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SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL ACTIVITY OF MIXED LIGAND (IMINE OF BENZIDINE AND 1,10-PHENANTHROLINE) COMPLEXES WITH Fe(II), Co(II), Ni(II) AND Cu(II) IONS

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Abstract. In this paper, binuclear metal complexes of the metal ions Fe(II), Co(II), Ni(II) and Cu(II) were synthesized by the reaction of the primary ligand (imine of benzidine) (H_2L) and the secondary ligand (1,10-phenanthroline) (L`) with these metal ions in a molar ratio of 1:2:2, respectively. The complexes were characterized using CHN elemental analysis, FT-IR, UV-Vis, magnetic susceptibility, molar conductivity, ^{1}H NMR, and TGA-DTA thermogravimetric analysis. According to the results obtained from the elemental analysis and spectral measurements where complexes of Fe(II), Co(II) and Ni(II) have octahedral geometry, while the complex with Cu(II) has a square planar geometry. All the prepared complexes are wholly stable and can keep for months without any significant change. The antibacterial activities of the prepared compounds were evaluated with regard to two bacteria species, gram-negative *Proteus* and *Kelbsiella*, by using diffusion agar plates. The inhibition zone diameter around the holes indicated the sensitivity of the bacteria to these compounds, where the *Klebsiella* bacteria were revealed to be more highly sensitive to these compounds than *Proteus* bacteria. All synthesized complexes showed more significant effects against *Kelbsiella* and *Protea* than the antibiotic (Amikacin).

Keywords: Schiff base, binuclear metal complexes, 1,10-phenanthroline, thermogravimetric analysis, biological activities.

1. Introduction

Imine compounds containing the azomethine (C=N) group are considered good coordinating ligands when they bear a functional group such as the hydroxyl, amine or thiol due to the formation of a five- or six-membered chelate with a metal ion.[1,2] Imine compounds and their transition metal complexes have attracted considerable interest due to their antibacterial,[3] antifungal,[4] antiviral,[5] antimalarial,[6] anticancer,[7] and antitumour[8] activities. Benzidine compounds form a variety of Schiff bases with aldehydes/ketones and are reported to be superior reagents in biological, pharmacological, clinical and analytical applications which are improved by complexation with transition metal ions.[9-11] Heterocyclic compound such as 1,10-phenanthroline (Phen) is a good ligand due to the presence of two-ring nitrogen atom with a localized pair of electrons.[12] A large number of mixed-ligand complexes involving 1,10-phenanthroline has been prepared by different researchers[12,13] due to their biological applications, structural properties and activity as corrosion inhibitors.

In this work, we synthesized a number of complexes with an imine ligand (H_2L) derived from salicylaldehyde and benzidine as the primary ligand and 1,10-phenanthroline (L`) as a co-ligand, and the metal ions Fe(II), Co(II), Ni(II) and Cu(II) in a molar ratio of 1:2:2, respectively. We also estimated the antimicrobial activities of prepared complexes against *Proteus* and *Kelbsiella b*acteria.

2. Experimental

2.1. Materials and Reagents

All the chemicals and solvents for the prepared compound were of analytical grade. The methanol,

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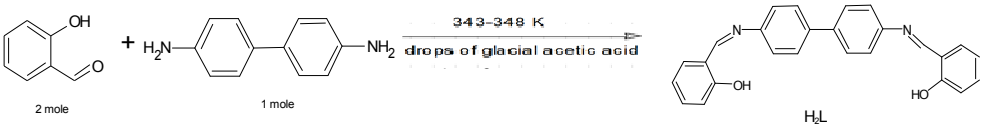
ethanol, glacial acetic acid, DMF, DMSO and other solvents used were of high purity and supplied by BDH. Benzidine, salicylaldehyde, 1,10-phenanthroline and metals salts ($FeCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$), were supplied by BDH and Sigma-Aldrich. CHN elemental analysis was undertaken for the ligand and complexes using an Euro EA Elemental Analyzer. Infrared spectra for the ligand and complexes were recorded *via* a Fourier transform-infrared (FT-IR) spectrometer using a KBr disk in the frequency range of 4000–400 cm^{-1} using a Shimadzu Corporation 8000S FTIR spectrometer. All electronic spectra of the prepared compounds have been recorded in the region of 200–1100 nm using a Shimadzu UV-240 UV-visible recorder spectrometer using dimethylformamide (DMF) as a solvent at the concentration of $1 \cdot 10^{-3}$ M. Magnetic susceptibilities obtained for the complexes were found at room temperature using a Magnetic Susceptibility Balance-MSBMKI. Molar conductivity was measured using a Jenway Ltd-4071 Digital conductivity meter using DMF as a solvent at the concentration of $1 \cdot 10^{-3}$ M. Melting points were measured using a Stuart melting point apparatus.

2.2. Synthesis of Primary Ligand (H_2L)(9)

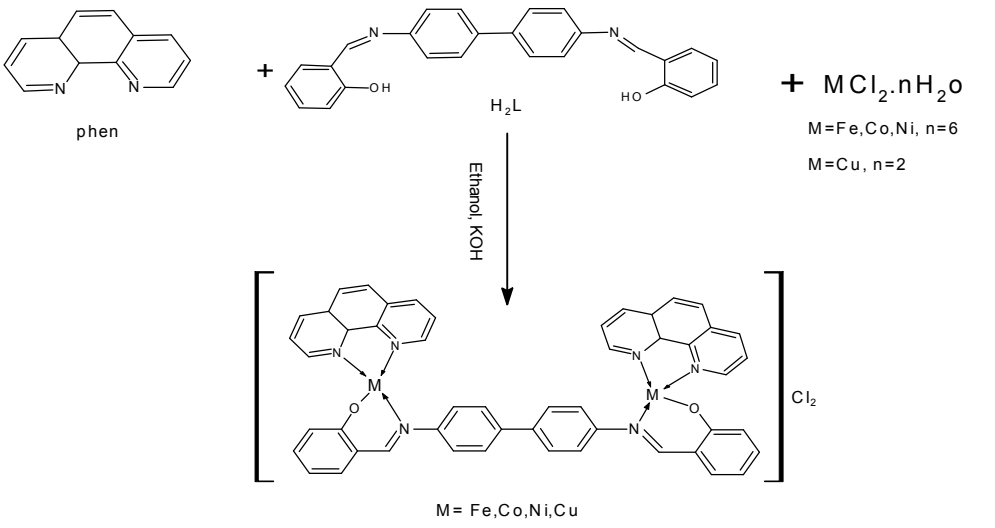
The ligand (H_2L) was prepared from the reaction of 0.032 mol salicylaldehyde with 0.016 mol benzidine in 25 mL absolute ethanol and 1-2 drops of glacial acetic acid, which was then refluxed at 343 K in a water bath for 2–3 h. The product which was separated out on subsequent cooling was filtered off. A yellow precipitate was obtained and then recrystallized from a hot mixture of 5 mL ethanol, 2 mL distilled water and 5 mL acetone. The product yield was almost 75 %, and a melting point was 491 K. The synthesis of the ligand is shown in Scheme 1.

2.3. Synthesis of the Binuclear Complexes

0.392 g (1 mmol) of H_2L ligand was added to the ethanolic solution of potassium hydroxide and 0.364 g (2 mmol) of 1,10-phenanthroline(phen) in a 100 mL round-bottomed flask. The appropriate amount of ethanolic solution of each metal salt, namely [$FeCl_2 \cdot 6H_2O$], [$NiCl_2 \cdot 6H_2O$], [$CoCl_2 \cdot 6H_2O$] and [$CuCl_2 \cdot 2H_2O$] was added in a ratio of 1:2:2 for H_2L:1,10-phenanthroline:metal salt. The reaction mixture was refluxed for about 3 h at 328 K. The resulting product was filtered and washed using a hot ethanol and finally dried for 24 h. The synthesis of the complexes is shown in Scheme 2.



Scheme 1. Synthetic route for the preparation of ligand (H_2L)



Scheme 2. General reaction for synthesis of prepared complexes

2.4. Antibacterial Activity

In this study, the antibacterial activity of the (H_2L) ligand and its prepared complexes was tested in DMSO as a solvent against the growth of two pathogenic microbes (*Proteus sp.* and *Klebseilla sp.*) which are representative of gram-negative bacteria, which were obtained and identified from the laboratories of the Biology Department, College of Science, University of Kerbala, Iraq. The microbes isolated were first activated by the development of bacteria in a nutrient broth medium,[14] after which the well diffusion assay method was used to determine the antibacterial activity of the prepared compounds.

To determine the antibacterial activity of the complexes against the studied bacteria we prepared a stock of the young bacteria (at an age of 24 h) by transferring a colony to a physiological saline solution and controlling its turbidity with the first tube of a standard McFarland tube then spreading it onto Muller Hinton Agar and leaving the dishes for 15 min to infuse the medium with a bacterial legation. A hole was placed in the centre of each dish using a sterile corky borer induplicate rate for each compound, then 100 µl of the prepared solutions were added to these holes using a micropipette, and which were then placed in the incubator at 310 K for 24 h. The inhibition zone was then measured around each hole,[15] and compared with Amikacin (10 mg disc) following the standard method of Bauer *et al*.[16]

3. Results and Discussion

The binuclear complexes prepared by reaction of H_2L with 1,10-phenanthroline and the metal salts were added in the ratio 1:2:2 (H_2L:1,10-phenanthroline:metal salt). The complexes were characterized by means of elemental analysis, infrared and UV-Vis spectra, ^1H NMR, magnetic susceptibility and thermal analysis.

3.1. Physical Properties and Elemental Analysis of the Ligand and its Complexes

The physical properties and CHN element analysis are reported in Table 1, where the latter for the ligand and its compounds almost correspond to the theoretical results calculated for the suggested formulae. Physical features (melting point (MP) and colour) for H_2L and its complexes can be seen, which show that the colour of the ligand differs from the colours of the synthesised complexes, and the high melting points indicate high photostability and stability in air.

3.2. IR Spectroscopic Investigations

The IR absorption spectra of the Schiff base for the ligand (H_2L), as shown in Fig. 1, showed the absence of absorption bands for stretching vibrations (symmetrical and asymmetrical) of the secondary amine NH_2 of benzidine and the stretching vibration of the carbonyl group (C=O) of salicylaldehyde, and the appearance of a stretching vibration for the azomethine group (–C=N) at 1610 cm^{-1} and a broad band at 3465 cm^{-1}, which belong to hydroxyl group.[17] The stretching frequency of the hydroxyl group ν(O–H) is absent in the IR spectra of all prepared complexes (see Fig. 1), which confirms coordination *via* the hydroxyl oxygen atom. It was also observed that all the absorption bands associated with the azomethine group (C=N) for the Schiff base and 1,10-phenanthroline appeared in the same region and were shifted to lower and higher frequencies due to coordination with metal ions *via* the nitrogen atom. The new bands appeared in the regions of 536–623 and 445–538 cm^{-1} likely due to the formation of M–O and M–N bonds, respectively.[5,18-20]

Table 1. Physical properties and elemental analysis for the ligand (H_2L) and its complexes

Compound	Molecular weight, g/mol	Elemental analysis, % (Found / Calcd.)			Color	MP, K	Yield, %
		C	H	N			
H_2L	392.46	79.25 (79.57)	5.14 (4.89)	7.14 (6.95)	Bright yellow	482	80
$[Co_2(H_2L)(L`)_2]Cl_2$	939.63	63.91 (63.29)	3.65 (2.99)	8.94 (8.46)	Brownish orange	296	74
$[Cu_2(H_2L)(L`)_2]Cl_2$	948.85	63.29 (63.56)	3.61 (3.13)	8.86 (8.42)	Brown	569	68
$[Ni_2(H_2L)(L`)_2]Cl_2$	939.15	63.95 (64.22)	3.65 (3.53)	8.95 (8.32)	Greenish yellow	515	75
$[Fe_2(H_2L)(L`)_2]Cl_2$	933.45	64.34 (64.01)	3.67 (3.23)	9.00 (8.89)	Dark brown	507	65

Table 2. Some IR data for H_2L and its complexes (cm^{-1})

Compounds	υ(C-H) aliphatic	υ(C-H) aromatic	υ(C=N)	υ(M–N)	υ(M–O)
H_2L	2984.76	3053.42	1610.61	–	–
$[Co_2(H_2L)_2(L`)]Cl_2$	2989.76	3053.42	1618.33	551.66	443.64
$[Fe_2(H_2L)_2(L`)]Cl_2$	2989.76	3051.49	1618.33	549.73	443.64
$[Ni_2(H_2L)_2(L`)]Cl_2$	3055.35	3363.97	1620.26	549.10	443.64
$[Cu_2(H_2L)_2(L`)]Cl_2$	3051.49	3390.34	1608.69	540.09	445.57

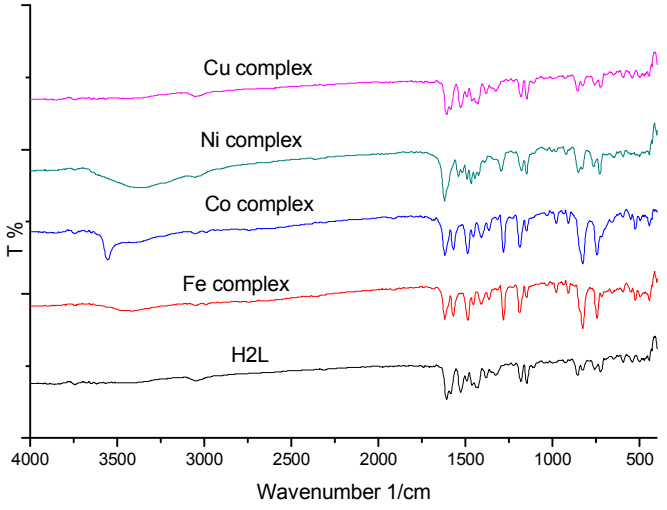


Fig. 1. IR spectra of H_2L and its complexes

3.3. Electronic Spectra, Molar Conductivity, and Magnetic Susceptibility

The electronic spectrum of the,H_2L ligand, as shown in Fig. 2, displayed two absorption bands, with the first at 222 nm belonged to the (π–π*) transition and the second band at 356 nm belonged to the (n–π*) transition.[21] The electronic spectrum of the $[Fe_2(H_2L)_2(L`)]Cl_2$ complex, as shown in Fig. 3, exhibits two peaks, the first intense peak at 246 nm being due to the ligand field transitions, and the second broad band at 371 nm being due to the charge transition.[22] The conductivity of the $[Fe_2(H_2L)_2(L`)]Cl_2$ complex was 135.3 µS/cm,,which indicates a conductivity of 1:2, while the magnetic moment for this complex was 5.25 B.M,,which indicates four single electrons in a tetrahedral environment.[23] The electronic spectrum of the $[Co_2(H_2L)_2(L`)]Cl_2$ complex (Fig. 4) showed a broad, low-intensity band at 256 nm which is due to the ligand field transitions, ,and a second high-intensity band at 370 nm which is due to the charge transition. The magnetic susceptibility (5.04 B.M) and molar conductivity (161.5 µS/cm) measurements indicated that the complex is paramagnetic and electrolytic (ratio 1:2), which indicates a tetrahedral geometry around the Co(II) ion.[24] The electronic spectrum of the $[Ni_2(H_2L)(L`)_2]Cl_2$ complex (Fig. 5) showed two bands at 250 and 269 nm, corresponding to a ligand field transition, while a charge transfer band appeared at 371 nm and a d-d transition band at 693 nm belonging to υ_2:($^3T_{1(F)} \rightarrow {}^3T_2$) in the tetrahedral geometry of Ni(II) complexes.[22] The magnetic susceptibility was 3.75 B.M and the molar conductivity measurement in DMF was 156 µS/cm in type 1:2, which indicated that the complex is paramagnetic and electrolytic. From these results, tetrahedral geometry around Ni(II) can be suggested.[22,25] The spectrum of the $[Cu_2(H_2L)_2(L`)]Cl_2$ complex (Fig. 6) exhibited two peaks. The first high-intensity peak at 249 nm was due to the ligand field transition, while the second broad band at 370 nm was due to the charge transfer transition. These transitions indicate a square planar geometry around the Cu(II) ion.[20] The Cu(II) complex shows a value of μ_{eff} =1.73 µV. The observed magnetic moments of Cu(II) show one unpaired electron with a paramagnetic kind and propose a square planer geometry in terms of Jahn-Teller effect. The molar conductivity measurement was 168 µS/cm, indicating that the complex was the electrolytic one. According to these data, a square planar geometry around the Cu(II) ion can be suggested.[26]

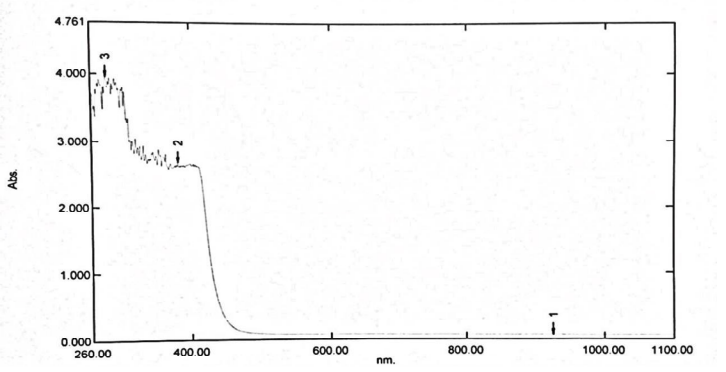


Fig. 2. UV-Vis spectrum for H_2L ligand

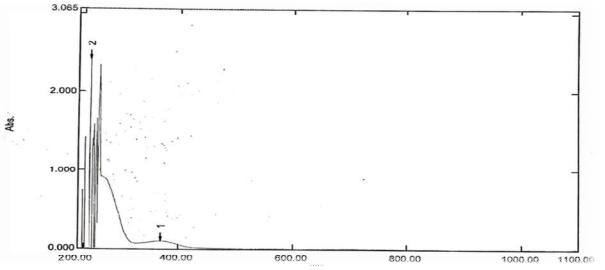


Fig. 3. UV-Vis spectrum for $[Fe_2(H_2L)(L`)_2]Cl_2$

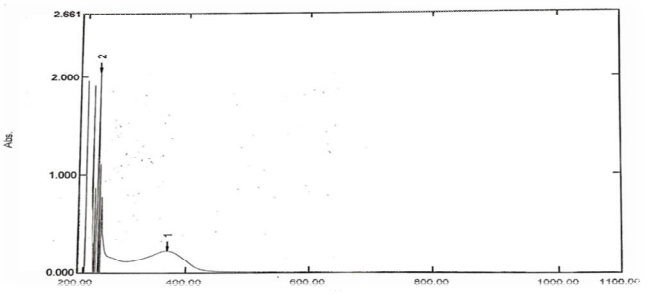


Fig. 4. UV-Vis spectrum for $[Co_2(H_2L)(L`)_2]Cl_2$

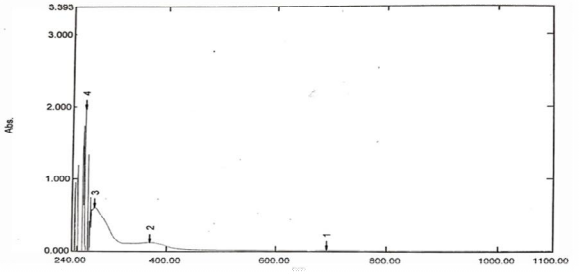


Fig. 5. UV-Vis spectrum for $[Ni_2(H_2L)(L`)_2]Cl_2$

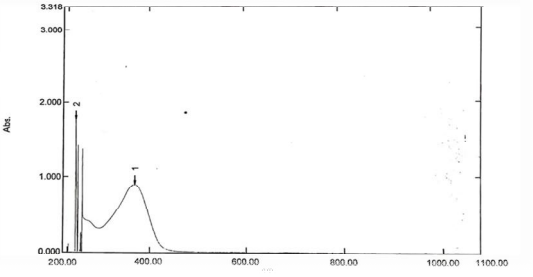


Fig. 6. UV-Vis spectrum for $[Cu_2(H_2L)(L`)_2]Cl_2$

3.4. ^{1}HNMR Spectra

The ^{1}HNMR spectra (Figs.7-12) were recorded for the Schiff base ligand (H_2L) and its metal complexes in DMSO as the solvent and showed the following chemical shifts; multiple signal chemical shifts between 6.97–7.89 ppm belong to the protons in aromatic rings, the singlet chemical shift at 9.01–9.10 ppm is attributed to the proton attached to C=N group.[27] The ^{1}H NMR spectrum of the ligand (H_2L) showed the hydroxyl protons appeared at δ = 13.27 ppm. The chemical shifts of the hydroxyl disappeared in all complexes, while those of the C=N group shifted due to coordination with the metal ion.

3.5. Thermogravimetric Analyses (TGA/DTA)

Table 3 and Figs. 13-17 show the thermal decomposition steps of the ligand H_2L and their metal complexes *via* the TGA and DTA techniques within the range of 303–1173 K at a heating rate of 20 K/min under a nitrogen atmosphere. Found and calculated weight loss, thermal range, decomposed compounds and produced compounds are shown in Table 3. Ionic chlorine molecules that were not directly coordinated to the metal ion were found to be lost at lower temperatures. The stages of decomposition reflect the nature of the binding

between the metal and ligand atoms and the stability of the complexes.[28] The later steps appeared to have left the metal ion with oxygen or alone, which reflects the affinity of the metal atoms towards oxygen, according to Pearson's law;[29] finally, a general trend in the thermolysis steps was observed in the earlier stages, where the small molecules were first to be lost, followed by the larger molecules.

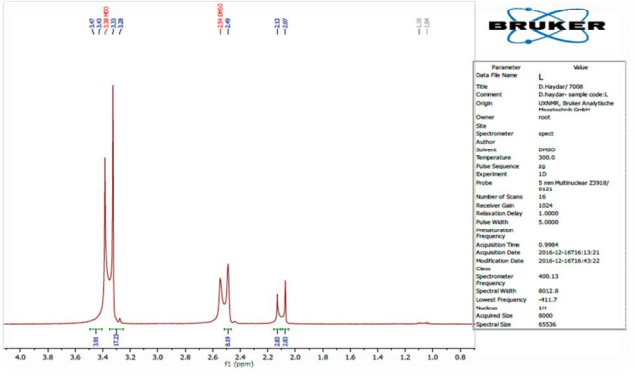


Fig. 7. ^{1}H NMR spectrum for the H_2L ligand

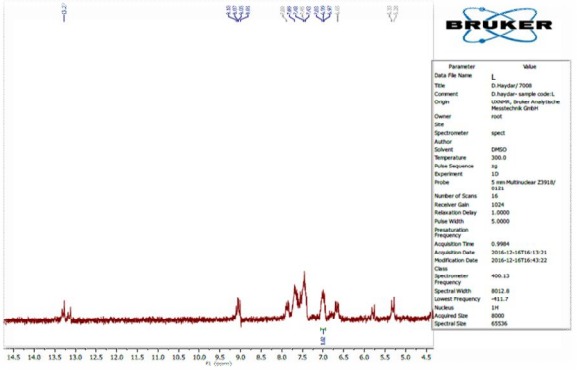


Fig. 8. ^{1}H NMR spectrum (zoom) for the H_2L ligand

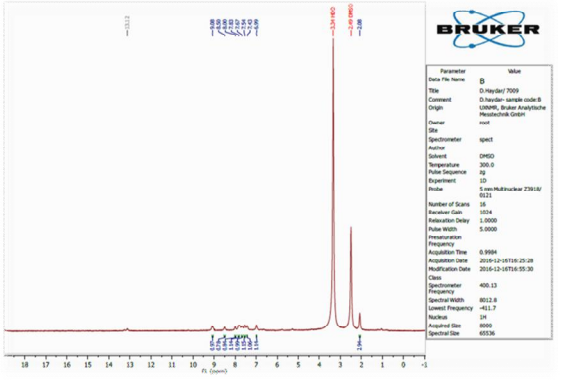


Fig. 9. ^{1}H NMR spectrum for the Fe(II) complex

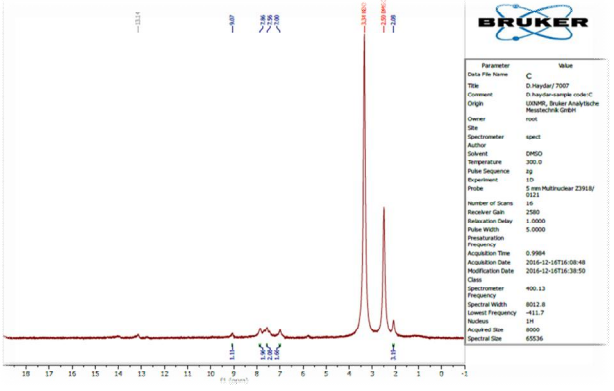


Fig. 10. ^{1}H NMR spectrum for the Co(II) complex

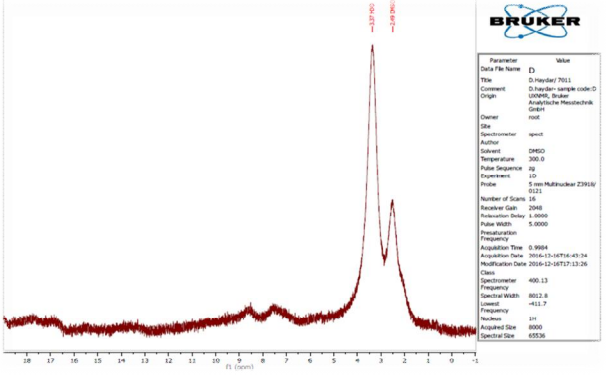


Fig. 11. ^{1}H NMR spectrum for the Ni(II) complex

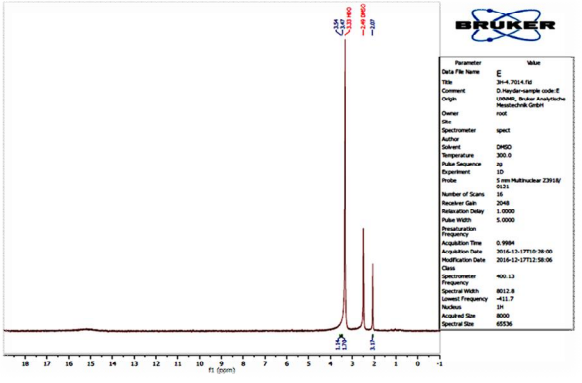


Fig. 12. ^{1}H NMR spectra for the Cu(II) complex

Table 3. Thermal decomposition of the H_2L ligand and its metal complexes

Compound	Molecular weight, g/mol	Weight loss, %		Thermal range, K	Decomposed compounds	Produced compounds
		Found	Calcd.			
H_2L	392	78	76.959	343–728	↓ $2(C_7H_6O)$, (C_6H_4N)	C_6H_4N
		24	22.959	728–973	↓ C_6H_4N	0
$[Fe_2(H_2L)(L`)_2]Cl_2$	933.45	7.35	7.60	973–633	↓ Cl_2	$C_{50}H_{34}Fe_2N_6O_2$
		19.12	19.28	633–798	↓ $C_{12}H_8N_2$	$C_{38}H_{26}Fe_2N_4O_2$
		19.12	19.29	798–983	↓ $C_{12}H_8N_2$	$C_{26}H_{18}N_2O$ FeO, Fe
$[Co_2(H_2L)(L`)_2]Cl_2$	939.63	7.3	7.55	303–378	↓ Cl_2	$C_{50}H_{34}Co_2N_6O_2$
		19.09	19.16	378–563	↓ $C_{12}H_8N_2$	$C_{38}H_{26}Co_2N_4O_2$
		38.18	38.36	563–878	↓ $C_{24}H_{16}N_4$	$C_{14}H_{10}Co_2O_2$
$[Ni_2(H_2L)(L`)_2]Cl_2$	939.15	7.35	7.56	373–633	↓ Cl_2	$C_{50}H_{34}Ni_2N_6O_2$
		22.06	22.3	633–758	↓ $C_{14}H_{10}O_2$	$C_{36}H_{24}Ni_2N_6$
		19.11	19.20	758–1073	↓ $C_{12}H_8N_2$	$C_{24}H_{16}N_4$ 2Ni
$[Cu_2(H_2L)(L`)_2]Cl_2$	948.07	11.11	11.28	473–603	↓ C_7H_5O	$C_{43}H_{29}Cl_2N_6O$, 2Cu
		7.9	7.5	603–671	↓ Cl_2	$C_{43}H_{29}N_6OCu$, CuO
		19.07	19.01	671–803	↓ $C_{12}H_8N_2$	$C_{31}H_{21}N_4$,CuO Cu
		19.00	19	803–1008	↓ $C_{12}H_8N_2$	$C_{19}H_{13}N_2$, CuO, Cu

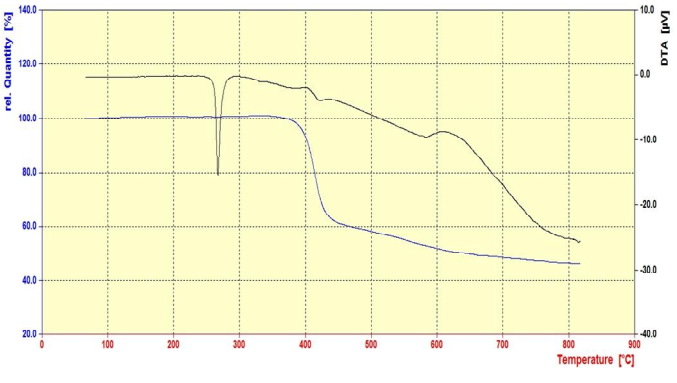


Fig. 13. TGA and DTG thermographs of H_2L

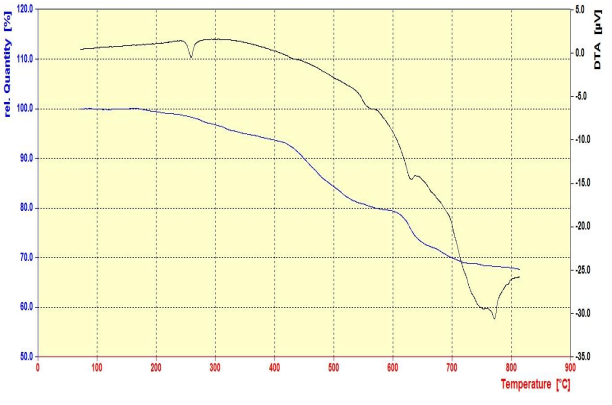


Fig. 14. TGA and DTA thermographs of $[Fe_2(H_2L)(L`)_2]Cl_2$

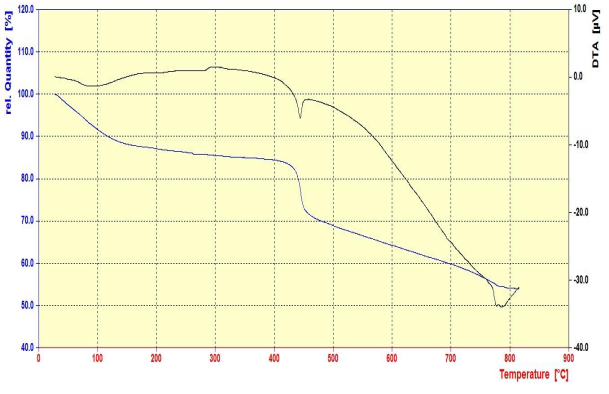


Fig. 15. TGA and DTA thermographs of $[Co_2(H_2L)(L`)_2]Cl_2$

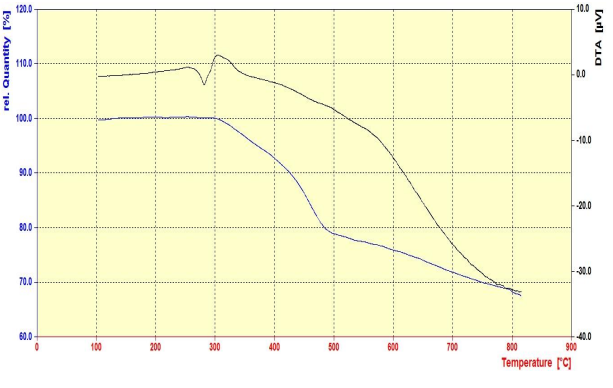


Fig. 16. TGA and DTA thermographs of $[Ni_2(H_2L)(L`)_2]Cl_2$

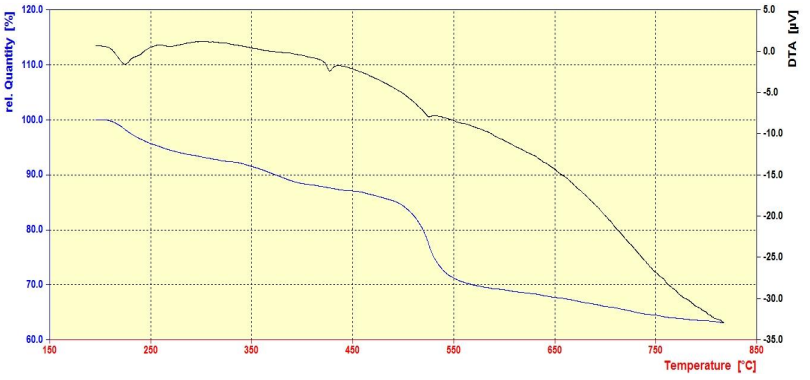


Fig. 17. TGA and DTA thermographs of $[Cu_2(H_2L)(L`)_2]Cl_2]$

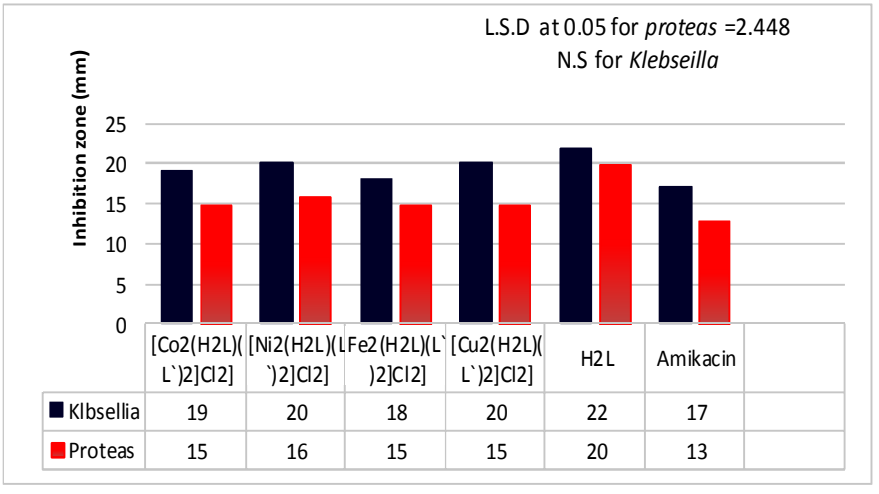


Fig. 18. Inhibition zone (mm) produced due to the prepared compounds against *Proteas* and *Klebseilla*

3.6. Antibacterial Activity

The primary ligand and its metal complexes were studied against two bacterial species, which were gram positive and gram negative (*Kelbsiella* and *Proteas*), as shown in Fig. 18, using diffusion agar plates. The sensitivity of bacteria for these compounds have been studied through inhibition zone diameters around the wells. The ligand (H_2L) was more highly effective against both *Kelbsiella* and *Protea* than the complexes. *Klebsiella* has a higher sensitivity for these complexes than the *Proteas* bacteria. All of the ligands and their complexes showed more significant effects against *Kelbsiella* and *Protea* than the antibiotic (Amikacin). Many metal complexes are essential to living bacteria as structural proteins and using in oxidation–reduction processes but a high concentration of these elements has an inhibitory effect, which is mainly due to altering the conformational structures of proteins, and affecting the nucleic acid and plasma membranes integrity. The toxicity of these complexes included reactive oxygen species (ROS), reduced enzyme and non-enzyme antioxidant, deactivation of enzymes, damage to the plasma membrane and restricted electron transport.[30]

4. Conclusions

Metal ion complexes of Co(II), Ni(II), Cu(II) and Fe(II) for the mixed ligands (imine of benzidine (H_2L) and 1,10-phenanthroline (L`)) were synthesized and characterized. Through the measurements of the electrical conductivity of the complexes, it was found that all of them conducted in a 1:2 ratio. FT-IR measurements elucidated the fact that the Schiff base ligand (H_2L) coordinated with metal ions as a bidentate ligand via its nitrogen and oxygen atoms, and that 1,10-phenanthroline coordinated by the two nitrogen atoms. According to physical measurements and the magnetic moments determined, it was clear that most of complexes had

tetrahedral geometries, with the exception of the Cu(II) complex which had a square planar geometry. Thermogravimetric analysis indicated that the chlorine in most complexes that was not directly coordinated to the metal ions was lost at lower temperatures, and the latest steps appeared to have left the metal ion with oxygen or alone, which reflects the affinity of the metal atoms for oxygen. The antimicrobial activity of the complexes indicates that the ligand (H_2L) was more effective against both *Kelbsiella* and *Protea* than the complexes as determined from their growth and sensitivity.

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СИНТЕЗ, ХАРАКТЕРИСТИКА І БІОЛОГІЧНА АКТИВНІСТЬ СУМІШІ ЛІГАНДІВ (ІМІНУ БЕНЗИДИНУ ТА 1,10-ФЕНАНТРОЛІНУ) ТА ЙОНІВ Fe(II), Co(II), Ni(II) ТА Cu(II)

Анотація. *За реакцією первинного ліганду (іміну бензидину) (H_2L) та вторинного ліганду (1,10-фенантролін) (L`) з йонами металів Fe(II), Co(II), Ni(II) та Cu(II) у мольному співвідношенні 1:2:2 синтезовані бінуклеарні металічні комплекси. За допомогою елементарного аналізу, FT-IR, UV-VIS, магнітної сприйнятливості, молярної провідності, ^{1}H ЯМР та термогравіметричного аналізу TGA-DTA визначено характеристику комплексів. Показано, що комплекси з Fe(II), Co(II) і Ni(II) мають восьмигранну геометрію, тоді як комплекс з Cu(II) має квадратну площинну геометрію. Всі синтезовані комплекси стійкі і можуть зберігатися місяцями без суттєвих змін. З використанням дифузійних агарових пластинок проведено оцінку антибактеріальної активності одержаних сполук стосовно двох видів бактерій, грампозитивної та грамнегативної (Kelbsiella та Proteus). Встановлено, що бактерія Klebsiella є більш чутливою до цих сполук, ніж Proteus. Показано, що синтезовані сполуки мають більший вплив на бактерії у порівнянні з антибіотиком (Амікацин).*

Ключові слова: *основа Шиффа, бінуклеарні металічні комплекси, 1,10-фенантролін, термогравіметричний аналіз, біологічна активність.*