

PACS numbers: 81.07.Nb, 81.16.Fg, 87.19.xb, 87.64.Cc, 87.64.kj, 87.64.km, 87.85.Rs

Synthesis and Characterization of Two Ligand Polydentals and Their Complexes with Cobalt(II) and Copper(II) Derived from Pyridine-2,6-Dicarbohydrazide and Studying the Biological Activity of Complexes

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Two tridentate-type Schiff-bases' ligands: 2,6-bis[(salicylidene) hydrazinocarbonyl] pyridine (*L*) and 2,6-bis[(3-methoxysalicylidene) hydrazinocarbonyl] pyridine (*L'*) are synthesized from the reaction of pyridine-2,6-dicarbohydrazide with salicylaldehyde and 3-methoxy salicylaldehyde. The co-ordination behaviour of the (*L*) and (*L'*) towards Cu(II) and Co(II) ions is investigated. The reaction of the Schiff-base ligands (*L*) and (*L'*) with cobalt(II) and copper(II) ions in 1:3 molar ratio affords polynuclear metal complexes. The shifts of the some IR-bands' spectra of synthesized complex in the selected vibrational bands in FT-IR indicate that Schiff bases behave as trilydentate ligands and co-ordinate to metal ions from phenolic oxygen atoms, amide and azomethine nitrogen atoms. The structure of the metal complexes exhibits octahedral arrangements. The antibacterial activity of the ligand (*L*) and its metal complexes against two bacterial species is studied. The Co(II) complex indicates a good inhibition activity. The structures of the ligands are elucidated by FT-IR, ¹H-NMR, and UV-Vis electronic spectra. The characterization and structure elucidation of the complexes are achieved by FT-IR, UV-Vis electronic spectra.

Два Шиффових ліганди тризубного типу: 2,6-біс[(саліциліден) гідразінокарбоніл] піридин (*L*) і 2,6-біс[(3-метоксисаліциліден) гідразінокарбоніл] піридин (*L'*) синтезуються в результаті реакції піридин-2,6-дикарбогідразиду з саліциловим альдегідом і 3-метоксисаліциловим альдегідом. Досліджено координаційну поведінку йонів (*L*) і (*L'*) щодо йонів Cu(II) та Co(II). Реакція Шиффових лігандів (*L*) і (*L'*) з йонами

Кобальту(II) та Купруму(II) в молярному співвідношенні 1:3 створює комплекси поліядрових металів. Зсуви спектрів синтезованого комплексу деяких ІЧ-діапазонів у вибраних коливних смугах у Фур'є-перетворі інфрачервоної спектроскопії вказують на те, що Шиффові основи поводяться як триліdentатні ліганди та координуються на йони металів з атомів фенольного Оксигену, атомів амідного й азометинного Нітрогену. У структурі металевих комплексів проявляються октаедричні розташування. Вивчено антибактеріальну активність ліганду (*L*) та його металевих комплексів щодо двох видів бактерій. Комплекс Со(II) вказує на хорошу гальмівну активність. Структури лігандів з'ясовуються за електронними спектрами Фур'є-перетвору інфрачервоної спектроскопії, ¹H-ЯМР й у видимій і ультрафіолетовій областях світла. Характеризація та з'ясування структури комплексів досягаються електронними спектрами Фур'є-перетвору інфрачервоної спектроскопії й у видимій і ультрафіолетовій областях світла.

Key words: pyridine-2,6-dicarbohydrazide, Schiff bases, polynuclear complexes, polydentate ligands.

Ключові слова: піридин-2,6-дивуглеводазид, Шиффові основи, поліядрові комплекси, полідентатні ліганди.

(Received 29 August, 2022)

1. INTRODUCTION

Schiff bases are a very important class of organic compounds, because of their ability to form complexes with transition metal ions [1–3] and of their pharmacological properties. It is due to the presence the group imine (or azomethine) (–CH=N–) in its structure, they play an important role in the field of pharmaceuticals field [4–5]. Their complex have a vital role as antibacterial and antifungal [6, 7] and antitumor [8]. The pharmacological use of azo compounds originates from the discovery of the antibacterial action of prontosil on streptococcal infection [9]. Furthermore, azo compounds were reported to show a variety of biological activities including antibacterial [10], antifungal [11], pesticidal [12], antiviral [13] and anti-inflammatory [14] activities. On other side, azo compounds are highly important, well known, and widely used in the textile, paper, and colouring agents for foods, cosmetics, dyes and plastics industries. They play an important role in emerging technologies application like liquid crystals, organic photoconductors and non-linear optics [15]. The goal of this research is to synthesize new Schiff bases and mineral complexes to obtain new compounds of industrial importance. In the recent years, multifunctional dihydrazones containing amide, azomethine and phenolic functions in duplicate have attracted a lot of attention, mainly due to their potentiality to yield

homo- and heteropolynuclear complexes. The polynuclear complexes are of interest in the areas such as multimetallic, enzymes, and homogeneous and heterogeneous catalysis [16].

The ligating diversity of such ligands has prompted us to design and synthesize (*L*, *L'*) and to study its chelating behaviour towards different transition metal ions such as cobalt(II) and copper(II).

2. EXPERIMENTAL

2.1. Apparatus and Chemicals

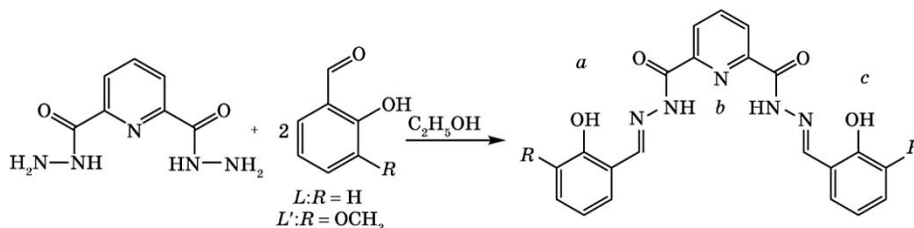
(pyridine-2,6-dicarbohydrazide by Sigma-Aldrich), (3-methoxy salicylaldehyde by Sigma-Aldrich), (salicylaldehyde by MERCK), cobalt(II)-chloride 6-hydrate 97% (by SCP), copper(II)-chloride 97% (by BDH), absolute ethanol (by CHEMLAB), absolute methanol (by CHEMLAB).

UV/Vis spectroscopy (model: HITACHI U-1900), spectrum NMR proton device 400 MHz model Bruker by Switzerland company, optical absorption spectrum infrared device model FT-IR-4100 from the Japanese company Jasco, rotary evaporator 4.91 model from the German company Normschiff, thin layer chromatographic of aluminium coated by Silica Gel 60F254 measuring 20×20 from the German company Merck.

2.2. Experimental Procedure

2.2.1. Synthesis of the Ligand (*L*) and (*L'*)

The *L* and *L'* ligands were synthesized by adding pyridine-2,6-dicarbohydrazide (0.6 g, 3 mmol) in absolute ethanol (20 ml), a solution of salicylaldehyde (0.6 ml, 6 mmol) or 3-methoxy salicylaldehyde (0.9 g, 6 mmol) in the same solvent (20 ml) was added, and refluxed for 7 h. The precipitated (*L*) and (*L'*) were filtered, washed with hot water followed by hot ethanol, air dried and recrystallized from 2-ethoxyethanol. Ligands as cream and yellow crystals was obtained with a yield of (70%) and (72%), respectively.



Scheme 1. Synthetic route for *L* and *L'*.

2.2.2. Synthesis of Metal Complexes

Ligands *L* (0.040 g, 1 mmol) or *L'* (0.046 g, 1 mmol) were boiled under reflux with sodium hydroxide (0.080 g, 2 mmol) in 75% aqueous ethanol (10 ml) for 30 min. The metal (II) chloride (Co and Cu) (3 mmol) dissolved in ethanol (10 ml) was added and the mixture was refluxed further for 7–8 h. The precipitate obtained was filtered, washed with distilled water and dried in air.

2.3.3. Evaluation the Antibacterial Activity of Complexes

Two Petri plates were prepared using (agar medium 11), the first plate cultured with the gram-positive bacteria (*Staphylococcus aureus*) and the second plate cultured with gram-negative bacteria (*Escherichia coli*). Six samples were prepared in each plate.

The first is the complex $[LCo_3(H_2O)_7Cl_2]:[LCo_3(H_2O)_7Cl_2]$ with a concentration of (50 µg/ml) using dimethyl sulfoxide (DMSO) as a solvent. The second is the complex $[LCo_3(H_2O)_7Cl_2]:[LCo_3(H_2O)_7Cl_2]$ at a concentration of (100 µg/ml) in (DMSO) as a solvent. The third sample is the complex $[LCu_3(H_2O)_7Cl_2]:[LCu_3(H_2O)_7Cl_2]$ at a concentration of (50 µg/ml) in (DMSO). The fourth is the complex $[LCu_3(H_2O)_7Cl_2]:[LCu_3(H_2O)_7Cl_2]$ at a concentration of (100 µg/ml) in (DMSO). The fifth is the augmentin as a reference using a concentration of (25 µg/ml) in (DMSO). The sixth is the (DMSO). The samples were placed in a pre-prepared Petri plate, and the areas of inhibition were compared with the reference sample.

3. RESULTS AND DISCUSSION

3.1. Characterization of Ligands and Their Complexes

The Schiff base (*L*) was prepared by the condensation of pyridine-2,6-dicarbohydrazide and salicylaldehyde in their 1:2 molar ratio. The second Schiff base (*L'*) was prepared by the condensation of pyridine-2,6-dicarbohydrazide with 3-methoxy salicylaldehyde in their 1:2 molar ratio. Both ligands were obtained after reflux and then on cooling as cream and yellow precipitates. The properties (colours, yield and the melting points) and their complex are presented in Table 1 and 2.

3.2. Infrared Spectra

The infrared spectra indicate a stretching absorption for $\nu(C=N)$, $\nu(N-H)$ and $\nu(O-H)$. The IR data of the spectra of Schiff base lig-

TABLE 1. Molecular weight and melting point of the ligands.

Compounds	Molecular weight	Colour	Yield, %	M.P., °C
<i>L</i>	403.39	Cream	70	295–297
<i>L'</i>	463.45	Yellow	72	300–302

TABLE 2. Molecular weight and melting point of the different complexes.

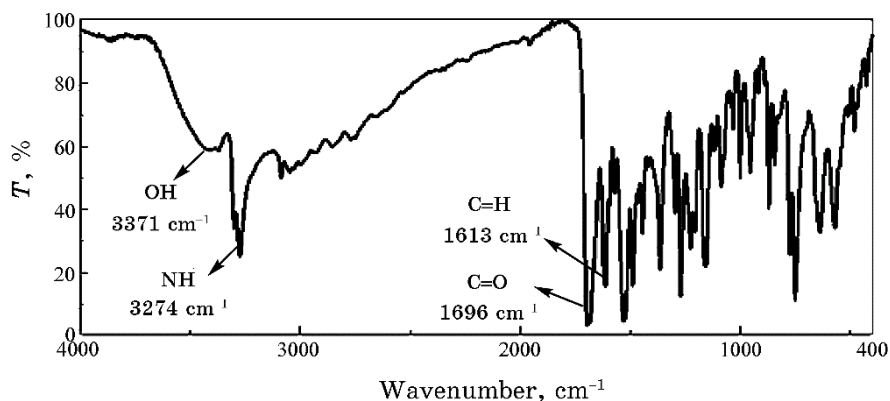
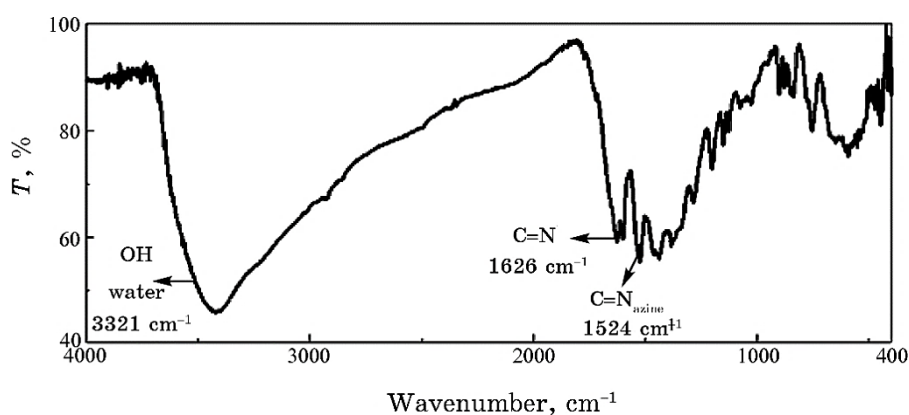
Complexes	Molecular weight	Colour	Yield, %	M.P., °C
[<i>LCo</i> ₃ (H ₂ O) ₇ Cl ₂]	773.17	Brown	86	> 300
[<i>LCu</i> ₃ (H ₂ O) ₇ Cl ₂]	787.01	Reddish brown	63	> 300
[<i>L'Co</i> ₃ (H ₂ O) ₇ Cl ₂]	833.22	Brown	72	> 300
[<i>L'Cu</i> ₃ (H ₂ O) ₇ Cl ₂]	847.06	Green	81	> 300

TABLE 3. Characteristic infrared absorption frequencies [cm⁻¹] of the ligand and complexes.

Compounds	$\nu(\text{O-H}), \text{cm}^{-1}$	$\nu(\text{N-H}), \text{cm}^{-1}$	$\nu(\text{C=O}), \text{cm}^{-1}$	$\nu(\text{C=N}), \text{cm}^{-1}$	$\nu(\text{C=N})_{\text{azine}}, \text{cm}^{-1}$	$\nu(\text{O-H})_{\text{water}}, \text{cm}^{-1}$
<i>L</i>	3371	3274	1696	1613	—	—
[<i>LCo</i> ₃ (H ₂ O) ₇ Cl ₂]	—	—	—	1626	1524	3421
[<i>LCu</i> ₃ (H ₂ O) ₇ Cl ₂]	—	—	—	1617	1533	3423
<i>L'</i>	3454	3240	1672	1609	—	—
[<i>L'Co</i> ₃ (H ₂ O) ₇ Cl ₂]	—	—	—	1624	1530	3418
[<i>L'Cu</i> ₃ (H ₂ O) ₇ Cl ₂]	—	—	—	1615	1542	3434

ands (*L* and *L'*) and their complexes are presented in Table 3.

The IR spectra of the complexes were compared with those of the free ligands in order to determine the coordination sites that may be involved in chelation. In all the complexes, the bands due to $\nu(\text{O-H})$ and $\nu(\text{N-H})$ were absent, indicating the complex formation through phenolic oxygen and amide nitrogen *via* deprotonation [17, 18]. The absence of amide band and presence of a new strong and broad band centred in all the complexes was assigned to the stretching frequency of newly formed C=N–N=C azine moiety indicating the co-ordination of amide oxygen and nitrogen through enolization and deprotonation [19]. The azomethine vibration has shifted to

Fig. 1. IR absorption spectra of ligand (*L*).Fig. 2. IR absorption of $[LCo_3(H_2O)_7Cl_2]$.

higher wave number in all the complexes indicating the co-ordination of azomethine nitrogen to the metal.

3.3. Electronic Spectral (UV) Data

The data of the electronic spectra of the ligand and its complexes are given in Table 4. The spectrum of Schiff base (*L*) presented three bands in the UV interval at 275 nm assigned to ($n \rightarrow \pi^*$), 297 and 335 nm assigned to ($\pi \rightarrow \pi^*$) transitions, respectively.

The electronic spectra of the $[LCo_3(H_2O)_7Cl_2]$ in DMSO has three bands at 450, 542 and 690 nm. These bands may be assigned to the transitions ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$, respectively (Fig. 7). The position of these bands suggests an octahedral structure [20].

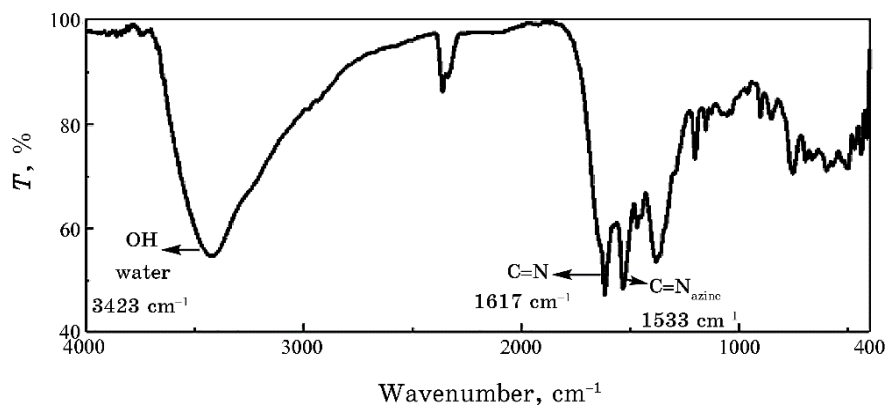


Fig. 3. IR absorption of $[LCu_3(H_2O)_7Cl_2]$.

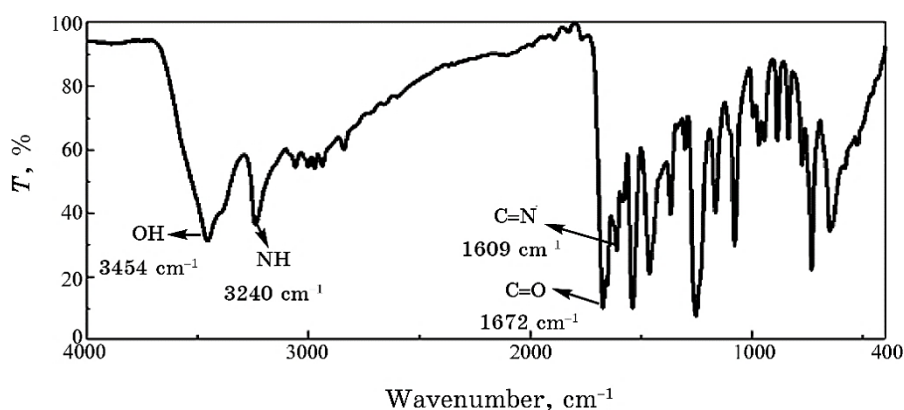
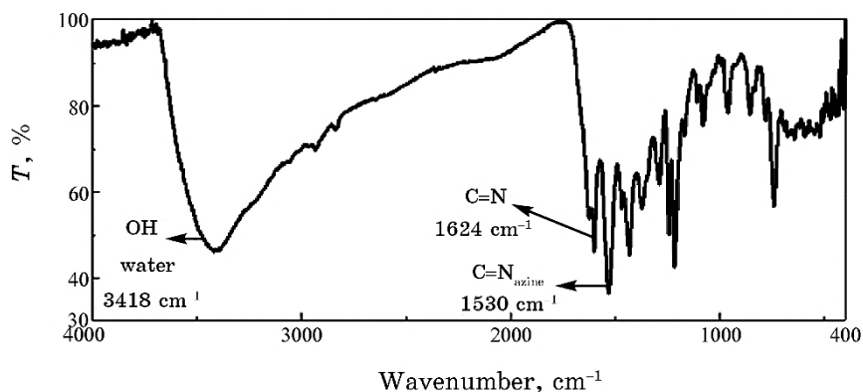
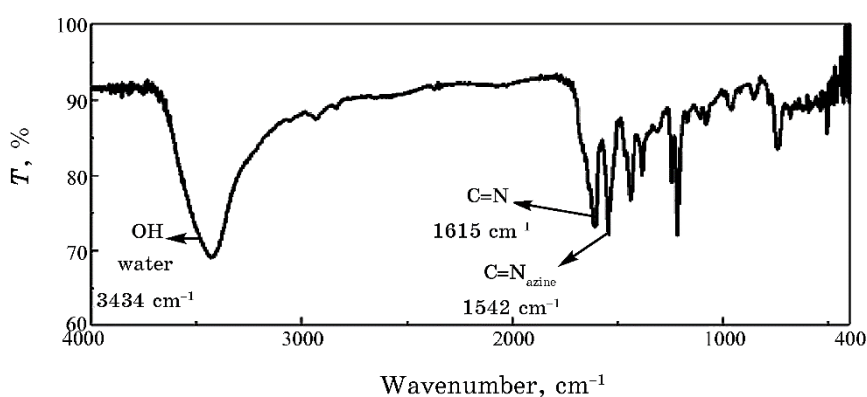


Fig. 4. IR absorption of L' .

The electronic spectra of the $[LCu_3(H_2O)_7Cl_2]$ in DMSO has two band. A band centred at 520 nm, observed as an envelope in copper(II) complex, assigned to the ${}^2B_{1g} \rightarrow {}^2A_{1g}$ reveals the octahedral geometry and another band at 415 nm was due to charge transfer transition (Fig. 8). The position of this band suggests an octahedral structure [21].

3.4. 1H -NMR Spectroscopic Measurements

1H -NMR spectra of the Schiff base ligand L revealed its formation by the presence of (HC=N) proton signal at ($\delta = 8.96$ ppm) and proton signal for hydroxyl at ($\delta = 11.16$ ppm). The 1H -NMR spectroscopic measurements of L , L' Schiff bases are given in Table 5.

Fig. 5. IR absorption of $[L'Co_3(H_2O)_7Cl_2]$.Fig. 6. IR absorption of $[L'Cu_3(H_2O)_7Cl_2]$.

3.5. Determination of Molar Ratio of ($M:L$) by Furnace

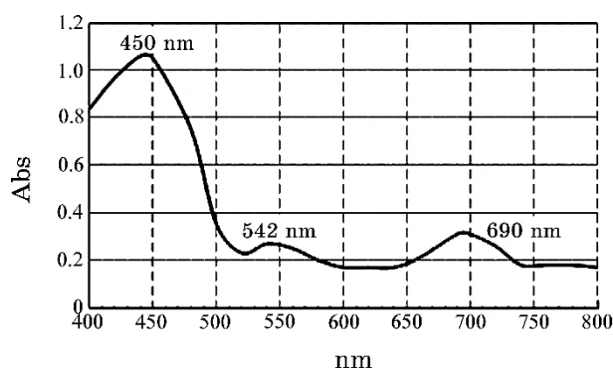
Analyse of metal ions followed dissolution of the solid complex (0.1 gr) in hot concentrated nitric acid, HNO_3 , then, these sample were sintered at $800^\circ C$ for 1.5 h in a furnace (Carbolite Furnace, CWF 1200), and then, cooled at room temperature in desiccators; after that, we notice that the formed compound is CuO (black colour) (0.0289 gr):

$$\left. \begin{array}{l} Cu \leftarrow CuO \\ 63.546 \text{ gr} \quad 79.545 \text{ gr} \\ \text{gr} \quad \quad 0.0289 \text{ gr} \end{array} \right\} X = 0.0231 \text{ gr} .$$

So, the complex contains (0.0231 gr) of copper metal; we suggest structure of this complex and account the amount of copper in it

TABLE 4. Electronic spectral data and geometries of ligand and complexes.

Compounds	Electronic spectra, nm	Assignments	Geometry
<i>L</i>	297, 335 275	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	
$[LCo_3(H_2O)_7Cl_2]$	450 542 690	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$	Octahedral
$[LCu_3(H_2O)_7Cl_2]$	415 520	$({}^2B_{1g} \rightarrow {}^2A_{1g})$ $({}^2E_g \rightarrow {}^2T_{2g})$	Octahedral
<i>L'</i>	307, 330 295	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	
$[L'Co_3(H_2O)_7Cl_2]$	441 560 680	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$	Octahedral
$[L'Cu_3(H_2O)_7Cl_2]$	435 568	$({}^2B_{1g} \rightarrow {}^2A_{1g})$ $({}^2E_g \rightarrow {}^2T_{2g})$	Octahedral

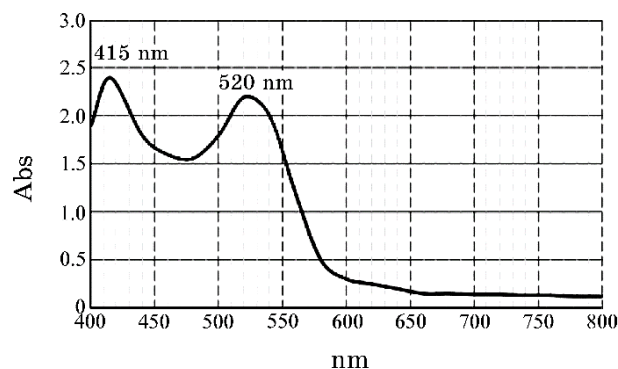
**Fig. 7.** UV absorption spectra of $[LCo_3(H_2O)_7Cl_2]$.

with the practical value to determine the correct structure.

Copper complex with *L*:

molecular weight 787 gr contain 190.64 gr of copper metal
 weight of disjointed sample 0.1 gr contain *Y* gr of copper metal } \rightarrow
 $\rightarrow Y = 0.0242$ gr.

When we compare between *X*, *Y*, we notice that $X \cong Y$. So, the complex has a polynuclear structure (Fig 11):

Fig. 8. UV absorption spectra of $[LCu_3(H_2O)_7Cl_2]$.TABLE 5. The 1H -NMR spectroscopic measurements of L , L' Schiff bases.

Compounds	1H -NMR (δ -ppm)
L	11.16 (s , 2H, OH)
	8.96 (s , 2H, H_4 , H_4')
	12.46 (s , 2H, H_3 , H_3')
	8.23 (t , 1H, $J = 6.7$, H_1)
	8.44 (d , 2H, $J = 7.5$, H_2 , H_2')
	7.64 (d , 2H, $J = 10.0$, H_5 , H_5')
	6.93 (t , 2H, $J = 9.4$, H_2 , H_6 , H_6')
	7.43 (t , 2H, $J = 8.8$, H_7 , H_7')
L'	6.9 (d , 2H, $J = 11.3$, H_8 , H_8')
	12.42 (s , 2H, OH)
	8.87 (s , 2H, H_4 , H_4')
	10.66 (s , 2H, H_3 , H_3')
	8.31 (t , 1H, $J = 9.1$, H_1)
	8.36 (d , 2H, $J = 9.9$, H_2 , H_2')
	7.3 (d , 2H, $J = 5.9$, H_5 , H_5')
	6.8 (t , 2H, $J = 8.2$, H_6 , H_6')
7.14 (t , 2H, $J = 12.1$, H_7 , H_7')	
	3.81 (s , 2H, OCH_3)

$$\text{Yeild} = \frac{X}{Y} = \frac{0.0231}{0.0242} = 95.4\%.$$

Analyse of metal ions followed dissolution of the solid complex (0.1 gr) in hot concentrated nitric acid, HNO_3 , then these sample were sintered at $800^\circ C$ for 1.5 h in a furnace (Carbolite Furnace, CWF 1200) and then cooled at room temperature in desiccators; after that, we notice that the formed compound is CuO (black colour)

(0.0273 gr).

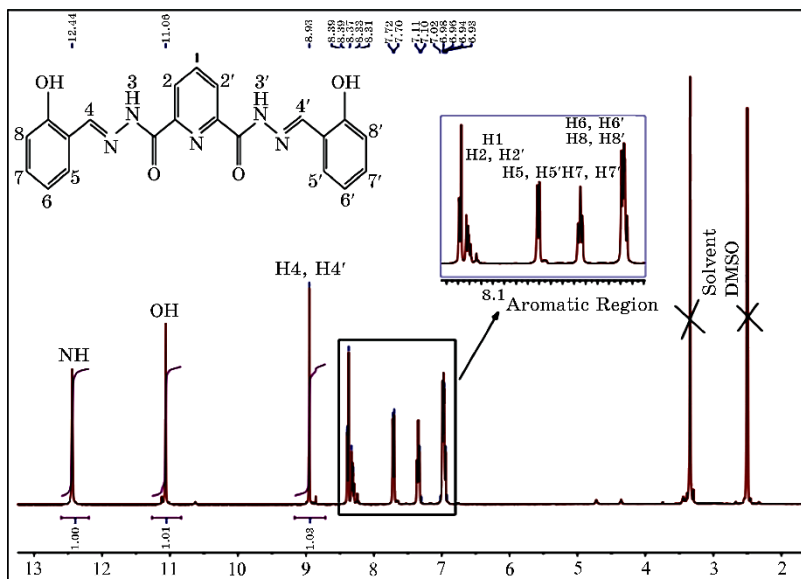


Fig. 9. $^1\text{H-NMR}$ spectrum of *L* (400 MHz, DMSO, $\delta_{\text{TMS}} = 0$).

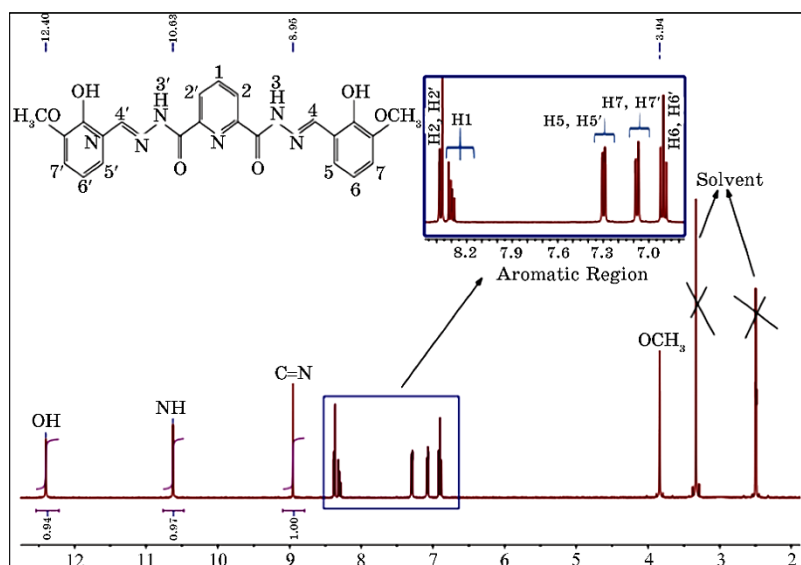


Fig. 10. $^1\text{H-NMR}$ spectrum of *L'* (400 MHz, DMSO, $\delta_{\text{TMS}} = 0$).

$$\left. \begin{array}{r} \text{Cu} \leftarrow \text{CuO} \\ 63.546 \text{ gr} \quad 79.545 \text{ gr} \\ \text{gr} \quad \quad 0.0273 \text{ gr} \end{array} \right\} X = 0.0218 \text{ gr} .$$

So, the complex contains (0.0218 gr) of copper metal; we suggest structure of this complex and account the amount of copper in it with the practical value to determine the correct structure.

Copper complex with L' :

$$\left. \begin{array}{l} \text{molecular weight } 847 \text{ gr contain } 190.64 \text{ gr of copper metal} \\ \text{weight of disjointed sample } 0.1 \text{ gr contain } Y \text{ gr of copper metal} \end{array} \right\} \rightarrow$$

$$\rightarrow Y = 0.0225 \text{ gr} .$$

When we compare between X , Y , we notice that $X \cong Y$. So, the complex has a polynuclear structure (Fig. 12):

$$\text{Yeild} = \frac{X}{Y} = \frac{0.0218}{0.0225} = 96.8\% .$$

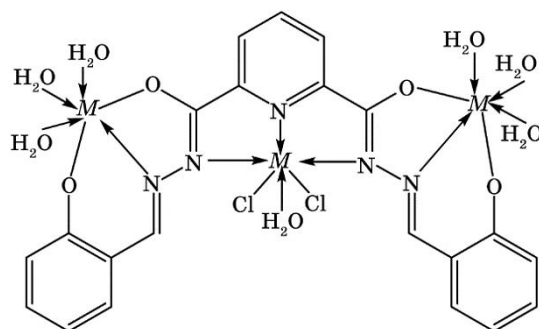


Fig. 11. The proposed structure for the L complexes.

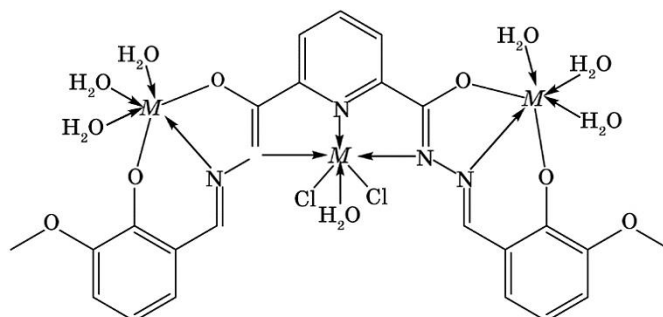


Fig. 12. The proposed structure for the L' complexes.

3.6. Evaluation the Antibacterial Activity of Complexes $[LCO_3(H_2O)_7Cl_2]$ and $[LCu_3(H_2O)_7Cl_2]$

The biological activity of complexes was studied on two strains of bacteria: *Staphylococcus aureus* and *Escherichia coli*. The incubation was for 30 minutes at a temperature of 37°C. Meanwhile, the tablets contain a food medium and sterile. The zone of inhibition is measured with a graduated ruler. The samples (5 and 6) showed a fort activity against the *bacteria* compared to the augmentin.

Figure 13 shows the areas of inhibition. The results are recorded in Table 6.

4. CONCLUSIONS

Two ligands L and L' have been synthesized. The crystal structure of L and L' reveals clearly the presence of donor sites in the trident

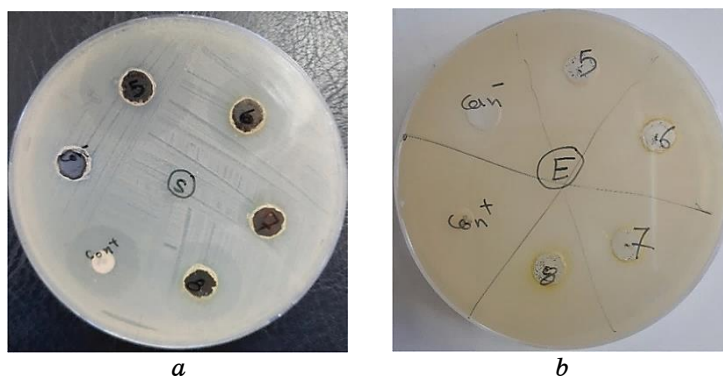


Fig. 13. The zones of inhibition against to the growing of *Staphylococcus aureus* and *Escherichia coli*, in different concentrations.

TABLE 6. The activity of the complexes calculated by measuring diameter of the inhibition zone [mm].

No.	Sample	Concentration	Mean of zone diameter, mm	
			<i>St. aureus</i>	<i>E. coli</i>
5	$[LCO_3(H_2O)_7Cl_2]$	$50 \mu\text{g}\cdot\text{ml}^{-1}$	26	0
6		$100 \mu\text{g}\cdot\text{ml}^{-1}$	12	0
7	$[LCu_3(H_2O)_7Cl_2]$	$50 \mu\text{g}\cdot\text{ml}^{-1}$	14	12
8		$100 \mu\text{g}\cdot\text{ml}^{-1}$	23	13
Con ⁺	Augmentin	$25 \mu\text{g}\cdot\text{ml}^{-1}$	21	21
Con ⁻	DMSO	—	0	0

compartmental mode. Both L and L' act as a nonadentate tri-compartmental ligand by coordinating through hydrazonic carbonyl oxygen, hydrazonic nitrogen and phenolic oxygen [in the two side compartments (a and c)] and through pyridyl nitrogen and two hydrazonic nitrogens [in the central compartment (b)] as shown in the scheme 1.

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