Almadani et al. *Iraqi Journal of Science, 2025, Vol. 66, No. 10, pp: 4091-4099*
DOI: 10.24996/ijs.2025.66.10.7

ISSN: 0067-2904

Synthesis of Schiff Base Complexes and Study their Applications as Catalysts for Esterification of Acetic Acid

Enas A Almadani, Dalal M Ibrahim*, Sara A Saleh
Department of Chemistry, Faculty of Science, Omar Al-Mukhtar University, Albyda, Libya

Received: 16/2/2024 Accepted: 17/10/2024 Published: 30/10/2025

Abstract

Schiff bases and their metal complexes have been found to exhibit high catalytic activity in a wide range of organic reactions, and their stability in the presence of moisture and high temperatures makes them particularly useful as catalysts in reactions that require elevated temperatures. In this study, new Schiff base (L) 2-((3-nitrophenylimino) methyl) phenol and new copper (II) and cobalt (II) complexes were synthesized from 3-nitrophenylamine with salicylaldehyde. The complexes were prepared by weighing the metal chloride and dissolved in methanol. The synthesised samples were characterized by FT-IR, UV-vis, SEM, and EDX and tested for catalytic activity as homogenous catalysts for esterification reactions. The free ligand's υ(C=N) stretching vibration was verified by the peak in the FT-IR spectra. The shift of this band to a lower frequency in the metal complexes' spectra, indicates that azomethine nitrogen participated in the coordination of metal ions in comparison to the parent ligand, metal complexes displayed a porous area, which might result from the ligand's cooperative contribution to the voids contracting for the metal ions to cause complications. The SEM image of the Schiff base had a surface morphology that was non-uniform, spherical, and crystalline. Synthesised catalysts were able to give the highest acid conversions of up to 77% since transition elements have the highest oxidation state when combined with Schiff bases, which also increase their Lewis acidity relative to the ligand. The esterification of acetic acid with ethanol using Co-complex at 80 ºC during the three hours of reaction time showed the highest acid conversions of 77%, and the conversion ratio using the Cu-complex was 76% at the same conditions, while the acid conversions without catalysts and with the ligand were 63.4% and 70.2%, respectively.

Keywords: Schiff bases, complexes, catalysts.

1. Introduction

Schiff bases and their complexes are a class of versatile compounds that are formed through the condensation reaction between primary amines and carbonyl compounds and have found extensive applications in various industrial fields. In addition, there are many different biological activities, such as antifungal, antiproliferative, antibacterial, antiviral, antimalarial, and antipyretic qualities [1- 3]. A significant number of Schiff base complexes have good catalytic activity in a variety of reactions and the presence of moisture. Their applications in both homogeneous and heterogeneous catalysis have been extensively reported in the past few years. Since complexation typically increases activity, knowledge of the properties of both ligands and metals might result in the synthesis of compounds with high levels of activity [4]. Research on the coordination behavior of these compounds has notably increased due to the impact of specific metals on their biological activity and their inherent chemical interest as

---

*Email: dalal.m.ibrahim@oum.edu.ly

multidentate ligands. In both homogeneous and heterogeneous reactions, Schiff base complexes of transition metal ions are effective catalysts. The biological activity of these complexes is influenced by several factors, including the type of ligands employed, the coordination sites involved, and the specific metal ions utilized, resulting in varying levels of activity [5]. The characteristics of different molecular systems are determined by the intermolecular hydrogen bonding between the OH and the C=N atom of the Schiff base, which is also important for many biological mechanisms [6]. Proton transfer is recognized as essential to the physicochemical characteristics and useful applications of Schiff bases, A basic chemical phenomenon known as intramolecular electron transfer pertains particularly to redox activities that take place in both synthetic and natural electron-transfer systems [7]. Research into systems containing copper, iron, zinc, and cobalt has generated a great deal of interest because these metals are trace elements displaying a wide range of pH, and they exhibit high biological activities when coordinated with certain metalloproteins; hence, they are used in different physiological processes. These metals can facilitate oxygen transport, electronic transfer reactions, or the storage of ions. Among the most commonly manufactured industrial organic chemicals are esters.

Fischer esterification is the most widely used method for synthesizing esters; however, it has significant drawbacks, including poor conversion and a lengthy reaction time that are mostly related to equilibrium establishment. Paints and varnishes, medicines, plastics and coatings, solvents like insecticides and herbicides, and biofuels like biodiesel, ethyl acetate, and methyl acetate are some of the most common examples of esterification products. Esters are widely used in food goods as flavorings and preservatives, as significant perfume ingredients, and in the soap and cosmetics sector [8-9]. This study aims to synthesise new Schiff base (L) (3-nitrophenylamine) and new copper (II) and cobalt (II) complexes using 3-nitrophenylamine with salicylaldehyde. Then use the synthesized ligand and complexes as catalysts in the esterification of acetic acid.

2. Materials and Method

2.1 Preparation of Ligand and metal complexes

Five grams of 3-nitrophenylamine 0.04mol were combined with 4ml of salicylaldehyde and 40ml of methanol. Leave the solution for 2 to 3 hours at room temperature until the solid product is formed. The resulting mixture was filtered to obtain the ligand as a crystalline powder, which was then washed with diethyl ether to purify it. The recrystallization process is done by hot ethanol.

2.2 Preparation of metal complexes

The formation of the new complex involves dissolving 0.25g of metal chloride 0.002mol from CuCl2 or CoCl2 dissolved in methanol, followed by 0.5g of the ligand that is completely dissolved in ethanol. The ligand-to-metal ratio is maintained at L:M (2:1). The complex solution is then heated on a stirrer for 1-2 hours until the color changes and then filtered to get the complex. The complexes were prepared by weighing the metal chloride and dissolved in methanol. The prepared samples were characterized by FT-IR, UV-vis, and melting point measurements (SEM and EDX) and tested for catalytic activity as homogenous catalysts for esterification reactions.

2.3 Catalytic Activity

The catalytic performance of the ligands and complexes was evaluated by conducting the esterification reactions of acetic acid and ethanol. The reactions were conducted in a stirred batch reflux system, where a two-neck round bottom flask was equipped with a water-cooler condenser, a thermometer, and a magnetic stirrer. The reactions were conducted at different reaction temperatures and different reaction times. The conversion of acetic acid was calculated using the following equation (1) [6].

$$\text{Percentage of conversion (\%)} = \frac{ai-at}{ai}\ x\ 100 \qquad (1)$$

3. Result and Discussion

3.1 Melting point measurements

Table 1 illustrates the melting points of ligands and complexes obtained via the melting point device.

Table 1: Melting points for both complexes and ligands

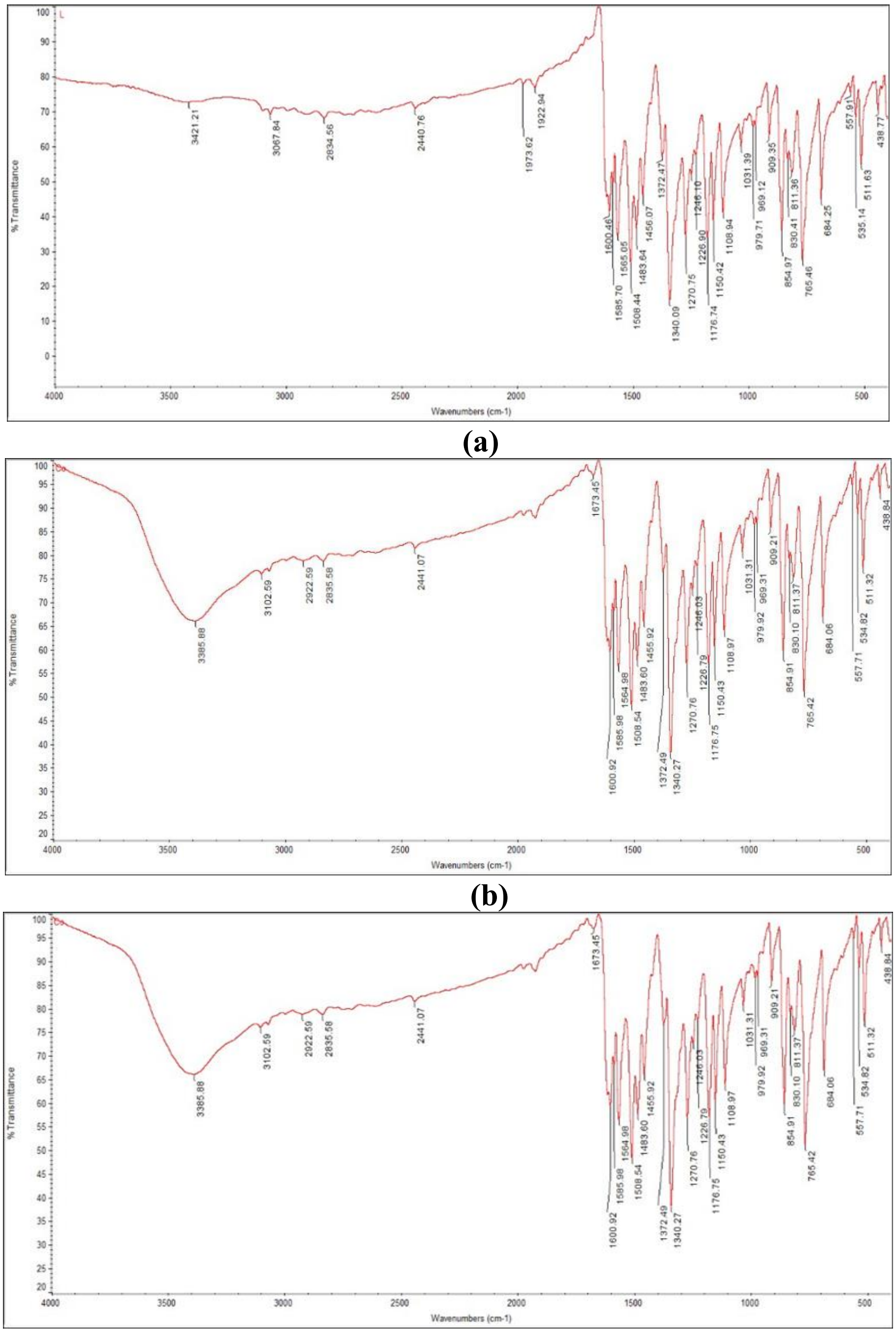
Complex	Melting point
Cu complex	186 ºC
Co complex	182-185 ºC
Schiff base	163 ºC

3.2 FTIR Spectroscopy

The IR spectrum of the ligand confirms the formation of an imine bond (-C=N-H). The actual band at 1627 cm-1 is assigned to the stretching vibration of the imines group, and the aromatic C-H band has the region 3037–3047 cm-1 in the ligand. Additionally, the OH vibrational stretch for the ligand occurred at 3473 and 3477 cm-1, respectively, as shown in Figure 1 (a). After complexation, the signals shifted downward in all the metal complexes. Due to the paramagnetic effect of all the M(II) ions. The appearance of new peaks was also considered as indication peaks. By comparison, it could be noticed that the υ(C=N) stretching vibration recorded at 1627 cm^{-1} for the free ligand shifted to a lower wavenumber position at 1603.5 cm^{-1}, accordingly the surrounding of the ligand had changed. In addition, the peak Co and Cu complexes of the M-O and M-N were observed at wavelengths of 500 and 438 cm-1, as shown in Figures 1 (b) and 1 (c).

3.3 Scanning Electron Microscopy (SEM)

Figure 2 presents the SEM images of Co-L and Cu-L complexes. It was noted that for non-symmetrical shapes, there was a transformation of the shape into a crystalline particle with a mixture of non-uniform spherical and crystalline shapes. The SEM image of the complex Cu-L shows a non-uniform crystal cluster shape, while the ligand shows uniform spherical crystal rectangle shapes. This variation may be attributed to the influence of the metal complex used to determine the morphology and particle size of the immobilized ligand, Cu-complex, and Co-complex [9]. SEM is a technique that provides high-resolution images of the surface form of a specimen, by rastering a focused beam of electrons across the specimen, thereby yielding a fine detail of its topography and morphology. Both electrons and atoms of the sample will interact, generating a variety of signals that result in providing information about the surface morphology and compositions of the sample.



(a)

(b)

(c)

Figure 1: FTIR Spectra of (a) ligand (L), (b) Cu(II) complex, (c) Co(II) complex.

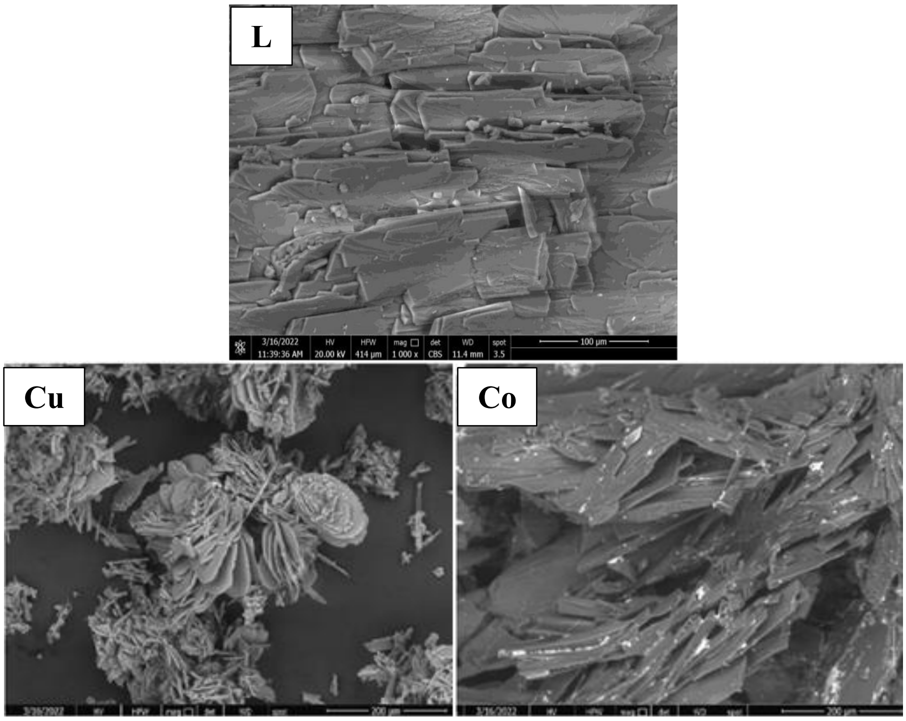


Figure 2: SEM images of Ligand and metal complexes

3.4 Energy Dispersive X-ray Spectroscopy (EDX)

The EDX data indicated that all samples contained elements, such as oxygen (O), carbon (C), nitrogen (Ne), and calcium (Ca). These elements represented the components of Ligand. It can be seen from Table 2 that the mean composition of elements in Ligand was O2 and N for all samples, which were in the range of 62–70% and 16–27%, respectively.

Table 2: Elemental compositions (Atomic) from EDX analysis of ligands and Complexes

Sample	C	N	O	Ca	CI	Cu	Co
Ligand	56.09	14.60	20.92	0.06			
Cu-Complex	53.76	8.36	19.83	0.13	10.71	6.91	
Co-Complex	56.24	16.85	23.32	0.14	1.66		0.52

3.5 Electronic spectra of the Ligand Complexes

The electronic spectra of the ligands and complexes are summarized in Table 3. Figure 3 shows different bands in the ranges of 200–250 nm and 300–400 nm can be seen in the electronic spectra of the ligand and metal complexes. The ligand (L) spectra exhibit a highly intense band with a wavelength of 250 nm, which is attributed to (π→π*) transitions. The C=N chromophore. The complex's UV-Vis spectrum showed two absorption peaks: at 250 nm and 380nm for (π→π*) and (d-d) transitions in the ligand field, at 370 nm for (n→π*), which is shifted due to the donation of lone pair electrons from nitrogen and oxygen atoms to the metal ions, and the last too broad peak at (350–380 nm) due to the charge transfer transition, which is responsible for the complex's deep orange color and is clear evidence of the metal ion coordination with nitrogen and oxygen atoms on two ligands.

Table 3: UV-VIS spectral data of ligands and complexes

Compound	**Ligand**	**Complex Co**	**Complex Cu**
λmax (nm)	250	250	250
	370	381	380

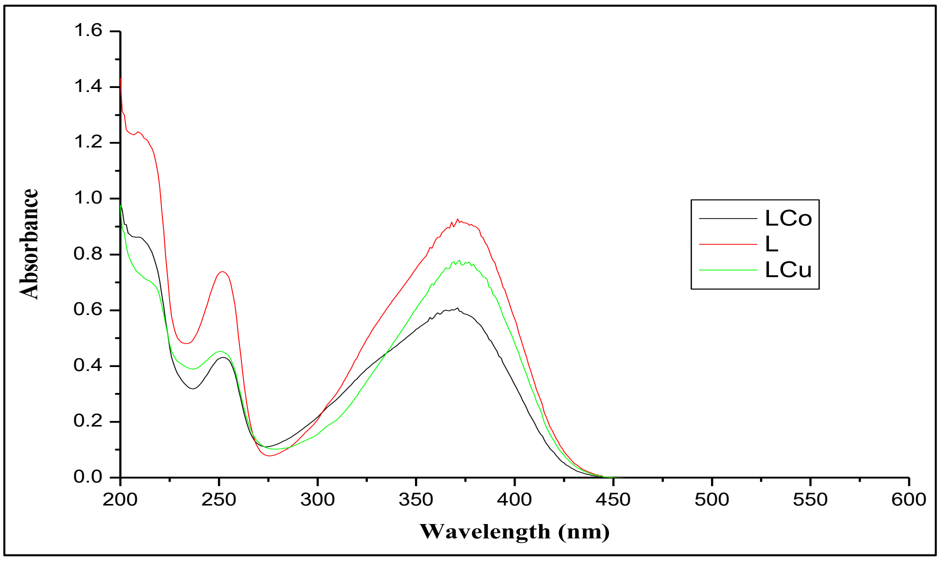


Figure 3: UV-visible spectrum analysis

3.6 Optimization of Esters Produced *via* the Conventional Method

The reactions were studied by either using ligands or complexes while fixing the other conditions.

3.6.1 Effects of Catalysts

The esterification of acetic acid with ethanol using catalysts at 80 °C is illustrated in Figure 4. It can be observed that the reaction occurred without a catalyst, and ligand complexes at 80 °C only gave 43.6 to 70.2% acid conversions, respectively. Compared to other transition metals (MCs), the first row of transition metals (TMMs) represents a particularly promising family of molecules with greater potential for application in the catalysis sector [8]. The Co and Cu complex catalysts resulted in a high acid conversion: 77.14% for Co-Complex and 76.4% for Cu-Complex. The acid conversion without catalysts and with the ligand as a catalyst was 63.4% and 70.2%, respectively. SEM analysis was done to analyze the morphology of the surface and it indicated that metal complexes had a more porous structure compared to the parent ligand. This could be explained by the fact that coordination of the ligand with metal ions contracted the voids, leading to the formation of a more porous region. This provided additional evidence for the complexities involved, which resulted in a slightly higher acidic conversion compared to the reaction with ligand and without catalyst.

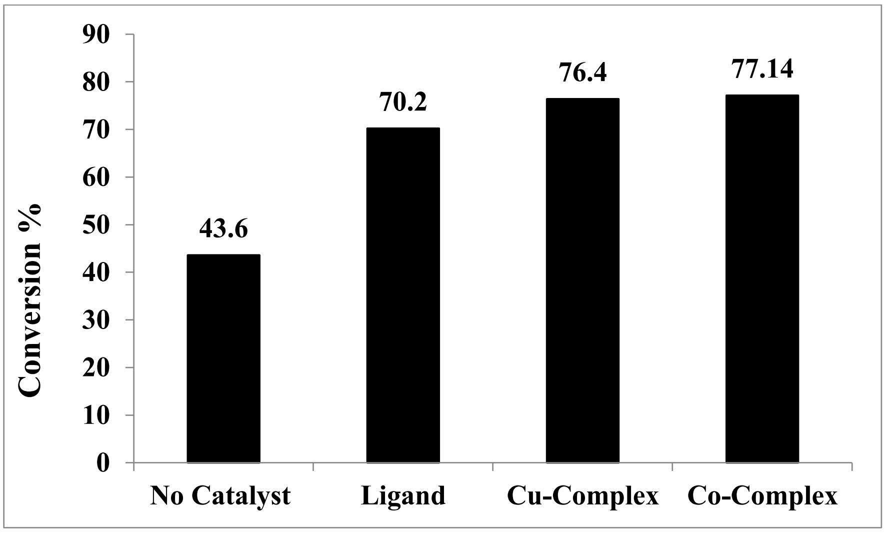


Figure 4: Effects of catalyst on esterification of acetic acid with ethanol at 80 ºC after 3 hours.

3.6.2 Effect of temperature

The reaction temperature had a strong effect on the esterification reaction. The study of the effect of temperature on the esterification reactions was carried out at various reaction temperatures while keeping the other parameters constant. Figure 5 illustrates the impact of three distinct reaction temperatures: 40, 60, and 80 ºC on the esterification of acetic acid with methanol. The results demonstrated that a rise in reaction temperature positively impacted the proportion of acetic acid conversion. The percentage of acid conversion increased with increasing the reaction temperature values from 40 ºC (69.71%), 60 ºC (71.83%), and 80 ºC (77.14%) at 180 min and Co-Complex. This can be explained by the use of ethanol as solvent, whose boiling point rose to 78.3°C, where the reaction could be under reflux conditions, thus minimizing vapour losses and establishing better reaction conditions [9].

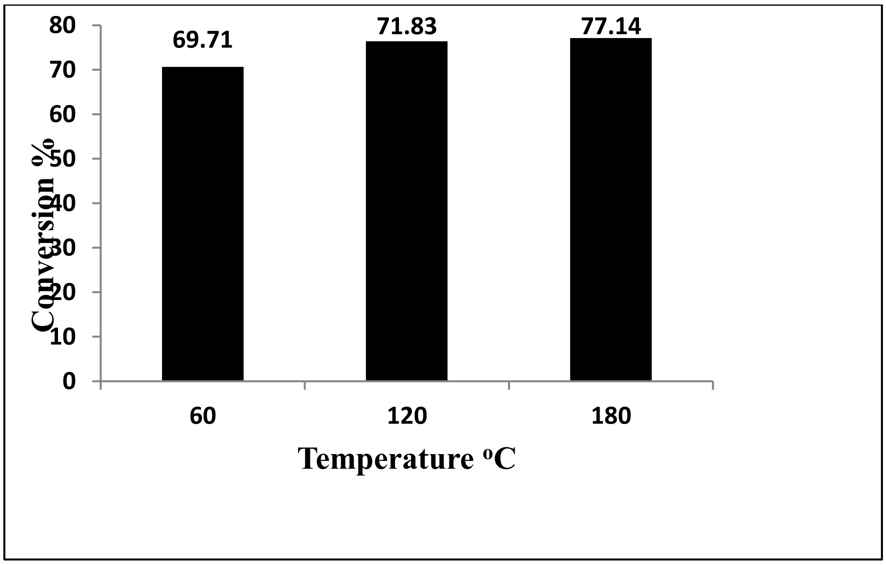


Figure 5: Effects of temperature on esterification of acetic acid with ethanol Reaction condition: Catalyst; Co-Complex, Reaction time; 3 hours

3.6.3 Effects of reaction time

Esterification reactions were carried out at various reaction times while keeping the other parameters constant. The reaction time profile for the esterification reaction of acetic acid with ethanol-catalyzed Co-Complex at 80 ºC is shown in Figure 6 The conversion of acetic acid increased with longer reaction times, as shown in Figure 6. During the first 60 minutes of the reaction time; the conversion percentage was 70.69%. Then, as the reaction time grew, the conversion percentage increased as well, reaching a percentage value of 77.14% after 180 minutes. 180 minutes later, the reaction had reached equilibrium, and the yield remained constant. Given the reversible nature of the reaction, a further increase in reaction time may have shifted the reaction backward [9]. The esterification reaction was expected to have a gradual increase in acid conversion with the increase in reaction time [10].

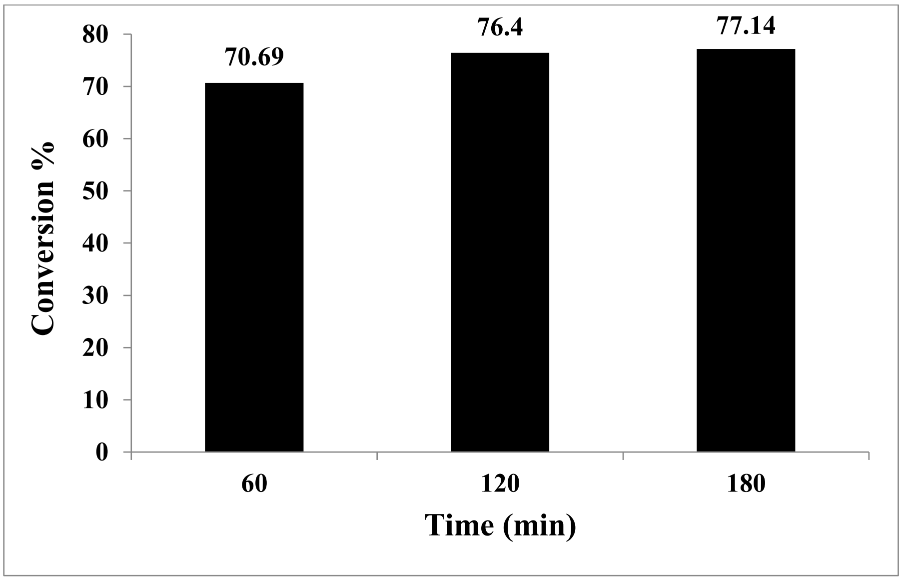


Figure 6: Effects of reaction time on esterification of acetic acid ethanol Reaction condition: Catalyst; Co-Complex, Reaction temperature; with 80 oC.

Conclusion

Two metal complexes have been synthesized from copper (II), cobalt (II), and ligand; the ligand and metal complexes have been used as catalysts for the esterification reaction. FT-IR, UV-vis, SEM, and EDX were used to characterize the ligand and metal complexes. The catalytic activities of these synthesized catalysts (Co and Cu complexes) were studied through the esterification reaction. Prepared catalysts gave the highest acid conversions of up to 77%. A main advantage of the proposed compounds is their biological activity. However, additional research is needed to expand the applicability of the proposed compounds. For instance, because of their structural variety, it is of great interest to create more novel derivatives of Schiff bases and their complexes with other transition metals.

References

[1] S. I. Al-Saeedi, L. H. Abdel-Rahman, A. M. Abu-Dief, S. M. Abdel-Fatah, T. M. Alotaibi, A. M. Alsalme, and A Nafady, "Catalytic oxidation of benzyl alcohol using nanosized Cu/Ni schiff-base complexes and their metal oxide nanoparticles," *Catalysts*, vol. 8, p. 452, 2018. https://doi.org/10.3390/catal8100452

[2] D. Ibrahim, H. Mohammem, and H. Lasema, "Synthesis and Characterization New Schiff Base Derivatives and Their Complexes with Zn (II) and Ni (II)," *Journal of Applied Chemistry*, vol. 12, pp. 24-34, 2019. DOI: 10.9790/5736-1208022434

[3] H. A. Al-Zubaidi, A. Z. Al-Bassam, and S. S. Alabdullah, "Facile Synthesis of Copper Nanocubes in Aqueous Phase for Catalytic Esterification Using Green-Conditions," *Iraqi Journal of Science*, 2024. https://doi.org/10.24996/ijs.2024.65.2.5

[4] M. J. Abubakar, M. Husaini, and A. H. Nuhu, "Synthesis and characterization of schiff base of 3-[(2-Hydroxy-phenylimino)-methyl]-6-methoxy-quinolin-2-ol and its metal complexes and their evaluation for antibacterial and antifungal activity," *Algerian Journal of Engineering and Technology*, vol. 2, pp. 029-036, 2020. http://dx.doi.org/10.5281/zenodo.3945251

[5] D. M. Ibrahim and S. A. Abdel-Latif, "Complexation, spectroscopic, thermal, magnetic and conductimetric studies on some 8-(arylazo) coumarins with divalent transition metal ions," *IOSR Journal of Applied Chemistry*, vol. 5, pp. 40-50, 2013.

[6] A. Szady-Chelmieniecka, E. Grech, Z. Rozwadowski, T. Dziembowska, W. Schilf, and B. Kamienski, "Multinuclear NMR study of the intramolecular hydrogen bond in Schiff–Mannich bases," *Journal of Molecular Structure*, vol. 565, pp. 125-128, 2001. https://doi.org/10.1016/S0022-2860(00)00788-2

[7] D. Lakhe and K. V. Mangaonkar, "Synthesis, characterization and antimicrobial activity of mixed ligands complexes of Mn (II), Co (II), Ni (II), Cu (II) and Fe (III) ions with N (5-nitro-2-hydroxybenzylidene)-2-chorobenzylamine and N-(5-nitro-2-hydroxy benzylidene)-4-aminobenzene-1-sulfonamide," *Journal of Chemical and Pharmaceutical Research*, vol. 4, pp. 4897-902, 2012.

[8] V. Lekha, J. George, S. Aswathi, and K. Rajesh, "Invitro Biological Studies and Characterisation of Schiff Base Complexes of Co (Ii), Cu (Ii), Ni (Ii) and Zr (Iv) Using Dfmpm and 2, 2-Diphenylethanamine," *Annals of the Romanian Society for Cell Biology*, vol. 25, pp. 12768-12782, 2021.

[9] Z. Khan, F. Javed, Z. Shamair, A. Hafeez, T. Fazal, A. Aslam, et al., "Current developments in esterification reaction: A review on process and parameters," *Journal of Industrial and Engineering Chemistry*, vol. 103, pp. 80-101, 2021. https://doi.org/10.1016/j.jiec.2021.07.018

[10] O. N. Syazwani, U. Rashid, M. S. Mastuli, and Y. H. Taufiq-Yap, "Esterification of palm fatty acid distillate (PFAD) to biodiesel using Bi-functional catalyst synthesized from waste angel wing shell (Cyrtopleura costata)," *Renewable Energy*, vol. 131, pp. 187-196, 2019. https://doi.org/10.1016/j.renene.2018.07.031