




Schiff Base Catalysts for the Oxidation of Benzyl Alcohol to Benzaldehyde

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Abstract

Catalysts are crucial in promoting sustainability by facilitating chemical transformations under milder conditions, saving energy, and reducing pollution and by-product formation. In this work, we aimed to synthesize and characterize Schiff base complexes of copper, nickel, cobalt in benzyl alcohol oxidation, three asymmetric Schiff bases derived from 2,2'-(propenylenedioxy) di benzaldehyde bis(thiosemicarbazone) After that, catalytic activity of Schiff base complexes (Cu(II), Ni(II) and Co(II)) was investigated on the benzyl alcohol oxidation. Ni(II) complex served as an effective catalyst in converting benzyl alcohol to benzaldehyde with 89% conversion in the presence of *tert*-butyl hydroperoxide (TBHP) oxidant. Moreover, in the catalytic tests performed using *tert*-butyl hydroperoxide (TBHP), hydrogen peroxide (H₂O₂) and *m*-chloroperbenzoic acid (*m*-CPBA) oxidants, the highest product conversion (95% benzaldehyde conversion) was achieved in the presence of *tert*-butyl hydroperoxide (TBHP). In this study, in which the effect of the substrate-catalyst ratio on catalytic activity was investigated, the reaction was completed at the end of 1 hour at 90 °C in DMF solvent using 2.05×10⁻⁶ mol catalyst, 1.02×10⁻³ mol oxidant, and homogeneous catalysis system.

Keywords: Catalysts, Schiff bases, ligands, metal complexes, alcohol oxidation

1. Introduction

Schiff bases are extensively utilized organic materials with a broad range of applications, including catalysis [1], polymer stabilization [2], intermediates in organic synthesis [3], the food industry [4], pigments [5], dyes [6], chemo sensors [7], and more [8]. Moreover, Schiff bases demonstrate useful catalytic biological performance [9]. Metal Schiff base complexes have been thoroughly examined as homogeneous catalysts in diverse oxidation reactions [10].

Today, using economical and environmentally friendly solvents, especially water, is of great importance in terms of green chemistry [11,12]. Improving processes and protocols results in increased sustainability and efficiency [6]. Scientists prioritize green chemistry approaches that employ innovative recyclable, heterogeneous, or phosphine-free catalysts [13,14]. Catalysts are important in promoting sustainability by facilitating chemical transformations under milder conditions, saving energy, and reducing pollution, and by-product formation [15].

The catalytic oxidation of alcohols to aldehydes and ketones is crucial in various industries, including

agrochemicals, fragrances, dyes, pesticides, cosmetics, flame retardants, food flavorings, vitamins, and pharmaceuticals [16–22]. Benzyl alcohol (BA) is a crucial intermediate in the synthesis of various organic compounds, including benzylic alcohols, which are important in medicinal chemistry and as synthetic intermediates [23–25]. It can be converted through oxidation processes into benzaldehyde, which is widely used in medicine, dyes, perfumes, and various other fields [26,27].

Transition metal complexes are widely used as catalysts to promote the oxidation of alcohols [28]. Due to the high abundance, low cost, and low toxicity of the first-row transition metals, we aimed to synthesize and characterize Schiff base complexes of copper, nickel, cobalt in benzyl alcohol oxidation, three asymmetric Schiff bases derived from 2,2'-(propenylenedioxy) di benzaldehyde bis(thiosemicarbazone) After that, catalytic activity of Schiff base complexes (Cu(II), Ni(II) and Co(II)) was investigated on the benzyl alcohol oxidation. Ni(II) complex served as an effective catalyst in converting benzyl alcohol to benzaldehyde with 89% conversion in the presence of TBHP oxidant.

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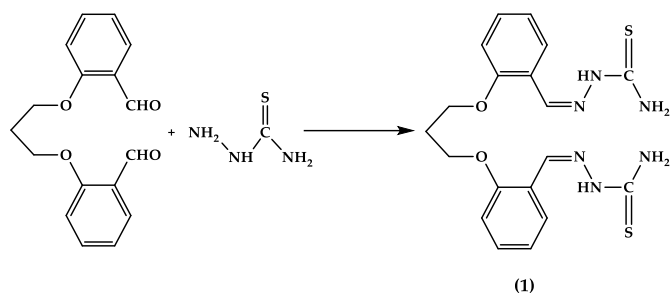


Figure 1. Synthetic reaction of 2,2'-(propenylenedioxy)di benzaldehyde bis(thiosemicarbazone)

In photocatalytic studies where all three complexes were used as catalysts, benzaldehyde was determined as the main product and benzoic acid as the by-product in the light of the data obtained.

2. Experimental

2.1. Materials

The details of the materials, equipment, and photocatalytic procedure used are given in Supplementary Information. 2,2'-[propane-1,3-diylbis(oxy)] di benzaldehyde was prepared according to the literature [29].

2.2. Methods

2.2.1. General Procedure for Synthesis of 2,2'-(propenylenedioxy)di Benzaldehyde Bis(thiosemicarbazone) (1)

2.84 g (10 mmol) dialdehyde and 1.82 g (20 mmol) thiosemicarbazide were dissolved in 25 mL ethanol (EtOH) and boiled under reflux for 10 hours. The mixture was then added to 50 mL of cold water and the precipitated solid was filtered through the glass crucible. The raw solid material obtained was dissolved in ethyl alcohol in hot water, 1 g of activated charcoal was added, boiled for 30 minutes, and filtered, then left to crystallize at room temperature. After this, the white solid precipitated in amorphous form was filtered and dried over P₂O₅ in a vacuum desiccator. Mp: 223 °C. Yield:75%. IR (KBr disc, cm⁻¹): 3419 (=N-H), 3275-3158 (NH₂), 1597 (C=N), 1245(C-O). ¹H-NMR(DMSO-d₆)/ppm δ: 11.37 (s, 2H, =N-H), 8.47 (s, 2H, N=CH), 7.88-8.07 (d, 4H, NH₂), 6.91-8.1 (m, 8H, Ar-H), 4.24 (t, 4H, -OCH₂), and 2.48 (p, 2H, -CH₂-). Mass (ESI) Calculated: 430.55, Found: 431.44 [M+H]⁺. Elemental analysis (C₁₉H₂₂N₆O₂S₂) (%): Calculated: C, 53.0; H, 5.2; N, 19.5. Found: C, 52.9; H, 5.3; N, 19.6.

2.2.2. General Procedure for Synthesis of Schiff Base Metal Complexes (2-4)

2,2'-(propenylenedioxy) dibenzaldehyde bis(thiosemicarbazone) (1) (2.15 g, 5 mmol) was dissolved in 10 mL dimethyl formamide (DMF) and metal salts (0.85 g, 5mmol) solution dissolved in 20 mL

EtOH was added dropwise. The mixture was boiled under reflux for 5 hours. The reaction was monitored by thin-layer chromatography while the solution was being mixed. It was determined that the reaction ended after 5 hours. At the end of this period, 1 mL of hot water was added dropwise to the hot mixture, and the mixture was allowed to crystallize. Then, the precipitated greenish-brown solid was filtered through the glass crucible, washed with H₂O, EtOH, and Et₂O, respectively, and dried over P₂O₅ in a vacuum desiccator.

2.2.2.1. Cu(II) complex 2

300 °C < Mp Cu(II) complex was obtained in 65% yield. FT-IR (ATR), ν_{\max} (cm⁻¹): 3441, 3337 (-NH), 2937, 2920, 2849 (AlipH), 1660, 1600 (C=N).Elemental analysis (C₁₉H₂₂CuN₆O₂S₂C₁₂) Calculated (%): C, 40.38; H, 3.90; N, 14.90; Cu, 11.25. Found: C, 40.32; H, 3.70; N, 15.15; Cu, 11.0. Mass (ESI Calculated: 492.08, Found: 491.53 [M-H]⁺.

2.2.2.2. Ni(II) complex 3

300 °C < Mp Ni(II) complex was obtained in 60% yield. FT-IR (ATR), ν_{\max} (cm⁻¹): 3160 (=N-H), 3437, 3384, 3312, 3260 (-NH), 3080 (ArH), 2951 (Alip H), 1667, 1588 (C=N), 1046 (C=S). ¹H-NMR (400 MHz, δ , ppm, DMSO): 9.74 (s, CH=N, 2H), 8.09 (s, N-NH, 2H), 8.04 (s, NH=C, 2H), 7.27-7.16 (m, Ar-H, 8H), 4.29 (t, J: 8.02, CH₂-O, 4H), 1.10-1.06 (m, Alip.CH₂, 2H). ¹³C-NMR (400 MHz, δ , ppm, DMSO):161.11, 158.77, 157.38, 157.01, 149.88, 135.28, 134.28, 126.09, 125.55, 117.50, 116.18, 69.03, 49.11, 35.27, 20.30. Elemental analysis (C₁₉H₂₂Ni-N₆O₂S₂C₁₂). Calculated (%): C, 40.75; H, 3.95; N, 15.0; Ni, 10.50. Found: C, 40.90; H, 4.15; N, 14.65; Ni, 10.75. Mass (ESI): m/z = Calculated: 487.23, Found: 487.15 [M]⁺.

2.2.2.3. Co(II) complex 4

300 °C < Mp The Co(II) complex obtained an 80% yield. FT-IR (ATR), ν_{\max} (cm⁻¹): 3161 (=N-H), 3438, 3385, 3314, 3262 (-NH), 3030 (ArH), 2986, 2952, 2882 (Alip.H), 1666 (C=N), 1043 (C=S). Elemental analysis (C₁₉H₂₂CoN₆O₂S₂C₁₂). Calculated (%): C, 40.72; H, 3.96; N, 15.0; Co, 10.52. Found: C, 40.56; H, 4.0; N, 15.30; Co, 10.8. Mass (ESI): Calculated: 487.46, Found: 487.31 [M]⁺.

3. Results and Discussion

3.1. Synthesis and Characterization

2,2'-(propenedioxy) dibenzaldehyde bis(thiosemicarbazone), was synthesized by the reaction of 2,2'-[propane-1,3-diylbis(oxy)] dibenzaldehyde and thiosemicarbazide in ethanol (Fig. 1). Spectroscopic and physical results support the proposed structure. Copper(II), nickel(II), and cobalt(II) complexes (2-4) of 2,2'-(propenylenedioxy)dibenzaldehyde bis(thiosemicarbazone) ligand were prepared (Fig. 2).

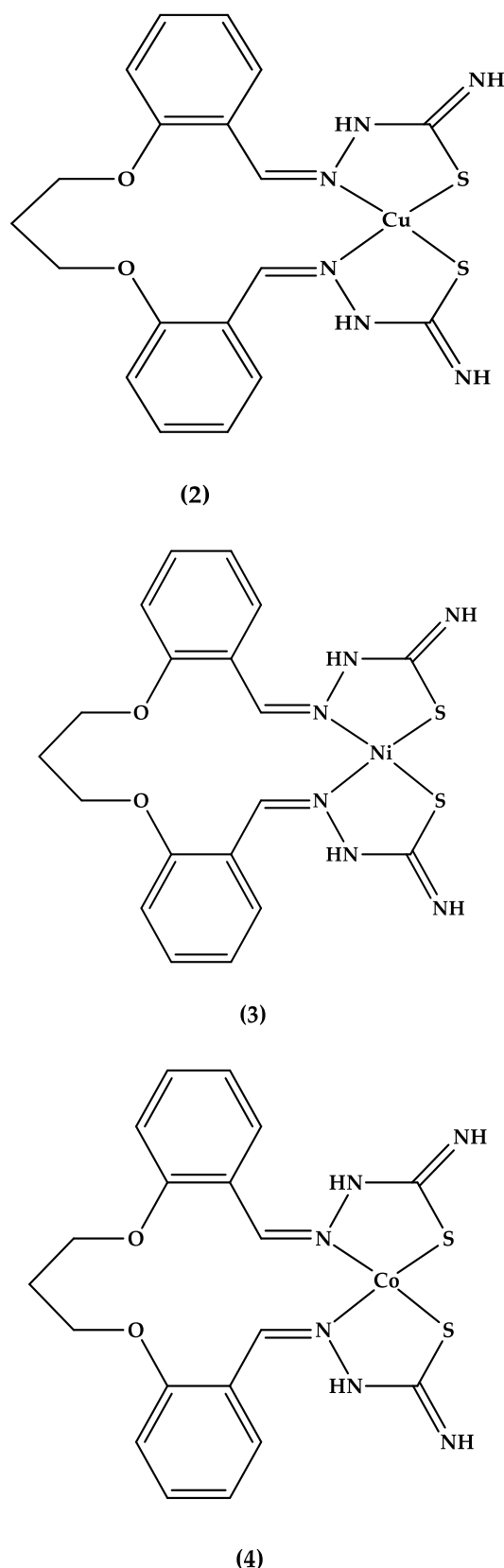


Figure 2. The structure of Cu(II), Ni(II) and Co(II) complexes (2-4)

The N₆S₂ donor set in the proposed structure of the ligand is available. This donor atom group is suitable for forming complexes with metal ions in a one-to-one ratio. Mononuclear Cu(II), Ni(II), and Co(II) complexes of the present ligand were prepared, and the structures were elucidated by spectroscopic methods.

In the IR spectrum of (1), the doublet $\nu(-\text{NH}_2)$ at 3419-3274 cm^{-1} , the $\nu(-\text{NH})$ group at 3157 cm^{-1} , the $\nu(\text{C}=\text{N})$ group observed at 1597 cm^{-1} and the vibration band observed at 1043 cm^{-1} confirms the existence of the $\nu(\text{C}=\text{S})$ group (S. Fig. 1). The shift in the frequencies of the characteristic vibration bands of $\nu(\text{N}-\text{H})$, $\nu(-\text{NH}_2)$, $\nu(\text{C}=\text{N})$, $\nu(\text{C}=\text{S})$ in the IR spectra to lower or higher frequencies of 5-60 cm^{-1} indicates the formation of complexes [30]

In the $^1\text{H-NMR}$ spectrum of (1), there are multiple CH₂-1 protons observed at 2.48 (2H) ppm, triplet OCH₂-2 protons observed at 4.24 (4H) ppm, multiplet aromatic ring protons observed at 6.91-8.1(8H) ppm and 7.88-8.07 (4H) ppm. It was interpreted that the doublet broad singlets observed belonged to $-\text{NH}_2$ the singlet observed at 8.5 (2H) ppm belonged to $-\text{NH}$ protons, and the singlet observed at 11.37 ppm belonged to HC=N protons (Fig. 3). Additionally, the signals at 7.88 and 11.37 ppm could not be observed because it was replaced by deuterium after the addition of D₂O. This confirms the existence of $-\text{NH}$ protons that can replace deuterium. When the integral values of the signals in the $^1\text{H-NMR}$ spectra are examined, the expected proton distributions are observed. The signal at 2.48 ppm corresponds to 2H, the signal at 4.24 ppm corresponds to 4H, the signal at 6.91-8.1 ppm corresponds to 8H, the signal at 7.88-8.07 ppm corresponds to 4H, and the signal at 11.37 ppm corresponds to 2H.

10 signals from 10 carbon atoms with different chemical environments were observed in the $^{13}\text{C-NMR}$ spectrum, which is an expected situation for the structure. These results confirm the structure and the $^{13}\text{C-NMR}$ resonance values are 27.1 C-1, 39.2 C-2, 138.8 C-3, 126.4 C-4, 122.7 C-5, 121.1 C-6, 112.9 C-7, 131.8 C-8, It shows the presence of C-9, C-9, and 178.1 C-10 carbons (Fig. 4) In the mass spectra of (1) 431.44 $[\text{M}+\text{H}]^+$ was seen and elemental analysis results confirm the structure (S. Fig. 2).

Metal complexes (2-4) were characterized by IR, UV-Vis, mass, and elemental analysis. The IR spectrum of metal complexes (2-4) were not different from each other and aromatic vibration bands at 3000-3100 cm^{-1} , aliphatic vibration bands at 2950-2850 cm^{-1} , $=\text{N}-\text{H}$ around at 3160 $-\text{NH}_2$ at 3400-3200 cm^{-1} , C=N at 1580-1600 cm^{-1} , C=S around at 1100-1050 cm^{-1} (S. Fig. 3–S. Fig. 5).

Table 1. Physical data of ligand and metal complexes

Compound	Empirical formula	Color	Yield	MS(m/z)	μ^{eff}
(1)	C ₁₉ H ₂₂ N ₆ O ₂ S ₂	white	75	430	-
(2)	C ₁₉ H ₂₂ CuN ₆ O ₂ S ₂ Cl ₂	green-brown	70	492	1.76
(3)	C ₁₉ H ₂₂ NiN ₆ O ₂ S ₂ Cl ₂	matt red	61	488	2.80
(4)	C ₁₉ H ₂₂ CoN ₆ O ₂ S ₂ Cl ₂	brown	80	487	4.34

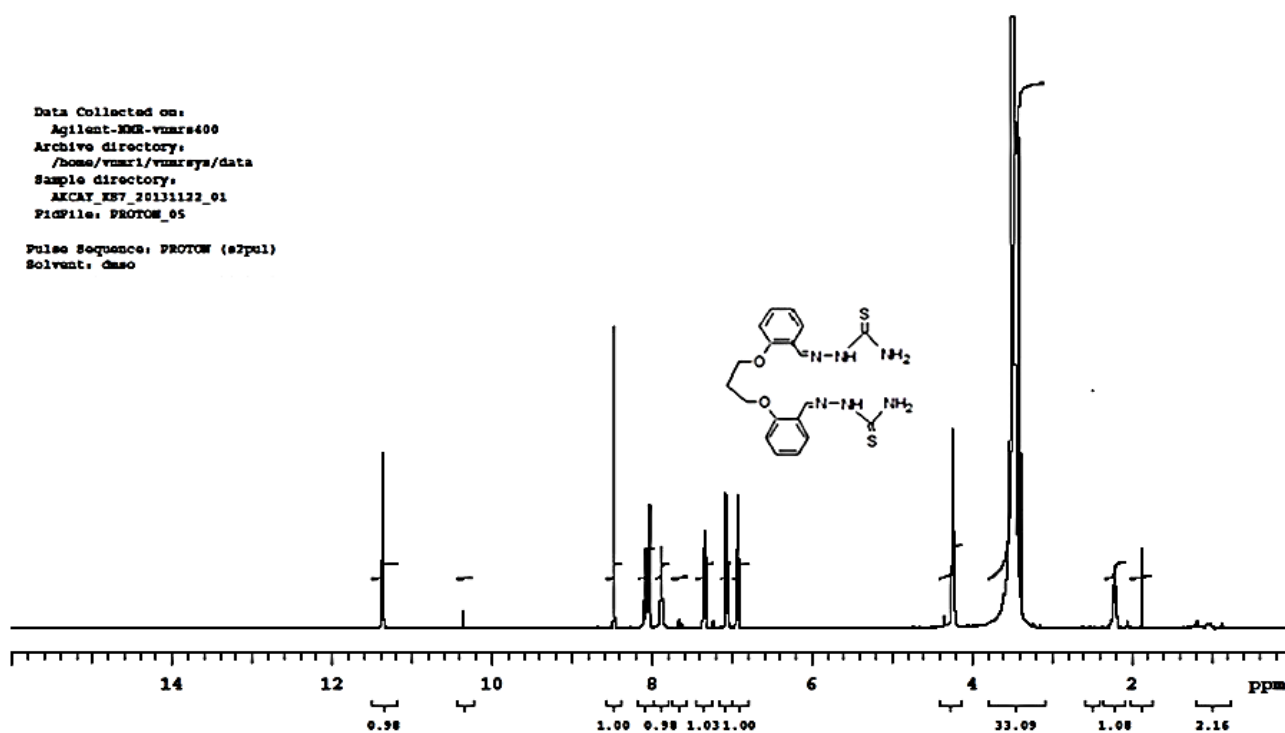


Figure 3. $^1\text{H-NMR}$ spectrum of (1)

It is widely known that $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of paramagnetic metal-centered complexes could not be taken, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of Cu(II) and Co(II) metal complexes (2 and 4) were not taken [31–33]. Mass spectra of metal complexes signals were m/z : 491.53 $[\text{M-H}]^+$ for Cu(II) complex (2), m/z : 487.15 $[\text{M}]^+$ for Ni(II) complex (3), and m/z : 487.31 $[\text{M}]^+$ for Co(II) complex (4) (S. Fig. 6–S. Fig. 8).

Magnetic moment measurements were made for all complexes at room temperature. The obtained values are given in Table 1. While the magnetic moment for the

mononuclear Cu(II) complex (2) was theoretically 1.73 BM, the finding of 1.76 BM as a result of the measurements showed that this complex created a normal magnetic moment. This value belonged to the Cu(II) ion belonging to the unpaired single-spin d^9 system and the structure was interpreted as a square plane. The value of 2.80 B.M. found for the Ni(II) complex (3) confirms the existence of the d^8 system and the presence of two unpaired spins. This result was interpreted as the formation of Ni(II) complex. The solid-state magnetic moment value of 4.34 B.M. found for the

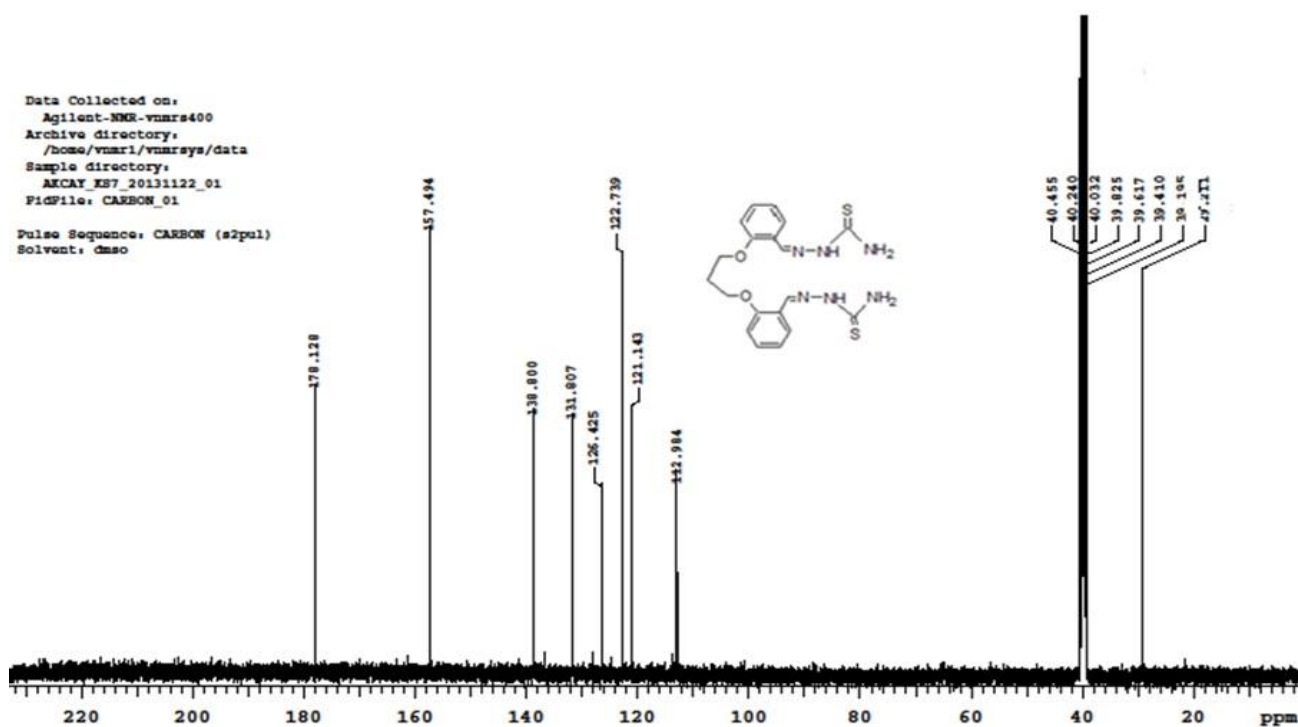


Figure 4. $^{13}\text{C-NMR}$ spectrum of (1)

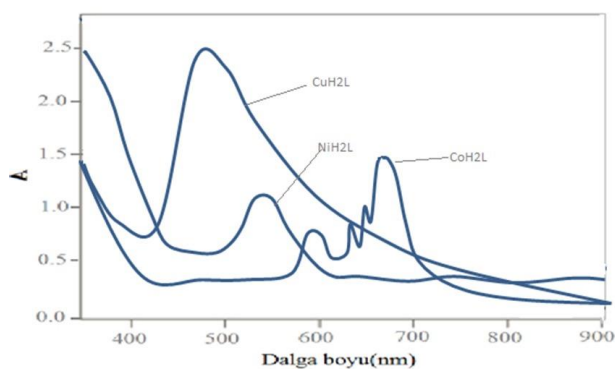


Figure 5. UV-Vis spectrum of Cu(II), Ni(II), and Co(II) complexes (2-4)

Co(II) complex (4) corresponds to three unpaired electrons, in which case it was interpreted that the Co(II) complex (4) has a tetrahedral structure [34–36]

UV-Vis spectra of ligands and complexes were taken in DMF (Fig. 5). Absorption bands are given in Table 4. The absorbances observed at 280–300 nm of the UV-Vis spectra of the ligand (1) and its Cu(II), Ni(II), and Co(II) complexes (2–4) were interpreted as $\pi-\pi^*$ transitions, and the absorbances observed at 320–360 nm were interpreted as $n-\pi^*$ transitions. The 480 nm d-d transition observed in the UV-Vis spectrum of Cu(II) complex was interpreted as the environment of the Cu(II) ion having a square plane geometry [37]. Only a single broad peak was observed in the electronic transition spectrum of Ni(II) complex, which was interpreted as a geometry between a distorted square plane and tetrahedral around the metal atom [38]. Transitions at 675, 660, 645, and 600 nm were observed in the UV-Vis spectrum of Co(II) complex, and among these bands, the transition at 675 nm is allowed and corresponds to the $^4A_2(F) \rightarrow ^4T_1(P)$ transition. The other bands at 660, 645, and 600 nm correspond to the prohibited transitions $^4A_2(F) \rightarrow ^2E(G)$, $^4A_2(F) \rightarrow ^2T_1(G)$, and $^4A_2(F) \rightarrow ^2T_2(G)$, respectively. These values observed for the Co(II) complex were interpreted as tetrahedral geometry [39]. The proposed structures of Cu(II) and Ni(II) Co(II) Schiff base complexes appear to be consistent with spectroscopic studies.

3.2. Catalytic Studies

In catalytic studies, a stock solution of 25 mg of catalyst in 100 ml of DMF was prepared and stored in the refrigerator. The purpose of choosing a homogeneous catalytic reaction system in this study is that the catalyst can provide higher selectivity and higher product conversion since all reactants are in the same phase. For the catalysis system that took place under homogeneous conditions, oxidants (H_2O_2 , TBHP, and *m*-CPBA), substrate (benzyl alcohol), and solvent (DMF) were used at 90 °C. As a result of the tests carried out without a catalyst or oxidant, no more than 2% product conversion was detected. The results obtained from all catalytic tests can be seen in Table 2.

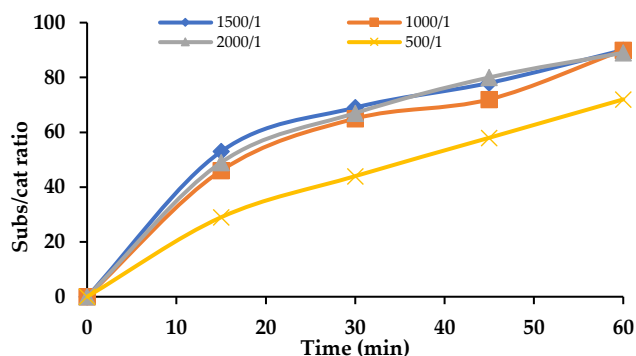


Figure 6. Substrate catalyst ratio in the oxidation of benzyl alcohol with (3)

To investigate the effect of the substrate catalyst ratio on the catalytic activity, the relationship between 1.05×10^{-3} mol, 2.05×10^{-3} mol, 3.08×10^{-3} mol, 4.10×10^{-3} mol benzyl alcohol amounts and 2.05×10^{-6} mol Ni(II) complex was investigated (Fig. 6). As the amount of benzyl alcohol increases from 1.05×10^{-3} moles to 2.05×10^{-3} moles, the activity of the nickel catalyst increases, meaning the total product conversion increases from 72% to 89%. When 3.08×10^{-3} mol and 4.10×10^{-3} mol benzyl alcohol were used with nickel Schiff base complexes as catalysts, the total product conversion was determined as 90%. Unfortunately, no significant increase in product selectivity was determined despite the high product conversion (Fig. 7).

After the substrate/catalyst ratio was determined as 1000/1, catalytic studies using this ratio were also repeated using cobalt(II) and copper(II) Schiff base complexes. In the catalytic study where Cu(II) Schiff base complex was used as a catalyst, 60% product conversion was determined with 600 as the turnover number, and Co(II) Schiff base complex was used as a catalyst, 65% product conversion was determined with 650 as turnover number (Fig. 8a and Fig. 8b).

Table 2. All catalytic results with (2, 3, and 4) in the oxidation of benzyl alcohol to aldehyde

Subs./cat. R.	Oxidant	Catalyst	Sol.	Conv. (%)	Benz. Sel. (%)	TON
500/1	TBHP	3	DMF	72	65	360
1000/1	TBHP	3	DMF	89	95	890
1500/1	TBHP	3	DMF	90	78	1350
2000/1	TBHP	3	DMF	90	70	1820
1000/1	H_2O_2	3	DMF	66	57	660
1000/1	<i>m</i> -CPBA	3	DMF	45	35	450
1000/1	TBHP	2	DMF	60	60	600
1000/1	TBHP	4	DMF	65	59	650
Without cat.	TBHP	3	DMF	< 2	—	—
1000/1	without ox.	3	DMF	< 2	—	—

Subs./cat. R.: Substrate/Catalyzer Ratio, Sol.: Solvent, Conv.: Conversion, Benz. Sel.: Benzaldehyde Selectivity,

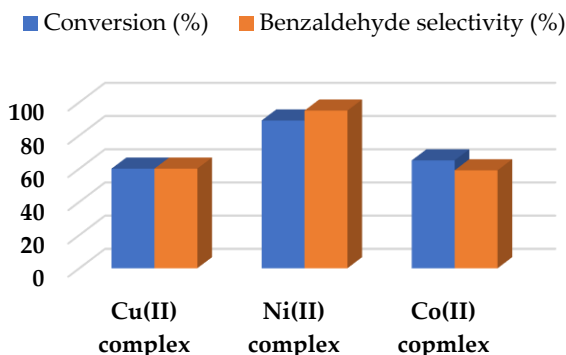


Figure 7. Conversion (%) and benzaldehyde selectivity (%) of (3)

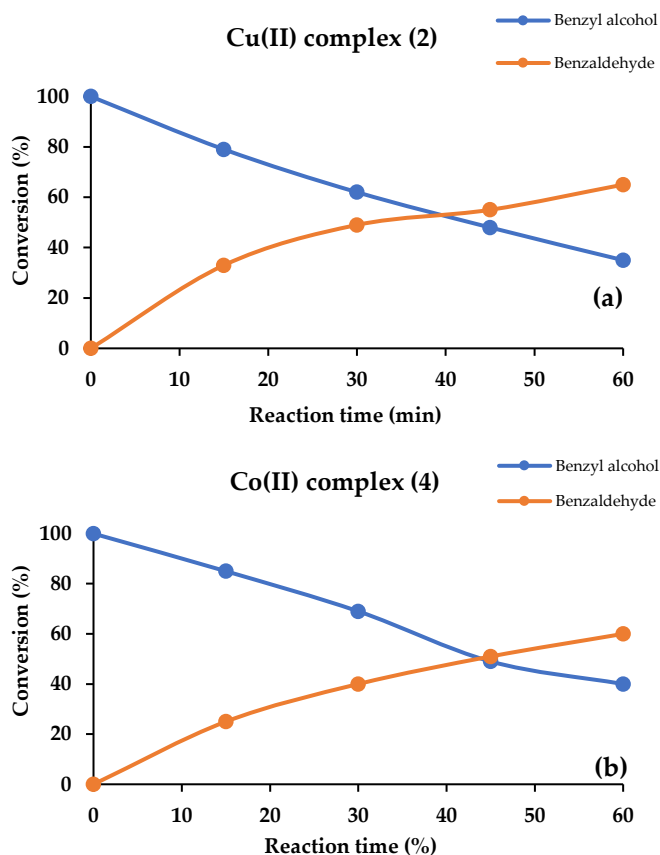


Figure 8. Benzaldehyde conversion with (2) (a) and (4) (b)

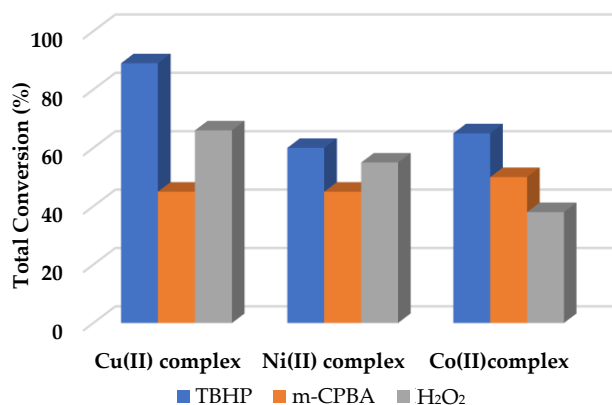


Figure 9. Oxidant type effect on benzyl alcohol oxidation with (2–4)

Table 3. All works using Schiff base complexes as catalysts in the oxidation reaction of benzyl alcohol in the last decade

Catalyst	SM	Ox.	Sol.	RT	RT (°C)	C/S	Ref.
Cu(II)SB ^a	MWCN	TBHP	1,4-dioxane	30 min	80	93/nr	[44]
*Cu(II)SB ^b	—	O ₂	water	24 h	70	>99/>99	[45]
Co(II)SB ^c	GO	H ₂ O ₂	free	40 min	25	95/70	[46]
Cu/NiSB ^d	MONP	H ₂ O ₂	DMSO	2 h	70	94/98	[47]
*Cu(II)SB ^e	—	O ₂	MeCN	1 h	25	99/nr	[48]
Co(II)SB ^f	—	H ₂ O ₂	water	80 min	82	85/100	[49]
Mo(VI)SB ^g	—	TBHP	free	2 h	25	92/98	[50]
**V(V)SB ^h	—	H ₂ O ₂	MeCN	1 h	80	21.5/85	[51]
Cu(II)SB ⁱ	Fe ₃ O ₄ @SiO ₂	TBHP	MeCN	2 h	nr	95/63	[52]
Ni(II)SB	—	TBHP	DMF	1 h	90	89/95	This work

SM: Supporting Material, Ox.: Oxidant, Sol.: Solvent, RT: Reaction Time RT: Reaction Temperature, C/S: Conversion/ Selectivity, Ref.: Reference

^aThese works were carried out in a basic aqueous solution in the presence of TEMPO [(2,2,6,6-tetramethylpiperidin-1-yl)oxyl] radical.

^{**}This work was carried out in the presence of co-catalyst HNO₃ with assisted light and ultrasound.

Cu(II)SB^a: commercially available, Cu(II)SB^b: Copper(II)-(2,2,6,6-tetramethylpiperidine-1-oxyl) complex, Co(II)SB^c: Different Schiff base complexes were prepared by immobilizing three aldehydes (4-Hydroxybenzaldehyde, 2-hydroxybenzaldehyde, and 2-Pyridinecarboxaldehyde), Cu/NiSB^d: Cu and Ni Schiff-base complexes, namely ahpvCu, ahpnCu, and ahpnNi, incorporating imine ligands derived from the condensation of 2-amino-3-hydroxypyridine, with either 3-methoxysalicylaldehyde (ahpv) or 4-nitrobenzaldehyde (ahpn), Cu(II)SB^e: Bearing the *N*-(*X*)-1-(furan-2-yl)methanimine ligands, Co(II)SB^f: synthesized with 1-(4-dimethylaminobenzyl-idenethiosemicarbazide (ABTSC) and 1-(2-pyridinylcarboxyl-idenethiosemicarbazide (TCTS), Mo(VI)SB^g: ioxidobis[2-(*E*)-p-tolyliminomethylphenolato]molybdenum(VI) complex, V(V)SB^h: Oxidovanadium (V) complex, Co(II)SBⁱ: Complex name was not identified, commercially taken.

Three different oxidants (TBHP, H₂O₂ and *m*-CPBA) were used to investigate the effect of the oxidant type on the catalytic system. Catalytic tests using Ni(II) Schiff base complex showed that the best oxidant source was TBHP with 95% benzaldehyde selectivity. The lowest product conversion for the same catalytic system was obtained at 45% when *m*-CPBA was used (Fig. 9). It is widely known that the peroxidative oxidation process proceeds via radical species [40–42]. Kani and co-workers investigated the reaction mechanism of catalytic oxidation of different organic compounds using TBHP and Mn(II) complexes in aqueous acetonitrile reaction medium using various radical scavengers [43]. In the first step, the oxidant (TBHP) coordinates to metal center (i) via the non-bonding electrons. Due to the bond dissociation energies of the peroxy and the O–H bonds in the TBHP, *tert*-butoxyl and hydroxyl radicals can be formed on the metal ions in the structure(ii). The *tert*-butoxy radical can leave the scaffold and further interact with another TBHP to form a *tert*-butyl hydroperoxyl radical ((CH₃)₃COO•) and *tert*-butanol ((CH₃)₃COH) by a rapid follow-up reaction. The cycle continues as the hydroxyl radicals become a hydroxyl ion by abduction of an electron from metal ion to form metal-(OH) (iii).

Table 4. Electronic transitions of ligand and metal complexes, (λ_{max} in nm)

Compound	π–π*	n–π*	d-d bant
(1)	280	320	—
(2)	290	321	480
(3)	298	356	540
(4)	292	363	675, 660, 645, 600

The oxidized structure (iii) reacts with another TBHP molecule to form water and a manganese hydroperoxo species (iv). At this stage, possibly due to the rigid coordination geometry of (iv), the metal-O bond is cleaved, leaving the *tert*-butyl peroxy radicals and oxidation state of metal is reduced via electron transfer to recover initiate center (i). Thus, a new catalytic cycle can begin [43].

When we look at the oxidation studies of benzyl alcohol carried out in the last 10 years, we see that the majority of them were carried out using copper, cobalt, vanadium, iron, zinc Schiff bases and their modified forms with various support materials (TiO₂, CeO₂, MCM-41, multi-walled carbon nanotube, rGO, etc.) [44–52]. All works are summarized in Table 3. In these studies, the use of support material extended the durability and life of the catalyst and made it more active and product-selective. In our study, high product conversion and product selectivity were achieved without the need for any support material with Nickel Schiff base, which is rarely used in literature.

4. Conclusion

2,2'-(propenylenedioxy)dibenzaldehyde bis(thiosemicarbazone) (1) and Cu(II), Ni(II), and Co(II) complexes (2-4) were characterized with different spectroscopic methods. Then, their photocatalytic performances were investigated on the oxidation of benzyl alcohol by changing oxidant type, substrate/catalyst ratio. In the catalytic study where Cu(II) Schiff base complex was used as a catalyst, 60% product conversion was determined with 600 as the turnover number, and Co(II) Schiff base complex was used as a catalyst, 65% product conversion was determined with 650 as turnover number. In this study, where homogeneous catalytic reaction system was used, catalysts and their selectivities were investigated on benzyl alcohol oxidation reaction and the results were quite satisfactory. However, the presence of all reactants together with the catalyst limited the recovery and reusability studies of the catalysts. Among the Schiff base complexes, the Ni(II) complex (3) was determined as the most active catalyst with an 890 TON value in the DMF solution. Ni(II) Schiff base complexes, of which there are limited studies in the literature, show not only high conversion but also high product selectivity in this study, revealing the potential of these complexes in catalytic applications.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could

have appeared to influence the work reported in this paper.

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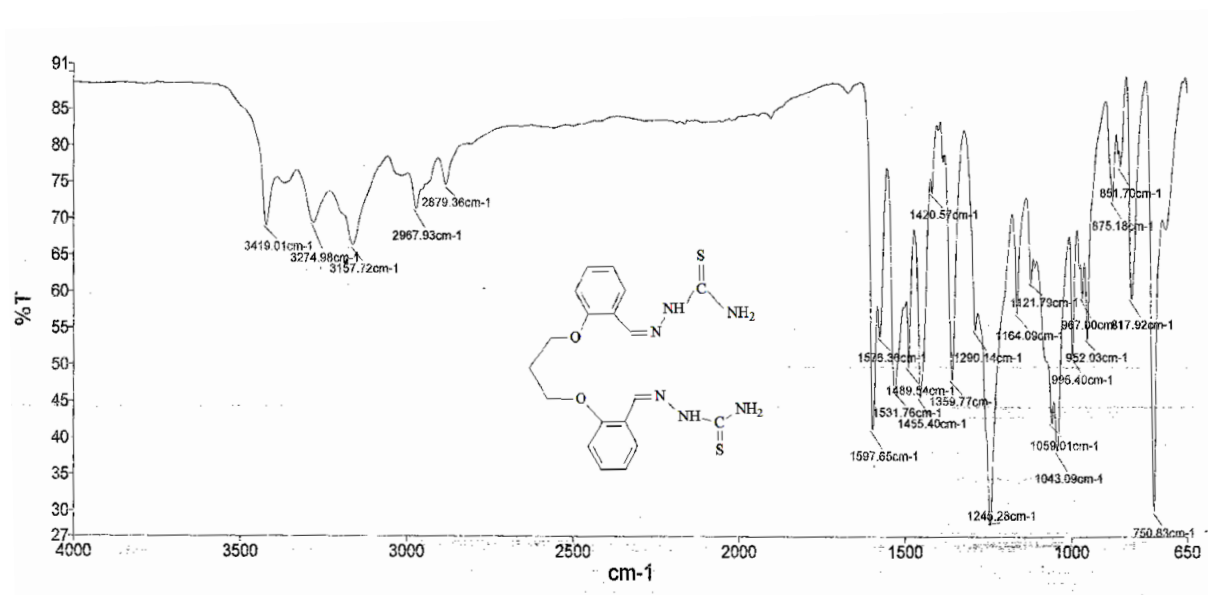
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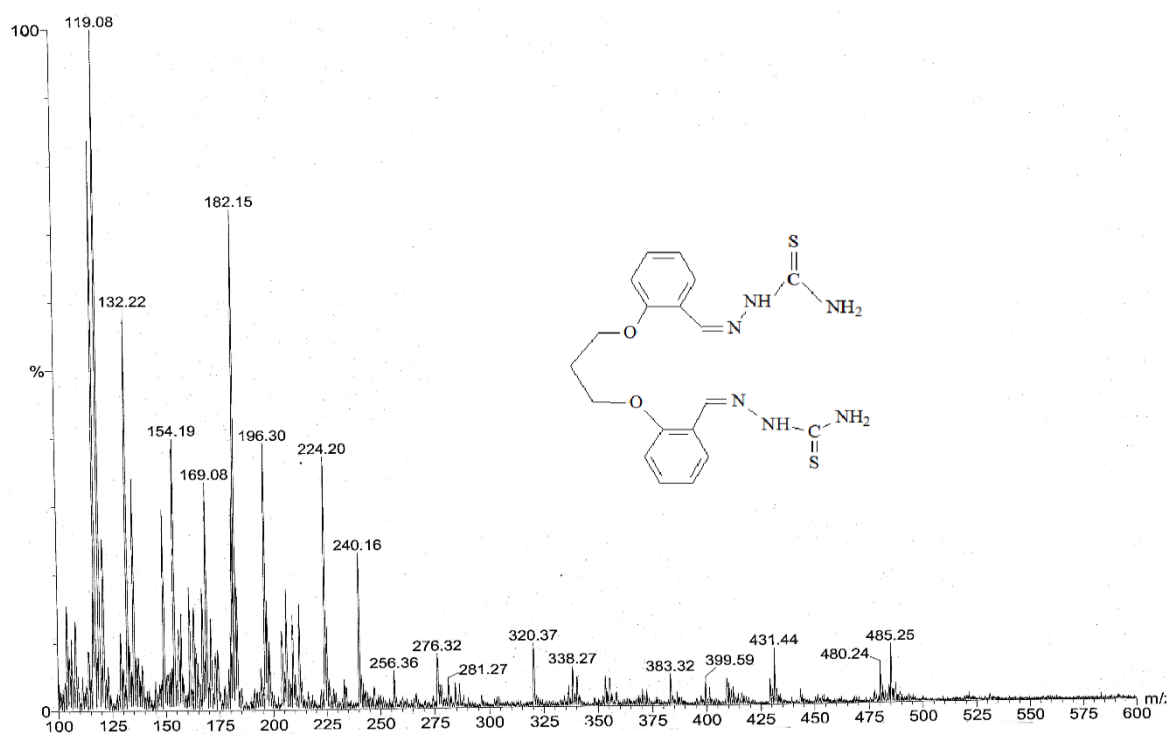
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SUPPLEMENTARY INFORMATION

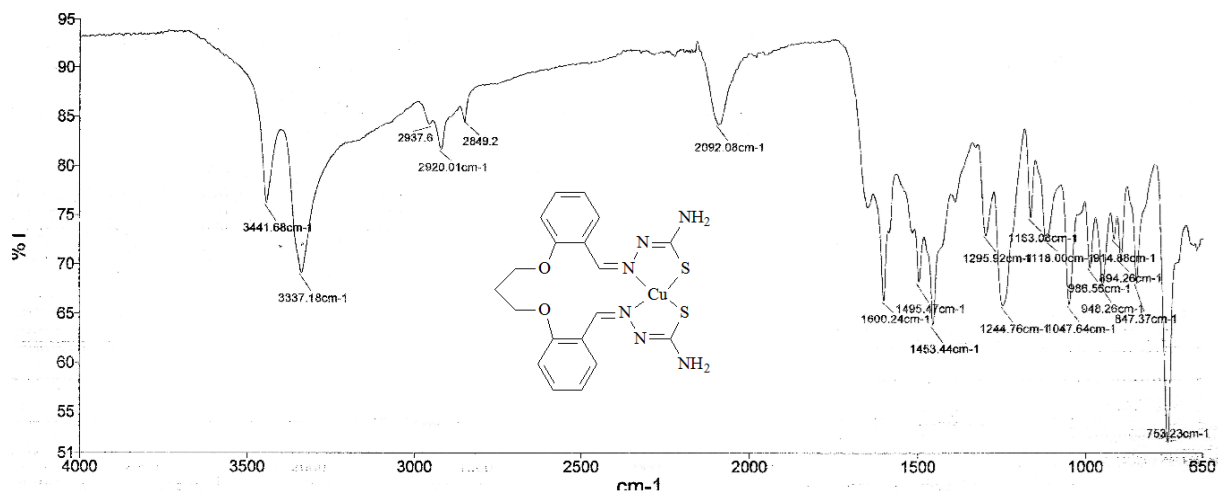
Schiff Base Catalysts for the Oxidation of Benzyl Alcohol to Benzaldehyde



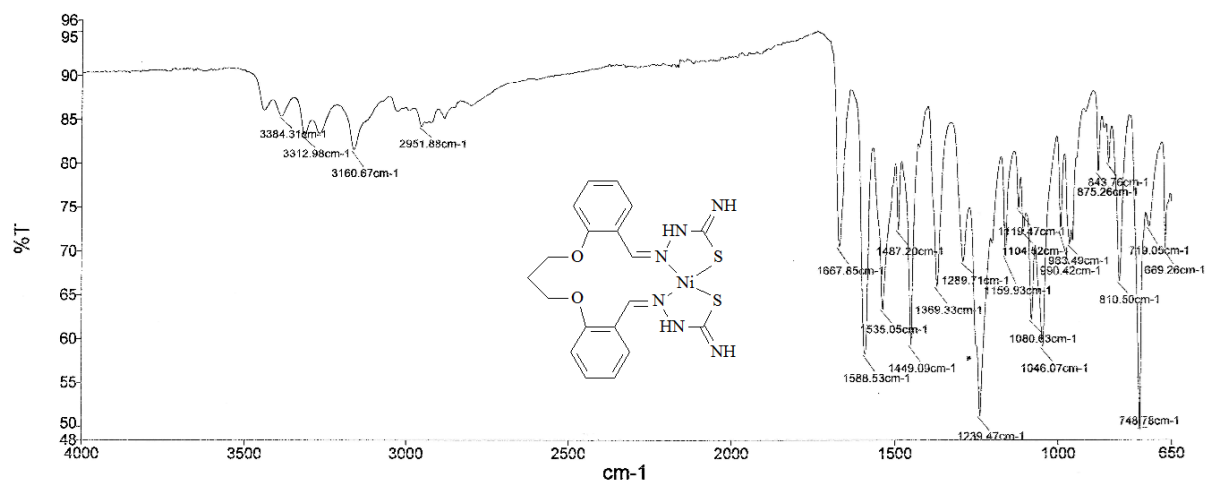
Supplementary Figure 1. IR spectrum of (1)



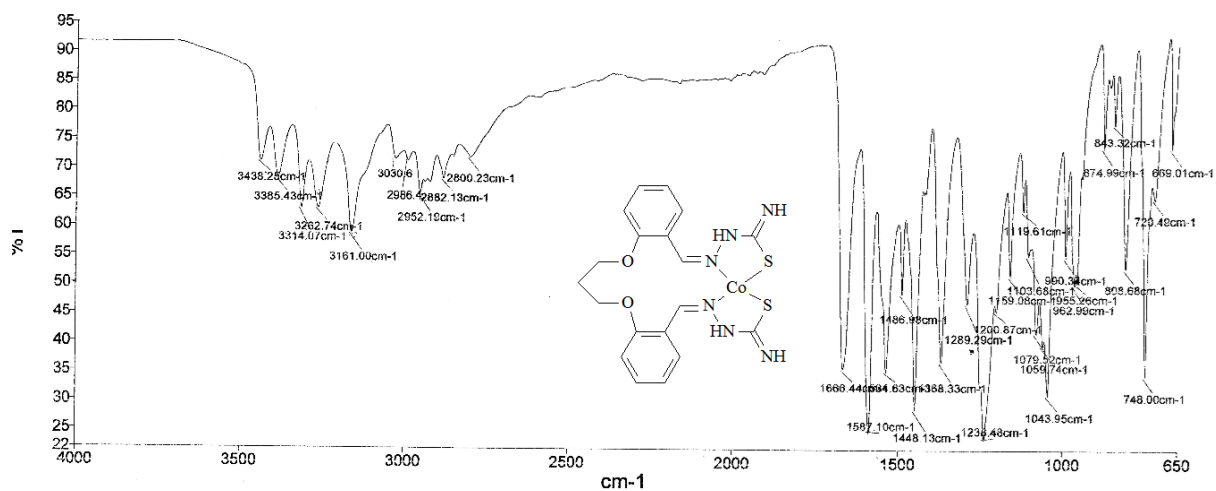
Supplementary Figure 2. Mass spectra of (1)



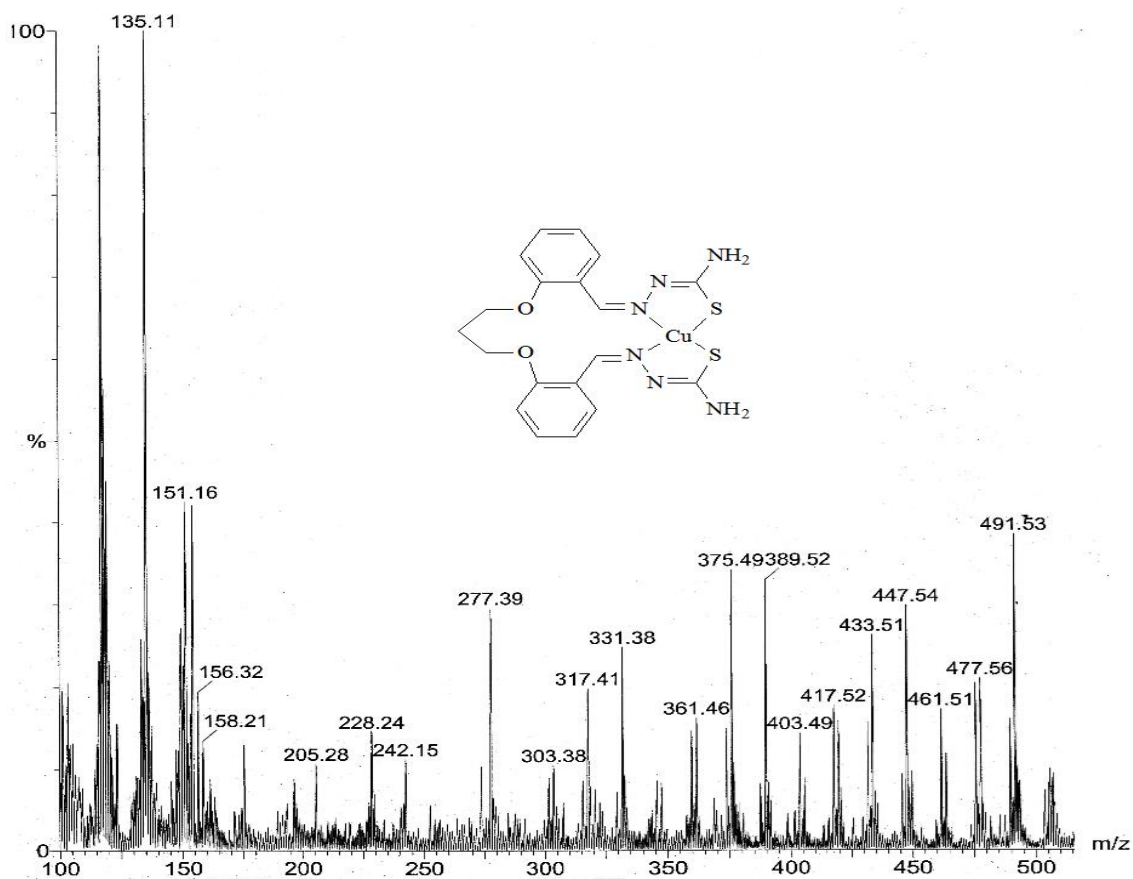
Supplementary Figure 3. IR spectrum of (2)



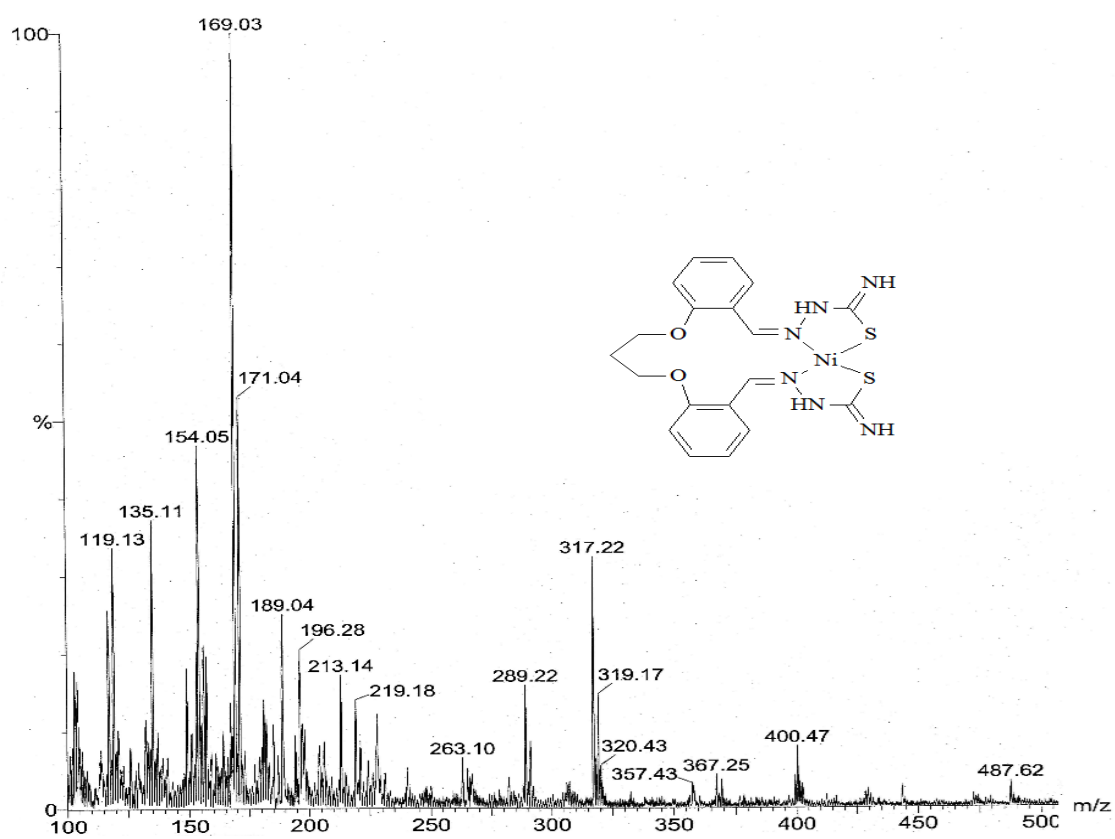
Supplementary Figure 4. IR spectrum of (3)



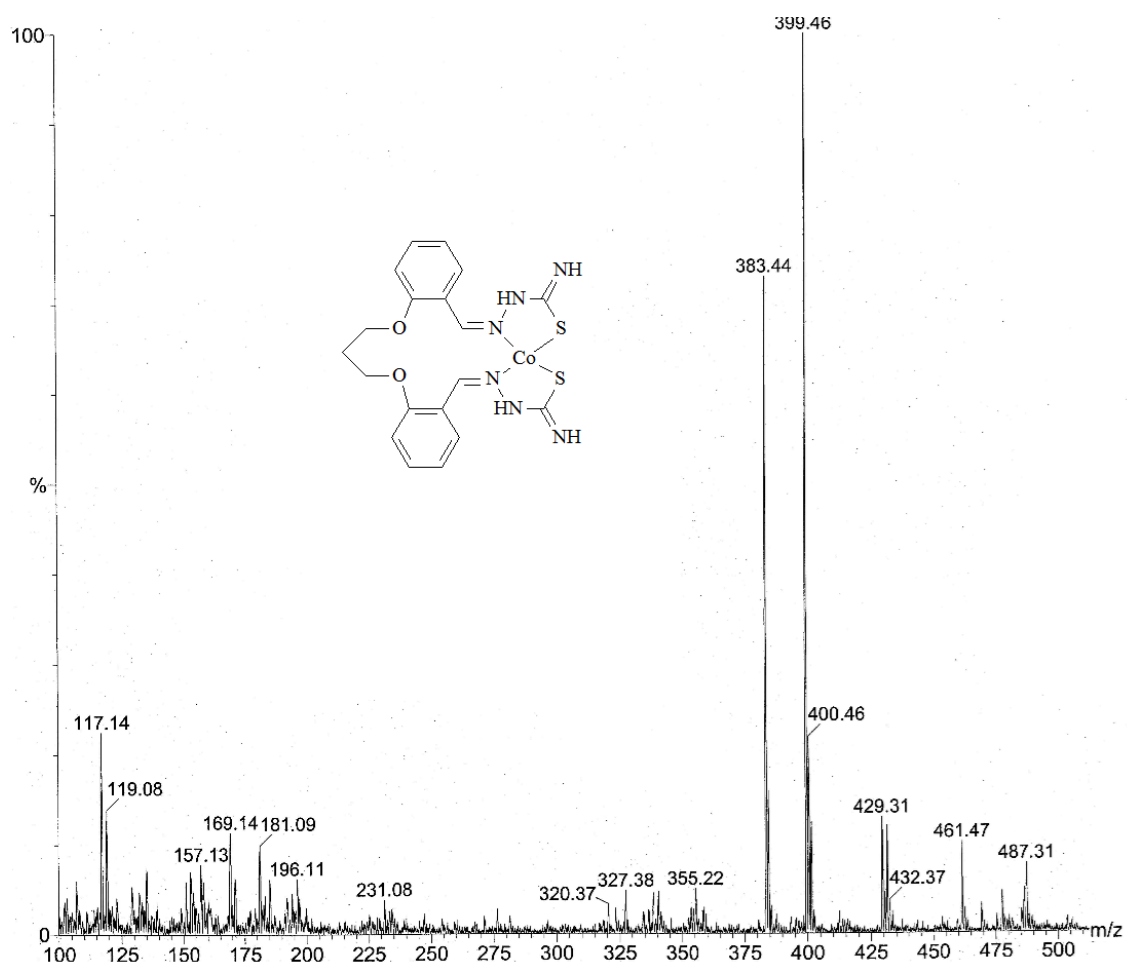
Supplementary Figure 5. IR spectrum of (4)



Supplementary Figure 6. Mass spectra of (2)



Supplementary Figure 7. Mass spectra of (3)



Supplementary Figure 8. Mass spectra of (4)