



Mixed Ligand Complexes of Copper(II) and Cobalt(II) with Hydrazones Derivatives and ortho-Vanillin: Syntheses, Characterizations and Antimicrobial Activity

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ABSTRACT

The purpose of this paper was to synthesis new mixed-ligand Cu(II) and Co(II) metal complexes utilizing bidentate and tridentate donor hydrazones derivatives as primary ligands and ortho-Vanillin as co-ligand. The obtained compounds were characterized by elemental analysis, Infrared, UV-Vis., ¹H-NMR, Mass spectra, molar conductance, thermal analysis and atomic absorption spectroscopy (ASS). Spectroscopic analysis results indicated that the hydrazone ligand (L₁) behave as tridentate (ONO) and forms metal complexes having distorted square planar geometry. While the ligands (L₂, L₃ and L₄) behave as bidentate (NO) and forms metal complexes having octahedral geometry around the central metal atoms. The antimicrobial potentials were assessed for the ligand (L₂) and its metal complexes only and were screened against six types of bacterial strains and one fungal strain. The antimicrobial activities results of the tested compounds showed enhanced activity of the complexes over their parent ligands.

Keywords: Hydrazones, ortho-Vanillin, Mixed Ligand Complexes, Antimicrobial Activity

INTRODUCTION

Transition coordination compounds containing hydrazones as ligands is still important field of investigation because of its interesting structural features and their biological significance^{1,2}. Hydrazones are important ligands, which played a significant role in the progress of Inorganic chemistry of the metal complexes. These ligands easily form stable coordination compounds with metal ions³. Hydrazones can also coordinate with several transition

metal cations, like copper(II), iron(III), vanadium and zinc(II)⁴⁻⁷. Hydrazones and their complexes are having great medicinal applications like anti-fungal, anti-inflammatory, anti-bacterial, anti-tuberculostatic, antimicrobial and anti-cancer agents⁸⁻¹¹. Due to the importance of such ligands, many studies found that mixed ligand complexes are different from traditional complexes in the point they have at least two different ligands linked with central metal ion in the complex. Synthesis and characterization of new mixed ligand is increasing day by day and researchers are involved in this field¹²⁻¹⁵.



From the importance mentioned above we are encouraged to prepare new copper and cobalt complexes using hydrazone derivatives and o-vanillin as mixed ligands.

MATERIALS AND METHODS

Chemicals

All chemicals used in this work: Copper(II) chloride, Cobalt(II)chloride, methyl benzoate, hydrazine hydrate, benzaldehyde, salicylaldehyde, anisaldehyde, vanillin, o-vanillin (L_6) were obtained from local market and used in experimentation without purification. The benzoic acid hydrazide and hydrazone derivatives (L_1 – L_4) were prepared in the laboratory following the published methods in literature¹⁶.

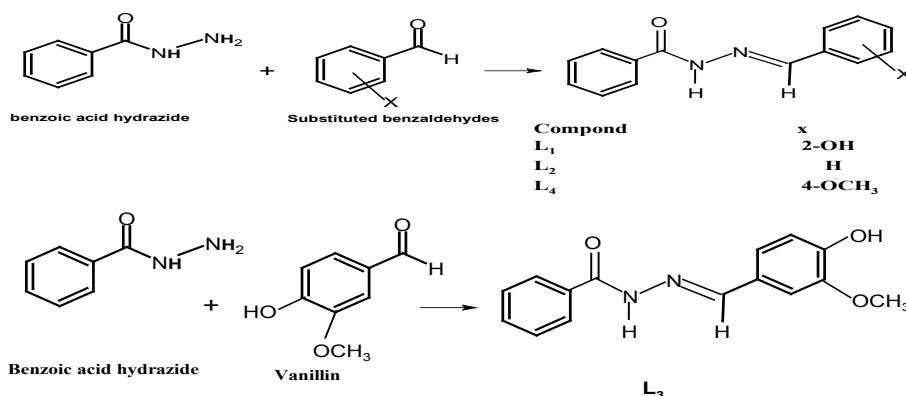
Instruments

Melting points of the synthesized ligands and complexes were measured using Electrothermal melting point apparatus (Cat NO. TA9100). Elemental analysis were recorded on a Leco VTF-900 CHN-S-O 932 version 1.3x instrument (Thermo Fisher Scientific-USA). Infrared spectroscopy was recorded on Nicolet IS50 FT-IR spectrophotometer in the spectra range of 4000–400 cm^{-1} . UV-Visible absorption analysis was performed utilizing UV-Visible double beam spectrophotometer of Thermo Scientific Evolution-300 model and using DMF as solvent. The Thermo Scientific Exactive Triversa Nanomate mass spectrometer instrument was used to measure mass spectra of the obtained

compounds. Molar conductivities of metal complexes in DMF solutions at a concentration of 0.001M were measured using Hanna instrument HI8633 N Multi-range conductivity meter. Thermogravimetric analysis (TGA) were performed on Shimadzu analyzer 50 in nitrogen atmosphere (100 ml/min) at a heating rate 10°C/min. The ^1H NMR spectra were performed by using Varian Mercury-400 BB (400 MHz) spectrometer using TMS (^1H) as standard. Atomic absorption spectroscopic studies of the formed GPZ-metal complexes were carried out using MODEL 210 VCP atomic absorption spectrophotometer (Buck Scientific, USA), detection limit 0.1 ppm and integration time 3 s. The flame used was acetylene-air mixture. A Shimadzu atomic absorption flame spectrophotometer model AA. 640-13, slit width 0.2 nm, relative noise 1.0, detection limit 0.6 ppm and integration time 3 s. The flame used was an acetylene-air mixture.

Synthesis of Hydrazone derivative ligands (L_1 – L_4)

The Hydrazone derivatives (L_1 – L_4) (Scheme 1) were prepared by condensation of Benzoic acid hydrazide (1.36 g, 10 mmol) in 50 mL of ethanol with an aldehyde compound (benzaldehyde, salicylaldehyde, vaniline, anisaldehyde) (10 mmol) in absolute ethanol (10 mL). add few drops of glacial acetic acid to the reaction mixture. The mixture was heated under reflux for 4 h and then allowed to cool at room temperature. The precipitate was filtered and washed with ethanol. The obtained product was recrystallized using ethanol to get pure solid¹⁶.



Scheme 1. Hydrazone derivatives ligands

Synthesis of Mixed Ligand Cu(II) and Co(II) Complexes

An ethanolic solution of hydrazone

derivatives (L_1 – L_4) as a primary ligand (1 mmol) and ethanolic solution of o-vanillin (L_6) as a co-ligand (1 mmol), were added slowly into warm aqueous

solution of Copper(II) chloride (CuCl_2) or Cobalt(II) chloride (CoCl_2) (1 mmol). The mixture was refluxed for five hours with stirring. The obtained precipitates were filtered, washed many times with cold ethanol and finally dried under desiccator.

Antimicrobial Activity

The antibacterial potency for both free ligands and their Co(II) and Cu(II) complexes were tested using three *Gram-positive* bacterial strains namely *Staphylococcus aureus*, *Enterococcus faecalis*, and *Group B streptococcus* (GBS) and three *Gram-negative* bacterial strains namely *Proteus Mirabilis*, *Escherichia coli*, *Klebsiella pneumoniae*. The antifungal potency was tested against the yeast *Candida albicans* only.

RESULTS AND DISCUSSION

The complexes of copper and cobalt were synthesized by the reaction of Cu^{2+} and Co^{2+} metal salts with hydrazone derivatives (L_1 – L_4) as primary ligands and o-vanillin (L_6) as secondary ligand. All the prepared complexes were colored and stable in open air. The obtained metal complexes were soluble

in DMF and DMSO. The ligands and their Cu^{2+} and Co^{2+} complexes were characterized using physico-chemical techniques. The physical properties data of the hydrazone derivatives ligands (L_1 – L_4) and their Cu^{2+} and Co^{2+} complexes are presented in Table 1.

Elemental analysis and values of molecular conductance for the synthesized complexes are listed in Table 2. The elemental analysis of the Co(II) and Cu(II) complexes are in agreement with the proposed chemical formula. It confirmed the presence of water molecules in the complexes by thermal analysis.

The values of molar conductance for prepared complexes (1-7) were measured in 1×10^{-3} M DMSO solutions are listed in Table 2. The values are within the range 13.9 – $20.8 \text{ Ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ for the complexes (2-7) suggest a non-electrolyte character of the tested compounds. While, the measured values (91.2 – $93.7 \text{ Ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) of molar conductance for the complexes (1 and 2) indicating 1:1 electrolytic nature of these complexes¹⁷. Molar conductivity measurements are agreed with the formula of the metal complexes.

Table 1: The physical properties data for ligands (L_1 – L_4) and their Cu^{2+} and Co^{2+} complexes

Compound	Molecular Formula	Yield%	Color	MP (°C)	Mol. Wt.
L_1	$\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_2$	82%	Pale yellow	179	240.25
L_2	$\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}$	60%	Brownish yellow	195	224.25
L_3	$\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_3$	72%	Brownish yellow	124	270.28
L_4	$\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_2$	92%	White	157	254.28
$[\text{Cu}(\text{L}_1)\text{L}_6]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ (1)	$\text{C}_{22}\text{H}_{26}\text{Cl}_2\text{CuN}_2\text{O}_9$	65%	Brown	300	596.9
$[\text{Co}(\text{L}_1)\text{L}_6]\text{Cl}_2 \cdot 4.5\text{H}_2\text{O}$ (2)	$\text{C}_{22}\text{H}_{27}\text{Cl}_2\text{CoN}_2\text{O}_{9.5}$	85%	Dark green	300	601.29
$[\text{Cu}(\text{L}_2)\text{L}_6]\text{Cl}_2 \cdot 5.5\text{H}_2\text{O}$ (3)	$\text{C}_{22}\text{H}_{30}\text{Cl}_2\text{CuN}_2\text{O}_{9.5}$	66%	Brown	300	608.93
$[\text{Co}(\text{L}_2)\text{L}_6]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (4)	$\text{C}_{22}\text{H}_{23}\text{Cl}_2\text{CoN}_2\text{O}_6$	76%	Dark green	300	541.26
$[\text{Cu}(\text{L}_3)\text{L}_6]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (5)	$\text{C}_{23}\text{H}_{23}\text{Cl}_2\text{CuN}_2\text{O}_7$	74%	Brown	300	573.89
$[\text{Co}(\text{L}_3)\text{L}_6]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (6)	$\text{C}_{23}\text{H}_{23}\text{Cl}_2\text{CoN}_2\text{O}_7$	65%	Dark green	300	569.27
$[\text{Cu}(\text{L}_4)\text{L}_6]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (7)	$\text{C}_{23}\text{H}_{23}\text{Cl}_2\text{CuN}_2\text{O}_6$	80%	Brown	300	557.89

Table 2: Elemental analysis and molar conductance values for the complexes

Compound	Cald. (Found)%						Molar conductivity $\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$
	C	H	N	O	Cu	Co	
$[\text{Cu}(\text{L}_1)\text{L}_6]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ (1)	43.26 (44.46)	4.39 (4.62)	4.69 (4.28)	24.12 (24.25)	10.64 (10.48)	-	93.7
$[\text{Co}(\text{L}_1)\text{L}_6]\text{Cl}_2 \cdot 4.5\text{H}_2\text{O}$ (2)	43.94 (43.73)	4.52 (4.32)	4.2 (4.42)	25.26 (25.52)	-	9.8 (9.58)	91.2
$[\text{Cu}(\text{L}_2)\text{L}_6]\text{Cl}_2 \cdot 5.5\text{H}_2\text{O}$ (3)	43.4 (43.82)	4.96 (4.72)	4.6 (4.95)	24.94 (24.76)	10.43 (10.84)	-	15.7
$[\text{Co}(\text{L}_2)\text{L}_6]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (4)	48.81 (48.55)	4.28 (4.13)	5.17 (5.52)	17.73 (17.98)	-	10.88 (10.96)	13.9
$[\text{Cu}(\text{L}_3)\text{L}_6]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (5)	48.13 (47.86)	4.04 (4.35)	4.88 (4.64)	19.51 (19.21)	11.07 (11.32)	-	14.3
$[\text{Co}(\text{L}_3)\text{L}_6]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (6)	48.52 (48.72)	4.07 (4.23)	4.92 (5.25)	19.67 (20.12)	-	10.35 (10.67)	18.5
$[\text{Cu}(\text{L}_4)\text{L}_6]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (7)	49.51 (49.85)	4.15 (4.34)	5.02 (5.39)	17.2 (17.52)	11.39 (11.69)	-	20.8

Infrared Spectra

A significant absorption bands for the free organic ligands (L_1 - L_4) were observed in the ranges 3010–3050 cm^{-1} , 1600–1640 cm^{-1} , 1630–1690 cm^{-1} and 3210–3260 cm^{-1} . These bands are assigned to N-H, -CH=N, C=O and OH stretching respectively. Important observed IR absorption bands for ligands and their Cu^{2+} and Co^{2+} complexes are recorded in Table 3. IR spectrum of $[\text{Co}(\text{L}_2)\text{L}_6\text{Cl}_2]2\text{H}_2\text{O}$ (4) complex is shown in Figure 1.

On comparing the observed IR spectra of the ligands with that observed for the corresponding metal complexes it is noted that the bands due to the (OH) group for the ligand (L_1) were disappeared in the spectra of the complexes (1 and 2). This observation indicate deprotonation of the OH group and binding to the metal ions through the oxygen atom¹⁸. In the IR spectrum of the complexes (5 and 6) it was observed that the bands due to OH group present in the L_3 ligand in the range (3170 – 3200 cm^{-1}) slightly shifted to lower frequency. The characteristic band of the carbonyl group $\nu(\text{C}=\text{O})$ that observed at 1630-1690 cm^{-1} in the spectrum of the free ligands (L_1 - L_4), shifted to lower frequency (by 10-20 cm^{-1}) in the spectrum of the complexes indicating complexation with metal

ions¹⁸⁻²¹. The formation of azomethine group ($\nu(\text{C}=\text{N})$) was confirmed by the appearance of bands in the range 1600-1640 cm^{-1} in the infrared spectra of the free ligands (L_1 - L_4). These bands were shifted to lower frequency and appeared at the range of (1540–1595 cm^{-1}) in the infrared spectra of the metal complexes¹⁻⁷. This blue shift in the IR wavelength of the metal complexes indicating the coordination of the N atom of the -CH=N- group to the metal ions^{3,22}.

In the infrared spectra of the copper(II) and cobalt (II) complexes¹⁻⁷ a new broad bands were observed in the range 3380-3450 cm^{-1} can be assigned to the $\nu(\text{OH})$ vibrations indicating the presence of water molecules^{23,24}. These bands were not observed in the spectra of the free ligands (L_1 - L_4). This was supported by TGA analysis. The observed bands in the region 520 - 550 and 450-490 cm^{-1} assigned to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ respectively²⁵. This indicates that the ligands (L_2 - L_4 and L_6) are bidentate and bind to metal ions through N atom of the -CH=N- and O atom of the $>\text{C}=\text{O}$ group. While, the ligand(L_1) behaves as tridentate ligand and bind to the metal ions through the N atom of the -CH=N-, O atom of the $>\text{C}=\text{O}$ and the O atom of -OH group.

Table 3: IR Spectroscopic data (cm^{-1}) of the ligands (L_1 - L_4) and their copper(II) and cobalt (II) complexes

Compound	H ₂ O	OH	NH	C=N	C=O	M-N	M-O
L_1	-	3260	3050	1600	1680	-	-
$[\text{Cu}(\text{L}_1)\text{L}_6\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ (1)	3400	-	3070	1550	1600	451	530
$[\text{Co}(\text{L}_1)\text{L}_6\text{Cl}_2 \cdot 4.5\text{H}_2\text{O}$ (2)	3390	-	3070	1555	1610	450	550
L_2	-	-	3050	1600	1690	-	-
$[\text{Cu}(\text{L}_2)\text{L}_6\text{Cl}_2] \cdot 5.5\text{H}_2\text{O}$ (3)	-	-	3060	1550	1605	480	525
$[\text{Co}(\text{L}_2)\text{L}_6\text{Cl}_2]2\text{H}_2\text{O}$ (4)	3400	-	3070	1545	1605	460	540
L_3	-	3210	3030	1600	1640	-	-
$[\text{Cu}(\text{L}_3)\text{L}_6\text{Cl}_2]\text{H}_2\text{O}$ (5)	3450	3170	-	1595	1680	470	530
$[\text{Co}(\text{L}_3)\text{L}_6\text{Cl}_2]\text{H}_2\text{O}$ (6)	3380	3200	3070	1580	1650	490	520
L_4	-	-	3010	1600	1630	-	-
$[\text{Cu}(\text{L}_4)\text{L}_6\text{Cl}_2]\text{H}_2\text{O}$ (7)	3390	-	3070	1540	1610	480	540

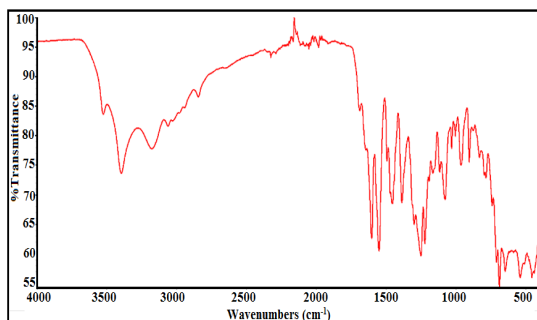


Fig.1. IR spectrum of $[\text{Co}(\text{L}_2)\text{L}_6\text{Cl}_2]2\text{H}_2\text{O}$ (4) complex

UV-Visible absorption Spectrum

The electronic absorption spectra of copper and cobalt complexes(1–7) were recorded in 10^{-3} $\text{mol}\cdot\text{L}^{-1}$ in DMSO solution, displayed many bands in the range of 200 to 600 nm (Figs. 2 and 3). In case of complexes (1, 3, 4, 5 and 6), the absorption bands around 320–360 nm were assigned to the intra-ligand charge transfer transitions of the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ charge transfer transitions^{26,27}. The complexes (1-7) also showed peaks at 490–409 nm which can be assigned to a metal-to-ligand charge transfer (MLCT)

transition^{28,25}. The lower energy bands at 600-670 nm can be assigned to a d-d transition in complexes (1 and 4) and are ascribed to the d-d transition and are characteristic for the 6-coordinated metal complexes (octahedral)^{29,30}.

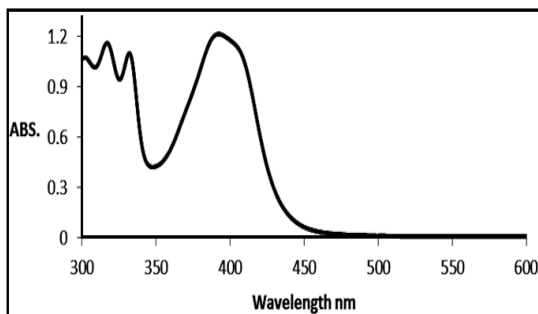


Fig. 2. The UV-Visible spectrum of [Cu(L₁)L₆]Cl₂·4H₂O (1)

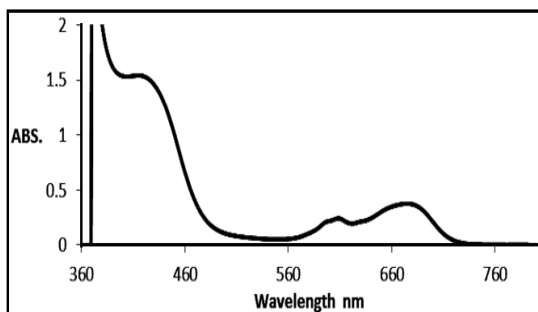


Fig. 3. The UV-Visible spectrum of [Co(L₂)L₆Cl₂]·2H₂O (4) complex

¹H NMR Spectra

The ¹H NMR spectra of the prepared ligands and their complexes were recorded in DMSO-d₆ and the internal standard used was tetra methyl silane (TMS). The ¹H NMR spectral data for [Cu(L₁)L₆]Cl₂·4H₂O (1) and [Co(L₂)L₆Cl₂]·2H₂O (4) complexes are shown in Fig. 4 and 5. The ¹H NMR spectra of the ligands (L₁ and L₂) showed signal at δ 8.65 ppm which is caused by the NH group. This signal was shifted to higher field in the spectra of metal complexes (1 and 4). The signal which assigned to the OH proton in the primary hydrazine ligand (L₁) and that in the co-ligand (L₆) was absent in the spectra of the metal complexes (1 and 4) supporting the deprotonation of the hydroxyl group in both ligands and coordination through the oxygen atom with the central metal ion³¹. The signal corresponding to the azomethine proton appeared at 7.87 and 7.88 ppm in the spectra of ligands, this signal is shifted to higher field in the spectra of metal complexes (1 and 4) due

to the coordination of azomethine nitrogen with metal ion and observed at 7.82 and 7.57 ppm³².

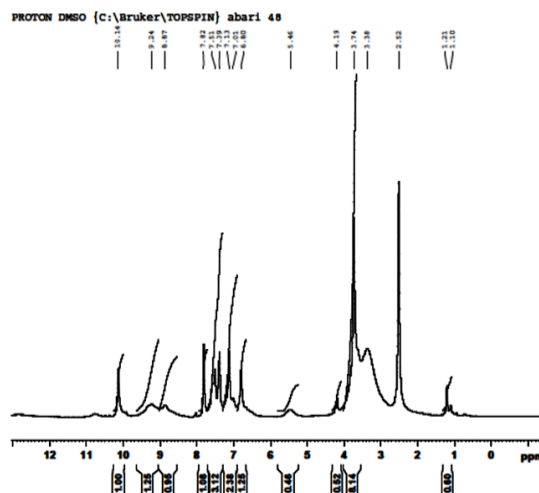


Fig. 4. ¹H NMR spectrum of [Cu(L₁)L₆]Cl₂·4H₂O (1) complex

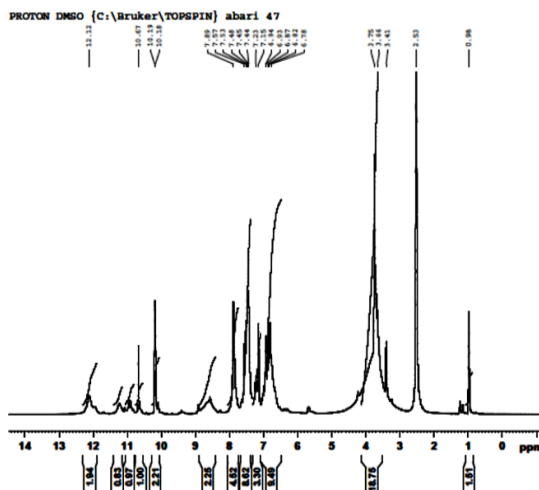


Fig. 5. ¹H NMR spectrum of [Co(L₂)L₆Cl₂]·2H₂O (4) complex

Thermogravimetric Analysis

Thermogravimetric curve of [Co(L₂)L₆Cl₂]·2H₂O (4) complex represents three decomposition steps (Fig. 6). The first step ended at nearly 250°C indicating the loss of two molecules of hydrated H₂O molecules and one molecule of HCl gas (obs.21%; calcd. 20.41%)³³. The next two steps started from 250°C and ended at 600°C, correspond to decomposition of the ligands leading to the final residue at 600°C as metal oxide (CoO), the remaining weight loss (obs./cal. 49.85/44.5) corresponds to the mixture of metal oxide and some ashes as a final pyrolysis product³⁴.

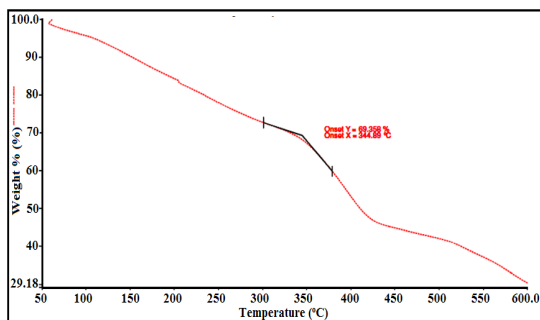


Fig. 6. Thermogravimetric (TGA) curve of $[\text{Co}(\text{L}_2)\text{L}_6\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ (4) complex

Mass Spectra

The mass spectra were recorded in order to confirm the theoretically calculated molecular weight according to the proposed structure. The molecular ion $[\text{M}+1]^+$ of the $[\text{Cu}(\text{L}1)\text{L}_6]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ (1) complex appears at $m/z = 598.25$, which matches the theoretically calculated molecular weight of (596.9 m/z), and this proves and supports the proposed structures. The molecular ion peak for the complex $[\text{Co}(\text{L}1)\text{L}_6]\text{Cl}_2 \cdot 4.5\text{H}_2\text{O}$ (2) was observed at 602.17 m/z , which is in accordance with the formula weight for this complex (calculated 601.29 m/z). Also, the mass spectrum for the complex $[\text{Cu}(\text{L}_2)\text{L}_6\text{Cl}_2] \cdot 5.5\text{H}_2\text{O}$ (3) showed a peak at 608.08 m/z , which is in accordance with its calculated formula weight (608.93 m/z). This confirms the formula proposed for these complexes. The mass spectra of some synthesized complexes are shown in Figures 7- 9.

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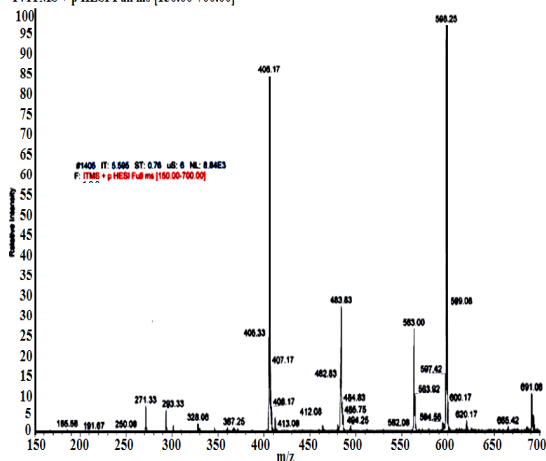


Fig. 7. Mass spectrum of $[\text{Cu}(\text{L}1)\text{L}_6]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ (1) complex

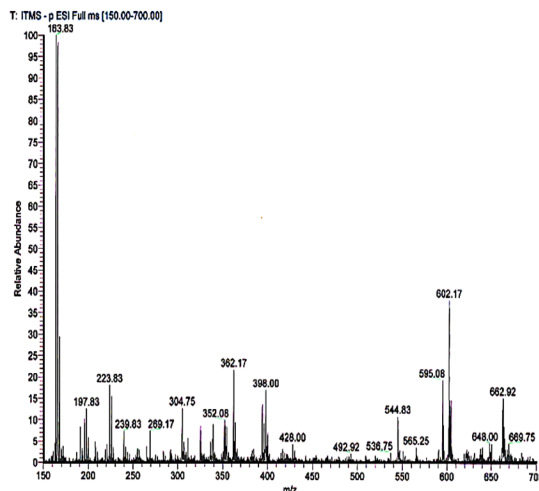


Fig. 8. Mass spectrum of $[\text{Co}(\text{L}1)\text{L}_6]\text{Cl}_2 \cdot 4.5\text{H}_2\text{O}$ (2) complex

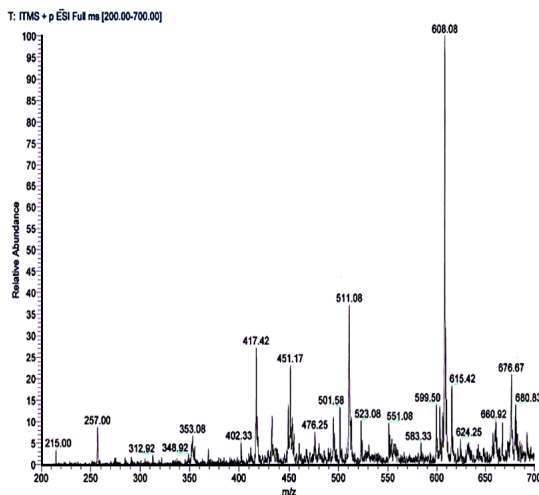


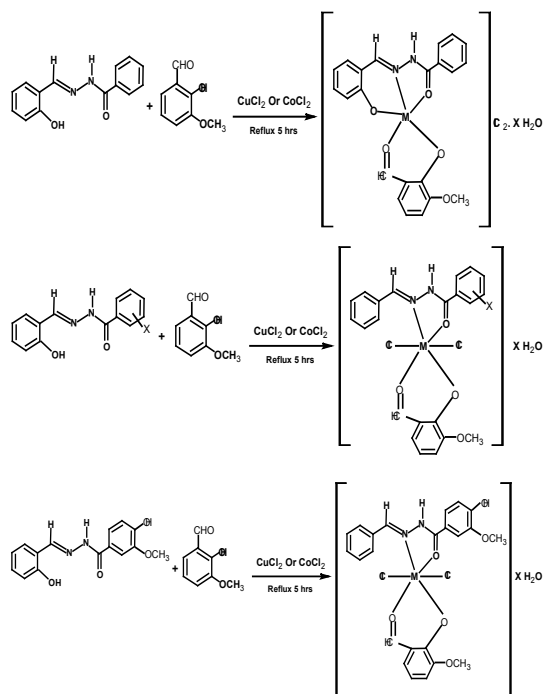
Fig. 9. Mass spectrum of $[\text{Cu}(\text{L}2)\text{L}_6\text{Cl}_2] \cdot 5.5\text{H}_2\text{O}$ (3) complex

From above results, we concluded that the hydrazone derivatives ligands ($\text{L}_2\text{-L}_4$) act as a bidentate ligand coordinate at the metallic ions through the oxygen atom of the free $\text{C}=\text{O}$ and N atom of the azomethane group forming stable five membered ring. While ligand L_1 acts as tridentate forming stable five and six membered rings. Moreover, the co-ligand (*o*-vanillin) acts as bidentate and coordinates to metal ions through oxygen atom of the hydroxyl and aldehydic groups forming six membered rings.

On the basis of the previous observations, it is suggested that the metal complexes (3-7) with bidentate ligands ($\text{L}_2\text{-L}_4$) showed an octahedral geometries while the proposed structure of the metal

complexes (1 and 2) with the tridentate ligand L_1 are of distorted square-pyramidal geometries.

The the proposed structure of the complexes 1-7 are shown below (scheme 2).



Scheme 2. Suggested structures of the Cu (II) and Co(II) complexes

Antimicrobial activity

The ligand (L_2) and its prepared corresponding

metal complexes (3 and 4) were assessed for microbial susceptibility against three *Gram-positive* and three *Gram-negative* bacteria strains. In addition, the antifungal assay was done against one kind of pathogenic fungus *Candida albicans*. The screening of the tested compounds was carried out at fixed concentration of 10^{-3} g/mL in DMSO solvent. The zones of complete inhibition (in mm) were measured in order to track the microbial susceptibility. The observations are recorded in Table 4. The results indicated that organic ligand (L_2) did not give activity against nearly all types of bacteria (*Gram-positive* bacteria and *Gram-negative* bacteria) except the *Enterococcus Faecalis* (inhibition zone of 16 mm). The tested metal complexes (3 and 4) showed antifungal activity against the pathogenic fungus *C. Albicans* with highest sensitivity with an inhibition zone equal to 26 and 21 mm respectively. The increased antifungal activity of the prepared metal complexes may be returned to chelation that increases the permeability of the chemicals and may be returned to metal ion (Cu^{2+} and Co^{2+}).

The results indicated that the examined Cu^{2+} and Co^{2+} complexes (3 and 4) have highest antibacterial activity against *Gram-positive* bacteria and *Gram-negative* bacteria compared to the free ligand (inhibition zones of 7-27 and 8-24 mm respectively).

Table 4: Antimicrobial activity of the ligand L_2 and its metal Complexes

Antibacterial Activity	200 (100) µg/disc						Antifungal Activity
	Gram-positive Bacteria			Gram-negative Bacteria			
Comp. No.	S.e	S. a	E. f	E. a	P. m	P. a	Yeast C. a
L_2	0	0	16	0	0	0	0
$[\text{Cu}(\text{L}_2)\text{L}_6\text{Cl}_2] \cdot 5.5 \text{H}_2\text{O}$ (3)	27	27	25	7	7	7	26
$[\text{Co}(\text{L}_2)\text{L}_6\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ (4)	24	14	16	8	20	14	21

S. e: *Staphylococcus epidermidis* (ATCC 12228); S. a: *Staphylococcus aureus* (ATCC 25923); E. f: *Enterococcus faecalis* (ATCC 29212); E. c: *Escherichia coli* (ATCC25922); P. m: *Proteus merabilis*(ATCC 13376); P. a: *Pseudomonas aeruginosa* (ATCC 27853); C. a: *Candia albican*(ATCC10231).

CONCLUSION

New series of copper (II) and cobalt (II) complexes incorporating with some mixed ligands containing hydrazone moiety as primary ligands and o-vanillin as co-ligand have been

synthesized. The ligands (L_1 - L_4) and their Cu^{2+} and Co^{2+} complexes were characterized by elemental analysis, Infrared, UV-Visible, $^1\text{H-NMR}$, Mass spectra, molar conductance, thermal analysis and atomic absorption spectroscopy (ASS). The observed data indicated that the ligands (L_2 - L_4 and

L_6) behave as bidentate ligands while the ligand (L_1) behaves as tridentate ligand. The analyses data for Cu(II) and Co(II) complexes suggested that the complexes (3-7) with bidentate ligands (L_2 - L_4 and L_6) showed an octahedral geometries. While, the structure of the Cu(II) and Co(II) complexes (1 and 2) with tridentate ligand (L_1) suggested distorted square-pyramidal geometries. The o-vanillin ligand coordinates to metal ion through oxygen atoms of the hydroxyl and aldehydic groups forming six membered ring.

The antibacterial results show that the ligand L_2 and its copper and cobalt complexes (3 and 4) have highest antibacterial activity against *Gram-positive* bacteria and *Gram-negative* bacteria

compared to the free ligands. On the other hand, the antifungal activity of the metal complexes (3 and 4) showed highest antifungal activity against the pathogenic fungus *C. Albicans* compared to the free ligands.

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Conflict of Interest

The authors declare no conflict of interest.

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