

RESEARCH ARTICLE

Synthesis, Characterization and Anticorrosion Studies of New Co(II), Ni(II), Cu(II), and Zn(II) Schiff Base Complexes

Awf A. R. Ahmed¹, Enass J. Waheed^{2*}, Ahmed T. Numan³

¹ General Directorate of Education Baghdad Rusafa First, Ministry of Education, Iraq

^{2,3} Department of Chemistry, College of Education for Pure Sciences, Ibn -Al-Haitham, University of Baghdad, Baghdad, Iraq.

Received: 10th March, 2021; Revised: 24th April, 2021; Accepted: 29th May, 2021; Available Online: 25th June, 2021

ABSTRACT

The research included preparation of new Schiff base (L) by two steps: preparation of precursor [bis(2-formyl-6-methoxyphenyl) succinate] (P) by reacting (3-methoxy salicyl aldehyde) with (succinoyl dichloride) as first step then react the prepared precursor (P) with (ethanedioamide) to have the new Schiff base [bis(2-((ethane thioyl imino) methyl)-6-methoxy phenyl) succinate] (L) as second step. Characterized compounds based on Mass spectra, ¹H, ¹³CNMR (for ligand (L)), FT-IR and UV spectrum, melting point, molar conduct, %C, %H, and %N, the percentage of the metal in complexes %M, magnetic susceptibility, while study corrosion inhibition (mild steel) in acid solution by weight loss. These measurements proved that by (Oxygen, Nitrogen, and Sulfur) atoms in the ligand, the metal ions are coordinated in a tetradentate form, and the tetrahedral structure of these complexes is suggested. Based on the measurement of micro elemental analysis (CHNS), the molar ratio appeared (2:1) (M:L). The complexes of [M₂(L)Cl₂]Cl₂ type, where M= Cobalt(ii), Nickel(ii), Copper(ii) and Zinc(ii). These products were determined aligned with two classes of bacterial; bacteria (G⁺) and (G⁻). The antibacterial effect of the metal complexes is greater than that of the ligand (free), according to the results of the bacterial activity test for the compounds. Results of corrosion inhibition of (L) and their complexes were determined by method (weight loss) in (0.2M) hydrochloric acid solution for mild steel.

Keywords: Schiff base, 3-methoxysalicylaldehyde, Metal complexes, corrosion inhibition.

International Journal of Drug Delivery Technology (2021); DOI: 10.25258/ijddt.11.2.32

How to cite this article: Ahmed AAR, Waheed EJ, Numan AT. Synthesis, Characterization and Anticorrosion Studies of New Co(II), Ni(II), Cu(II) and Zn(II) Schiff Base Complexes. International Journal of Drug Delivery Technology. 2021;11(2):414-422.

Source of support: Nil.

Conflict of interest: None

INTRODUCTION

By reacting ketone or aldehyde with any primary amine in specific conditions, we obtain Schiff bases. According to the structural composition, the compounds of imine or azomethine (Schiff base) are analog of nitrogen for (ketone or aldehyde), in (C=O) group was replaced by group (CH=N). Ligands of Schiff base are readily synthesized, and their complexes are formed by reacting with almost all metal ions.^{1,2} Due to the exciting and essential properties of Schiff bases and their complexes, a large number of them have been studied, for example, the complex ability towards some toxic metals and the transfer of an amino group, the catalytic activity of biological activity in the hydrogenation of olefins, color properties.³ Numerous reports over the past few years have shown applications of Schiff bases to biology, including antifungal, antimalarial, antibacterial, anticancer, anti-inflammatory, and antiviral activity. Also, it participates in many reactions as a catalyst such as reduction of thionyl chloride, aldol reaction,

epoxidation of alkenes, the reduction reaction of ketones, hydrosilylation of ketones, oxidation of organic compounds, Diels–Alder reaction, polymerization reaction, Henry reaction, anti-diabetic performances and anti-oxidant, anti-corrosion activity.^{4,5} In many enzyme reactions containing the reaction of (carbonyl or amino group) of a compound with an enzyme, Schiff bases were a vital intermediate.^{6,7} Because of the great interest in the remarkable structures of their metallic complexes, the wide range of practical applications for them has been widely studied. It can create multidentate complexes with two or more metals at its center, which is unique. It has been found that Schiff base ligands which are coordinated with metals such as zinc and cobalt exhibit many biological activities and more potent compared to free ligands due to the presence of the metal moieties. The Schiff bases with less or no activity became more powerful when chelation with metal ions was indicated in many reports. Due to the ability of Schiff bases to bind metals, they are often used as ligands in coordination

*Author for Correspondence: enasshassanali@gmail.com

chemistry to form metal complexes.⁸⁻¹⁰ Vanillin is the main flavor component in vanilla beans and is a pleasant aromatic compound. Vanillin is widely used as an ingredient in foods and animal feeds as a primary alternative to natural vanilla. It serves as a pharmaceutical intermediate, odor-masking product, a food flavoring, and as a fragrance in perfumes. A massive number of vanillin-derived Schiff bases complexes have been reported 225-231.¹¹

In this research work, we mention the formation of ligands and their complexes, the tetradentate Schiff bases ligand (L) formed from the condensation of the precursor (P) with ethanethioamide, and the resulting ligand (L) was reacted with Co(ii), Ni(ii), Cu(ii), and Zn(III) to obtain solid complexes. The prepared compounds were diagnosed in several different ways.

MATERIALS AND METHODS

Chemicals and Measuring Tools

Entirely used elements are of the maximum purity (BDH, Fluka, or Merck) without refining. Elemental Analyzer EURO EA 3000, Micro elemental analysis for carbon, hydrogen, and nitrogen has been determined. Absorption spectrums have been documented by Shimadzu Uv-160 spectrophotometer for complexes solution in Dimethylsulfoxide (DMSO) at laboratory temperature with (1 cm) cell of quartz. FT-IR spectrums have been documented with Shimadzu-FTIR-8300, in (4000–400) cm^{-1} range via potassium bromide disc and (4000–200) cm^{-1} range via CsI disc. Using the conductivity meter EUTECH CON 150, the conductivity measurements at laboratory temperature and (10^{-3}) M concentration of the sample solution in the Dimethyl sulfoxide solvent were conducted. With the Sherwood Scientific's Magnetic Susceptibility Balances, magnetic moments (μ_{eff} BM) at 25°C have been identified. The metallic ratios have been measured using an atomic absorption procedure by Shimadzu AA-680 Shimadzu.¹

H-NMR spectrum had been calculated on a 300 MHz NMR spectrometer in DMSO. The antibacterial screening was done at the Biology Department at the University of Baghdad, Iraq. By a Stuart SMP10 Melting Point Apparatus with an open capillary tube, the melting point of the prepared compounds was measured. A corrosion test was done at the Chemistry department. Using the potentiometer titration method on a (686 titro processor: 665 dosimat-Metrohm Swiss), the chlorine content was determined in the prepared compounds at Ibn Sina Company Baghdad, Iraq.

Formulation of New Schiff base Ligand (L)

The synthesis of the (L) includes two steps: The first one is a synthesis of the precursor (P) which was resulted from the reaction of 3-methoxy salicylaldehyde with succinoyl dichloride. The second step was the synthesis of the new Schiff base ligand by the concentration of the product of step one (P) with ethanethioamide in absolute ethanol.

1-Formulation of Precursor (P)

To 3-methoxy salicylaldehyde (10mmole, 1.5215g) in absolute ethanol (15 mL) was added potassium hydroxide (5 mmole,

0.28 g) in water (5 mL). The mixture was warmed, and succinoyl dichloride (10mmole, 1.5498 g) has been added dropwise to the reaction flask with continuous stirring for (1–3) hours until the appearance of the precipitate. Then, after filtering the precipitate with diethyl ether, it was washed and allowed to dry at lab temperature, yield: 72.1%, m.p: (105)°C.

2-Formulation of New Schiff Base Ligand (L)

(L) has been organized by condensing (P) compound (10 mmole, 3.8636 g) that liquefied in (15 mL) absolute ethanol and refluxed with (10 mmole, 0.7513 g) of ethanethioamide for 3 hours and then by adding a few drops of glacial acetic acid were added, a distinct solution (color) is found. The prepared L, has isolated after the mixture volume has lessened to half through vaporization and recrystallization using absolute hot ethanol (Figure 1) and allowed to dry at lab temperature. Scheme 1 shows how the ligand formulation yields: 64.8%, m.p: 155°C.

Formulation of Metal Complexes

The ethanolic solution (15 mL) of the corresponding metal chloride salts ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, and ZnCl_2) (10mmole, (4.7586 to 2.7256 g) was mixed with the ethanolic solution (15 mL) of ligand Schiff base (L) (10 mmole, 3.8206 g) and then refluxed for 4 hours. The product has been filtered; then, it was washed and at laboratory temperature allowed to dry with absolute ethanol at laboratory temperature. The metal complexes were synthesized at a ratio of (2:1) (M:L). Table 1 illustrates some properties of these compounds.

Gravity Measurements

By diluting the reagent degree of 37% hydrochloric acid with double distilled water, a solution (0.2 M) HCl was syntheses. In order to conduct inhibition studies, inhibitor solutions at concentrations of 100, 300, and 900 parts per million were

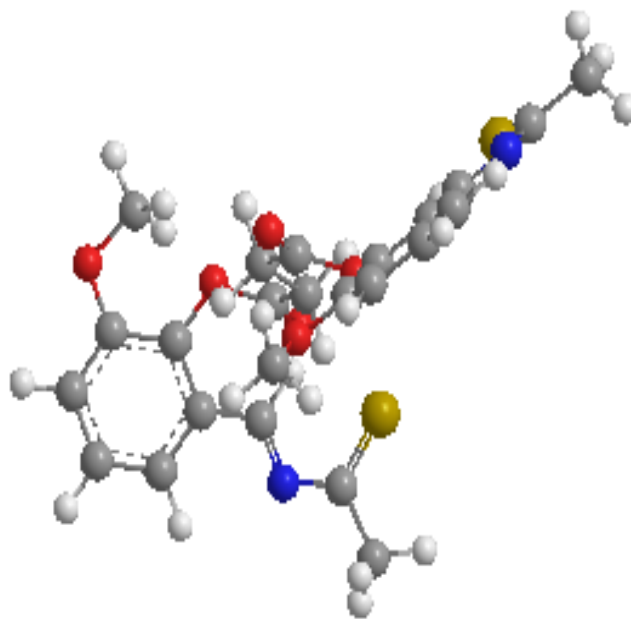
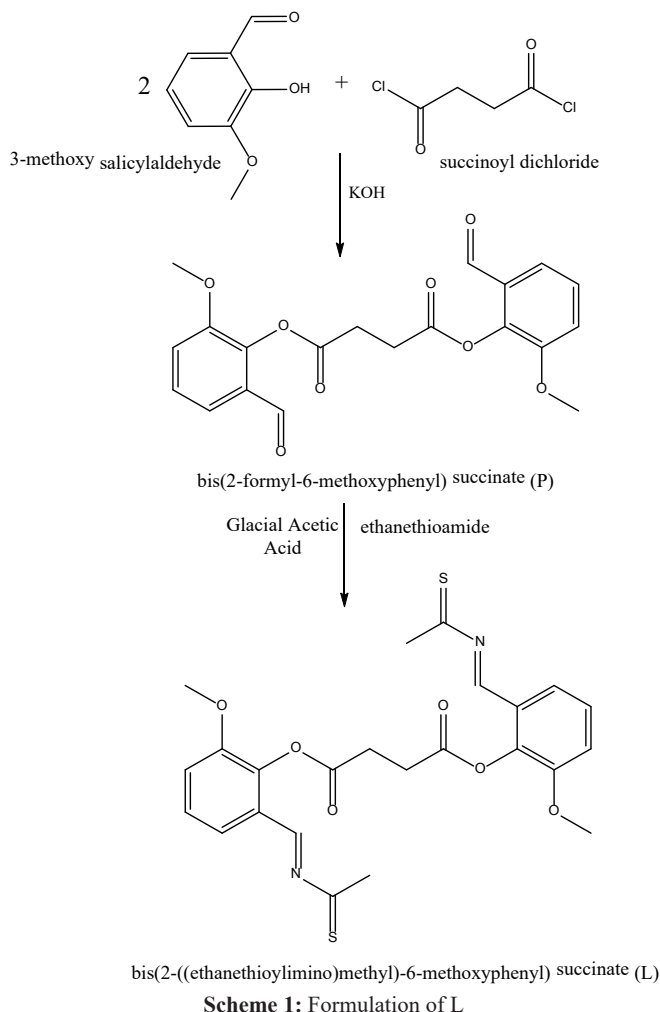


Figure 1: 3D –Structure of (L)

used, which were syntheses by dissolving the amount of ligand (L) and its metallic complexes in 80 mL of (0.2 M hydrochloric acid). Beakers with a capacity of 100 mL are labeled from 1 to 16, each containing (0.2 M hydrochloric acid) solution, and have been used in a weight loss experiment. Empty, the first beaker was reserved, while the rest of the beakers contained a ligand (L) and its metallic complexes at concentrations of 100, 300, and 900 parts per million. At lab temperature, it has all placed. With emery paper, mild steel

coupons having 10×10×1 mm size were abraded, and MeOH, MeCOMe, and H₂O were washed, then dried, and weighed. With the help of glass holders, the coupons were immersed in the prepared solutions for 3 days. Before immersion, weights of the specimens were observed. The specimens were removed after being immersed for 72 hours in the solutions, polished (emery papers), washed (distilled water), degreased (acetone), dried in the oven, and then weighed again. The loss of the W weights was calculated by the following equation:-



$$\Delta W = \frac{m_1 - m_2}{A} \dots \dots \dots (1)$$

m_1 = the mass of the specimen (before corrosion)
 m_2 = the mass of the specimen (after corrosion)
 A = the exposed area of the specimen

Through the following equation, the corrosion rate was calculated (mm^{-1})¹²:

$$\text{Corrosion rate, CR} = \frac{87.6 \times W}{D \cdot A \cdot t} \dots \dots \dots (2)$$

W = the weight loss (mg).
 D = the density of the specimen (7.85 g/cm³)
 A = the surface area of the specimen (cm²)
 t = the time of exposure of the sample (hours)

Through the following equation, the efficiency of the inhibitor was calculated¹³:

$$\text{Inhibition efficiency, \%IE} = \frac{\Delta W_1 - \Delta W_2}{\Delta W_1} \times 100 \dots \dots \dots (3)$$

ΔW_1 = the weight loss without inhibitor
 ΔW_2 = the weight loss with inhibitor

Biological Activity Study

The newly synthesized ligand and all complexes have been investigated alongside bacteria (*S. aureus*)(G⁺) and bacteria (*E. coli*)(G⁻) species by disk diffusion operation.^{14,15} Muller Hinton Agar was used to culture the test bacteria. By using (DMSO) as a solvent and with a single concentration (C) 1×10⁻³M, the chemical solutions used in the biological study were prepared. At 37°C, the dishes wire incubated for an entire day. The formed inhibiting region by compounds against the specific tested bacterial strain can evaluate the antibacterial efficacies of the prepared compounds. In order to calculate the

Table 1: Some physical data of the prepared compounds

Com.	Color	M.wt	m. p (°C)	Found (Calc.) (%)						Λ_M (cm ² Ω ⁻¹ Mol ⁻¹)
				M	C	H	N	S	Cl	
(L)	Pale Yellow	500.58	155 °C	-	57.60 (57.59)	4.82 (4.83)	5.59 (5.60)	12.82 (12.81)	-	-
Co(II)-Complex	Green	760.25	250 °C	15.59 (15.50)	37.90 (37.92)	3.19 (3.18)	3.69 (3.68)	8.43 (8.41)	18.67 (18.65)	79.13
Ni(II)-Complex	Light Brown	755.85	261 °C	15.42 (15.45)	37.95 (37.94)	3.17 (3.18)	3.70 (3.69)	8.45 (8.47)	18.63 (18.65)	76.25
Cu(II)-Complex	Pale Green	769.48	287 °C	16.50 (16.52)	37.44 (37.46)	3.13 (3.12)	3.66 (3.64)	8.33 (8.32)	18.40 (18.41)	71.21
Zn(II)-Complex	Yellow	773.14	269 °C	16.95 (16.94)	37.30 (37.28)	3.11 (3.13)	3.63 (3.62)	8.28 (8.29)	18.45 (18.43)	63.01

area of growth inhibition for each sample, the average volume obtained for three individual replicates was used.

RESULTS AND DISCUSSION

General Considerations

The compounds are colored crystalline powders that have higher melting points than the ligand; the compounds were dissolved in common solvents such as ethanol, dimethylformamide, dimethyl sulfoxide, and thermally stable. Their atomic absorbance measured results for all complexes have shown approximated magnitudes as compared them with theoretical values.

Physical Characteristics and Elemental Investigation

The physical characteristics and outcomes taken from CHN investigation and metal substances of the arranged compounds are explained in Table 1. The investigative values had been acceptable with planned magnitudes. The molecular procedure

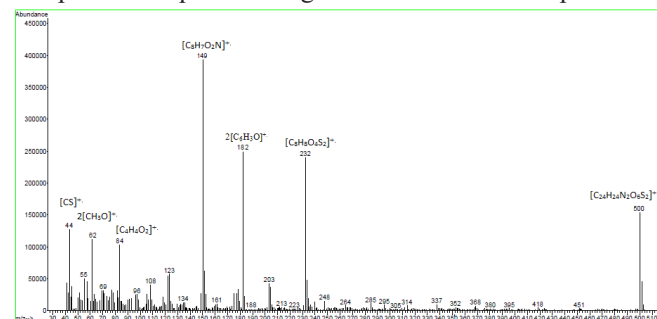


Figure 2: Mass band of (L)

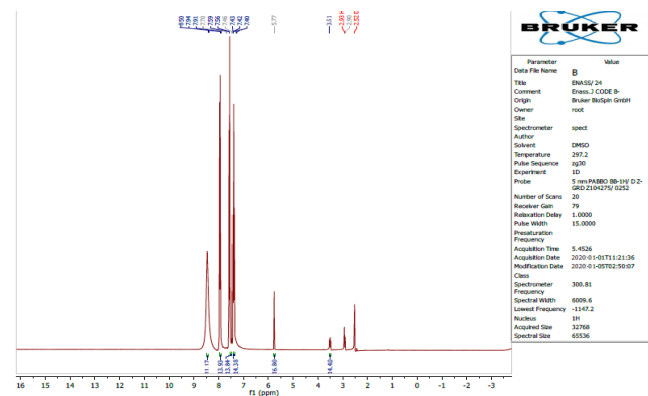


Figure 3: ¹H-NMR band of Schiff base ligand (L)

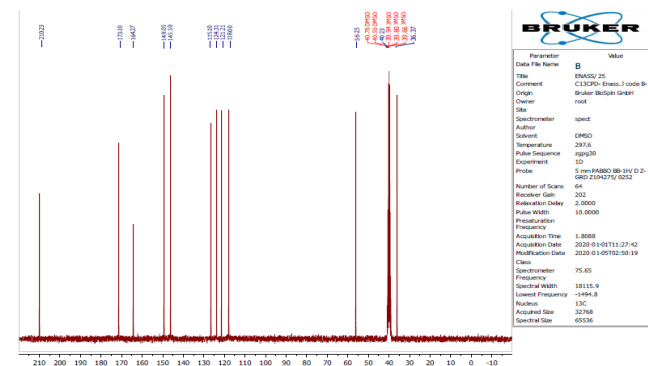


Figure 4: ¹³C-NMR band of Schiff base ligand (L)

of L and its metallic complexes had been proposed in relation to these data jointly with those acquired from spectral in addition to the magnetic susceptibility of metal complexes. Every (2:1) metal to solid ligand complex has been separated.

Mass Band of Ligand (L)

The mass band of (L) as in Figure 2 depicts $[M]^+$. A peak at m/z 500 related to $[C_{24}H_{24}N_2O_6S_2]^+$ ion. The peaks at $m/z=232$, 182, 149, 84, 62, 44, and others are due to different fragments. The intensity of the remaining peaks are in line corresponds to their abundance. Other fragments are summarized in Table 2.^{16,17}

NMR Studies for the Ligand (L)

A strong signal appeared at (8.35-8.20 ppm) for the spectrum (¹HNMR) in ligand, Figure 3 related to the proton of azomethine group, which was confirmed by the appearance of a signal at (164.27–162.51 ppm) for spectrum (¹³CNMR) in ligand, Figure 4.

At (7.300–7.120 ppm) all aromatic protons and their absorption were counted. Finally, a signal appeared at (4.01 ppm) for the spectrum (¹HNMR) related to methoxyl protons of ligand resulting from 3-methoxy salicylaldehyde, which was confirmed by the appearance of signals at (56.60–56.25 ppm) for the spectrum (¹³CNMR). The other results are summarized in Tables 3 and 4.¹⁸⁻²⁰

FT-IR Spectrums Study

In Table 5, data for (FT-IR) spectra of (L) and its metallic complexes are presented, which could be involved in chelation process to identify the coordination sites that could be; the spectra of the FT-IR complexes were compared with those of the ligand (free) as in Figures 5 and 6. When making the comparison, it was observed that a band appeared at

Table 2: Mass spectral details of (L)

Fragments	Formula weight $g.mole^{-1}$	Relative abundance%
$[C_{24}H_{24}N_2O_6S_2]^+$	500	33.33
$[C_8H_8O_4S_2]^+$	232	53.33
$[C_6H_3O]^+2$	182	55.56
$[C_8H_7O_2N]^+$	149	88.89
$[C_4H_4O_2]^+$	84	24.44
$2[CH_3O]^+$	62	27.78
$[CS]^+$	44	28.89

Table 3: Show data (¹H-NMR) and chemical shift in (DMSO-d⁶) for (L)

Comp.	Active groups	ppm (δ)
(L)	H of C1 -CH=N group	8.50 (s)
	H of C2 aromatic group	(7.91-7.94) (d)
	H of C3 aromatic group	(7.59-7.56) (d)
	H of C4 aromatic group	(7.43-7.40) (t)
	3H of C5	5.77 (s)
	2H of C6	3.51 (t)
	3H of C7	2.9 (s)

(1649 cm^{-1}) in the ligand (free) spectrum due to the vibration of the stretching $\nu(\text{C}=\text{N})$. In the spectrum (FT-IR) of the complexes, it was observed that this band was shifted to

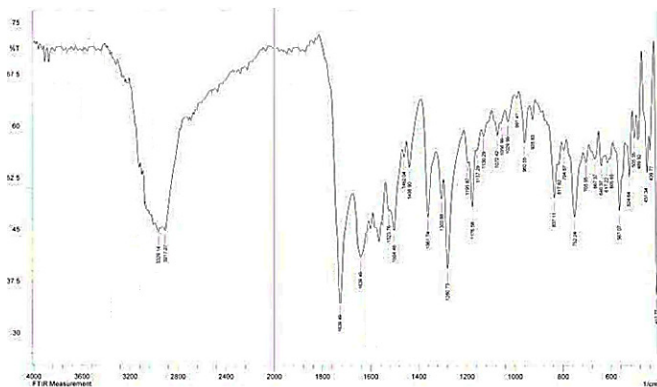


Figure 5: FT-IR band of ligand (L)

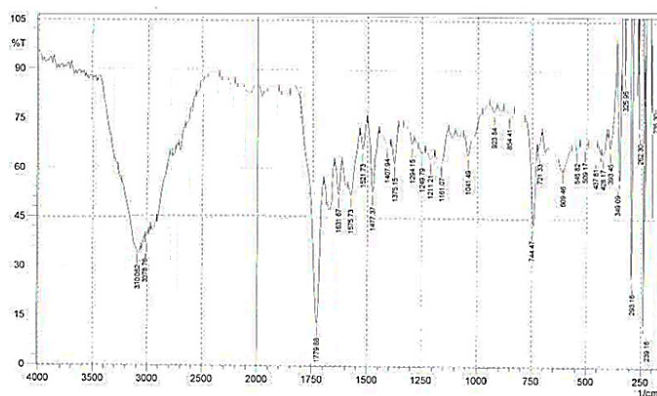


Figure 6: FT-IR band of ion complex of Co(II) with ligand (L)

Table 4: Show data (^{13}C -NMR) and chemical shift in (DMSO- d_6) for (L)

Comp.	Active groups	ppm (δ)
(L)	C for $-\text{CH}=\text{N}$	164.27
	C for thioamide	210.23
	C for carbonyl group	172.10
	C for benzene group	149.05
	C for benzene group	145.50
	C for benzene group	125.10
	C for benzene group	124.31
	C for benzene group	121.21
	C for benzene group	118.00
	C for methyl group	56.25
	C for aliphatic group	40.23
	C for methyl group	36.37

Table 5: FTIR data for the prepared compounds (cm^{-1})

Comp.	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}-\text{O})$	$\nu(\text{C}=\text{S})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{S})$	$\nu(\text{M}-\text{Cl})$
$\text{C}_{24}\text{H}_{24}\text{N}_2\text{O}_6\text{S}_2$ (L)	1649	1723	1280	1072	-	-	-	-
Co(II)-Complex	1631	1725	1294	1041	509	437	393	325
Ni(II)-Complex	1632	1725	1298	1037	505	431	405	293
Cu(II)-Complex	1630	1723	1295	1041	448	470	430	315
Zn(II)-Complex	1634	1722	1297	1050	447	441	420	331

wavenumbers (lower) (1630–1634) cm^{-1} . This confirms the contribution of (N) in (CH=N) group in coordination and emergence of new frequencies due to bands (M-N) in regions (447–509) cm^{-1} .^{21,22} In the ligand spectrum, a medium band appeared at (1280) cm^{-1} due to the stretching vibration of (C-O), while its displacement has been observed in the spectrum of metallic complexes to (1294–1298) cm^{-1} . This confirms the contribution of the oxygen of C-O group in coordination and the emergence of new frequencies due to the bands (M-O) in the regions (431–470) cm^{-1} . A band (C=S) was detected in the ligand at (1072) cm^{-1} while it was observed in the spectra of the complexes at (1037–1050) cm^{-1} . This confirms the contribution of the Sulfur of thiol group in coordination and the emergence of new frequencies due to bands (M-S) in the regions (393–430) cm^{-1} .^{23,24} In addition, in the regions (293–331) cm^{-1} of the complex spectra, it was observed that new bands appeared, returning to $\nu(\text{M}-\text{Cl})$ frequency.²⁵⁻²⁷

UV-Vis. Spectrums Study

The electronic transition study of the (L) and its complexes was carried out in (DMSO). Two distinct bands were observed at (35087 and 28985) cm^{-1} , which corresponds to the ($\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$) transitions of the azomethine group, respectively, Figure 7.²⁸ This confirms the occurrence of coordination between (L) and the metal ions shift these transitions to frequencies (lower) in electronic spectra of all prepared compounds. The UV-Vis. spectrum of Co complex appears several absorption bands at (36363, 25000, 19960, and 16233) cm^{-1} attributed to (IL, CT, $^4\text{A}_{2(\text{F})} \rightarrow ^4\text{T}_{1(\text{P})}$ and $^4\text{A}_{2(\text{F})} \rightarrow ^4\text{T}_{1(\text{F})}$), respectively, which indicate a tetrahedral geometric.²⁹ The electronic of Ni(II) complex, Figure 8 displayed new absorption peaks at (35587, 28571, 23419 and 12048) cm^{-1} which related to (IL, IL, CT, and $^3\text{T}_1 \rightarrow ^3\text{T}_{1(\text{P})}$) transitions respectively, suggesting tetrahedral structure around Nickel (II) ion.³⁰ The UV-Vis. of Copper (II) complex appeared at (33333 and 10526) cm^{-1} attributed to (IL and $^2\text{T}_2 \rightarrow ^2\text{E}$) transition that tetrahedral geometric Copper (II)

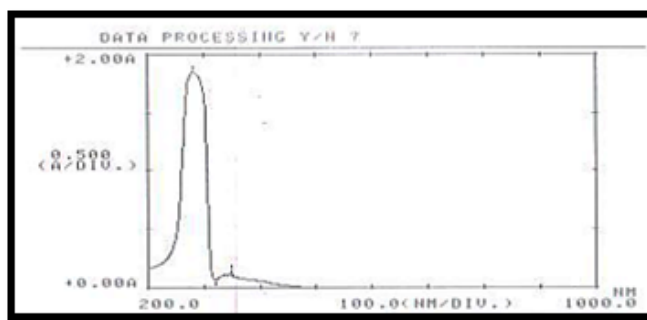


Figure 7: Absorbance band of ligand (L)

ion.³¹ The UV-Vis. spectrum the prepared Zn (II) complex show tow bands at (35087 and 25000) cm^{-1} which are due to the transitions: (IL and CT), respectively, which indicate a tetrahedral geometry.³² The spectral details have been depicted in Table 6.

Elemental Analysis Study

There was found great agreement between the results of the experimental element analysis with the results of theoretical calculations for all the complexes prepared. The complexes were prepared in ratio 2:1 [metal]:[L], a general form $[\text{M}_2(\text{L})\text{Cl}_2]\text{Cl}_2$ type, where M=Co (ii), Ni (ii), Cu (ii) and Zn (ii) and this is what was deduced from the data of the elemental analysis showed in Table 1.

Magnetic Measurements

The tetrahedral environment around the cobalt (ii) ion, this is what magnetic moment μ_{eff} . (4.87) BM has shown for the cobalt complex because there are three unconnected electrons. Ni (ii) complex exhibits μ_{eff} . (3.11) BM at lab temperature based on dualistic uncombined electrons. This refers to a tetrahedral geometry nearby the Ni (ii) ion. The μ_{eff} . of the copper complex (1.75) BM that refers to a tetrahedral geometry,^{33,34} listed in Table 6.

Conductivity Measurements

All compounds display electrolytic properties according to measurements of molar conductivity at range (79.13–63.01)

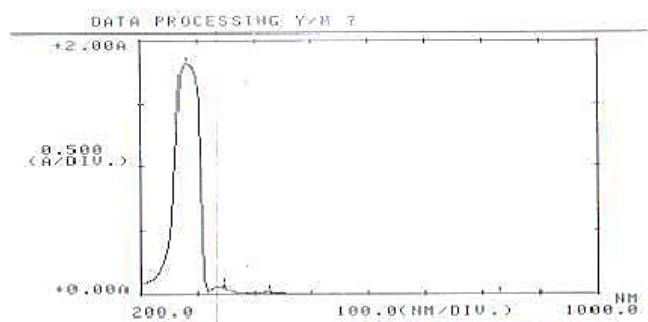


Figure 8: Absorbance band of Ni (II) complex

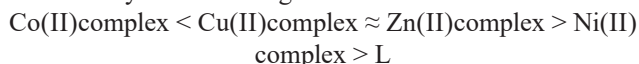
Λ_M ($\text{cm}^2 \Omega^{-1} \text{mol}^{-1}$) in (DMSO) as a solvent in (10^{-3}M) at lab temperature.^{35,36} In Table 1 the measured conductivity values are listed.

Determination of Chloride Content in the Compounds

The presence of chloride in the metal complexes. This was confirmed by the positive chloride ion test for all the prepared metal compounds listed in Table 1.³⁷

Corrosion Inhibition (Mild Steel) by the Prepared Compounds

Gravity data of (mild steel) were performed in (the absence and presence) of 100, 300, and 900 parts per million of compounds in the same solution at laboratory temperature to study the effect of prepared compounds on the corrosion of mild steel in (0.2 M) of hydrochloric acid. The percentage inhibition efficiency and the corrosion rate were calculated from the 72-hour weight loss results given in Table 7. An observed behavior in the inhibition of corrosion towards corrosion (mild steel) in a solution of (0.2 M) of hydrochloric acid was inferred from data obtained from the ligand and its metallic complexes. The % IE of the (L) on (mild steel) may be explained based on N, O, and S atoms besides π electron interaction of aromatic ring with the unshared p electrons of the coupons. The inhibition efficiency in metallic complexes is greater than free ligand due to its molecular planarity and larger size. Thus the efficiency can be arranged as follows:



The disparity in the solubility and stability of the compounds in the solution (acid) is the main reason for the difference in the inhibition efficiency. It was also found by increasing the concentration of compounds, the efficiency of inhibition increases. The corrosion inhibition can be explained by obtaining the adsorption of inhibitor on the surface of the metal and the compounds acting as inhibitors of absorption. The reason for the increased damping efficiency at higher concentration is to cover the metal more with inhibitor particles.^{38,39}

Table 6: (Magnetic and Uv-Vis) data in DMSO solutions.

Compound	μ_{eff} (BM)	Band position (λ_{nm})	ν (cm^{-1})	Extinction coefficient ϵ_{max} $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$	Assignment
$\text{C}_{24}\text{H}_{24}\text{N}_2\text{O}_6\text{S}_2$ (L)	----	285	35087	1852	$\pi \rightarrow \pi^*$
		345	28985	155	$n \rightarrow \pi^*$
Co(II)-Complex	4.87	275	36363	1686	IL
		400	25000	10	CT
		501	19960	9	${}^4\text{A}_{2(\text{F})} \rightarrow {}^4\text{T}_{1(\text{P})}$
		616	16233	44	${}^4\text{A}_{2(\text{F})} \rightarrow {}^4\text{T}_{1(\text{F})}$
Ni (II)-Complex	3.11	281	35587	1815	IL
		350	28571	76	IL
		427	23419	20	CT
		830	12048	1	${}^3\text{T}_1 \rightarrow {}^3\text{T}_1(\text{P})$
Cu(II)-Complex	1.75	300	33333	2073	I.L
		950	10526	56	${}^2\text{T}_2 \rightarrow {}^2\text{E}$
Zn(II)-Complex	0	285	35087	1954	I.L
		400	25000	9	C.T

C.T = Charge Transfer I.L=Intra Ligand T.h=Tetrahedral

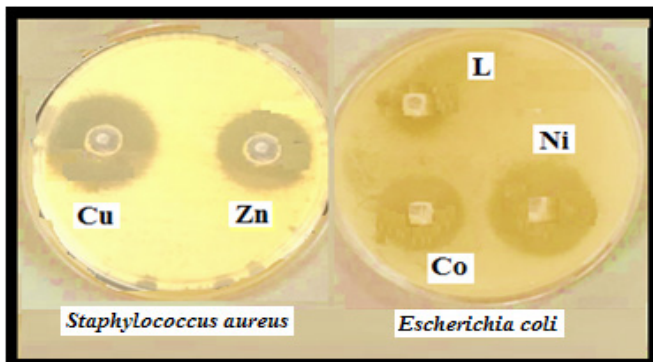
Table 7: Corrosion inhibition data for the prepared compounds

Baker NO.	Compound	C/mg.L ⁻¹	Initial wt. mg/cm ²	Final wt. mg/cm ²	Wt. loss mg/cm ²	CR/mm.y ⁻¹	E.I %	θ
1	Blank 0.2 M HCl	-	878	388.00	490	75.94	-	-
2	Blank + L	100	871	617.88	253.11	39.23	48.34	0.4834
3		300	853	608.98	244.02	37.82	50.20	0.5020
4		900	864	656.44	207.56	32.17	57.64	0.5764
5	Blank + Co(II)-complex	100	773	547.18	225.82	35.44	53.91	0.5391
6		300	781	586.66	194.34	30.12	60.03	0.6003
7		900	759	629.89	129.11	20.01	73.65	0.7365
8	Blank + Ni(II)-complex	100	719	466.66	252.34	39.11	48.50	0.4850
9		300	783	564.15	218.85	33.92	55.33	0.5533
10		900	728	577.00	150.89	23.38	69.20	0.6920
11	Blank + Cu(II)-complex	100	747	504.28	242.72	37.62	50.46	0.5046
12		300	752	551.54	200.46	31.07	59.09	0.5909
13		900	766	628.38	137.62	21.33	71.91	0.7191
14	Blank + Zn(II)-complex	100	812	565.85	246.15	38.15	49.76	0.4976
15		300	856	661.99	194.01	30.07	60.41	0.6041
16		900	834	693.02	140.98	21.85	71.22	0.7122

where θ is surface coverage = $1 - \frac{\Delta W_1 - \Delta W_2}{\Delta W_1}$

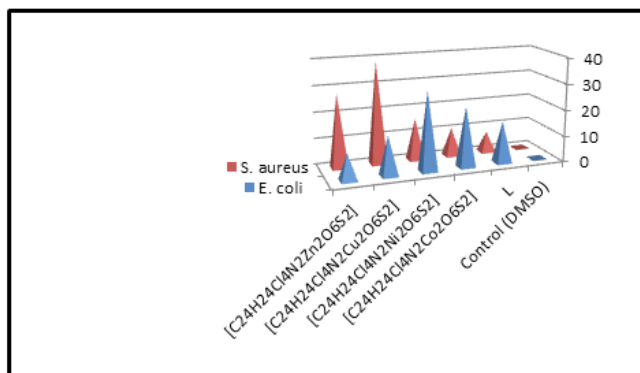
Table 8: Antibacterial efficacy data for the prepared compounds

Com.	<i>E. coli</i> (G ⁻)	<i>S. aureus</i> (G ⁺)
Control (DMSO)	-	-
C ₂₄ H ₂₄ N ₂ O ₆ S ₂ (L)	+++	+
Co (II) - Complex	++++	++
Ni (II) - Complex	++++	+++
Cu (II) - Complex	+++	++++
Zn (II) - Complex	+++	++++


Figure 9: Antibacterial efficacy of prepared compounds

Anti-biological Study

Using disk diffusion operation, the potential of the prepared compounds as antibacterial agents was evaluated against selected species (G⁺) bacteria (*S. aureus*) and (G⁻) bacteria (*E. coli*). In Table 8, Figures 9 and 10, measured areas of inhibition against the growth of different bacteria are shown. The action mechanism of antibacterial drugs is discussed under four headings, inhibition of cell wall, protein synthesis inhibition, nucleic acid inhibition, and cell membrane function inhibition. Finally, it was found that the antibacterial efficacy of Co(ii), Ni(ii), Cu(ii), and Co(ii) complexes was greater compared with the free ligand.^{40,41}


Figure 10: Statistical depiction for the antibacterial action of prepared compounds

Probable Shape

The prepared ligand L behaves as tridentate when coordinated with the selected metal ions Co(ii), Ni(ii), Cu(ii), and Zn(ii) in mole ratio (M:L) (2:1) through the oxygen atom for (C-O) group of 3-methoxy salicylaldehyde, the sulfur atom for (C=S) group of ethanethioamide and the nitrogen atom for (CH=N) group of Schiff base and this is confirmed by the measurements made for the prepared compounds, including ¹H, ¹³C-NMR, spectroscopic studies, mass spectral, elemental microanalysis, magnetic moment, metal content, and molar conductivity and all complexes have tetrahedral geometry around metal ion (Figure 11).

CONCLUSION

In this research, the preparation and representation of prepared complexes of ligand (L) were accomplished by the means of elemental analyses, M%, mass spectrum, UV-Vis, FTIR, and ¹H, ¹³C-NMR measurements. Magnetic susceptibility measured results verify the tetrahedral structure of the complexes. It was also found that complexes' biological

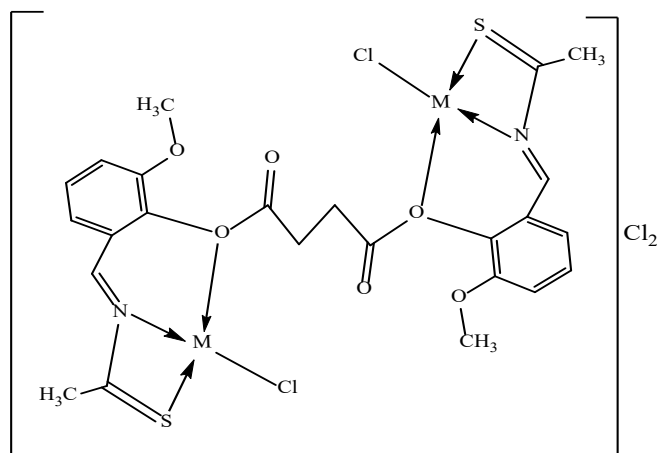


Figure 11: The suggested structure of prepared complexes where, M=Co(ii),Ni(ii),Cu (ii) and Zn(ii)

action and corrosion testing are greater than that of the ligand.

ACKNOWLEDGMENT

The author presents his sincere thanks to the Department of Chemistry and laboratory workers and the distinguished professors for their continuous scientific support during research.

REFERENCES

- Al-Azawi K, AL-Duhaidahawi DL, Al-Amiery A, Kadhum AA. Synthesis of Schiff base Metal Complexes with Motivating Scavenging Potential Studies. *Free Radicals and Antioxidants*. 2019 Apr 1;9(1):1-4.
- Kareem EK, Lateef SM, Drea AA. Study of Preparation and Identification of some metals complexes of New Schiff Base Ligand type (NNO) Derived from Isatin. *J. of Multifunc mater. and Photosci*. 2015;6(1):1-10.
- Ebrahimi Z, Davoodnia A, Motavalizadehkakhky A, Mehrzad J. Synthesis, characterization, and molecular structure investigation of new tetrahydrobenzo [b] thiophene-based Schiff bases: A combined experimental and theoretical study. *Eurasian Chemical Communications*. 2020 Feb 1;2(2):170-180.
- Namdeo P, Bhardwaj A, Verma SK. Synthesis Of Mixed Ligand Metal Complex Of Cu (II) With Schiff Base And Thioacetamide. *International Journal of Engineering Technologies and Management Research*. 2017 Dec 31;4(12):24-26.
- Yesmin MF, Hossain MS, Nasira S, Uddin N, Ashrafuzzaman M, Haque MM, Banu LA. Cu (II) and Ni (II) Complexes of Schiff Base: Synthesis, Characterization and Antibacterial Activity. *International Journal of Advanced Research in Chemical Science (IJARCS)*. 2020;7(1):9-15.
- Sherif OE, Abdel-Kader NS. DFT calculations, spectroscopic studies, thermal analysis and biological activity of supramolecular Schiff base complexes. *Arabian Journal of Chemistry*. 2018 Jul 1;11(5):700-713.
- Palanimurugan A, Dhanalakshmi A, Selvapandian P. Electrochemical behavior, structural, morphological, Calf Thymus-DNA interaction and in-vitro antimicrobial studies of synthesized Schiff base transition metal complexes. *Heliyon*. 2019;5:1-10.
- Abou-Hussein AA, Linert W. Synthesis, spectroscopic, coordination and biological activities of some organometallic complexes derived from thio-Schiff base ligands. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 2014 Jan 3;117:763-771.
- Khalaji AD. Nano-sized Cobalt (II) Schiff Base Complexes: Synthesis, Characterization and Thermal Studies. *Chemical Methodologies*. 2020;4(2):34-39.
- Sobola AO, Watkins GM. Antimicrobial activity and Cu (II) complexes of Schiff bases derived from ortho-aminophenol and salicylaldehyde derivatives. *Journal of chemical and pharmaceutical research*. 2013;5(10):147-154.
- Gueye A, Tamboura FB, Planeix JM, Gruber N, Gaye M. Synthesis and spectroscopic study of transition metal complexes of tridentate ligand formed by direct condensation of o-vanillin and 2-aminophenol: X-ray structural characterization of the zinc (II) complex. *European Journal of Chemistry*. 2018 Dec 31;9(4):281-286.
- Nazir U, Akhter Z, Janjua NK, Asghar MA, Kanwal S, Butt TM, Sani A, Liaqat F, Hussain R, Shah FU. Biferrocenyl Schiff bases as efficient corrosion inhibitors for an aluminium alloy in HCl solution: a combined experimental and theoretical study. *RSC Advances*. 2020;10(13):7585-7599.
- Bouchouit M, Said ME, Ali MK, Bouacida S, Merazig H, Chaouche NK, Chibani A, Zouchoune B, Belfaitah A, Bouraiou A. Synthesis, X-ray structure, theoretical investigation, corrosion inhibition and antimicrobial activity of benzimidazole thioether and theirs metal complexes. *Polyhedron*. 2016 Nov 24;119:248-259.
- Berk B, Ertaş M, Biltekin SN. Synthesis, antimicrobial activity studies and molecular property predictions of schiff bases derived from ortho-vanillin. *Acta Pharm. Sci.*, 2017; 55 (1): 1-10.
- Munde AS, Shelke VA, Jadhav SM. Synthesis, Characterization and Antimicrobial Activities of some Transition Metal Complexes of Biologically Active Asymmetrical Tetradentate Ligands. *Pelagia Research Library*, 2012;3(1):175-182.
- Bożejewicz D, Witt K, Kaczorowska MA, Ośmiałowski B. The copper (II) ions solvent extraction with a new compound: 2, 6-bis (4-methoxybenzoyl)-diaminopyridine. *Processes*. 2019 Dec;7(12):954.
- Sahib SK, Karem LK. Some Metal Ions Complexes Derived From Schiff Base Ligand with Anthranilic Acid: Preparation, Spectroscopic and Biological Studies. *Baghdad Science Journal*. 2020;17(1):99-105.
- Waheed EJ, Ahmed AA. Synthesis, Characterization, Thermal Study, Biological Activity and Corrosion Inhibition of New Ligand Derived from Butanedioyl Dichloride and Some Selective Transition Metal Complexes. *Journal of Global Pharma Technology*. 2019;11(2):379-391.
- Prakash V, Suresh MS. Preparation characterization, ¹H, ¹³C NMR study and antibacterial studies of Schiff bases and their Zn (II) chelates. *Res J Pharm Biol Chem Sci*. 2013;4(4):1536-1550.
- Sarhan BM, Lateef SM, Waheed EJ. Synthesis and Characterization of Some Metal Complexes of [N-(1, 5-dimethyl-3-oxo-2-phenyl-2, 3-dihydro-1H-pyrazol-4-ylcarbamothioyl) acetamide]. *Ibn AL-Haitham Journal For Pure and Applied Science*. 2017 Mar 16;28(2):102-115.
- Abu Bakar SN, Kassim K. Synthesis and Characterization of a Novel Schiff Base Derived from 2,4,6-trimethyl-mphenylenediamine with o-vanillin and Its Metal Complexes. *Conference Paper*. 2010: 5-7.
- Uyar Z, Erdener D, Koyuncu İ. Synthesis, Characterization, and Cytotoxic Activities of a Schiff Base Ligand and Its Binuclear

- Copper(II) and Manganese(III) Complexes. *JOTCSA*. 2017;4(3): 963-980.
23. De A, Ray HP, Jain P. Synthesis, characterization, molecular docking and DNA cleavage study of transition metal complexes of o-vanillin and glycine derived Schiff base ligand. *Journal of Molecular Structure*. 2020;1199:126901.
 24. Nora H, Shaalan A. Synthesis, characterization and biological activities of Cu(II), Co(II), Mn(II), Fe(II), and UO₂(VI) complexes with a new Schiff base hydrazone: O-hydroxyacetophenone-7-chloro-4-quinolinehydrazone. *Molecules*. 2011;16:8629-8645.
 25. Nakamoto K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1986.
 26. Saranya R, Rajasekaran J, Selvaraj SJ. Synthesis and Characterization of Biologically Important Zn (II), Cu (II) AND Co (II) Metal Complexes in the 3d- Series. *Journal of Chemical and Pharmaceutical Sciences*. 2017;(1):64-73.
 27. Yesmin MF, Camellia FK, Bashar M. Synthesis, Characterization and Investigation of Antimicrobial Activity of a New Schiff Base, 2-(((2-((4-hydroxy benzylidene) amino)ethyl)imino)methyl) Phenol and Its Cu(II) and Ni(II) Complexes. *Asian Journal of Chemical Sciences*. 2020;7(2):30-38.
 28. Sridevi G, Antony SA, Angayarkani R. Schiff Base Metal Complexes as Anticancer Agents. *Asian Journal of Chemistry*. 2019;31(3):493-504.
 29. Ciolan F, Patron L, Mureseanu M. Synthesis and Characterization of Cu(II), Ni(II) and Co(II) Binuclear Complexes with a new Schiff base (1,3-bis[ortho-(2-carboxy-phenyliminomethyl)-phenoxy]propane). *REV. CHIM. (Bucharest)*. 2012;63(1): 34-39.
 30. Ameen AM, Buttrus NH, Hassan OK. Synthesis and Characterization of some New Dinuclear Complexes of Ni(II), Pd(II) and Pt(II) with Bulky Substituted Thioether Ligands. *The Eurasia Proceedings of Science, Technology, Engineering & Mathematics (EPSTEM)*. 2019;6:43-51.
 31. Haque MM, E-Zahan MK, Banu LA. Synthesis and Characterization with Antineoplastic, Biochemical, Cytotoxic, and Antimicrobial Studies of Schiff Base Cu(II) Ion Complexes. *Bioinorganic Chemistry and Applications*. 2015;3(8):1-7.
 32. Sarhan BM, Kadhim NJ, Wheed EJ. Stability constant of some Metal Ion Complexes of (6-(2-Amino-2-(4-hydroxy phenyl)-acetamido)-3, 3--dimethyl-7-oxo-4-thia-1-aza-bicyclo [3, 2, 0] heptanes-2-carboxylic acid (Amoxicillin). *Ibn AL-Haitham Journal For Pure and Applied Science*. 2017 Apr 24;26(3):245-253.
 33. Carlin R, Van A. *Magnetic Properties of Transition Metal Compounds*. New York, Springer-Verlag, 1977.
 34. Kafi-Ahmadi L, Shirmohammadzadeh L. Synthesis of Co (II) and Cr (III) salicylidenic Schiff base complexes derived from thiourea as precursors for nano-sized Co₃O₄ and Cr₂O₃ and their catalytic, antibacterial properties. *Journal of Nanostructure in Chemistry*. 2017 Jun;7(2):179-190.
 35. Andruh M. The exceptionally rich coordination chemistry generated by Schiff-base ligands derived from o-vanillin. *Dalton Transactions*. 2015;44(38):16633-16653.
 36. El-Ajaily MM, Al-Noor TH, Albarki NS. Antifungal Activity of Some Mixed Ligand Complexes Incorporating Schiff Bases. *J Bacteriol Mycol*. 2020;7(1):1122-1127.
 37. Salehi M, Faghani F, Kubicki M, Bayat M. New complexes of Ni (II) and Cu (II) with tridentate ONO Schiff base ligand: synthesis, crystal structures, electrochemical and theoretical investigation. *Journal of the Iranian Chemical Society*. 2018 Oct;15(10):2229-2240.
 38. Mahross MH, Efil K, Seaf El-Nasr TA. Synthesis, Characterization and Corrosion Inhibition of N'-Phenylbenzohydrazide Derivative Metal Complexes: Experimental and Quantum Chemical Studies. *Chem*. 2019;2(9):1-24.
 39. Kashyap S, Kumar S, Ramasamy K, Lim SM, Shah SA, Om H, Narasimhan B. Synthesis, biological evaluation and corrosion inhibition studies of transition metal complexes of Schiff base. *Chemistry Central Journal*. 2018 Dec;12(1):1-10.
 40. El-Sonbati AZ, Mahmoud WH, Mohamed GG. Synthesis, characterization of Schiff base metal complexes and their biological investigation. *Appl Organometal Chem*. 2019:1-16.
 41. Obaid SM. Synthesis, Spectral and Antibacterial Activity of Mixed Ligand from Lanthanum (III) Complexes of Schiff Base Ligand with Some Amino Acids. *Journal of Global Pharma Technology*. 2019;11(3):88-99.