

Synthesis, characterization and selective oxidation using a new copper (II) Schiff base complex derived from Alanine and 4-chloro3-formyl coumarin

Malihe Ebrahimpour^a, Ghodsieh Bagherzade^{a,*}, Seyed Ali Akbar Sajadi^b, Rouhollah Khani^a

^aDepartment of Chemistry, Faculty of Sciences, University of Birjand, P.O. BOX 97175-615, Birjand, Iran

^bSharif University of Technology, Tehran, P.O. BOX 11155-8639, Iran

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Abstract

A novel Schiff-base ligand (L: 2-[(4-chloro-2-oxo-2H-chromen-3-ylmethylene)-amino] propionic acid) was prepared from the reaction of 4-chloro3-formylcoumarin and alanine amino acid. Copper (II) complex was synthesized from the reaction of the ligand with Cu (OAc)₂ · H₂O in ethanol. The ligand and its metal complex were characterized by elemental analysis (CHN), ICP, thermal analysis (TGA), Fourier transform infrared spectroscopy (FT-IR), ¹HNMR, and ¹³C NMR techniques. The complex was found to be an efficient catalyst and reusable in the selective oxidation of sulfides to the corresponding sulfoxides without the formation of any sulfone using the green oxidant, H₂O₂, at room temperature and under solvent-free conditions.

Keywords: Amino acid; Schiff base; copper complex; catalyst; selective oxidation; oxidation of sulfides.

Introduction

During the past years, significant attention has been paid to the chemistry of Schiff bases and their metal complexes [1-3]. Schiff bases are an important group of ligands in coordination chemistry [4-6]. The condensation of primary amines and carbonyl compounds produces Schiff base that was reported by Hugo Schiff in 1864 [7] for the first time. The general structure of these compounds was represented by the general formula R₃R₂C=NR₁. Schiff bases are generally excellent chelating agent with metals [8], especially when a functional group like OH or SH is present near to the azomethine. Complexes of Schiff bases

with some transition metals like Cu (II) [9], Co (II), Ni (II), Zn (II) [10], Ti (IV) [11], Sn (IV), and Te (V) [6] show notable biological properties [12] and catalytic activity [13-15]. Schiff base complexes have many advantages such as cheapness, easy synthesis, selectivity in reactions and chemical and thermal stability, therefore they are an important and attractive group of catalysts for a variety of organic reactions.

Oxidation of sulfides is one of the fundamental and important reactions in organic chemistry because the oxidation process leads to the removal of sulfides which are toxic, funky, and existing in many homemade and

*Corresponding author: Ghodsieh Bagherzade

Tel: +98 (56) 32345192, Fax: +98 (56) 32345191

E-mail: gbagherzade@gmail.com, bagherzadeh@birjand.ac.ir

industrial wastewaters [19]. Moreover, oxidation products like sulfoxides are very important intermediates and are useful in biological molecules and medicinal chemistry which are obtained through selective oxidation of the corresponding sulfides [17].

Oxidation reaction has been tested with a wide variety of reagents and catalysts [18-21]. But that method suffers from serious disadvantages, namely high temperature [22], long reaction times [23], high cost, and generation of unfavorable by-products for the environment. The synthesis of a new, mild, simple, and efficient Schiff base complex has a significant value. In this study, the copper Schiff base complex was used as a reusable catalyst for the selective oxidation of sulfides to sulfoxides at short time, solvent-free condition, and room temperature.

Since amino acid participant in the formation of ligand has both nitrogen and oxygen, they readily coordinate with transition metal ions and show interesting physical, chemical, and potentially beneficial chemotherapeutic properties [24]. In the oxidation of sulfides, several oxidants can be used, such as hydrogen peroxide [25], molecular oxygen [26], tert butyl hydroperoxide [19], iodobenzene diacetate [27], sodium hypochlorite [28] and Urea-hydrogen peroxide/uronium hydrogen sulfate [29]. Among these oxidants, aqueous hydrogen peroxide is a pleasant choice, because of its easy availability, cheapness, easy operation, its compatibility with the environment, and generates innocuous water as the only by-product in the reaction [30]. To begin this study, thioanisole was chosen as an appropriate model and influence of different reaction parameters, such as the amount of reagent, oxidant, catalyst, temperature, time, and solvent in order

to find out the optimum conditions for the oxidation reaction.

Sulfoxidation was also studied with different catalysts and the results were compared with the results of our synthesized Schiff base complex. In all cases, our synthesized catalyst, in milder conditions and in shorter time had higher efficiency.

Experimental

General

All the chemicals and solvents employed for the synthesis were purchased from Merck or Aldrich chemical companies and used without further purification. 4-Chloro3-formylcoumarin was synthesized by using literature procedures [31].

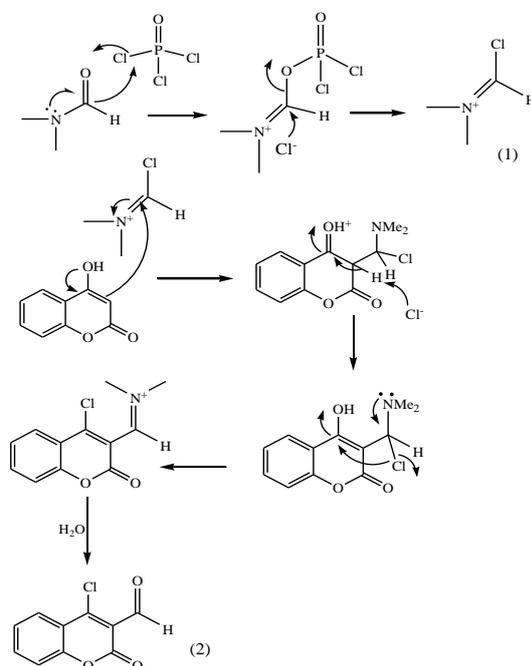
The Fourier transform infrared (FT-IR) spectra were recorded on a Shimadzu FT-IR spectrometer (4000 to 400 cm^{-1}) in KBr pellets. ^1H NMR and ^{13}C NMR spectra were recorded in ppm in CDCl_3 on a Bruker Avance DPX-400 and 250 instrument using TMS as an internal standard. The C, H, and N contents were determined using Costech 4010 CHNS elemental analyzer. Thermal gravimetric analysis (TGA) was performed using flowing N_2 at a heating rate of 10 $^\circ\text{C min}^{-1}$ on a Shimadzu thermogravimetric analyzer (TG-50). The contents of copper in the sample were determined by inductively coupled plasma-optima emission spectrometry (ICP-OES) using a Perkin Elmer Optima 8000. The purity of the products and the progress of the reactions were checked by thin layer chromatography (TLC) and Gas chromatography (GC). GC analyses were performed on Shimadzu GC-17A.

Synthesis of 4-chloro3-formylcoumarin

Phosphorus oxychloride (5.4 mL, 60 mmol) was added dropwise and with

stirring to dry N,N-Dimethylformamide (DMF) (20 mL) at 0 °C (cooled in ice). The prepared reagent cooled in ice, was added dropwise and with stirring to a solution of 4-hydroxy coumarin (3.2 g, 20 mmol) in dry DMF (15 mL). After adding all the formylating agent, the reaction mixture had reached 55

65°C. It was then cooled and poured onto crushed ice. The yellow precipitate was filtered off and recrystallized from 2:1 acetone–water to give yellow crystals (3 g, 72%), mp 125 °C. The mechanism of this reaction was shown in Scheme1.



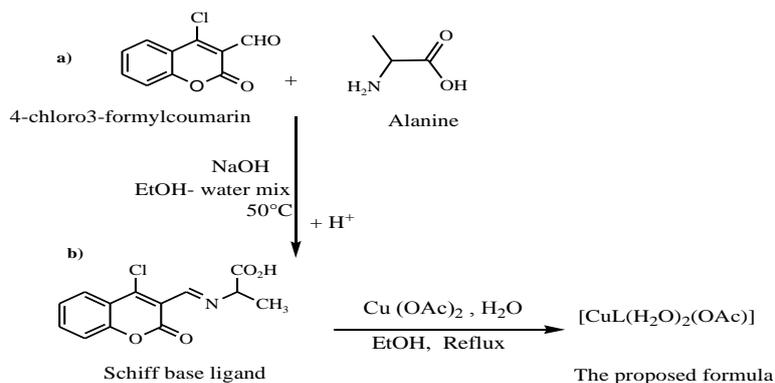
Scheme 1. Mechanism of synthesis of 4-Chloro-3-formylcoumarin from 4- hydroxycoumarin

Synthesis of Schiff base ligand

The Schiff base ligand was synthesized as per the following literature procedure [32].

Alanine (10 mmol, 0.89 g) was added to an aqueous solution (30 mL) of sodium hydroxide (10 mmol, 0.4 g), and the mixture was stirred for 30 min. After completion of CO₂ evolution, the warm solution of 4-chloro-3- formyl coumarin (10 mmol, 2.08 g) in 15 mL EtOH was added dropwise with stirring to an aqueous solution. The reaction was allowed to proceed for 90 min at 50 °C with stirring. The solvent was

removed by rotary evaporator until a milky color precipitate was formed. The solid product was purified by recrystallization from H₂O/EtOH mixture (2.37 g; 85%) Monosodium-Schiff base (1.00 mmol) was dissolved in 30 mL H₂O and this solution was adjusted to a pH 5.0-6.0 with 0.5 M HCl solution. The white solid was filtered off, washed with cold ethanol, dried and recrystallized from ethanol (1.99 g; 89.37%). The product was characterized by ¹H NMR, ¹³C NMR, CHN, and IR spectroscopy (Scheme 2a).



Scheme 2. Synthesis of (a) Schiff base ligand (b) its copper complex

Synthesis of $[\text{Cu}(\text{L})(\text{H}_2\text{O})_2(\text{OAc})]$ complex

For the synthesis of the copper Schiff base complex (Scheme 2b), Schiff base ligand (5 mmol, 1.39 g) were dissolved in 25 mL ethanol. Also, $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (5 mmol, 0.998 g) was separately dissolved in 50 mL ethanol, then the metal solution was dropwise added to the ligand solution under magnetic stirring for 3-5 h at reflux condition. The reaction mixture was cooled to room temperature. The resulting precipitate of the complex was filtered and washed with ethanol and diethyl ether several times until clear filtrate. Finally, the green resulting powdered complex was dried under vacuum system, (1.7 g, 78%). as shown in Scheme 2b. The product was characterized by CHN, ICP and TGA (Figure 2).

General procedure for oxidation of sulfides

To find the optimized conditions, we investigated the oxidation of thioanisole as a model substrate using hydrogen peroxide. The results are summarized in Table 1. Hydrogen peroxide (2 mmol, 30%) was added to a mixture of thioanisole (1 mmol) and catalyst (0.5 mol %, 0.005 mmol, 2 mg), then the reaction mixture was stirred at 25 °C with a magnetic stirrer bar. The

progress and yield of the reactions were monitored by TLC and GC. After completion of the reaction, ethyl acetate, 3×2 mL was added, and the organic phase was extracted followed by evaporation of the solvent, on the other hand, the catalyst was washed with ethyl acetate and was recycled with a centrifuge.

Results and discussion

Catalyst characterizations

The FT-IR spectra of the ligand and complex can be seen in Figure 1. In the FT-IR spectrum of the ligand, a sharp band appeared at 1614 cm^{-1} , which is attributed to the vibrations of the imine group [33,34] and shows the successful preparation of the Schiff base ligand (Figure 1a), while in the FT-IR spectra of the Schiff base complex, this peak shifted to a lower wavenumber and appeared at 1591 cm^{-1} . This shift could be attributed to the weakening of the $\text{C}=\text{N}$ bonds on adduct formation and this can be explained by the donation of electrons from the nitrogen atom to the empty d-orbitals of the metal atom [35]. Also, the spectrum of the free ligand shows a strong band at 1718 cm^{-1} assigned to the carbonyl stretching vibration, while after its coordination to the metal ion, this band was observed at 1701 cm^{-1} for copper complex (Figure 1b).

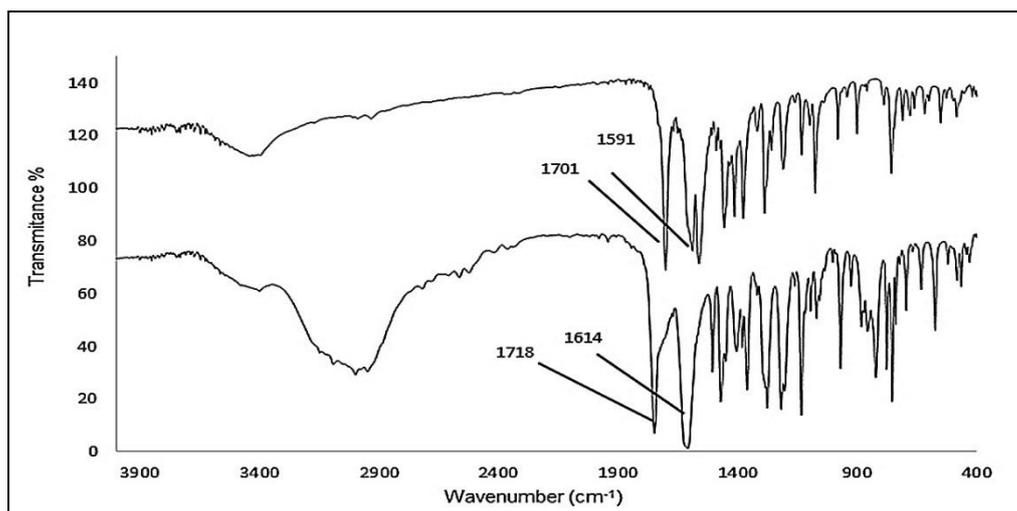


Figure 1. FT-IR spectra of (a) synthesized Schiff base ligand and (b) copper complex of Schiff base

The broadband in the region 2800 to 3300 cm^{-1} showed the presence of the intermolecular hydrogen bond due to carboxylic OH groups of Schiff bases, while this band disappears on complexation, due to chelation of the oxygen to the copper atom, and also The FT-IR spectra of complex exhibit characteristic bands of coordination water at the complex. 3450, 885, and 774 cm^{-1} assigned to $m(\text{OH}_2)$, $qr(\text{OH}_2)$, and $qW(\text{OH}_2)$ vibrations, respectively.

In the ^1H NMR spectra of the Schiff bases, the multiplet signals in the 7.23 to 7.86 ppm range are assigned to the carbon atoms of the aromatic ring. The chemical shift values of the azomethine hydrogen ($-\text{CH}=\text{N}-$) appeared at 8.160 ppm as singlet and integration intensity equivalent to one hydrogen. The ligand displays a singlet peak with integration equivalent to one hydrogen at 12.25 ppm corresponding to the hydrogen of the OH of an acidic group. Also, in the ^1H -NMR spectrum, the chemical shifts around 2.50 to 2.52 ppm can be attributed to the methylene and methine group protons of ligand, respectively, (see supplementary material).

The ^{13}C NMR spectra show 13 signals for the ligand. The signal for the

carbon atom of carboxylate appeared at 175.17 ppm and the peak at 163.49 ppm, assignable to the imine carbon atom that confirms the successful preparation of the Schiff base ligand and formation of imine band, Also, for carbon atoms attached to the chlorine and carbonyl group in the coumarin ring, signals appeared at 154.18 and 161.35 ppm, respectively. The signals for the carbon atoms of methine and methyl groups appeared at about 77.43 and 39.93 ppm, respectively and the signals of regions 151.60, 133.49, 125.45, 124.08, 123.86, 121.71, and 116.91 ppm are related to carbon atoms of coumarin ring (see supplementary material).

The chemical structure was confirmed by a combination of elemental analysis, ICP, and TGA analysis. The elemental analysis data showed the carbon (C), hydrogen (H), and nitrogen (N) contents in the ligand and complex and the amount of copper in the complex is determined by ICP spectrometer analysis. The characteristic data of the synthesized ligand and its metal complex were measured and copper complex shows 1:1 of metal: ligand stoichiometry ratio. Founded data of the

elemental analysis of the Schiff base ligand and synthesized Cu (II) Schiff base complex is in good agreement with the calculated values. By using the elemental analysis, ICP data can be a proposed formula of $[\text{CuL}(\text{H}_2\text{O})_2(\text{OAc})]$ for synthesized complex.

Anal. Calc. for the ligand ($\text{C}_{13}\text{H}_{10}\text{NO}_4\text{Cl}$): C 56.03, H 3.26, N 5.03. Found: C 57.1, H 3.69, N 5.1% and Anal. Calc. for copper (II) complex: C 41.3, H 3.47, N 3.21. Found: C 41.63, H 3.46, N 3.37%. ICP data showed that the Cu content was 15.1 wt %.

Thermal analyses give useful data about the thermal stability of the metal complexes and the metal-ligand bonds.

In the first step, TGA curve (Figure 2) of complex shows loss of 2 water molecules around 100 °C which corresponds to a weight loss of 8% (calculated weight loss is 8.25%). A further increase of temperature up to 250 °C leads to the elimination of organic fragment acetate with weight loss 13.27% (calculated weight loss is 13.46%). Further enhancement of temperature up to 600 °C leads to the decomposition of an organic moiety with the weight loss of 36.04% (calculated weight loss is 36.19%). Calculated weight loss of fragments in the proposed structure (Scheme 2b) was in good agreement with the founded weight loss of fragments in TGA curve.

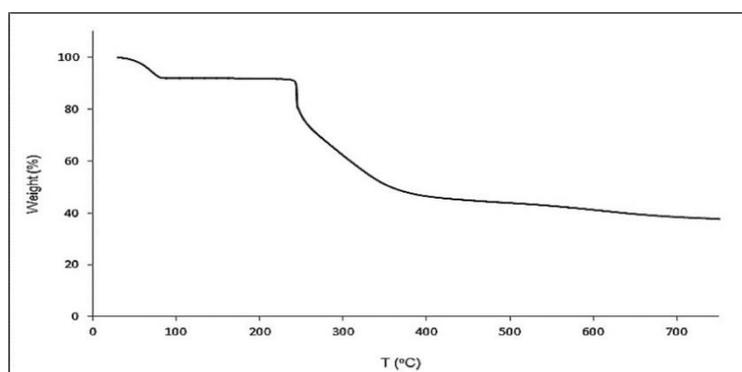


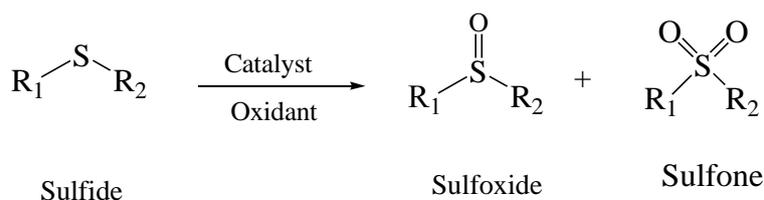
Figure 2. TGA curve of copper Schiff base complex driven of alanine and 4-chloro3- formyl coumarin between 25 °C-800 °C at a heating rate of 10 °C/min

Catalytic activity of the metal complex towards sulfide oxidation: Screening studies

Sulfoxides are important intermediates in the synthesis of a wide range of chemically and biologically active molecules. Syntheses of sulfoxides are usually achieved by oxidation of their corresponding sulfides. The oxidation of sulfides to sulfoxides is the most direct synthetic route to the latter, and numerous reagents and oxidative procedures are available for this transformation. However, many of them cause overoxidation to the

corresponding sulfones (Scheme 3). Hence, control of the reaction conditions plays an important role in avoiding the formation of oxidation side products, but this is often hard to achieve and therefore there is still considerable interest in the development of selective oxidants for this transformation [36,37].

In this study, selective oxidation of sulfides to the corresponding sulfoxide has been carried out using H_2O_2 as an oxidant and copper Schiff base complex as a catalyst.

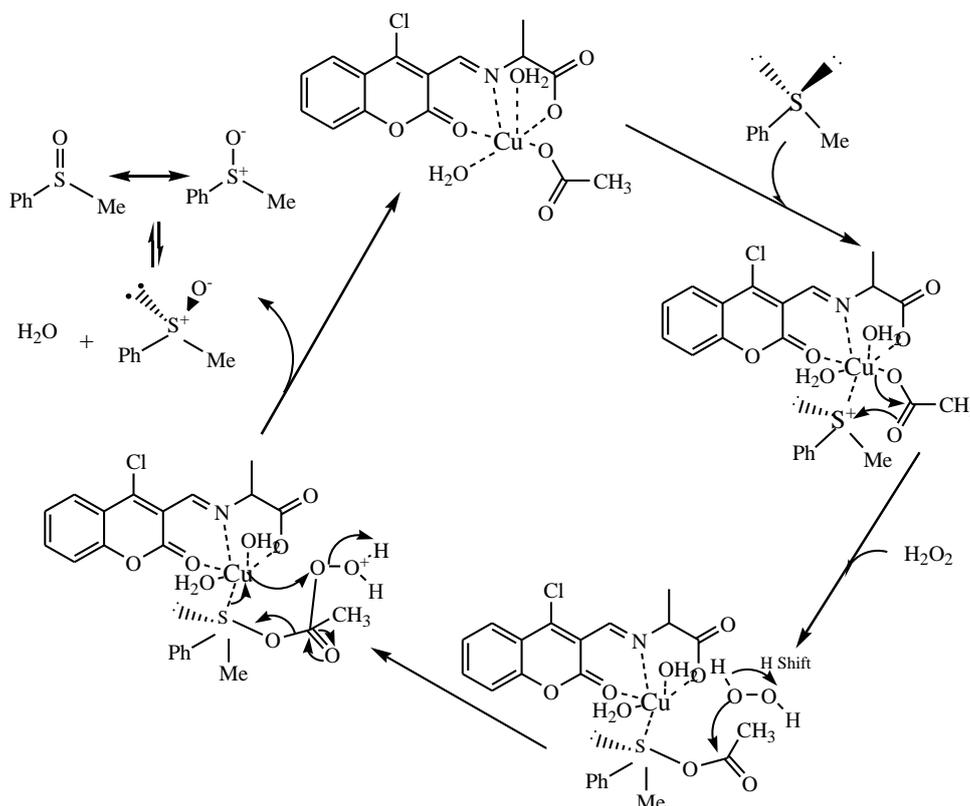


Scheme 3. Oxidation of sulfide

A possible mechanism for oxidation of the sulfide into the corresponding sulfoxides using H_2O_2 is shown in Scheme 4.

Table 1 shows the results of sulfides oxidation to their corresponding sulfoxides. In the current study, the formation of the sulfone is not observed

or the percentage of sulfone formed may be below the detection limit and the only product of the reaction was found to be sulfoxide in all cases. To investigate the efficiency of the copper complex of Schiff base as catalyst, it was applied in the selective oxidation of sulfide for obtaining sulfoxide.



Scheme 4. Proposed mechanism of selective oxidation of thioanisole

Primary studies were accomplished with thioanisole and H_2O_2 in the presence of catalytic amounts of $[\text{CuL}(\text{H}_2\text{O})_2 \text{OAc}]$ to find optimization reaction condition. A blank experiment

was performed in the absence of Catalyst that afforded only 10 % yield even after 12 h at room temperature. It emphasized that the presence of a catalyst was necessary for maximum

conversion. In order to have more investigations on the amount of catalyst on the product formation and reaction time, the model reaction was carried out in the presence of 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 mol% of the catalyst. 0.5 mol

% of catalyst were excellent for affording the desired sulfoxide. The increase in catalyst did not improve the yields. The results have been summarized in Figure 3.

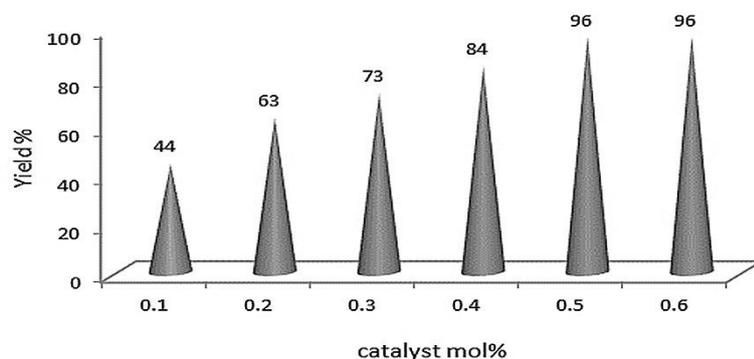


Figure 3. Optimization of amount of catalyst on oxidation of thioanisole, solvent-free conditions and room temperature within 45 min

The effect of temperature on the catalytic performance of synthesized catalyst was also studied (Figure 4). For this purpose, in solvent-free condition, different temperatures such as 25, 40, 60, and 75 °C were considered. Obviously, with an increase in the

temperature, selectivity for sulfoxide was decreased. Thus, 25 °C or room temperature is the optimum temperature for selective oxidation sulfide to sulfoxide without producing any sulfone.

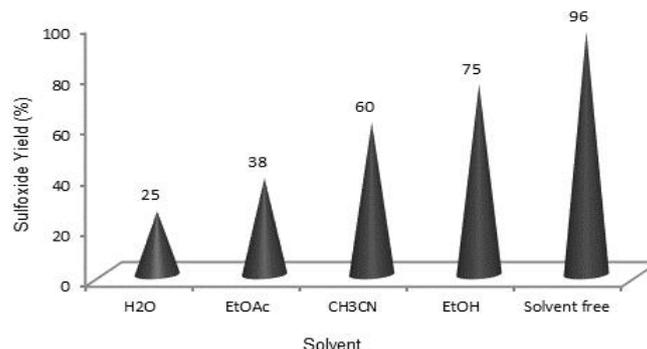


Figure 4. The screening of the temperature on the oxidation of thioanisole at solvent-free condition, 0.5 mol% catalyst, and H₂O₂ as oxidant

H₂O₂, TBHP, NaIO₄, KIO₄, and air also were used for check the effect of oxidant type. TBHP produced sulfone and sulfoxide with a yield of less than H₂O₂. On the other hand, air, KIO₄ and NaIO₄ and produced 10 - 30%

Sulfoxide. Thus, H₂O₂ has chosen as best oxidant due to a good yield, inexpensive cost, safe storage and also water generation as the only byproduct in the reaction, (Figure 5).

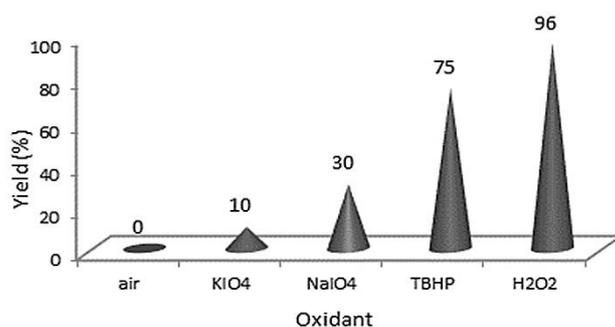


Figure 5. The screening of the amount of oxidant on the oxidation of thioanisole with synthesized catalyst in 45 min

On the other hand, the amount of oxidant in the oxidation of thioanisole has great influence. Figure 6 shows the effect of H₂O₂ concentration on

sulfoxidation. The amount of oxidation reaction was monitored using five different amounts of aqueous 30% H₂O₂ (1, 1.5, 2, 2.5, and 3 mmol).

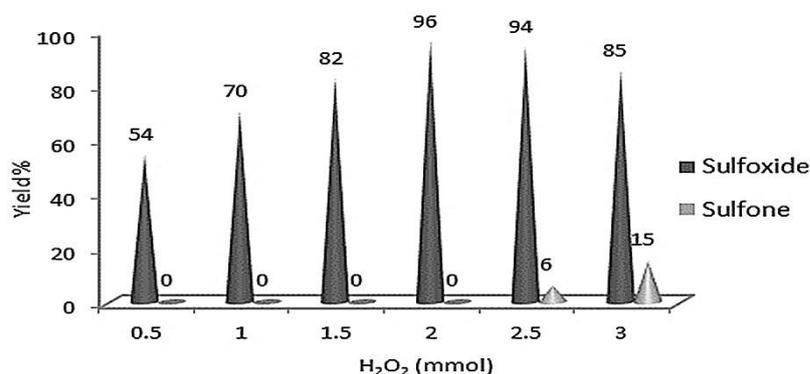
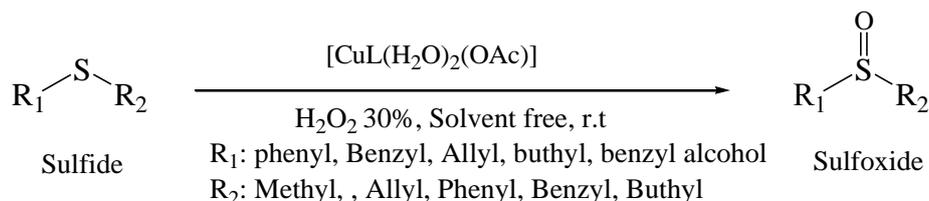


Figure 6. The screening of the amount of oxidant on the oxidation of thioanisole with the synthesized catalyst in 45 min, solvent-free conditions and at room temperature

Under the optimized conditions, thioanisole converted completely to sulfoxide at room temperature, solvent-free condition and in the presence of 0.5 mol% of [Cu L (H₂O)₂ (OAc)] and H₂O₂ within 45 min and 96% yield. In this way, sulfoxide was used as the only product (Scheme 3). To establish the general applicability of the method, various sulfides were subjected to the oxidation protocol under the catalytic influence. Table 1 shows the results obtained for the selective oxidation of these sulfides to the corresponding sulfoxides. All the reactions were run within a reasonable short time (1 to 3 h) and the sulfoxides were obtained in excellent yields (75 to 96%), therefore,

the reaction is selective for the transformation of sulfides to sulfoxides. Sulfides containing allyl and hydroxyl groups (Entries 2, 6, and 8) were selectively oxidized into their corresponding sulfoxides and these reactive functional groups remained intact. Diallyl sulfide was purely converted into diallyl sulfoxide without epoxidation. Although a catalyst may be active for C=C bond epoxidation and carbonylation of a hydroxyl group, but it is to be noted that high chemoselectivity of sulfoxidation was observed in the case of allyl phenyl sulfide and diallyl sulfide under the present reaction conditions.



Scheme 3. Selective oxidation of sulfides to sulfoxides with synthesized catalyst

Table 1. Catalytic oxidation of sulfides with new copper Schiff base complex in the solvent-free conditions and room temperature

Entry	Sulfides	Time (min)	Yield (%)
1		45	96
2		130	83
3		60	86
4		95	90
5		70	95
6		125	90
7		55	83
8		65	93

Reactions were run under solvent-free and room temperature (25°C) using H₂O₂ (2 mmol) and sulfides (1 mmol), in the presence of [Cu(L)(H₂O)₂OAc] (0.5 mol %). a) within 45 min. the yield of the reactions was monitored by TLC and GC. b) determined by NMR.

In order to determine the chemoselectivity of catalyst under the earlier mentioned conditions, some competitive reactions were studied. Thus, the competitive oxidation of sulfides in the presence of benzyl alcohol, benzaldehyde, and thioanisole was checked. These experiments show that the method is applicable for the chemoselective oxidation of sulfides to sulfoxides in the presence of the earlier mentioned ones. Functional groups can be considered as a useful practical method for the oxidation of sulfides to sulfoxides without appreciable

oxidation of other functional groups. The optimal reaction conditions for the chemoselective oxidation of sulfides is 0.2 mmol of sulfide, 0.2 mmol of the competitive substrate, 0.4 mmol of 30 % H₂O₂, 1 mol% of the catalyst at room temperature, and 1 h continuous stirring, (Table 1, Entries 3, 4 and 8). The recovery and reuse of a catalyst are one of the most important issues for practical applications. After the reaction the complex could be recovered conveniently from the reaction system by subsequent catalytic runs. The reaction of thioanisole with 0.5 mol%

of copper Schiff base complex was selected under the optimized conditions, after the reaction was completed, the mixture was filtered with centrifuge and residual catalyst was washed with ethyl acetate and dried and then the reused catalyst was utilized for 6 runs by using fresh substrate. The results presented in

Figure 7 confirmed that complex could be recovered and reused 6 runs without any significant loss of the catalytic activity. The recovered complex had been characterized by FT-IR (Figure 8). No significant changes in the FT-IR spectra of the complex had been observed even after reused for six times cycles.

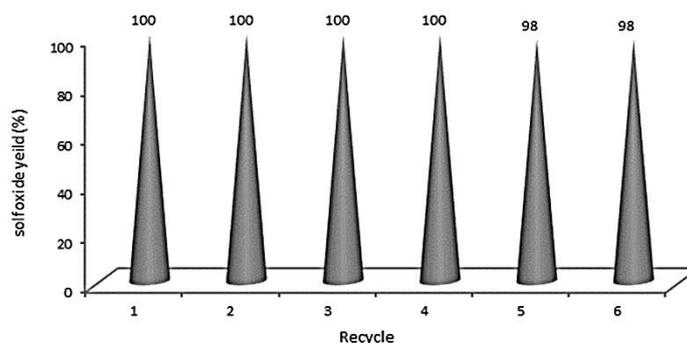


Figure 7. Catalyst recycling runs for sulfide oxidation with synthesized catalyst without significant loss of activity

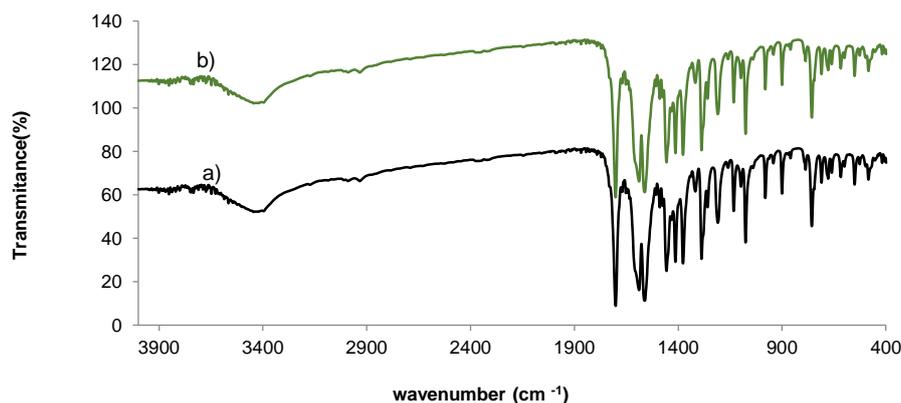


Figure 8. FT-IR spectra of the synthesized Schiff base complex (a) before and (b) after oxidation reaction of thioanisole during the re-use and without significant changes in the FT-IR spectrum

Eventually, the efficiency of newly synthesized catalyst for the oxidation reaction of thioanisole compared with results which have been reported (Table 2). The synthesized catalyst in

comparison with others that mentioned above, is efficient and in terms of the reaction time and yields are better, while less catalyst was required.

Table 2. Comparison of the catalytic activity synthesized copper Schiff base complex nanoparticles with some reported methods for the oxidation of thioanisole to the sulfoxide

Entry	Catalyst (mol%) ^{ref}	Conditions	Time(h)	Yield(%)
1	Cu(II) salt (5mol%) ¹⁹	t-BuOOH, CH ₃ CN, reflux	0.75	94
2	[Bmim][BF ₄](4ml) ³⁸	H ₂ O ₂ , RT	4	95
3	UHP, CC ³⁹	CDCl ₃ , O ₂ Irradiation :420 nm	1.5	57
4	Ru(II)(TMP)(CO) (0.2 mol%) ⁴⁰	TBHP	12	90
5	Cu Schiff base complex(0.01mmol) ⁴¹	H ₂ O ₂ , 50 °C	3	51
6	Zn Schiff base complex(0.01mmol) ⁴¹	H ₂ O ₂ , 50 °C	3	59
7	Cu(NO ₃) ₂ .3H ₂ O(10mol%) ⁴²	O ₂ , EtOH, 100 °C	10	39
8	Fe(NO ₃) ₃ .9H ₂ O(2.5 mol%) ⁴²	O ₂ , TFE, 80 °C	10	84
9	Vanadyl schiff base complex(0.1 mmol) ⁴³	H ₂ O ₂ , RT	8	90

Conclusion

In conclusion, a new chiral Schiff base ligand and its copper (II) complex from the reaction of 4-chloro3-formylcoumarin and alanine, amino acid as precursors was synthesized and characterized by elemental analysis, ICP, TGA, and spectral analysis like ¹H NMR, ¹³C NMR, UV-Vis, and FT-IR spectra. The effectiveness of this complex was demonstrated as catalysts for the green and selective oxidation of sulfides to the corresponding sulfoxides with hydrogen peroxide. In this system, the reactions can be carried out under solvent-free conditions as a green sustainable method using the copper complex as a catalyst in the presence of H₂O₂. An easy preparation method, mild reaction conditions, high yields of the products, short reaction times, and high selectivity and reusability, make this catalytic system very useful for oxidation reactions.

Acknowledgements

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Supplementary material

¹H NMR and ¹³C NMR of 4-chloro3-formylcoumarin and Schiff base ligand and products of sulfoxidation can be found in the supplementary material.

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