

SYNTHESIS OF SOME METAL ION COMPLEXES OF NEW IMIDAZOLE DERIVATIVE, CHARACTERIZATION, AND BIOLOGICAL ACTIVITY

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ABSTRACT. Imidazole complexes with high biological activity for some metal complexes prepared by a new imidazole ligand from the reaction of a 1,3-oxazole derivative with hydroxylamine and utilizing this ligand in the preparation of some metal ion complexes. Many of the techniques available for all prepared compounds, such as elemental analysis (CHNS), (FT-IR), (UV-Vis) spectra, and ¹H-NMR spectra, will be used in the diagnosis of these complexes, and the forms of the complexes will be deduced from the results obtained. The outcomes demonstrated that the octahedral geometries of all the produced complexes, except for the copper and palladium complexes, which were square planer shapes. The antimicrobial activity of both the ligand and its metal ionic complexes against various microbes was evaluated.

KEY WORDS: Imidazole, Oxazole, Spectral data, Bioactivity

INTRODUCTION

Imidazole, well known as 1,3-diaza-2,4-cyclopentadiene, is a planar, heteroaromatic molecule consisting of a five-membered ring structure containing three carbon (C) and two nitrogen (N) atoms in positions 1 and 3. It was initially referred to as glyoxalin and was first synthesized using glyoxal and ammonia [1]. Imidazole exhibits an amphoteric nature and is susceptible to both electrophilic and nucleophilic attacks. It possesses high stability under various conditions such as thermal, acidic, basic, oxidation, and reduction environments. The molecule demonstrates extensive intramolecular hydrogen bonding. Significantly, it is worth noting that it occurs in two isomeric forms that are equivalent, known as tautomer's, due to the flexibility of the molecular structure, a hydrogen atom can occupy any of the two nitrogen atoms.

Imidazole is categorized as an aromatic compound since it possesses a six of π -electrons, which includes a pair of electrons originating from protonated nitrogen atom and one electron from other four atoms within the ring structure. Imidazole complexes have significant relevance in numerous biological applications because the structure of imidazole contains two nitrogen atoms one of these nitrogen atoms is easy to coordinate with different metal ions [2].

Imidazole, a heterocyclic compound, exists in two tautomer forms where the hydrogen atom moves between its two nitrogen atoms. It was initially discovered by Debus *et al.* in 1858 through the reaction of dike tone, aldehyde, and ammonia. However, earlier in the 1840s, various derivatives of imidazole had already been found. Over time, the imidazole family has significantly expanded, and imidazole is now extensively utilized in numerous applications. These applications encompass diverse areas such as natural products and have contributed to the vital role imidazole play in various fields [3], medicinal chemistry [4], and material sciences for nonlinear optical application [5].

Certain imidazole derivatives serve as catalysts in industrial applications [6, 7]. Moreover, these imidazole derivatives have been employed as corrosion inhibitors for iron when exposed to acidic environments [8], on certain transition metals, such as copper [9] and carbon steel [10]. Imidazole is a compound that is not only found in various compounds used for photography [11]

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but is also utilized as a dopant in organic semiconductor matrix materials, organic semiconductor materials, and electronic or optoelectronic structural elements.

Many papers referred to those imidazole derivatives with hydrogen bond donor groups that act as reducing agents for cytotoxicity and used as antiviral agents [12, 13]. Imidazole has high anti-HIV inhibitory activity [14], and some derivatives of imidazole used in industries to reduce fly ash. Many researchers reported the imidazole complexes with highly biological activity of some metal complexes prepared by the reaction of new imidazole derivatives ligand with some transition metals. Because imidazole possesses these properties, this substance prepared from imidazole derivatives possesses two groups of oxygen atoms that can be ionized, forming a good Lewis base for forming effective complexes. Important in the direction of many antimicrobial applications, as indicated in this research [15].

The aim of this research is to synthesize and characterize various imidazole metal complexes (Mn, Co, Ni, Cu, and Pb) and evaluate their bioactivity against specific bacteria and fungi.

EXPERIMENTAL

Materials and methods

The ligand's ¹H-NMR spectra were obtained using a DMX-500 spectrophotometer (300 MHz) in DMSO-d₆. The melting points of the compounds were determined using a Gallenkamp MF B600 melting point device. Microelemental analyses (CHNS) for all prepared compounds were recorded using EA-034.mth. The percent contents of metal ions were determined using an atomic absorption spectrophotometer, specifically the Shimadzu-670 AA Spectrophotometer. The (IR) spectra were acquired by the FT-IR-8300 Shimadzu instrument over the wavenumber range of 4000-350 cm⁻¹. The magnetic susceptibilities of the prepared metal complexes were calculated using the magnetic susceptibility balance of Sherwood Scientific. The conductivity of all complexes was determined using the electrolytic accessibility determining set "Model MC-1-MarkV" with a platinum electrode (EDC 304) with 10⁻³ M in dimethylformamide (DMF) as the solvent. UV-Vis spectra of the prepared complexes were acquired using the UV-1650PC-Shimadzu Spectrophotometer, with measurements taken at a concentration of 10⁻³ M.

Synthesis of acetic acid derivatives

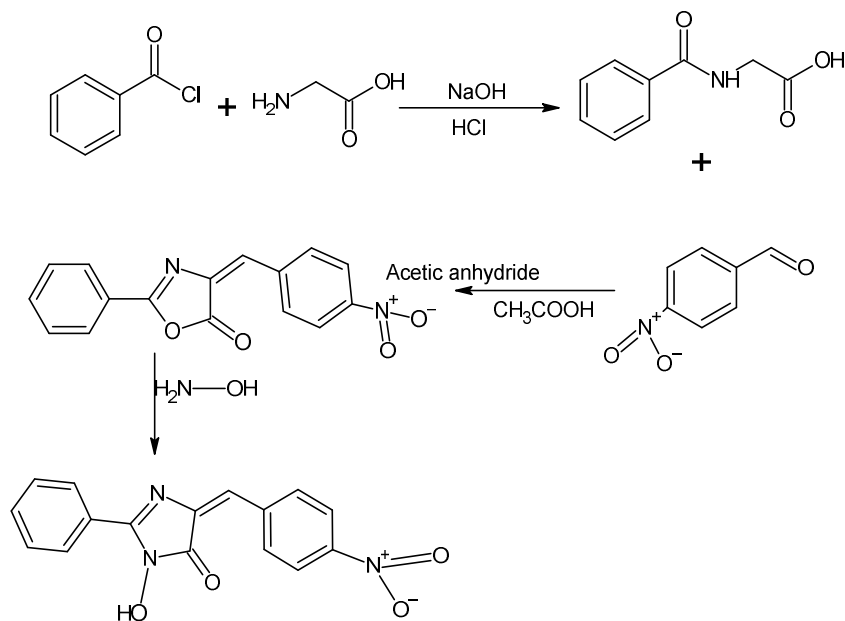
(24.7 g, 0.176 mol) of benzoyl chloride was added slowly to mixtures of (13.2 g, 0.176 mol) glycine was dissolved in (60 mL) of (10%) sodium hydroxide solution with stirring. The mixture was transferred to ice and made slightly acidic medium with hydrochloric acid. The white precipitate underwent filtration, washing, drying, and subsequent recrystallization from toluene [16]. This process resulted in a melting point range of (184-186 °C), with a yield of 78% (Scheme 1).

Synthesis of the ligand

(3.58 g, 0.02 mol) of phenyl carbonyl acetic acid and (3.022 g, 0.02 mol) of (4-nitrobenzaldehyde) were dissolved in a mixture of (20 mL) acetic anhydride and (5 mL) acetic acid. The obtained combination was subjected to reflux for a duration of 3 hours at 93 °C, poured onto ice bath and stirred for a period of 30 min. The yellow product obtained was subjected to filtration, washing, drying, and recrystallization using ethanol [17-18]. The finished product had a yield of 61% and a melting point of (190-193 °C) (Scheme 1).

(1.47 g, 0.005 mol) of the previously prepared product and (0.165 g, 0.005 mol) of hydroxyl amine hydrochloride (NH₂OH.HCl) (80%) was dissolved in 20 mL of benzene, then the mixture was refluxed for (3 h), poured onto ice bath, then filtrated. The filtered product underwent

washing, drying, and recrystallization from ethanol [20, 21], melting point (152-154 °C), yielding 82% (Scheme 1). ¹H-NMR (s. 5.23 (1H) for CH, s. 5.42 (2H) for (NH₂), m 7.42 for H of aromatic ring).



Scheme 1. Preparation of ligand (L).

Synthesis of metal ion complexes (S_1 - S_5).

The synthesis of all metal complexes in the study involved the reaction between the ligand and divalent metal ion salts in molar ratios, conducted in an ethanol medium. The ligand used in the synthesis acted as a bidentate coordinate throughout the oxygen atom and nitrogen atom through the prepared metal ion complexes, an ethanolic solution containing transition metal ion salts ($[\text{MnCl}_2 \cdot 4\text{H}_2\text{O}]$, $[\text{CoCl}_2 \cdot 6\text{H}_2\text{O}]$, $[\text{NiCl}_2 \cdot 6\text{H}_2\text{O}]$, $[\text{CuCl}_2 \cdot 2\text{H}_2\text{O}]$, and $[\text{PdCl}_2]$) (1 mmol) was added to the ligand solution (0.6 g, 2 mmol) in ethanol as the solvent. The mixture refluxed for 1.5 hours. Then the precipitate filtration (distilled water), washing with absolute ethanol, and then with distilled water before being dried in an oven [19, 20].

Complexes formation in solution

To determine the metal-ligand ratio of formation of prepared complexes, a sequence of solutions which have a concentration (10^{-3} M) were prepared of synthesized ligand metal ion complexes using dimethyl sulfoxide [DMF] as per solvent. The mole rate is determined from the absorbance and the mole ratio of the metal-ligand relationship [21] (Table 1).

Biological activity of the synthesized ligand and its metal complexes (S_1 - S_5)

E. coli and *Staph. Aurous* were isolated and purified from different clinical resources, and identified by usual methods; these bacteria were cultured in nutrient agar medium and keep warm

at 37 °C for 24 h preceding screening. The filter paper disk technique was used to determine the activity inhibition as shown by the diameter of zone inhibition. A filter paper of Whitman number four, with a diameter of 6 mm, was subjected to various concentrations of the ligand and its metal complexes, ranging from 50 to 200 µg/mL.

The control and solvent used was DMSO (dimethyl sulfoxide). Then dry in the oven at 60 °C for 10 h. The clear zone diameter in the region of the disks was calculated after 48 h of incubation at 37 °C. The nonexistence of a clear zone in the region of all disks refers to inactivity [19]. The new complexes (S1-S5) were also studied, they screened their (in vitro) growth of inhibition of activity against additional pathogenic, fungi, i.e., (*A. niger*) and (*P. chrysogenum*) on "potato dextrose agar" media then these fungi incubated at 30 °C for 72 h. The inhibitory activity of the growth of fungal was expressed in percentage terms, measure up to respective control plates [22].

RESULTS AND DISCUSSION

Elemental analyses

The elemental analysis, analytical and physical data of synthesized ligands and their complexes were shown in Table 1. The data from the elemental analysis obtained shows a strong agreement with the calculated values, indicating the accuracy of the proposed molecular and geometrical formula. The validation of the formula was further supported by measuring spectral data and magnetic moment. Additionally, the new complexes demonstrated solubility in common organic solvents such as CH₂Cl₂, CHCl₃, DMF, and DMSO, because show excellent solubility and non-aggregated species in common organic solvents such as dimethyl sulfoxide, dimethylformamide, chloroform and dichloromethane. All complexes showed very high melting points because they are salts with an ionic character in one way or another, and thus their melting points are very high.

Table 1. The elemental analysis and physical characteristics of the synthesized complexes.

Comp. sym.	Standard formula	M.wt (g.mol ⁻¹)	Color	M.P. (°C)	Yield	M:L	Elemental content analysis (%)			
							observed (calc.)			
							C	H	N	M
L	C ₁₆ H ₁₁ N ₃ O ₄	309.276	Greenish yellow	152-154	82%	--	62.136 (62.28)	3.585 (3.65)	13.557 (18.04)	----
S ₁	[Mn(L) ₂ (H ₂ O) ₂].Cl ₂	780.492	Yellow	185-187	65%	1:2	49.248 (49.26)	3.358 (3.56)	10.768 (14.34)	7.039 (6.99)
S ₂	[Co(L) ₂ Cl ₂].2H ₂ O	785.453	Greenish brown	236-238 dec.	59%	1:2	48.997 (48.98)	3.341 (3.54)	10.714 (14.21)	7.513 (7.48)
S ₃	[Ni(L) ₂ (H ₂ O) ₂].Cl ₂	784.182	Brown	256-258 dec.	55%	1:2	49.012 (49.00)	3.342 (3.59)	10.717 (14.35)	7.485 (6.99)
S ₄	[Cu(L) ₂].Cl ₂	753.004	Dark brown	220-222 dec.	78%	1:2	51.041 (51.06)	2.945 (3.10)	11.161 (14.85)	8.439 (8.40)
S ₅	[Pd(L) ₂].Cl ₂	795.878	Light brown	192-194	62%	1:2	48.292 (48.33)	2.786 (3.00)	10.559 (14.04)	13.371 (13.34)

$$* \text{ The percent Yield} = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} * 100\%$$

Infra-red spectroscopy of synthesized ligand (L) and its complexes

The spectrum of synthesized ligand appeared and (3411 cm⁻¹) related to ν(OH) group, this band shifted by (12-22) cm⁻¹ to low frequency in all IR-spectra of metal ion complexes, this indicating the participates of the (O) atom of ligand in the coordination process, FT-IR spectrum of the

prepared ligand appeared another bands at (1714 cm^{-1}) related to vibration of carbonyl group. This band changed in every prepared metal complexes and shifted by (15-21) cm^{-1} to a low frequencies in all spectra of the metal complexes as per illustrate in Table 2. This behavior indicated involvement of carbonyl group in the formation process of the complexes.

Metal ion complexes [S1 and S3] displayed medium bands in FTIR spectra in the region between (3353 cm^{-1} and 3342 cm^{-1}), this mentions the existence of coordinated molecules in the structure of these metal ion complexes, while the metal ion complex (S2) showed abroad band at 3452 cm^{-1} related to the hydrated water molecules this metal ion complex. New bands showed in all spectra of complexes in the low frequency those bands characteristic to $\nu(\text{M-N})$ and $\nu(\text{M-O})$ vibrations. These bands were detected at (531-522) cm^{-1} and (463-456) cm^{-1} , respectively [23, 24]. The low-frequency bands in the spectra of the complexes are characterized by bond $\nu(\text{M-N})$ and $\nu(\text{M-O})$ vibrations. Because the emitted mass of the metal ions is very high and its spectrum is inversely proportional to the emitted mass, it appears at low frequencies according to Hooke's law.

Cobalt mostly shows spectral transitions, but it showed two spectral transitions, and the third transition was calculated because it is in the near-infrared region, close to ultraviolet radiation, and it does not appear in the spectrum.

The main vibration modes of ligand and its metal ion complexes were recorded in Table 2.

Table 2. Characteristic infra-red data (cm^{-1}) of the synthesized ligand and its metal ion complexes.

Compound	L	S ₁	S ₂	S ₃	S ₄	S ₅
$\nu(\text{OH})$	3411(m)	3399(w)	3398(w)	3389(w)	3390(w)	3394(w)
$\nu(\text{C-H})$ aromatic	3076(m)	3072(m)	3078(m)	3072(m)	3070(m)	3068(m)
$\nu(\text{C=O})$	1714(s)	1701(s)	1688(s)	1703(s)	1697(s)	1694(s)
$\nu(\text{C=N})$	1627(s)	1620(m)	1621(m)	1624(m)	1618(m)	1621(m)
$\nu(\text{NO}_2)$	1344(s)	1344(s)	1344(s)	1066(m)	1340(s)	1342(s)
$\nu(\text{M-N})$	--	526(w)	531(w)	522(w)	527(w)	525(w)
$\nu(\text{M-O})$	--	463(w)	457(w)	457	456(w)	461(w)

Where from: "s": strong, "w": weak, "m": medium.

Electronic transition spectra and other measurements studies

The electronic spectrum of prepared ligand in "ethanol" showed bands at (240 nm, 41666.7 cm^{-1}), (272 nm, 36764.7 cm^{-1}) belonged to ($\pi \rightarrow \pi^*$) transitions, the another bands at (312 nm, 32051.3 cm^{-1}) related to ($n \rightarrow \pi^*$) transitions with higher intensity than the first band [18]. The coordination of the ligand with divalent transition ions appear as a novel band in the ultraviolet region belong to ligand transitions, at the same time, the d-d transitions are confirmed in the visible region. All bands at 300-400 nm could be referred to as M-L charge transfer. Table 3 illustrates positions of highest absorption bands of metal complexes with their assignments.

In the spectrum of brown Mn(II) complex (S1), The d-d transition bands are spin-forbidden, therefore that they are very weak and not easy to detect, though, it is sometimes feasible to distinguish between 6 and 4-coordination. The electronic spectrum of this complex showed the band at (690 nm, 14492.75 cm^{-1}) attributed to ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$ and band at (445 nm, 22471.9 cm^{-1}) related to ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_{2g} + {}^4\text{A}_{1g}$ [24]. These bands point to an octahedral geometry about Mn(II) ion [23, 24]; the measurement of the magnetic moment of this prepared complex which was set up to be (5.36 B.M.), this value refers to a high spin (d5) complex [19, 25]. While the complex has an ionic behavior in DMF (Table 3).

Table 3. Electronic spectra and other measurement data.

No.	ν_{\max} (cm ⁻¹)	Band assignment	B'	B	10Dq	Molar cond. S.cm ² .mol ⁻¹	μ_{eff} . (B.M.)	Proposed geometry
(S ₁)	14492.75 22471.9	⁶ A _{1g} → ⁴ T _{2g} ⁶ A _{1g} → ⁴ E _{2g} + ⁴ A _{1g}	--	--	--	168.36	5.36	O.h
(S ₂)	14880.95 18248.18 7538	⁴ T _{1g} → ⁴ A _{2g} (F) ⁴ T _{1g} → ⁴ T _{1g} (P) ⁴ T _{1g} → ⁴ T _{2g} (F) (calc.)	611	0.62	7183	17.48	4.18	O.h
(S ₃)	14814.81 21834.06 12147	³ A _{2g} → ³ T _{1g} (F) ³ A _{2g} → ³ T _{1g} (P) ³ A _{2g} → ³ T _{2g} (F) (calc.)	574	0.56	11066	172.58	3.29	O.h
(S ₄)	14598.54 20746.89	² B _{1g} → ² A _{1g} ² B _{1g} → ² B _{2g} + ² E _g	--	--	--	171.21	1.78	S.p
(S ₅)	20325.2 23640.66	¹ A _{1g} → ¹ B _{1g} ¹ A _{1g} → ¹ E _g	--	--	--	169.21	0.0	S.p

Greenish brown cobalt complex exhibited two transitions bands at (672 nm, 14880.95 cm⁻¹) and (548 nm, 18248.18 cm⁻¹), these transitions band could belong to the transitions [⁴T₁ → ⁴A₂(F)] (v2) and [⁴T₁ → ⁴T₁(P)] (v3), respectively [26], from the position of these transition bands this complex might have octahedral geometry, while the first transition (v1) was calculated for d7 of the "Tanaba-Sugano" chart, the calculated value of this transition was (7538) cm⁻¹, referred [⁴T₁ → ⁴T₂(F)] transition [15, 20]. In addition to conductivity measurement and magnetic susceptibility showed this complex has paramagnetic and non-ionic behavior.

Brown nickel complex showed two bands at (675 nm, 14814.81 cm⁻¹) and (458 nm, 21834.06 cm⁻¹) allocated to ³A₂ → ³T₁(F), (v2) and ³A₂ → ³T₁(P) (v3) transitions, respectively [27]. These transitions referred to octahedral "geometry surrounding "Ni(II) ion, while, the value of the first transition (v1) was calculated and found to be 12147 cm⁻¹, which might be related to the transition ³A_{2g} → ³T_{2g}(F) [21, 25, 27]. The magnetic susceptibility value for the nickel complex was (2.92 B.M.). This agrees with "octahedral geometry" about nickel ions, in addition to the molar conductivity measurements point to the electrolytic act of this metal complex.

While the spectrum of brown copper complex appeared band at (685 nm, 14598.54 cm⁻¹) attributed to ²B_{1g} → ²A_{1g} transition, and another band at (482 nm, 20746.89 cm⁻¹) which referred to ²B_{1g} → ²B_{2g} + ²E_g transition [25-27]. These transitions may be referred to as square planer geometry. The value of the magnetic moment for the same complex was found (1.78 B.M.), proving to this geometry around Cu(II) complex [18, 26, 28]. In addition, conductivity measurements confirm that the complex has ionic nature.

The UV-Vis spectrum of the palladium complex confirmed two bands, the first at (492 nm, 20325.20 cm⁻¹) belonged to ¹A_{1g} → ¹B_{1g}, while the second band at (423 nm, 23640.66 cm⁻¹) referred to ¹A_{1g} → ¹E_g transitions. These bands indicate the square-planar geometry for this complex. The magnetic susceptibility value and the conductance measurements of the palladium complex was found both diamagnetic and the complex has ionic behavior, therefore, it is be decided with square planer geometry surrounding Pd(II) ion [21, 25].

With regard to copper and palladium, it behaved like a square planar, and this is due to all spectroscopic studies, such as UV and its transitions, in addition to magnetic spectroscopy and chromatography, and it was proven that these two ions with this ligand give a flat square center, and this was proven by comparing these results with the published literature for the same two ions with regard to According to the measurements mentioned above in the text of the research [27, 28].

The activity of some complexes is considered an active part, and this is due to the nature of the metal ion bound to the ligand. This can be seen in copper complexes that have proven to be

highly effective, and palladium complexes in particular, in addition to numerous literatures that have indicated that copper-palladium complexes are highly effective. Because they are planar square complexes, they can change the nature of their symmetry from tetragonal to hexagonal, compared to complexes with octahedral symmetry, which cannot expand their symmetry envelope.

Chemical structure of metal complexes (S₁-S₅)

Drawing from those above micro elemental analysis results, physical and chemical analysis investigations, magnetic characteristics, and conductivity tests of metal complexes, the suggested geometrical structure may be the same as Figure 1.

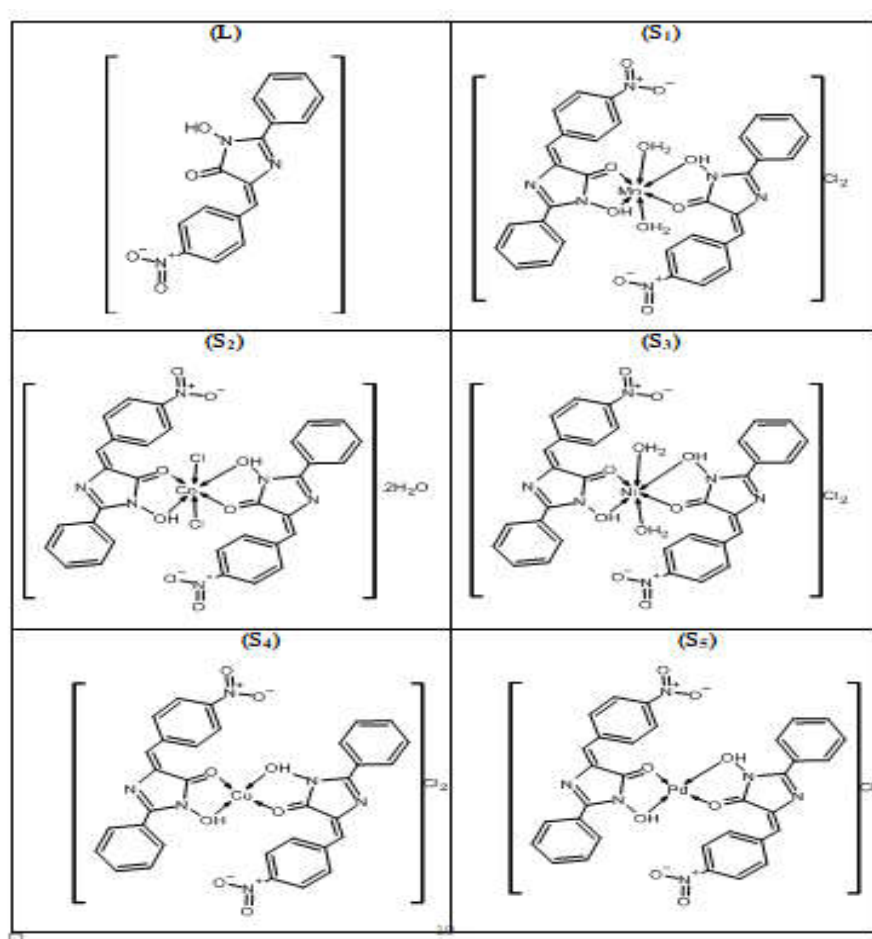


Figure 1. Proposed chemical structure of complexes (S₁-S₅).

Biological activity of prepared ligands and their metal ion complexes

All compounds were evaluated "*in vitro*" to determine their aptitude to inhibit the growth of selected bacteria (*E. coli* as gram-negative) and (*Staph. aureus* as gram-positive), in addition to their antifungal activity against *Candida albicans* and *Aspergillus flavus*. The results of the study can be found in Table 4. From the obtained results, the following points can be concluded: The inhibition activity was increased when the concentration of metal complexes increase. All metal complexes showed higher inhibition activity compared to the ligand. All of the prepared compounds inhibited microorganisms less than the standard drug chooses. The results showed that complexes display high inhibition activity against both sets of "organisms". The antifungal activity was increased when the ligand is coordinated with metal ions. The enhanced activity of metal ion complexes might be described based on Tweedy chelation theory [29]. This explained the "cell permeability" of the lipids "membrane" "surrounding the cell by soluble lipid resources which the cell favors, because the solubility of lipids is a significant reason to manage the antibacterial and antifungal action. The chelation theory referred to the metal ion polarity will be decreased to a larger size correlated to the overlapping of the orbital of the ligand and partial sharing of the positive charge of the metal ion with the donor atom in the ligand. While The increase in the inhibition of the activity of antifungal metal complexes might be related to the effectiveness of the transition metal ion on ordinary cell processes [29].

Table 4. Antibacterial and antifungal activity of ligand (L) and its complexes (S₁-S₅).

Comp. No.	Conc. of comp. (µg/mL)	<i>E. coli</i>	<i>Staph. aureus</i>	<i>Cand. albic</i>	<i>Asper. flavus</i>
(L)	50	6	5	1	3
	100	8	6	3	4
	150	9	6	5	5
	200	11	8	7	9
(S ₁)	50	11	12	8	9
	100	14	14	10	10
	150	16	15	11	11
	200	19	17	13	12
(S ₂)	50	10	11	9	10
	100	12	13	11	12
	150	17	18	12	13
	200	20	19	13	14
(S ₃)	50	11	12	9	10
	100	13	13	10	12
	150	17	17	13	14
	200	22	19	14	15
(S ₄)	50	14	14	10	10
	100	18	17	13	13
	150	20	18	15	15
	200	22	20	15	16
(S ₅)	50	12	12	11	10
	100	15	14	13	11
	150	18	18	14	13
	200	22	21	15	15
Tetracycline	200	30	32	--	--
Nystatin	200	--	--	36	33

CONCLUSION

A new imidazole ligand and its complexes were prepared in good yield and characterized. All of physical and chemical results, referred to some complexes have an octahedral geometry such as manganese(II), cobalt(II), and nickel(II) complexes, while, the other complexes, copper(II) and palladium(II) complexes exhibit square planar geometry. The study of biological activity showed the ligand and their metal complexes have antibacterial and antifungal activity, and the study of biological activity showed the complexes were more active compared with the ligand.

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