FULL PAPER

Revised: 8 December 2019



Applied Organometallic Chemistry

Dinuclear Zn(II) and tetranuclear Co(II) complexes of a tetradentate N₂O₂ Schiff base ligand: Synthesis, crystal structure, characterization, DFT studies, cytotoxicity evaluation, and catalytic activity toward benzyl alcohol oxidation

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Funding information Research Council of University of Guilan Two novel dinuclear Zn(II) and tetranuclear Co(II) complexes of a tetradentate N_2O_2 Schiff base ligand ($H_2L = N,N'$ -bis-(4-hydroxysalicylidene)-1,3-diaminopropane) were prepared. The structures of the H₂L ligand, $[4(Zn_2L(\mu O_2CCH_3)(O_2CCH_3)(H_2O))] \cdot 4CH_3OH \cdot 3H_2O$ (complex 1) and $[Co_4L_2(\mu - 1)] \cdot 4CH_3OH \cdot 3H_2O$ O₂CCH₃)₂(O₂CCH₃)₂]·2H₂O (complex 2) were unambiguously characterized by elemental analysis, mass spectrometry, Fourier-transform infrared spectroscopy (FT-IR), ¹H nuclear magnetic resonance (NMR), and UV-Vis spectroscopy. Single crystal X-ray diffraction studies revealed that two Zn(II) nuclei of 1 were connected through μ -phenolato and μ -acetato bridges and had distorted square pyramidal and distorted octahedral coordination geometries. Four Co(II) nuclei of 2, on the contrary, showed a Co₄O₄ cubane-like configuration in which Co(II) cations and O atoms were located at alternating corners of a distorted cube. Density functional theory studies at the B3LYP/6-31 G(d) level were carried out to gain an insight into the thermodynamic stability of the complexes. in vitro cytotoxicity of the ligand and the complexes were evaluated using the MTT assay against breast cancer MCF7 cells, melanoma cancer A375 cells, and prostate cancer PC3 cells as representative human cancer cell lines. Complex 1 showed a remarkable activity against A375 and PC3 cancer cell lines. In addition, 1 and 2 were used as precursors to produce zinc and cobalt oxide nanoparticles via pyrolysis technique. The resulting ZnO and Co₃O₄ nanoparticles were characterized using FT-IR spectroscopy, UV-Vis diffuse reflectance spectroscopy, powder X-ray diffraction, and field emission scanning electron microscopy. Then, these nanoparticles were used as heterogeneous catalysts in the oxidation of benzyl alcohol with hydrogen peroxide at room temperature. Both catalysts showed good recyclability with a negligible decrease in their efficiency during four catalytic cycles. The results of theoretical calculations showed that the most stable product was benzaldehyde, which is in good agreement with the obtained experimental results.

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KEYWORDS

nanoparticles, polynuclear complexes, Schiff base, selective oxidation, tetradentate ligand

1 | INTRODUCTION

Schiff bases are considered "exclusive ligands" because they play a key role in the development of coordination chemistry. Schiff base ligands are prepared easily and can be readily modified, both electronically and sterically.^[1,2] Schiff base ligands contain multiple potential donor sites, which allow them to bind metal ions with diverse coordination geometries such as bidentate and tridentate.^[3–6] Tetradentate Schiff base ligands also provide a suitable coordination platform for metal ions to provide diverse metallic complexes.^[7–10]

Salpn-type Schiff base ligands are an interesting class of tetradentate ligands with four donor sites (N_2O_2) .^[11] As shown in Scheme 1, salpn ligand provides an ideal environment for equatorial coordination to transition metal ions, leaving two axial sites open for coordination of extra ligands or substrates to produce metal complexes of higher coordination number.

Many dinuclear complexes of tetradentate N_2O_2 Schiff base ligands with various metal ions have been reported.^[12-16] The corresponding dinuclear Zn(II) complexes have a flexible coordination environment with a variety of geometries such as tetrahedral, square planar, trigonal bipyramidal, square pyramidal, and octahedral.^[17-21]

Among polynuclear transition metal complexes, tetranuclear clusters with cubane-like M_4O_4 core have been widely studied and have received considerable attention.^[22,23] However, reports on cobalt clusters of the type Co_4O_4 -containing cubane structure are scarce.^[24,25]

The synthesis and structural studies of polynuclear metal complexes with Schiff base ligands have increased in recent years because of their widespread applications in various fields such as catalysis, biological studies, and industrial systems.^[26–31]

Various methods for the synthesis of metal oxide nanoparticles are available, which include hydrothermal, solvothermal, sol–gel, microwave-assisted template-free, and microemulsion methods.^[32–35] However,



these methods have some drawbacks such as long reaction time and high cost. Therefore, using coordination metal complexes as a precursor can provide a simple and inexpensive method for the preparation of the desired metal oxide nanostructures.^[36,37] Among metal oxide nanoparticles, ZnO and Co₃O₄ have been widely studied owing to their applications in lithium-ion batteries and supercapacitors,^[38-40] sensing materials,^[41,42] semiconductors,^[44] cells.^[43] piezoelectric solar devices,^[45] UV-shielding materials,^[46] photochemical reactors,^[47] gas sensing,^[48] biology,^[49] agriculture,^[50] and food packaging.^[51] Moreover, ZnO and Co₃O₄ nanoparticles have been used as nontoxic and easy-torecvcle catalysts. for example, in oxidation reactions.^[52-54] Selective oxidation of benzyl alcohols to the corresponding aldehydes under mild reaction conditions has always been of interest to researchers, and the application of metal oxide nanoparticles such as ZnO and Co₃O₄ as heterogeneous catalysts is actively pursued.

In this study, we synthesized a tetradentate N_2O_2 Schiff base ligand (H₂L, Scheme 1) from 2,4dihydroxybenzaldehyde and 1,3-diaminopropane. To investigate the coordination modes of this ligand, two novel dinuclear Zn(II) and tetranuclear Co(II) complexes (1 and 2) were synthesized, and the structures of the ligand and the complexes were established using elemental analysis, mass spectrometry (MS), Fourier-transform infrared spectroscopy (FT-IR), UV-Vis, and ¹H nuclear magnetic resonance (NMR) spectroscopy. Single crystal X-ray crystallography studies confirmed that H₂L acts as a tetradentate ligand. The results from density functional theory (DFT) calculations (obtained using the B3LYP/6-31 G(d) basis set) were correlated to those obtained from experimental studies for complexes 1 and 2. Moreover, antiproliferative activity of the ligand and its complexes was examined against human MCF7 (breast cancer), A375 (melanoma cancer), and PC3 (prostate cancer) cell lines using MTT assay. In addition, we prepared ZnO and Co₃O₄ nanoparticles directly from complexes 1 and 2, respectively. The produced nanoparticles were characterized using FT-IR, powder X-ray diffraction (PXRD), and field emission scanning electron microscopy (FESEM) imaging. The nanoparticles were used as heterogeneous catalysts in selective oxidation of benzyl alcohol in the presence of hydrogen peroxide at room temperature.

2 | EXPERIMENTAL

2.1 | Materials and methods

All of the reagents and solvents were of analytical grade and used without further purification. Elemental analyses were performed on a Heraeus CHN-O-Rapid elemental analyzer. Electron impact mass spectroscopy (EIMS) was performed on an Agilent 6890 Series (detector: Agilent 5973 Network Mass Selective Detector, Agilent Technologies; ionization energy: 70 eV). FT-IR spectra were recorded on a Bruker Alpha spectrophotometer using KBr disks over the range of 4000-400 cm⁻¹. UV-Vis spectra were recorded on a Rayleigh UV-1800 spectrophotometer. ¹H NMR spectra were recorded in DMSO-d₆ using tetramethylsilane as an internal standard on a Bruker Avance III 300 MHz spectrometer at 298 K. UV-Vis diffuse reflectance spectra (DRS) were recorded in the wavelength range of 200-800 nm on a Scinco S-4100 spectrophotometer (Korea). The X-ray powder diffraction (XRD) data were recorded on a Philips PW1730 (Poland) with Cu Ka radiation ($\lambda = 1.5406$ Å). FESEM images of the synthesized nanoparticles were obtained using a Tescan Mira III scanning electron microscope (Tescan USA Inc., PA, USA). HPLC-grade methanol from Kermel Chemical Reagent Co. (Tianjin, China) was used for LC-MS analysis.

2.2 | Synthesis

2.2.1 | Synthesis of H_2L

 H_2L was synthesized by condensation of 1,3-diaminopropane with 2,4-dihydroxybenzaldehyde in methanol. Briefly, 1,3-diaminopropane (0.17 g, 2.00 mmol) was added dropwise solution of to а 2,4dihydroxybenzaldehyde (0.55 g, 4.00 mmol) in 25 mL of methanol at room temperature. The reaction mixture was then refluxed for 1 h with continuous stirring. After cooling to room temperature, the orange precipitate was filtered off and washed with methanol. Yield: 78%. EIMS (70 eV) m/z: 314.3 [H₂L⁺]. Anal. Calc. for C₁₇H₁₈N₂O₄ $(MW = 314.34 \text{ g mol}^{-1})$: C, 64.96; H, 5.77; N, 8.91. Found: C, 64.87; H, 5.82; N, 8.97%. IR (KBr, cm⁻¹): 3447 (s, $\nu_{\rm OH}$), 1641 (s, $\nu_{\rm C=N}$), 1236 (m, $\nu_{\rm PhO}$). UV–Vis: $\lambda_{\rm max}$ (nm) (ϵ , M⁻¹ cm⁻¹) (DMSO): ~280 (26250), 308 (24650), 410 (1850). ¹H NMR (DMSO-*d*₆, 300 MHz, ppm); δ: 12.92 (br, 2H⁸), 10.79 (br, 2H⁶), 8.34 (s, 2H³), 7.18 (d, 2H⁴, J = 8.40 Hz), 6.30 (dd, $2H^5$, J = 8.40 and 2.40 Hz), 6.23 (d, $2H^7$, J = 2.10 Hz), 3.58 (t, $4H^2$, J = 6.75 Hz), 1.95 $(m, 2H^1).$

2.2.2 | Synthesis of complex 1

A methanolic solution of Zn (OAc)₂·2H₂O (0.66 g, 3.0 mmol in 10 mL) was added dropwise to a solution of H_2L in the same solvent (0.63 g, 2.0 mmol in 15 mL). The orange color of the ligand faded gradually with simultaneous precipitation of a white microcrystalline compound. The reaction mixture was stirred for 45 min at room temperature. The crude product was then filtered off, washed with methanol, and recrystallized from MeOH/DMF. The solvent was partially evaporated, and several colorless single crystals suitable for X-ray crystallography were collected after 2 days. Yield: 71% (based on zinc). Anal. Calc. for $C_{22}H_{24}N_2O_9Zn_2\cdot 3/4(H_2O)$ $(MW = 603.4 \text{ g mol}^{-1})$: C, 43.79; H, 5.01; N, 4.64. Found: C, 43.55; H, 4.93; N, 4.78%. IR (KBr, cm⁻¹): 3448 (s, ν_{OH}), 1609 (s, $\nu_{C=N}$), 1552 (m, ν_{asCOO} -), 1450 (m, ν_{sCOO} -), 1217 (m, ν_{PhO}) 464 (w, ν_{Zn-N}). UV-Vis: λ_{max} (nm) (ϵ , M⁻¹ cm⁻¹) (DMSO): 286 (21300), 348 (16750). ¹H NMR (DMSO- d_6 , 300 MHz, ppm); δ : 9.53 (br, 2H⁶), 8.10 (s, $2H^3$), 6.97 (d, $2H^4$, J = 8.4 Hz), 6.21 (s, $2H^7$), 6.03 (d, $2H^5$, J = 8.4 Hz), 3.74 (br, $4H^2$), 3.39 (s, $3H^{11}$), 1.95 $(m, 2H^1), 1.83 (s, 3H^{10}).$

2.2.3 | Synthesis of complex 2

A methanolic solution of Co (OAc)₂·4H₂O (0.25 g, 1.0 mmol in 10 mL) was added dropwise to a suspension of H_2L in dichloromethane (0.31 g, 1.0 mmol in 15 mL). Color of the mixture immediately changed to dark brown. The reaction mixture was stirred for about 30 min at room temperature and then filtered, and the filtrate was allowed to stand for a few days. The solvent was partially evaporated, and several gray single crystals suitable for X-ray crystallography were collected after 5 days. Yield: 78% (based on cobalt). Anal. Calc. for $C_{42}H_{44}N_4O_{16}Co_4 \cdot 2(H_2O)$ (MW = 1132.56 g mol⁻¹): C, 44.54; H, 4.27; N, 4.95. Found: C, 44.67; H, 4.34; N, 5.02%. IR (KBr pellet, cm⁻¹): 3424 (s, ν_{OH}), 1622 (s, $\nu_{C=N}$), 1555 (m, νas_{COO} -), 1450 (m, νs_{COO} -), 1234 (m, ν_{PhO}), 465 (w, $\nu_{\text{CO-N}}$). UV-Vis: λ_{max} (nm) (ε , M⁻¹ cm⁻¹) (DMSO): 270 (31250), 368 (6300).

2.3 | Crystal structure determination

X-ray intensity data for complexes **1** and **2** were collected using graphite monochromatic Mo K α , $\lambda = 0.71073$ Å radiation on a four-circle κ geometry KUMA KM-4 diffractometer with a two-dimensional area CCDC detector. Data collection was made at low temperature (100 (1) K) using the CrysAlis CCD software.^[55] The ω -scan technique with $\Delta \omega = 1.0^{\circ}$ for each image was used for data collection. One image was used as a standard after every 40 images for monitoring of the crystal stability and data collection, and no correction on the relative intensity variation was necessary. Integration, scaling of the reflections, correction for Lorenz and polarization effects, and absorption corrections were performed using the CrysAlis Red program.^[55] The structures were solved by direct methods using SHELXT^[56] and refined using SHEXL-2018 program.^[57] The data were deposited in Cambridge Crystallographic Data Center with deposition number CCDC **1911571** for [4(Zn₂L(μ -O₂CCH₃) (O₂CCH₃)(H₂O))]·4CH₃OH·3H₂O (**1**) and **1916520** for $[Co_4L_2(\mu-O_2CCH_3)_2(O_2CCH_3)_2]\cdot 2H_2O$ (2). Details of the crystal parameters, data collection, and refinements for complexes 1 and 2 are summarized in Table 1.

2.4 | Theoretical calculations

Theoretical studies were performed using density functional theory (DFT) with the hybrid density functional (B3LYP)/6–31 G(d) basis set. All calculations were done using the Gaussian 03 program package^[58] without specifying any symmetry for the title compounds. No constraint was applied in the calculations, and all atoms were free to optimize.

TABLE 1 Crystal data and structure refinement for complexes 1 and 2

•	-	
Parameter	1	2
Empirical formula	$4(C_{21}H_{24}N_2O_9Zn_2)\cdot 4(CH_4O)\cdot 3(H_2O)$	$C_{42}H_{44}N_4O_{16}Co_4 \cdot 2(H_2O)$
Formula weight	2413.60	1132.56
Temperature (K)	100	100
Crystal system	Monoclinic	Monoclinic
Space group	$P2_{1}/n$	Сс
Unit cell dimensions		
a (Å)	16.779 (3)	11.6158 (3)
<i>b</i> (Å)	7.6128 (7)	19.6198 (3)
<i>c</i> (Å)	20.339 (4)	20.4742 (5)
α (deg)	90	90
β (deg)	112.07 (2)	93.316 (2)
γ (deg)	90	90
$V(\text{\AA}^3)$	2407.6 (7)	4658.25 (18)
Ζ	1	4
$D_{\rm x}$ (mg m ³)	1.723	1.615
$\mu (\mathrm{mm}^{-1})$	2.06	1.48
F (000)	1286	2320
Crystal size (mm)	$0.26\times0.18\times0.05$	$0.22\times0.12\times0.11$
θ range for data collection (deg)	2.62-26.00	2.78-29.41
Index ranges	$-20 \le h \le 20$	$-15 \le h \le 16$
	$-9 \le k \le 9$	$-27 \le k \le 26$
	$-25 \le l \le 25$	$-28 \le l \le 27$
Reflections collected	29301	71869
Independent reflections (R_{int})	4743 (0.089)	11697 (0.057)
Reflections with $I > 2\sigma(I)$	3516	9038
Data/restraints/parameters	4743/6/350	11697/2/617
Goodness-of-fit on F^2	1.05	1.06
Final <i>R</i> indexes $[I > 2\sigma(I)]$	$R_1 = 0.1110, wR_2 = 0.2263$	$R_1 = 0.0653, wR_2 = 0.1574$
Final <i>R</i> indexes [all data]	$R_1 = 0.1498, wR_2 = 0.2432$	$R_1 = 0.0917, wR_2 = 0.1750$
Largest difference in peak/hole $(e \text{ Å}^3)$	2.315/-0.836	1.70/-0.45

2.5 | In vitro cytotoxicity

The cytotoxic activity of the Schiff base ligand H₂L and its complexes 1 and 2 was evaluated against MCF7 (breast cancer), A375 (melanoma cancer), and PC3 (prostate cancer) cell lines using the MTT (3-(4,5dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) assay kit (Bio-Idea, Houston, TX). Briefly, MCF7, PC3, and A375 cells were seeded at 7×10^3 cells/well in 96well plates. A stock solution of each of the compounds 1, 2, and H₂L was provided in DMSO (10 mg mL⁻¹) and then diluted to different concentrations with culture medium (12.5, 25, 50, and 100 μ g mL⁻¹). A blank solution containing the same amount of DMSO was used as a control to monitor the activity of the solvent in this test. Solutions were added to the wells 24 h after cell seeding. Doxorubicin hydrochloride (DOX, 20 μ g mL⁻¹) was used as a reference drug. After 48 h of incubation, the medium was replaced with 100 µL of freshly prepared RPMI medium, and then 10 µL of the MTT solution (0.5 mg mL^{-1}) was added to each well. This was incubated for 4 h (5% CO₂, 37°C and 95% humidity). The solution was then removed, and 50 µL of dimethylsulfoxide (DMSO, 99.5%) was added to dissolve the formazan crystals. The plate was incubated for 15 min at room temperature with gentle shaking. The absorbance was read using an ELISA plate reader at 490 nm with a reference wavelength of 630 nm. The percentage of cell viability was calculated using the following equation:

Cell viability (%) = $[(A_{490} - A_{630})$ of treated cells/ $(A_{490} - A_{630})$ of control cells] × 100.

The cytotoxicity was evaluated based on the percentage of cell survival in a dose-dependent manner relative to the negative control and was calculated by a nonlinear regression using GraphPad Prism software. All tests were repeated in at least three independent trials.

2.6 | Preparation of nanoparticles

About 0.4 g of each of the complexes **1** and **2** was introduced into a crucible and heated in an electric furnace with a heating rate of 10° C min⁻¹ for an appropriate time (2 h at 650°C for complex **1** and 4 h at 400°C for complex **2**). The obtained nanosized metal oxides were characterized using FT-IR spectroscopy, UV–Vis diffuse reflectance spectroscopy (DRS), XRD, and FESEM.

2.7 | Oxidation reaction

All of the catalytic benzyl alcohol oxidation reactions were carried out in a glass reactor at room temperature. The effect of different reaction parameters such as the amount of H₂O₂, reaction time, and amount of catalyst was studied. The progress of the reaction was monitored either by TLC (*n*-hexan/ethyl acetate 4:1) or by GC. To identify possible reaction intermediates, LC–MS analysis was used. The mobile phase composition was water: methanol (40:60, v/v), and the flow rate was 1.0 mL min⁻¹. Mass spectra were acquired in the scan range of m/z 50–400.

2.8 | Computational study of the oxidation of benzyl alcohol

The optimized structures and energies of the stationary points were calculated using Gaussian09 program.^[59] Geometry optimization was performed at M062X/6-311 + g(d,p) level of theory. Single point calculations were carried out at the CCSD(T)/6-311 + g(d,p)//M062X/6-311 + g(d,p) level of theory to get more accurate energies along the reaction paths. The potential energy surface (PES) was obtained at 298.15 K and 1 atm. A proposed mechanistic pathway for the title reaction is depicted in Scheme 2. The harmonic vibrational frequencies were calculated at M062X/6-311 + g(d,p) level of theory to determine the nature of reactants, products, intermediates, and transition states. All of the species (except transition states) have real frequencies at M062X/ 6-311 + g(d,p) level of theory, whereas transition states have only one negative eigenvalue of the Hessian matrix, and therefore one imaginary frequency. The intrinsic reaction coordinate (IRC)^[60] calculations were carried out to ensure a correct connection between the transition state and corresponding minima along the reaction paths. Each IRC terminated upon reaching a minimum using the default criterion in Gaussian program.

3 | **RESULTS AND DISCUSSION**

3.1 | Description of the crystal structures

The dinuclear Zn(II) complex $C_{21}H_{24}N_2O_9Zn_2$ crystallizes as a methanol and water solvate, $(4(C_{21}H_{24}N_2O_9Zn_2)\cdot4(CH_3OH)\cdot3(H_2O))$ (1), in the monoclinic crystal system with a $P2_1/n$ space group. Methanol as solvent is ordered, whereas water molecule as solvent is disordered and occupies equivalent positions in 75%.



SCHEME 2 A proposed mechanistic pathway for the oxidation reaction of benzyl alcohol by H_2O_2 based on calculations at the CCSD(T)/6–311 + g(d, p)//M062X/6–311 + g(d,p) level of theory

The molecular structure of the dinuclear Zn(II) complex **1** together with the coordination polyhedra of the Zn ions are illustrated in Figure 1. The selected bond lengths and angles are given in Tables 2 and S1, respectively. Atom Zn1 is penta-coordinated by N_2O_2 donors of the L^{2-} unit (N1, N2, O1, and O4) and one O atom (O6) from the bridging acetate ion. Atom Zn2 is in a distorted octahedral coordination where the equatorial plane is occupied by two phenoxo O atoms (O1 and O4) from L^{2-} and two O atoms (O7 and O8) from the other acetate ligand. The axial positions are occupied by two O atoms (O5 and O1W) from bridging acetate ion and H₂O, respectively.

The tetranuclear Co(II) complex $C_{42}H_{44}N_4O_{16}Co_4$ crystallizes as a dihydrate, $C_{42}H_{44}N_4O_{16}Co_4 \cdot 2(H_2O)$ (2), in a monoclinic crystal system with a *Cc* space group. The molecular structure of the tetranuclear Co(II) complex together with the cubane-type $[Co_4O_4]$ core is shown in Figure 2. The asymmetric unit contains four crystallographically independent Co²⁺ cations, two \mathbf{L}^{2-} ligands, four acetate ligands, and two water molecules. The core of complex 2 is a cubane-like $[Co_4O_4]$ unit, with the Co(II) cations and O atoms from the two Schiff base ligands located at alternating corners of a distorted cube. Table 3 shows the Co-Co and Co-N/O coordination distances. The equatorial plane of Co(1) ion is occupied by the imine nitrogen atoms (N1 and N2) and two phenolic oxygen atoms (O1 and O4). The axial positions are occupied by two O atoms (O41 and O21) from the bridging acetate and the other L^{2-} ligand, with an O41-Co1-O21 angle of 162.5 (3). Atom Co2 also adopts a distorted octahedral geometry, with atoms O1 and O4 (from one L^{2-}) and O51 and O52 from acetate ligand in the equatorial plane. The axial positions are occupied by atoms O42 from the bridging acetate and O24 from the



FIGURE 1 (a) View of the molecular structure of complex **1**, showing part of the atom-numbering scheme. The water and methanol solvent molecules and all H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. (b) The coordination polyhedron of Zn(II) in complex **1**



Bond lengths	Experimental	Theoretical	Bond lengths	Experimental	Theoretical
Zn1-01	2.094 (7)	2.129	Zn2-01	2.040 (6)	2.143
Zn1-O4	2.035 (6)	2.120	Zn2-O4	2.033 (7)	2.147
Zn1-06	2.008 (7)	2.014	Zn2-O5	2.102 (7)	2.058
Zn1-N1	2.076 (8)	2.118	Zn2-07	2.306 (7)	2.122
Zn1-N2	2.050 (9)	2.088	Zn2-O8	2.109 (7)	2.146
Zn…Zn	3.0534 (18)	3.165	Zn2-O1W	2.140 (7)	2.344

TABLE 2 Selected bond lengths (Å) for complex 1

FIGURE 2 (a) View of the molecular structure of complex **2**. The water molecules and all H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. (b) The cubane-type $[Co_4O_4]$ core of complex **2**



TABLE 3 Selected bond lengths (Å) for complex 2

Bond lengths	Experimental	Theoretical	Bond lengths	Experimental	Theoretical
Co1-O1	2.089 (7)	2.291	Co3-O1	2.181 (6)	1.990
Co1-O4	2.087 (6)	2.064	Co3-O21	2.075 (7)	1.962
Co1-O21	2.165 (6)	2.083	Co3-O24	2.038 (6)	1.986
Co1-O41	2.102 (6)	1.958	Co3-O61	2.135 (7)	1.982
Co1-N1	2.044 (8)	2.016	Co3-N21	2.016 (8)	1.962
Co1-N2	2.053 (9)	2.074	Co3-N22	2.051 (8)	2.029
Co2-O1	2.058 (6)	1.957	Co4-O4	2.104 (6)	2.087
Co2-O4	2.103 (6)	2.070	Co4-O21	2.077 (6)	2.042
Co2-O24	2.137 (6)	2.121	Co4-O24	2.070 (6)	1.783
Co2-O42	2.019 (7)	1.939	Co4-O62	2.007 (6)	1.926
Co2-O51	2.070 (7)	2.176	Co4-071	2.120 (7)	1.912
Co2-O52	2.133 (7)	1.992	Co4-072	2.085 (7)	1.888
Co1…Co2	3.002	2.905	Co2…Co3	3.164	2.982
Co1Co3	3.314	3.207	Co2…Co4	3.222	3.147
Co1…Co4	3.186	3.126	Co3Co4	3.013	2.801

other L^{2-} ligand, with an O42–Co2–O24 angle of 169.8 (3)°. Atoms Co3 and Co4 exhibit similar coordination environments to Co1 and Co2, respectively. Two acetate groups connect Co1 and Co2, and Co3 and Co4,

respectively. All of the Co–O–Co and O–Co–O angles within the cubane core are larger than or smaller than 90° , indicating that the cubane is slightly distorted.^[25] The Co–O/N–Co and O/N–Co–O/N angles within the

cubane core are listed in Table S2. Although a number of cubane-type $[Co_4O_4]$ clusters have been reported thus far, this study is the first report on a cubane-type complex with the *N*,*N'*-bis-(4-hydroxy-salicylidene)-1,3-dia-minopropane ligand.

The arrangement of the dinuclear Zn(II) and tetranuclear Co(II) complexes is stabilized by two types of Hbonds. The crystal structure of **1** is established by O–H^{...}O and C–H^{...}O intermolecular interactions that form an extended three-dimensional network (Figure 3a), whereas for **2** the O–H^{...}O hydrogen bonding interactions lead to the formation of the two-dimensional layers parallel to the (001) plane (Figure 3b). These layers interact mainly by the van der Waals forces. The geometry of the hydrogen bonds is listed in Table 4.

3.2 | FT-IR spectra

In the FT-IR spectrum of the H₂L ligand, characteristic bands of the v(OH) and $v(C=N)_{imine}$ were observed at 3447 and 1641 cm⁻¹, respectively. Also, in the FT-IR spectra of complexes 1 and 2, broad bands of the v(OH) moieties were clearly observed at 3448 and 3424 cm⁻¹, respectively. Condensation of the primary amine group with benzaldehyde was confirmed by the disappearance of the NH stretching bands in the 3100-3400 cm⁻¹ region. The ν (C=N) stretching vibrations of complexes **1** and **2** were observed at 1609 and 1622 cm^{-1} , respectively. This represents a red shift to lower frequencies by about $20-30 \text{ cm}^{-1}$, which is a direct indication of the involvement of azomethine nitrogen in coordination. The $\nu_{as}(C=O)$ and $\nu_{s}(C=O)$ vibrations of the acetate ligands appeared in the 1450–1555 cm⁻¹ region.^[61] Also, ν (PhO) was shifted to lower frequencies in both complexes, which indicates that the M-O bond was formed between the metal ion and the ligand.^[62] In addition, the spectra of complexes 1 and 2 showed corresponding ν (Co–N) and ν (Zn–N) vibrations at 464 and 465 cm⁻¹, respectively.

3.3 | Electronic absorption spectra

The electronic absorption spectra of the complexes and the free ligand were recorded at room temperature $(2 \times 10^{-5} \text{ M in DMSO}, \text{ Figure 4})$. The Schiff base ligand H₂L showed characteristic absorption bands at 280, 308, and 410 nm. The highly intense bands at 280 and 308 nm were assigned to $\pi \to \pi^*$ and $n \to \pi^*$ transitions of the H₂L, respectively, and the broad band at about 410 nm was attributed to intraligand charge transfer.^[63] On the contrary, in the electronic spectra of **1** and **2**, distinct bands at 348 and 368 nm arising from $n \rightarrow \pi^*$ transitions of the imine groups and MLCT transitions^[64–66] and intense bands at higher energy (286 and 270 nm for **1** and **2**, respectively) associated with the aromatic $\pi \rightarrow \pi^*$ intraligand charge-transfer transitions were observed.^[67] In the visible region, complex **1** showed no appreciable absorption bands above 450 nm, indicating the absence of *d*–*d* transitions which is in accordance with the *d*¹⁰ configuration of the Zn(II). Complex **2**, however, showed low-intensity bands in the range of 550–700 nm due to its expected *d*–*d* transitions.

3.4 | ¹H NMR spectra

¹H NMR spectra of the H₂L ligand and its zinc complex were recorded at 298 K in DMSO-d₆ (Figures S1 and S2). In the ¹H NMR spectrum of the ligand, the protons' broad peaks of phenolic OH⁸ and OH⁶ moieties were observed at 12.9 and 10.8 ppm, respectively. The aromatic protons of the ligand resonated in the range of 6.2-7.2 ppm and unambiguously assigned according to their coupling constants (see Section 2.2.1). The expected singlet for the proton of the imine moiety (H³) was observed at 8.3 ppm. Multiplets of the aliphatic protons H¹ and H² were also observed at 1.9 and 3.6 ppm with expected multiplicities and coupling constants. In the ¹H NMR spectrum of complex **1**, the broad peak at 9.5 ppm was attributed to remaining phenolic protons (OH⁶). The disappearance of the phenolic OH⁸ proton signal in the spectrum of complex 1 indicates the deprotonation of the ligand and having taken part in the bond formation to metal through oxygen. The aromatic and imine protons also appeared in the anticipated positions. In addition to the aforementioned signals, the spectrum of complex 1 exhibited five singlets at 1.8, 2.7, 2.9, 3.4, and 8.0 ppm. The signals at 2.7, 2.9, and 8.0 ppm can be attributed to the traces of the DMF solvent.^[68] Thus, the singlets at 1.8 and 3.4 ppm can be assigned to the methyl groups of the acetate ligands (H^{10} and H^{11} , respectively).

3.5 | Electron impact mass spectroscopy

In the mass spectrum of the H_2L ligand, a molecular ion peak was observed at m/z 314.3 corresponding to its molecular weight (Figure S3). The spectrum also exhibited various fragments of the ligand. The information gathered from the EIMS data is in agreement with the elemental analysis and ¹H NMR results.

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FIGURE 3 Arrangement of (a) **1** and (b) **2** in the unit cell viewed along *a*-axis. Dashed lines represent the O-H…O hydrogen bonds that stabilized the structural architecture

^aA, acceptor; D, donor.

a) 0.6



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TABLE 4 Hydrogen bond geometries (Å, deg) in the crystal structures of 1 and 2

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D−H …A	D-H	H····A	D····A	D-H···A	Symmetry
1					
$O2-H2A\cdots O2W^{i}$	0.82(1)	1.83 (14)	2.370 (18)	2.370 (15)	-x + 1, -y + 1, -z + 1
C10-H10B····O2W ⁱⁱ	0.99	2.25	3.14 (2)	148	-x + 1/2, y - 1/2, -z + 1/2
C14-H14O6 ⁱⁱⁱ	0.95	2.59	3.522 (13)	167	-x + 1/2, y + 1/2, -z + 1/2
O3-H3…O2W	0.82(1)	1.87 (3)	2.661 (16)	162 (8)	
C16-H16…O7	0.95	2.27	3.176 (12)	158	
C16–H16···O1W ^{i}	0.95	2.62	3.344 (12)	134	-x + 1, -y + 1, -z + 1
C21–H21A…O7 ^{iv}	0.98	2.62	3.484 (13)	148	-x + 1, -y, -z + 1
O1W-H1WA···O 3^i	0.82(1)	2.10 (5)	2.808 (10)	145 (8)	-x + 1, -y + 1, -z + 1
O1W-H1WB····O7 ⁱ	0.82(1)	2.00 (4)	2.744 (9)	151 (8)	-x + 1, -y + 1, -z + 1
O9-H9…O1W	0.84	2.20	2.652 (10)	114	
2					
O2-H2A…O2W	0.84	1.80	2.621 (15)	164.6	
O3–H3…O61 ^{<i>i</i>}	0.84	1.85	2.670 (9)	165.5	x + 1/2, y + 1/2, z
O22-H22A…O42 ⁱⁱ	0.83	1.97	2.773 (9)	162.0	x + 1/2, y - 1/2, z
O23-H23…O1W	0.85	1.92	2.76 (2)	166.3	
01W-H1WA…071	0.89	1.91	2.796 (15)	175.5	

FIGURE 4 UV-Vis spectra of (A) H₂L, (B) complex 1, and (C) complex 2 (CA, B and $C = 2 \times 10^{-5}$ M and Cb = 2×10^{-3} M) in DMSO at room temperature

DFT calculations 3.6

The optimized structures of complexes 1 and 2, shown in Figure 5, are in good agreement with the results of single-crystal X-ray analysis. Tables 2, 3, S1, and S2 compare the theoretical bond distances and bond angles of the optimized structures with those obtained experimentally. Also, there is a good agreement between the theoretical and experimental data.

Frontier molecular orbitals, HOMO and LUMO, play an important role in the study of chemical reactivity and optical properties.^[69] The energy bandgap between HOMO and LUMO is an important parameter for determining the molecular properties such as stability and activity.^[70] The calculated HOMO and LUMO energies were found to be -4.88 and -1.48 eV for complex 1 and -3.81 and -3.22 eV for complex 2. The calculated HOMO-LUMO energy gaps were found to be 3.40 and 0.59 eV for complexes 1 and 2, respectively (Figure 6). Soft molecules have a small bandgap, and hard molecules have a large bandgap.^[71] The energy gap of complex 1 may indicate its good stability and low reactivity.^[72,73] On the contrary, the small bandgap of complex 2 indicates that its electrons are more easily excited from the ground

(c)

0.8



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state to the excited state. In addition, this gap refers to a complex with more polarity and conductivity, high chemical and biological activity, and low kinetic stability.^[74]

3.7 | In vitro antitumor activity

To evaluate the ability of the H_2L ligand and its complexes to inhibit cell proliferation, MCF7 (breast cancer), A375 (melanoma cancer), and PC3 (prostate cancer) cell lines were treated with different concentrations (12.5–100 μ g mL⁻¹) of each compound. The antiproliferative activity results and the observed cytotoxic effects (IC₅₀; concentration required for 50% cell growth inhibition) of these compounds are presented in Figure 7 and Table 5.

In the case of H_2L , an increase in the concentration resulted in an increase in the antiproliferative activity on the MCF7 cells and an adverse effect on A375 cell lines.

Complex 1, however, showed a remarkable activity against A375 and PC3 cancer cell lines with low IC_{50}



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concentrations (12.5, 25, 50, and 100 μ g mL⁻¹) of the (a) Schiff base ligand H₂L, (b) complex **1**, and (c) complex **2** on the proliferation of MCF7, A375, and PC3 cells

Compounds	IC ₅₀ (µM)		
	MCF7 (breast cancer)	A375 (melanoma cancer)	PC3 (prostate cancer)
H_2L	137.20	441.61	495.97
1	155.25	27.89	122.97
2	190.76	172.70	175.27
DOX	22.70	21.03	22.96

values in the entire range of concentrations. In comparison, complex **2** did not show convincing growth

inhibition on the tested cell lines, which indicates its low cytotoxic effect. These results emphasize that the cytotoxicity of dinuclear Zn(II) complex is higher than that of the tetranuclear Co(II) complex.^[75]

3.8 | Characterization of the nanoparticles

3.8.1 | FT-IR analysis

The FT-IR spectra of the nanoparticles obtained from thermal decomposition of complexes **1** and **2** are shown in Figure 8. Both spectra represent the expected nature of



FIGURE 8 FT-IR spectrum of (a) ZnO and (b) Co₃O₄ nanoparticles

metal oxides. In the FT-IR spectrum shown in Figure 8a, the broad band at 466 cm⁻¹ is attributable to the Zn–O stretching vibration mode and confirms the formation of ZnO nanoparticles. The broad peaks at about 3412 and 1638 cm⁻¹ are assigned to the O–H stretching and bending modes of the adsorbed water molecules, respectively.^[37,76] On the contrary, in the FT-IR spectrum shown in Figure 8b, two strong bands at 664 and 574 cm⁻¹ are attributable to Co–O stretching modes and confirm the formation of spinel Co₃O₄. The peak at 664 cm⁻¹ is attributed to the stretching vibration of Co²⁺–O^{2–} in tetrahedral holes and the band at 574 cm⁻¹

is related to the stretching vibration of $\text{Co}^{3+}-\text{O}^{2-}$ in octa-

3.8.2 | XRD analysis and morphology of the nanoparticles

X-ray diffraction patterns of the synthesized metal oxides confirmed the formation of ZnO and Co₃O₄ from complexes **1** and **2**. Figure 9e,g shows the XRD patterns for the obtained ZnO and Co₃O₄ nanoparticles, respectively. All of the diffraction peaks correspond to the hexagonal phase of ZnO (cell constants: a = 3.25, c = 5.21 Å, space group: *P63mc*, JCPDS card no. 01–080-0074) and cubic spinel structure of Co₃O₄ (cell constants: a = b = c = 8.085 Å, space group *Fd3m*, JCPDS card no. 78–1970).^[77,78]

The sharp and intense XRD reflections indicate high crystallinity of the samples. In addition, no reflection peaks from other phases were observed, which indicates the high purity of the samples. The average crystallite size (D) for each sample was calculated using the Debye–Scherrer equation:

 $D = 0.9\lambda/\beta \cos\theta,$

hedral holes.^[37]

where λ is the wavelength of X-rays (1.5406 Å for Cu K α), β is the full width at half maximum (FWHM) of the diffraction peak, and θ is the Bragg diffraction angle. The crystallite sizes of ZnO and Co₃O₄ were estimated to be 34 and 43 nm, respectively (Table 6). Morphology of the



FIGURE 9 FESEM images of (a,b) ZnO and (c,d) Co₃O₄, XRD patterns of (e,f) ZnO before and after using as catalyst, and (g,h) Co₃O₄ before and after using as catalyst

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TABLE 6 Information obtained from Debye–Scherrer equation

Compound	20	Θ	cosθ	$B_{1/2}$ (deg)	<i>B</i> _{1/2} (rad)	D (nm)
ZnO	36.1333	18.0950	0.9503	0.246	0.0043	34
Co ₃ O ₄	37.0306	18.5153	0.9482	0.1968	0.0034	43

obtained nanoparticles was also investigated using the FESEM technique. The FESEM images of the ZnO and Co_3O_4 nanoparticles are shown in Figure 9a–d. ZnO was obtained as almost uniform spherical nanoparticles, and Co_3O_4 was formed as polygonal nanoparticles.^[79] Although both polygonal and spherical morphologies have been reported for the latter, cubic spinel structure of Co_3O_4 has been deduced from XRD data in the corresponding literature.^[37,80–82]

3.8.3 | DRS analysis

UV–Vis DRS was used to elucidate the absorption behavior of the nanoparticles. Figure S4 shows the UV–Vis DRS spectra for the obtained ZnO and Co_3O_4 nanoparticles. As shown in Figure S4a, the ZnO nanoparticles exhibit an absorption edge at 363 nm, which may be attributed to the band-to-band transitions.^[83,84] On the contrary, Figure S4b shows two absorption bands in the range of 350–450 and 600– 800 nm for the Co_3O_4 nanoparticles. The first band can be attributed to the tetrahedrally coordinated Co^{2+} , and the second band can be attributed to the octahedrally coordinated Co^{3+} [85,86]

3.9 | Catalytic activity studies

To evaluate the catalytic activity of the ZnO and Co_3O_4 nanoparticles obtained from thermal decomposition of complexes **1** and **2**, the oxidation of benzyl alcohol was selected as a model reaction, and the effect of various parameters such as reaction time, temperature, amount of catalyst and amount of oxidant on the reaction yield, and selectivity was studied.

The amount of oxidant had a significant effect on the conversion and selectivity of the oxidation reaction (Tables 7 and 8). For both catalysts, increasing the amount of hydrogen peroxide increased the conversion proportionately. Higher amount of H_2O_2 , however, drastically decreased the selectivity due to the formation of by-products such as benzoic acid. Therefore, 10 mmol of H_2O_2 (30%) was used as the optimum amount of oxidant for each catalyst (Tables 7 and 8).

TABLE 7 Effect of the amount of H_2O_2 on the oxidation of 1.0 mmol of benzyl alcohol in the presence of 1.0 mg of ZnO at room temperature after 5 h

Entry	mmol of H ₂ O ₂	Conversion (%)	Selectivity (%)
1	2	60	99
2	5	64	99
3	10	71	98
4	15	82	87
5	30	98	63

TABLE 8	Effect of the amount of H ₂ O ₂ on the oxidation of
1.0 mmol of be	enzyl alcohol in the presence of 1.0 mg of Co ₃ O ₄ at
room tempera	ture after 12 h

Entry	mmol of H ₂ O ₂	Conversion (%)	Selectivity (%)
1	2	28	99
2	5	39	98
3	10	50	98
4	15	63	89
5	30	75	77

To optimize the amount of catalyst and the reaction time, the oxidation of benzyl alcohol with 10 mmol of H_2O_2 was carried out using 1.0, 2.0, 5.0, and 10.0 mg of each catalyst per millimole of the substrate at different time periods. As shown in Tables 9 and 10, increasing the amount of catalyst and time is in favor of conversion of benzyl alcohol. Amounts higher than 10.0 and 15.0 mg of

TABLE 9Conversion of 1.0 mmol of benzyl alcohol in thepresence of different amounts of ZnO at different time periods atroom temperature

Conversion (%) after					
Amount of catalyst (mg)	1 h	2 h	3 h	4 h	5 h
1.0	18	33	41	56	71
2.0	29	38	48	69	77
5.0	39	60	69	84	87
10.0	50	71	83	96	98

TABLE 10 Conversion of 1.0 mmol of benzyl alcohol in the presence of different amounts of Co_3O_4 at different time periods at room temperature

Conversion (%) after						
Amount of catalyst (mg)	1 h	3 h	6 h	9 h	12 h	
1.0	4	11	27	38	50	
2.0	12	21	33	41	59	
5.0	26	38	43	56	63	
10.0	37	50	55	64	71	
15.0	49	58	69	75	88	

ZnO and Co_3O_4 per millimole of benzyl alcohol, however, had an adverse effect on the selectivity. Therefore, the best results were obtained when 1.0 mmol of benzyl alcohol was transformed selectively to benzaldehyde in the presence of 10.0 mg of ZnO or 15.0 mg of Co_3O_4 at room temperature with 10.0 mmol of hydrogen peroxide after 5 or 12 h, respectively. To gain an insight into the stability of the catalysts, recovery of the ZnO and Co_3O_4 nanoparticles was evaluated and the results are shown in Figure 10. The catalysts were reused in successive cycles and showed negligible decrease in efficiency in terms of conversion after four runs. Decrease in conversion, however, was more



SCHEME 3 A proposed mechanism for the selective oxidation of benzyl alcohol in the presence of ZnO and Co_3O_4 nanoparticles



 $\begin{array}{ll} FIGURE \ 10 & \mbox{Reusability of (up) ZnO and} \\ (bottom) \ Co_3O_4 \ in \ the \ oxidation \ of \ benzyl \\ alcohol \end{array}$



FIGURE 11 The PES of the oxidation reaction of benzyl alcohol to benzaldehyde at CCSD(T)/6-311 + g(d,p)//M062X/6-311 + g(d,p) level of theory

significant for the Co_3O_4 nanoparticles during four cycles (up to 9%).

At the end of each run, the catalyst was recovered by centrifugation, washed with water, dried at 100°C for 1 h, and then reused with fresh starting materials. XRD patterns for the recycled catalysts of the fourth run are compared with those of the fresh catalysts in Figure 9e–h. The recycled catalysts showed no considerable change in their crystal structure.

A proposed mechanistic pathway, which is in line with the reported literature,^[87] is outlined in Scheme 3. It is believed that metal oxide nanoparticles convert 1 mmol of H_2O_2 to 2 mmol of hydroxyl radicals.^[88] When the hydrogen of the benzylic carbon is attacked by hydroxyl radicals, a benzyl radical intermediate as well as a molecule of water is formed. This benzyl radical then combines with the other hydroxyl radical to produce an intermediate containing two hydroxyl groups. Finally, dehydration of the latter produces the desired benzalde-hyde product.

To identify the intermediate of the oxidation reaction of benzyl alcohol to benzaldehyde, the reaction mixture was sampled after 1, 3, and 5 h, and was analyzed using LC–MS. As shown in Figure S5, m/z of the only intermediate detected in this reaction was 123.

As shown in PES (Figure 11), the reactants must undergo a series of continuous reactions to generate the product. Initially, an H-abstraction reaction occurred, and the hydrogen atom of the methylene group of benzyl alcohol was separated by H_2O_2 to form the radical intermediate 1 (IM1), H_2O , and 'OH. The barrier height of TS1 was calculated about 14.1 kJ mol⁻¹ at CCSD(T)/6-311 + g(d,p)//M062X/6-311 + g(d,p) level of theory. Afterward, the 'OH radical was added to IM1 and resulted in intermediate 2 (IM2) by passing over the TS2 with a 66.1 kJ mol⁻¹ barrier height. Finally, IM2 dissociated to water and benzaldehyde molecules by passing over the TS3 with a 73.9 kJ mol⁻¹ barrier height. As shown in Figure 11, the most stable species in PES is the benzaldehyde product.

4 | CONCLUSION

A tetradentate N_2O_2 Schiff base ligand (N,N'-bis-(4hydroxy-salicylidene)-1,3-diaminopropane, H_2L) was of 2.4synthesized via condensation dihydroxybenzaldehyde and 1,3-diaminopropane and was utilized in the preparation of two novel dinuclear Zn(II) and tetranuclear Co(II) complexes. All of the products were unambiguously characterized. Single crystal diffraction analysis showed that Zn²⁺ and Co²⁺ ions, in the corresponding di- and tetranuclear complexes, were connected though μ -phenolato and μ -acetato bridges. The calculated HOMO-LUMO energy gaps were found to be 3.40 and 0.59 eV for Zn(II) and Co(II) complexes, respectively. The in vitro cytotoxicity studies showed that complex 1 had the best antiproliferative activity on A375 and

PC3 cancer cells. In addition, thermal decomposition of the synthesized complexes resulted in pure nanostructured ZnO and Co_3O_4 , which were used as recyclable heterogeneous catalysts in selective oxidation of benzyl alcohol to benzaldehyde. Both catalysts showed excellent efficiency in terms of conversion and selectivity, along with acceptable recyclability.

ACKNOWLEDGEMENTS

We gratefully acknowledge the financial support from the Research Council of University of Guilan.

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How to cite this article: Sanatkar TH,

Khorshidi A, Janczak J. Dinuclear Zn(II) and tetranuclear Co(II) complexes of a tetradentate N₂O₂ Schiff base ligand: Synthesis, crystal structure, characterization, DFT studies, cytotoxicity evaluation, and catalytic activity toward benzyl alcohol oxidation. *Appl Organometal Chem.* 2020;e5493. <u>https://doi.org/10.</u> 1002/aoc.5493