsubscript{2}O was chosen as a model catalyst to discuss the impact factors as shown in Table 4. The TON value of CyOH increased from 0 to 34 when the ratio of H\textsubscript{2}O\textsubscript{2}/Cy changed from 0 to 1:1 (Table 4, entries 1-3), and then, decreased (entry 4). The same trend was observed for catalyst content (0.1–0.8 mg), and the maximum TON value (39) was obtained with 0.5 mg of catalyst (entries 3 and 5-7). More HNO\textsubscript{3} additive is not beneficial to produce CyOH; the best TON value (62) was achieved at 0.2:1 HNO\textsubscript{3}/Cy molar ratio (entries 6 and 8-10). The TON\textsubscript{CyOH} dropped remarkably if CH\textsubscript{3}CN was replaced by MeOH, EtOH or CH\textsubscript{2}Cl\textsubscript{2} (entries 11-13). In addition, the best temperature was 70°C (entries 9 and 14-17) and the optimal time was 4 h (entries 16 and 18-21). As a result, the best Cy conversion, TON value of CyOH and CyO were 88%, 78 and 19, respectively, under the optimal condition: 1:1 molar ratio of H\textsubscript{2}O\textsubscript{2}/Cy, 0.5 mg Zn(ClO\textsubscript{4})\textsubscript{2}·6H\textsubscript{2}O, 0.2:1 molar ratio of HNO\textsubscript{3}/Cy with the reaction time of 4 h in CH\textsubscript{3}CN at 70°C.

Since \textbf{2} and \textbf{3} were both synthesized with Zn(ClO\textsubscript{4})\textsubscript{2}·6H\textsubscript{2}O as the starting material, \textbf{3} was used as a model catalyst to compare with Zn(ClO\textsubscript{4})\textsubscript{2}·6H\textsubscript{2}O.

It can be seen clearly that Cy conversion was continually increasing, while the TON value of CyOH showed curves that reached maxima with time (Figure 7A) and H\textsubscript{2}O\textsubscript{2} contents (Figure 7B). The TON of CyOH reached a maximum value of 218 at 4 h and 310 when the ratio of H\textsubscript{2}O\textsubscript{2}/Cy was 0.6:1, respectively, and then decreased. These indicate that CyOH may be transformed to other by-products [38] with time or excess H\textsubscript{2}O\textsubscript{2} [39].

A series of solvents, CH\textsubscript{3}Cl\textsubscript{3}, CH\textsubscript{2}Cl\textsubscript{2}, EtOH, CH\textsubscript{3}OH and CH\textsubscript{3}CN (3 mL), were explored while keeping fixed the amount of Cy (7.064 mmol), n\textsubscript{catalyst} (complex \textbf{3})=1:14000, HNO\textsubscript{3} (0.942 mmol) temperature (40°C) and time (4 h), as shown in Figure 8. The order

| Entry | H\textsubscript{2}O\textsubscript{2}/Cy molar ratio | Catalyst (mg) | HNO\textsubscript{3}/Cy molar ratio | Solvent | Temp. (°C) | Time (h) | Con. (%) | TON\textsubscript{CyOH} | TON\textsubscript{CyO} |
|-------|----------------------------------|----------------|----------------------------------|--------|-----------|--------|--------|----------------|----------------|
| 1     | 0                                | 0.3            | 0:1:1                            | CH\textsubscript{3}CN | 60       | 4      | 16     | 0              | 0              |
| 2     | 0.6:1                            | 0.3            | 0:1:1                            | CH\textsubscript{3}CN | 60       | 4      | 45     | 29             | 0              |
| 3     | 1:1                              | 0.3            | 0:1:1                            | CH\textsubscript{3}CN | 60       | 4      | 72     | 34             | 15             |
| 4     | 2:1                              | 0.3            | 0:1:1                            | CH\textsubscript{3}CN | 60       | 4      | 68     | 31             | 15             |
| 5     | 1:1                              | 0.1            | 0:1:1                            | CH\textsubscript{3}CN | 60       | 4      | 67     | 0              | 0              |
| 6     | 1:1                              | 0.5            | 0:1:1                            | CH\textsubscript{3}CN | 60       | 4      | 71     | 39             | 17             |
| 7     | 1:1                              | 0.8            | 0:1:1                            | CH\textsubscript{3}CN | 60       | 4      | 65     | 11             | 2              |
| 8     | 1:1                              | 0.5            | 0                               | CH\textsubscript{3}CN | 60       | 4      | 54     | 7              | 0              |
| 9     | 1:1                              | 0.5            | 0:2:1                            | CH\textsubscript{3}CN | 60       | 4      | 69     | 62             | 15             |
| 10    | 1:1                              | 0.5            | 0:3:1                            | CH\textsubscript{3}CN | 60       | 4      | 63     | 42             | 14             |
| 11    | 1:1                              | 0.5            | 0:2:1                            | CH\textsubscript{3}OH | 60       | 4      | 60     | 21             | 10             |
| 12    | 1:1                              | 0.5            | 0:2:1                            | CH\textsubscript{3}CH\textsubscript{2}OH | 60       | 4      | 45     | 18             | 4              |
| 13    | 1:1                              | 0.5            | 0:2:1                            | CH\textsubscript{3}Cl\textsubscript{2} | 60       | 4      | 39     | 6              | 0              |
| 14    | 1:1                              | 0.5            | 0:2:1                            | CH\textsubscript{3}CN | 40       | 4      | 56     | 22             | 0              |
| 15    | 1:1                              | 0.5            | 0:2:1                            | CH\textsubscript{3}CN | 50       | 4      | 57     | 48             | 4              |
| 16    | 1:1                              | 0.5            | 0:2:1                            | CH\textsubscript{3}CN | 70       | 4      | 88     | 78             | 19             |
| 17    | 1:1                              | 0.5            | 0:2:1                            | CH\textsubscript{3}CN | 80       | 4      | 50     | 50             | 0              |
| 18    | 1:1                              | 0.5            | 0:2:1                            | CH\textsubscript{3}CN | 70       | 1      | 72     | 22             | 0              |
| 19    | 1:1                              | 0.5            | 0:2:1                            | CH\textsubscript{3}CN | 70       | 2      | 77     | 27             | 3              |
| 20    | 1:1                              | 0.5            | 0:2:1                            | CH\textsubscript{3}CN | 70       | 3      | 80     | 60             | 11             |
| 21    | 1:1                              | 0.5            | 0:2:1                            | CH\textsubscript{3}CN | 70       | 5      | 89     | 39             | 4              |
of CyOH TON value is CH₂Cl₂ (41) < CHCl₃ (43.5) < EtOH (45.7) < MeOH (78.8) < CH₃CN (218), which should be proportional to their dielectric constant, CHCl₃ (4.8) < CH₂Cl₂ (9.1) < EtOH (26.6) < MeOH (32.7) < CH₃CN (37.5). However, The TON values of CHCl₃ and CH₂Cl₂ do not conform to this rule, which may be affected by their polarity [40]; the higher polarity of CHCl₃ than CH₂Cl₂ make phases disperse more
uniformly, and the performance of the catalyst better, although the dielectric constant of CHCl3 is less than that of CH2Cl2.

The influence of reaction temperature on Cy oxidation was investigated under the conditions Cy (7.064 mmol), n_catalyst (complex 3): n_Cy = 1:14000, H2O2 (4.239 mmol), HNO3 (0.942 mmol), CH3CN (3 mL), and 4 h, as shown in Figure 9. The Cy conversion and TON of CyOH all rose to the maxima of 83% and 218 at 40 °C, respectively, and then fell with rising temperature, indicating that high temperature is not good for the Cy conversion and the formation of CyOH, and the selective Cy oxidation to CyOH with 3 can occur under very mild conditions (40 °C). Noticeably, the formation of CyO could only be detected beyond 60 °C, and climbed remarkably with temperature, which indicates that CyO is only produced at higher temperature when promoted by 3.

The catalytic properties of the three zinc complexes in the reaction of Cy (7.064 mmol), H2O2 (4.239 mmol), catalysts (n_catalyst:n_Cy = 1:14000), HNO3 (0.942 mmol), CH3CN (3 mL), 40 °C and 4 h are compared in Figure 10. It was found that the catalytic activities of 2 and 3 were higher than 1, which may result from their stronger electron-withdrawing effect of the ligands to expose more active metal sites. Furthermore, 3 has the highest ortho and conjugated effects of its ligand, which may be the reason why it has the best catalytic performance. The order of catalytic activity of the complexes is 3 > 2 > 1.

The catalytic performance of the zinc complexes were compared with that of their starting materials (Table 5). The total TON value was only 6 with Zn(CH3COO)2·2H2O, which could be improved to 95 when this starting material was replaced by its corresponding complex 1 (Table 5, entries 1 and 2). Similar phenomena happened for 2 and 3 and their starting material Zn(ClO4)2·6H2O (Table 5, entries 3-5). The TON value increased remarkably from 97 (Zn(ClO4)2·6H2O) to 168 (for 2) and 218 (for 3),
respectively. These indicate that 1-3 are all more effective than their starting materials. Additionally, the optimal reaction temperature dropped from 60 or 70 to 40 °C, and the amount of catalyst decreased from 0.0014 or 0.0013 to 0.0005 mmol when the zinc complexes were used as catalysts. This suggests that more mild reaction conditions can be used with 1-3 compared to their zinc starting material. Therefore, we have reason to believe that the synthesis of the zinc complexes can effectively promote the production of the main products under more mild and economical conditions. On the other hand, 3 shows the best catalytic activity and more mild reaction conditions compared to the catalytic results and conditions reported previously for other Zn complexes in Cy oxidation (Table 5, entries 6-9).

**Figure 10.** The effect of the type of catalysts on Cy oxidation. Reaction conditions: Cy (7.064 mmol), 1: [ZnL2(OAc)2]2CH3OH, 2: [ZnL(3-NA)2]·H2O and 3: [ZnL(2-NA)2] as catalysts (\(n_{\text{catalyst}:n_{\text{Cy}}}=1:14000\)), H2O2 (4.239 mmol), HNO3 (0.942 mmol), CH3CN (3 mL), 40 °C, 4 h.

**Table 5.** The catalytic comparison of Zn complexes to zinc salts as catalysts for Cy oxidation.

| Entry | Catalyst                  | Time (h) | Temp (°C) | \(n_{\text{catalyst}}\) (mmol) | Ref.  | Con. (%) | TON (CyOH + CyO) |
|-------|---------------------------|----------|-----------|---------------------------------|-------|----------|------------------|
| 1     | Zn(CH3COO)2·2H2O         | 4        | 60        | 0.0014                          | This work | 47       | 6                |
| 2[a]  | Complex 1                 | 4        | 40        | 0.0007                          | This work | 73       | 120              |
| 3     | Zn(ClO4)2·6H2O           | 4        | 70        | 0.0013                          | This work | 88       | 97               |
| 4[b]  | Complex 2                 | 4        | 40        | 0.0005                          | This work | 75       | 168              |
| 5[c]  | Complex 3                 | 4        | 40        | 0.0005                          | This work | 83       | 218              |
| 6     | Zn(PS)2                   | 12       | 100       | 0.0200                          | [41]  | 53       | 11               |
| 7     | Zn(PSNa)2                 | 12       | 100       | 0.0200                          | [41]  | 66       | 19               |
| 8[d]  | Zn2(\(H2L1\)2(ox)\(H2O\)2·4H2O | 4           | 40        | 0.0003                          | [42]  | –        | 160              |
| 9[e]  | Zn(\(H2L1\)(ad)·2H2O)     | 4        | 60        | 0.0007                          | [42]  | –        | 58               |

[a] HL = 2-amino-N’-(pyridin-2-ylmethylene)benzohydrazide; AC = acetate.
[b] HL = 2-amino-N’-(pyridin-2-ylmethylene)benzohydrazide; 3-NA = 3-nitrobenzoic acid.
[c] HL = 2-amino-N’-(pyridin-2-ylmethylene)benzohydrazide; 2-NA = 2-nitrobenzoic acid.
[d] \(H2L1\) = 2,6-di(5-methyl-1H-pyrazol-3-yl)pyridine; H2ox = oxalic acid.
[e] \(H2L1\) = 2,6-di(5-methyl-1H-pyrazol-3-yl)pyridine; H2ad = adipic acid.
3.6. Probable mechanism

To detect the intermediates formed in the catalytic process, changes in the UV–Vis spectrum were monitored during successive additions of dilute H$_2$O$_2$ solution dropwise to a 10 mL CH$_3$OH solution of 1.8 $\times$ 10$^{-3}$ M of 3, as shown in Figure 11. It can be seen that the band at 400 nm, which belongs to a ligand-to-metal charge transfer (LMCT) transition, decreased slightly in intensity. Together with the appearance of an increase in the intensity at 356 nm, we propose that active intermediates, which can transfer oxygen atom to the substrate and oxidize it to product, can be formed in the interaction of 3 with H$_2$O$_2$ [43].

Based on the above discussion, a mechanism was proposed (Scheme 3). Zn$^{II}$OL peroxido species are formed first by the reaction of H$_2$O$_2$ with Zn$^{II}$L complex (reaction 1)
[44], which can be supported by our results in Figure 11. Then, oxygen-centered radicals HOO• and HO• are produced (reaction 2). HO• radical must be the crucial intermediate in the formation of KA-oil products [45], for no CyOH or CyOOH can be detected when adding t-butanol (an HO• radical scavenger [46]) to our oxidation system when catalyzed by 3. HO• would further form the cycloalkyl radical Cy• upon H-abstraction from cycloalkane CyH (reaction 3) and cyclohexylperoxyl radical CyOO• by further reaction with oxygen (reaction 4). CyOOH can then be produced from CyOO• (reaction 5) and decomposed to CyO• and CyOO• radicals (reactions 6 and 7), which would then produce CyOH and CyO (reactions 8 and 9).

4. Conclusion

We synthesized three new Zn(II) complexes by the reaction of Zn(CH3COO)2·2H2O or Zn(ClO4)2·6H2O with HL, 3-nitrobenzoic acid or 2-nitrobenzoic acid in methanol, and demonstrated that the zinc ions in 1-3 are five-coordinate. The complexes show distorted square-based pyramidal geometries and adjacent molecules are connected by intermolecular hydrogen bonds. The catalytic performance of 1-3 are significantly improved compared to their zinc starting materials under more mild conditions for Cy oxidation, and the order is 3 > 2 > 1. Considering the best catalytic activity and more mild reaction conditions of 3 to zinc salts and referenced Zn complexes, the data presented here encourage a more comprehensive study of designing and synthesizing Zn(II) complexes containing hydrazone ligands as oxidation catalysts.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by the Young Science and Technology talent Seedling Project of Liaoning Provincial Department of Education (No. LQ2019024) and the National Natural Science Foundation of China (NSFC) (Grant No. 21576128).

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