



Received on 15 March, 2012; received in revised form 25 July, 2012; accepted 27 September, 2012

BINUCLEAR Fe(III), Co(II), Ni(II), Cu(II) AND ZN(II) COMPLEXES WITH SCHIFF BASE 4, 4'(1, 4-PHENYLENE BIS(AZAN-1-YL-1-YLIDENE)) BIS(METHAN-1-YL-1-1-YLIDENE)-1, 2-DIOL. SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL EVALUATION

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ABSTRACT

Condensation reaction of 1, 4-phenylene diamine and Protocatechu aldehyde in 1:2 molar ratio resulted in the formation of new Schiff base ligand 4, 4'(1,4-phenylene bis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-1-ylidene)-1, 2-diol; (H₄L). From the direct reaction of the ligand (**1**) with Co(II), Ni(II) and Cu(II) chlorides and Fe(III) and Zn(II) nitrates in 2M:1L molar ratio, the five new neutral complexes were prepared. The characterization of the newly formed compounds was done by ¹H-NMR, U.V-Vis and IR spectroscopy and elemental analysis. The data showed tetrahedral geometry for Co, Ni, Cu and Zn complexes (**3**, **4**, **5** and **6** respectively) and octahedral geometry for Fe complex (**2**). The *in-vitro* antibacterial activity against G^{+ve} bacteria (*B. subtilis* and *S. aureus*), G^{-ve} bacteria (*E. coli* and *P. aeruginosa*) and antifungal activity against (*C. albicans* and *A. niger*) of the metal complexes were studied and compared with that of free ligand. Also MIC of the compounds against test microorganisms were detected.

Keywords:

Binuclear,
Schiff bases,
Synthesis,
PCA,
MIC of biological evaluation

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INTRODUCTION: Some Schiff bases were tested for fungicidal activity, which is related to their chemical structure ¹, there metal complexes are important in biochemical process. For example, the transamination reactions are catalyzed by metals ions through the formation of intermediate Schiff bases containing vitamin B₆ ².

In the area of bioinorganic chemistry interest in Schiff base complexes has centered on the role of such complexes in providing synthetic models for the metal containing sites in metallo-proteins and enzymes ³. Schiff base ligands are potential anticancer drugs ⁴ and the anticancer activity of these metal complexes are enhanced in comparison to their free ligands ⁵.

3, 4-dihydroxybenzaldehyde, (Protocatechuaaldehyde, PCA) derivatives were evaluated and showed inhibition

for bacteria growth ⁶, antioxidants ⁷, antitumor ⁸, anticorrosion ⁹ and reagent in simple, rapid and highly sensitive analysis of Cr(VI) and (V) ¹⁰.

In the present work, new Schiff base derived from condensation of PCA and p-phenylene diamine and its complexes were prepared and investigated using the elemental analysis and UV-Vis, IR, ¹H-NMR spectral analysis as well as TGA and the biological activities including MIC were studied.

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MATERIALS AND REAGENTS: The analytical reagent grade (AR) 3, 4-Dihydroxy benzaldehyde, 1, 4-phenylene diamine, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ are Merk or Aldrich was used and Organic solvents used (methanol, ethanol, diethyl ether and acetone) were HPLC or extra pure grades and were used without further purification.

Instruments: Percentages of C, H and N were determined in the Microanalytical Laboratory. IR spectra were recorded using KBr pellets on a Perkin-Elmer 1430 Spectrometer for the region ($200\text{-}4000\text{cm}^{-1}$). Electronic spectra were measured in UV-Vis range (195- 1100 nm) using a Perkin-Elmer lambda 35 UV/Vis. The $^1\text{H-NMR}$ spectra were recorded on DEITAZ NMR 500 MHZ Spectrometer at the National Research Centre. The mass spectra were recorded on GC- MSA-QP 5050A Shimadzu. Magnetic susceptibility measurements were carried out at room temperature on a Sherwood Scientific Magnetic Balance. Antimicrobial activity experiments were carried out.

Synthesis of Schiff base ligand (H_4L) (1): The Schiff base ligand (H_4L , 1) was prepared by dropwise addition of hot ethanolic solution (25ml) 3,4-dihydroxy benzaldehyde (1.381 g, 0.005mole) to hot ethanolic solution of 1,4-phenylene diamine (0.5405g, 0.005mole), The reaction mixture was heated under reflux for 3 hr, evaporation of solvent at r.t. allowed to appear of fine dark orange crystals, filtered, washed with ethanol, acetone and diethyl ether and air dried. M.p. 160°C ; M.wt.-348.0; Anal. Calc. for $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_4$: C, 68.96; H,4.59; N, 8.0%, Found: C, 68.67; H,4.60; N, 7.75%; Main IR Peaks ($\text{KBr}, \text{Cm}^{-1}$): $\nu(\text{OH})3380$, $\nu(\text{C}=\text{N})1592$.

General procedures for the Preparation of complexes: The solid complexes; (**Fig. 10 and 11**) were prepared by drop-wise addition of an ethanolic solution of metal salts to an ethanolic solution of the ligand in 2:1 molar ratio metal salt: ligand, the reaction mixture refluxed for 3hr., the obtained precipitate was filtered and washed with ethanol, acetone and diethyl ether and air dried.

The complex, $\text{Fe}_2\text{L}(\text{H}_2\text{O})_6(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$; (2): Black solid. M.p. $>300^\circ\text{C}$; M.wt.723.68; Anal.Calc. for $\text{C}_{20}\text{H}_{28}\text{Fe}_2\text{N}_4\text{O}_{18}$: C,33.19; H,3.86; N,7.7; Fe,15.43%;

Found: C,33.48;H,3.4;N,6.77;Fe,15.00; Main IR Peaks ($\text{KBr}, \text{Cm}^{-1}$): $\nu(\text{C}=\text{N})1580$.

The complex, $\text{Co}_2\text{L}(\text{H}_2\text{O})_4 \cdot 5\text{H}_2\text{O}$; (3): Dark brown solid. M.p. 290°C ; M.wt.-623.8; Anal. Calc for $\text{C}_{20}\text{H}_{30}\text{Co}_2\text{N}_2\text{O}_{13}$: C,38.48; H,4.85; N, 4.48; Co,18.9%; Found: C, 38.45; H,4.25; N, 4.95; Co,18.25%; Main IR Peaks ($\text{KBr}, \text{Cm}^{-1}$) : $\nu(\text{C}=\text{N})1596$

The complex, $\text{Ni}_2\text{L}(\text{H}_2\text{O})_4 \cdot 3\text{H}_2\text{O}$; (4): Dark brown solid, M.p. $>300^\circ\text{C}$; M.wt.587.4; Anal.Calc. for $\text{C}_{20}\text{H}_{26}\text{Ni}_2\text{N}_2\text{O}_{11}$: C,40.82 ;H,4.4; N,4.70; Ni,19.95%; Found: C,40.56;H,4.06;N,4.75;Ni,19.1%; Main IR Peaks ($\text{KBr}, \text{Cm}^{-1}$) : $\nu(\text{C}=\text{N})1592$.

2.4.4. The complex, $\text{Cu}_2\text{L}(\text{H}_2\text{O})_4 \cdot 5\text{H}_2\text{O}$; (5)

Black solid. M.p. $>300^\circ\text{C}$; M.wt.649.0; Anal.Calc. for $\text{C}_{20}\text{H}_{30}\text{Cu}_2\text{N}_2\text{O}_{14}$: C,36.94 ;H,4.62; N,4.30; Cu,19.50%; Found: C,36.75;H,4.45;N,3.73;Cu,19.0%; Main IR Peaks ($\text{KBr}, \text{Cm}^{-1}$): $\nu(\text{C}=\text{N})1612$.

The complex, $\text{Zn}_2\text{L}(\text{H}_2\text{O})_4 \cdot 3\text{H}_2\text{O}$; (6): Brown solid. M.p. 190°C ; M.wt.- 608.8; Anal. Calc. for $\text{C}_{20}\text{H}_{26}\text{Zn}_2\text{N}_2\text{O}_{11}$: C, 39.94; H, 4.35; N, 4.60 Zn, 21.72%; Found: C, 40.07; H, 4.75; N,4.15; Zn,21.0; Main IR Peaks ($\text{KBr}, \text{Cm}^{-1}$) : $\nu(\text{C}=\text{N})1593$.

RESULTS AND DISCUSSION: The present Schiff base ligand H_4L ; (**Fig. 1**) was prepared by refluxing in ethanol an equimolar mixture of PCA and 1, 4-phenylene diamine. The structure of formed Schiff base was established by IR, $^1\text{H-NMR}$, mass and U.V-vis spectra as well as elemental analysis. All complexes were prepared by direct reaction between Schiff base ligand H_4L and corresponding salts. The obtained complexes are stable in air and have melting points above 150°C . They are insoluble in organic solvents such as diethyl ether and acetone, but soluble in DMF and DMSO. The elemental analysis data of the Schiff base and complexes (**Section 2**) are in well agreement with the expected structure.

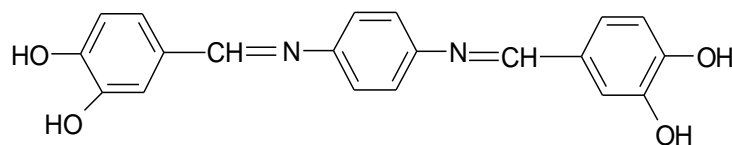


FIGURE 1: PROPOSED STRUCTURE OF (H_4L)

The molar conductance values of the synthesized complexes were determined using 10^{-3} M concentration in DMF as solvent, are in the range of $0.83 - 1.65 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. These values suggest non-electrolyte nature for these complexes¹¹.

Characterization of ligand (H₄L): The infrared spectrum of the Schiff base ligand (H₄L) in the region 200-4000 cm^{-1} showed a medium absorption band at 1592 cm^{-1} assigned to the C=N stretching vibrations, indicating the formation of the Schiff base linkage. Furthermore, the absence of C=O and $-\text{NH}_2$ stretching vibration in the spectra of the ligand related to aldehyde and amine, respectively, indicated the occurrence of Schiff base condensation¹².

The spectrum showed that a broad medium intensity band occurred at 3380 cm^{-1} assigned to νOH and the

phenolic $\nu\text{C-OH}$ stretching vibration was observed at 1287 cm^{-1} . The two weak intensity bands at 3929 and 2840 cm^{-1} corresponding to $\nu(\text{C-H})_{\text{ar}}$ and $\nu(\text{C-H})_{\text{aliph}}$ stretching vibration. $\nu\text{Ph-N}$ gave medium intensity band at 1172 cm^{-1} .

The $^1\text{H-NMR}$ spectrum of the Schiff base ligand (**Fig. 2-a, b**) showed signals lying at rang 8.9-9.7ppm were due to the resonance hydroxyl groups, the signals of OH groups lying at higher field side could be attribute to the contribution of the OH group intramolecular and intermolecular hydrogen bonds. Addition of D_2O to the pervious solution results disappearance of the signal due to proton exchange. The resonance of imine proton downfield shifted to (9.6 ppm) due to the strong shielding effect of the hydroxyl groups. Also the multiple signals lying in range 6.3-7.6 ppm were attributed to resonance of aromatic protons.

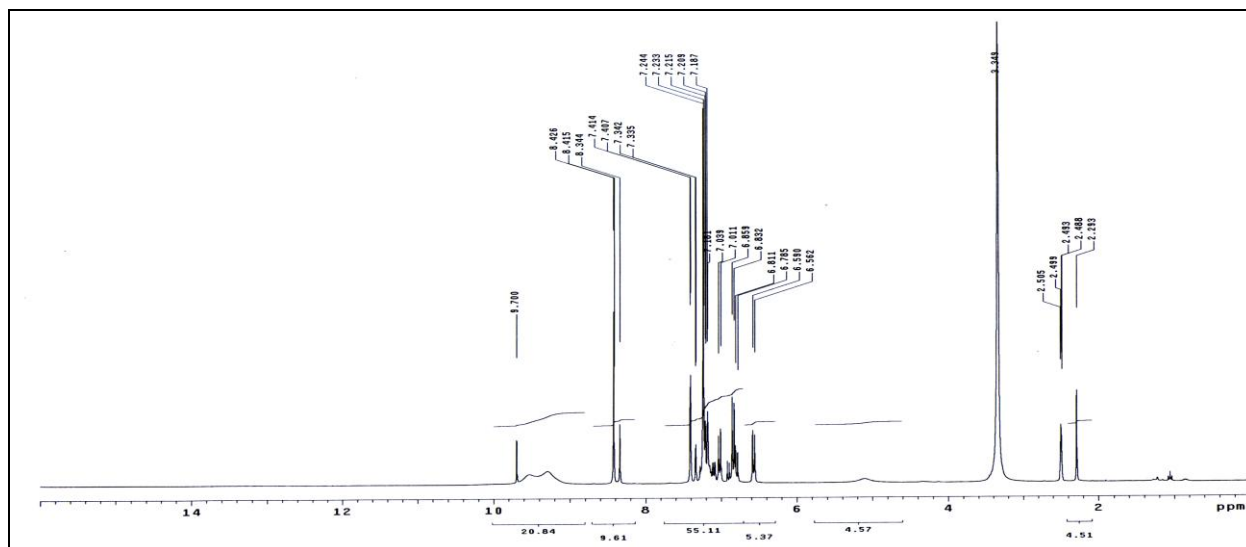


FIGURE (2a): THE $^1\text{H-NMR}$ SPECTRUM FOR (H₄L) IN (DMSO)

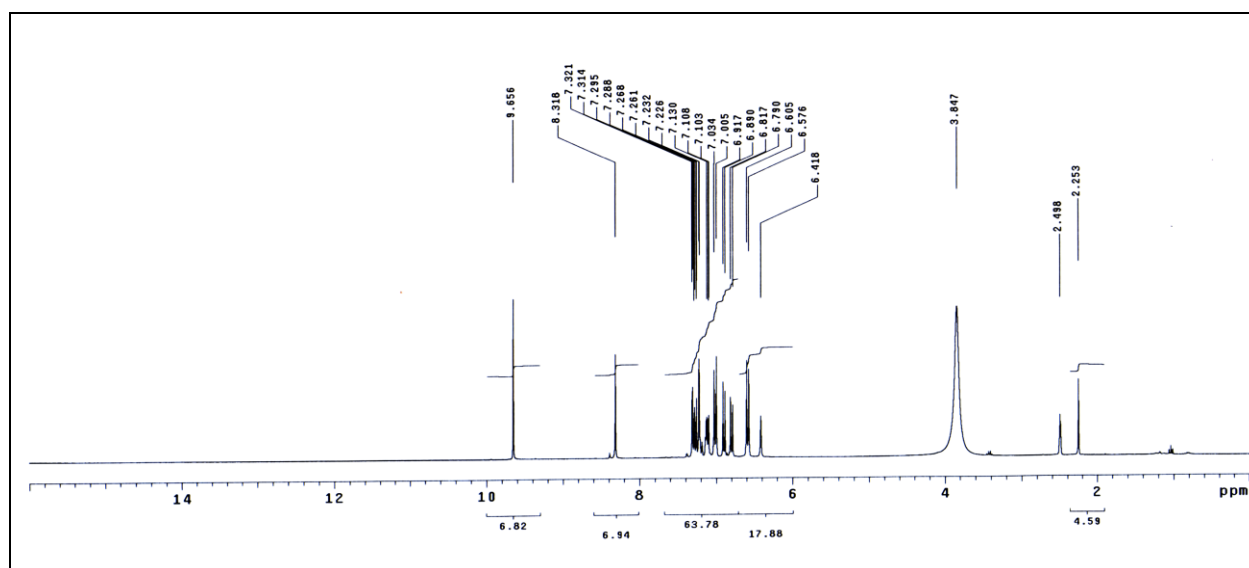


FIGURE (2-b) THE $^1\text{H-NMR}$ SPECTRUM FOR (H₄L) IN (DMSO+D₂O)

The electronic spectrum of the ligand in DMF displayed bands below 330nm which were attributed to intraligand $\pi-\pi^*$ and $n-\pi^*$ transitions of the benzene ring and azomethine group.

The mass spectrum of the free Schiff base ligand (**Fig. 3**) showed its molecular ion peak at $m/e=348$ which was coincidence with its formula weight.

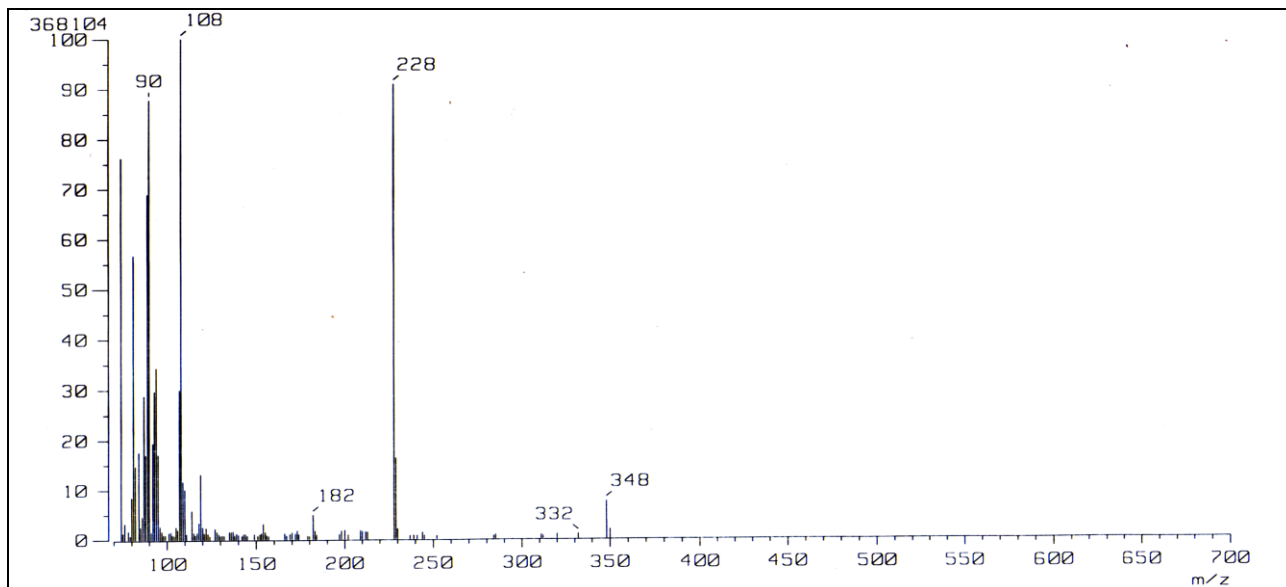


FIGURE 3: THE MASS SPECTRUM FOR (H₄L)

Characterization of the complexes:

- Infrared spectra:** The infrared spectra (**table 1**) of the complexes provide some information about the bonding in the complexes. The band in the IR spectrum of the ligand at 1592 cm^{-1} is found to be unaffected; this is characteristic feature for uncoordination through azomethine group¹³. Also, the $\nu_{\text{M-N}}$ bands were not appearing, due to uncomplexation via azomethine group. Deprotonation of all phenolic functions was confirmed by the lack of phenolic O-H stretching bands at 3380 indicating the Participation with the metal ion as $-\text{O}^-$, on the other hand very broad bands observed in the spectra of the complexes in the range ($3390\text{-}3427$) cm^{-1} considerable support

the presence of water molecules in the complexes¹⁴.

The band at 1287cm^{-1} in the free ligand ascribed to the phenolic C-O stretching vibration, this band was shifted to lower frequencies ($1185\text{-}1216\text{cm}^{-1}$) due to O- metal coordination¹⁵. The weak bands appeared in the far IR spectra between ($555\text{-}583$) cm^{-1} were attributed to $\nu_{\text{M-O}}$.

The infrared spectra of complexes (**2**) and (**6**) exhibited bands around 1543 , 1289 and 1125 cm^{-1} due to $\nu(\text{N=O})$, $\nu_{\text{asym}}(\text{NO}_2)$ and $\nu_{\text{sym}}(\text{NO}_2)$, respectively which were corresponding to nature of coordinated monodentate nitrate group¹⁶.

TABLE 1: THE IR SPECTRA DATA FOR COMPOUNDS (1-6)

Compound	$\nu(\text{OH})$	$\nu(\text{H}_2\text{O})$	$\nu(\text{CH})_{\text{ar.}}$	$\nu(\text{CH})_{\text{aliph.}}$	$\nu(\text{C=N})$	$\nu(\text{C-OH})$	$\nu(\text{Ph-N})$	$\nu(\text{M-O})$
1	3380	-	2929	2840	1592	1287	1172	-
2*	-	3414	2928	2863	1580	1216	1125	583
3	-	3390	2926	2853	1596	1200	1126	584
3	-	3391	2931	2840	1592	1203	1125	580
4	-	3427	2934	2842	1612	1199	1109	581
5*	-	3413	2927	2840	1593	1185	1122	555

*nitrate complexes

4. Thermal analysis: The thermogravimetric analysis (TGA); **Figures 5-8**, curves for complexes (**2, 3, 4 and 5**), respectively were obtained at a heating rate of 10⁰C/min and flowing nitrogen atmosphere over a

temperature range of 20–1000C and recorded in **table 2**. The decomposition temperature and the weight losses of the complexes were calculated from TGA data.

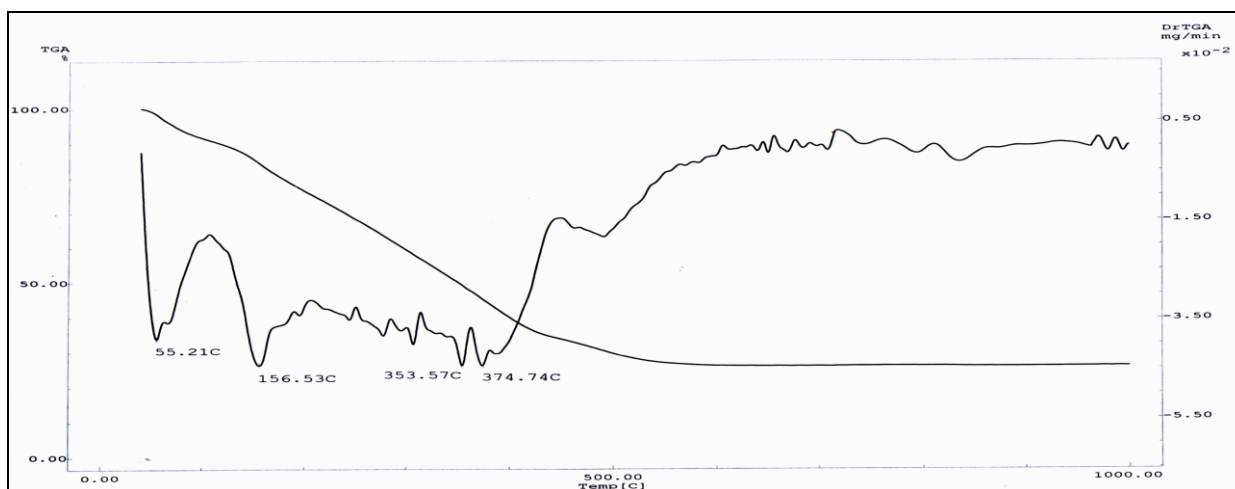


FIG. 5: TG AND DTG OF COMPLEX (2)

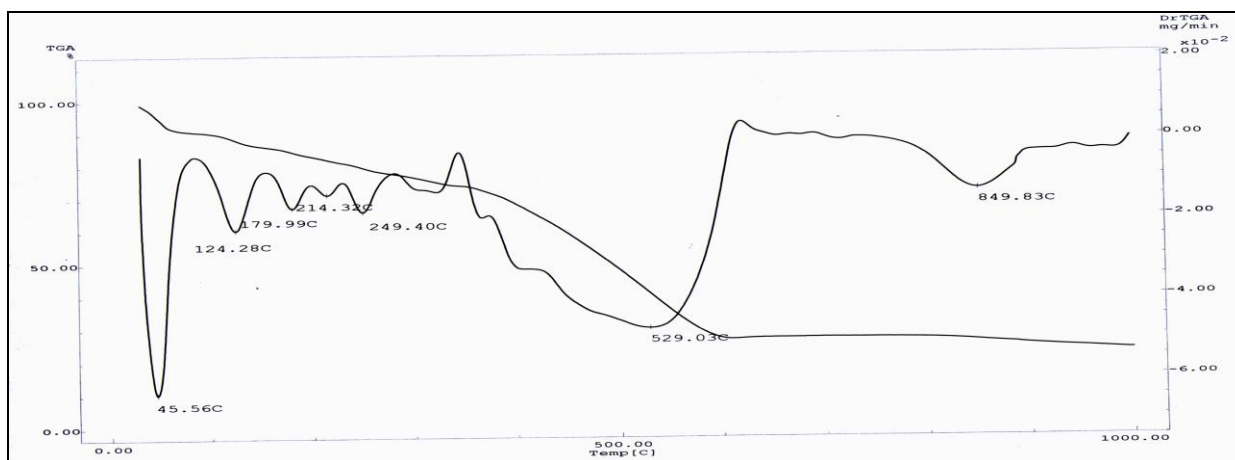


FIG. 6: TG AND DTG OF COMPLEX (3)

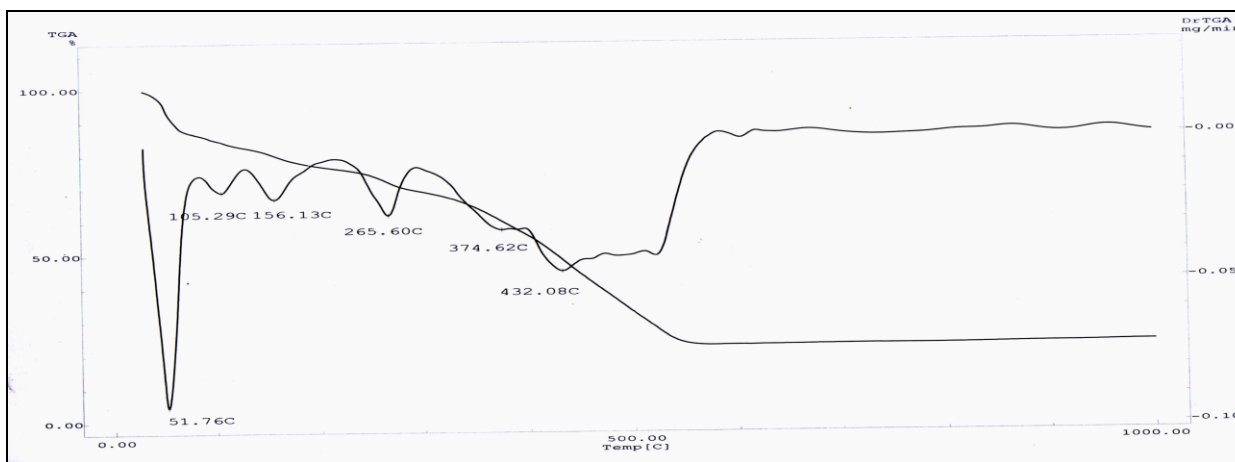


FIG. 7: TG AND DTG OF COMPLEX (4)

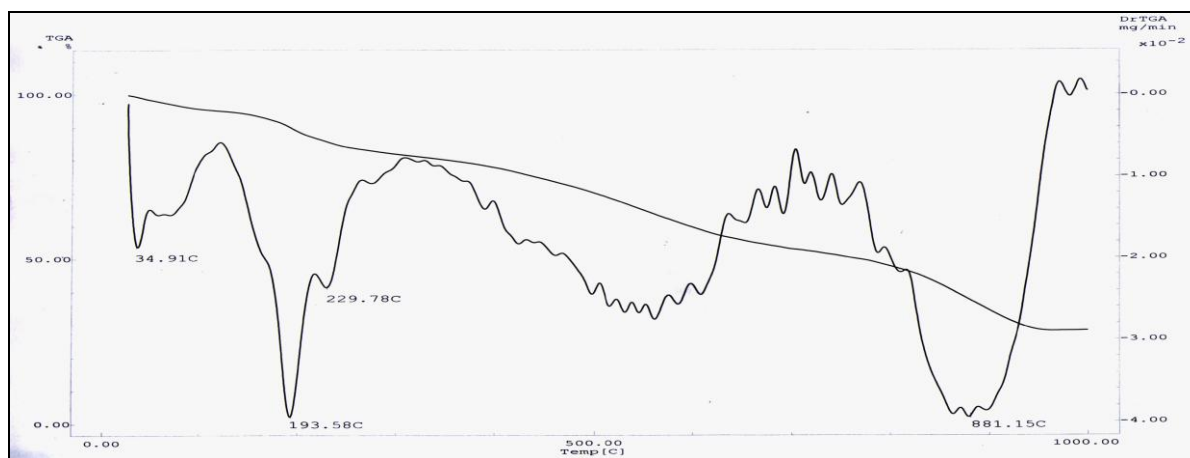


FIG. 8: TG AND DTG OF COMPLEX (6)

TABLE 2: THERMAL GRAVIMETRIC ANALYSIS FOR COMPOUNDS (2, 3, 4 AND 6)

Compound No.	Stages	Calculated	Found	Assignment
2	First Step	4.97	5.49	Two Crystalline H ₂ O
	Second Step	14.9	13.03	Six Coordinated H ₂ O
	Third and Fourth Step	56.31	55.03	Decomposition of Organic part of ligand + 2HNO ₃
	Residue	25.36	25.86	1.15 Fe ₂ O ₃
3	First Step	8.65	8.21	Three Crystalline H ₂ O
	Second Step	5.77	4.6	Two Crystalline H ₂ O
	Third and Fourth Step	13.14	12.18	Two Coordinated H ₂ O 2NO ₂ +
	Fifth and Sixth step	50.33	51.21	Decomposition of Organic part of ligand
	Residue	24.00	23.5	2CoO
4	First Step	12.25	12.42	Three Crystalline H ₂ O + One Coordinated H ₂ O
	Second Step	6.1	4.80	Two Coordinated H ₂ O
	Third and Fourth Step	13.27	12.65	One Coordinated H ₂ O + 2NO
	Fifth Step	48.00	47.52	Decomposition of Organic part of ligand + 1HCl
	Residue	22.89	22.80	1.8 NiO
6	First Step	5.95	4.67	Two Crystalline H ₂ O
	Second Step	14.96	13.18	One Crystalline H ₂ O + Four Coordinated H ₂ O+
	Third and Fourth Step	52.65	53.76	Decomposition of Organic part of ligand
	Residue	27.1	28.23	2ZnO

5. **ESR Spectra:** The ESR spectrum of complex **5** ; Fig. 9 is axial shape and having symmetric bands with two "g" value, $g_{\parallel} = 2.25$ while $g_{\perp} > 2.0027$ characteristic of complex with $^2B_1(d_{x^2-y^2})$ orbital ground state . The average g values were calculated according to the equation $g_{av.} = 1/3[g_{\parallel} + 2g_{\perp}]$, which obtained equal=2.14. The **5** complex exhibit $g_{\parallel} < 2.3$, suggesting covalent character of copper - ligand

in present complex. The complex **5** having $G = 3.12$, so there are exchange coupling between Cu (II) centers in the solid state. The g factor derives strongly from complex (**5**) because of strong spin – orbit coupling. The ESR spectral parameter of Copper(II) in complex having tetrahedral geometry around Cu(II) ion . These data are well consistent with other reported values [22].

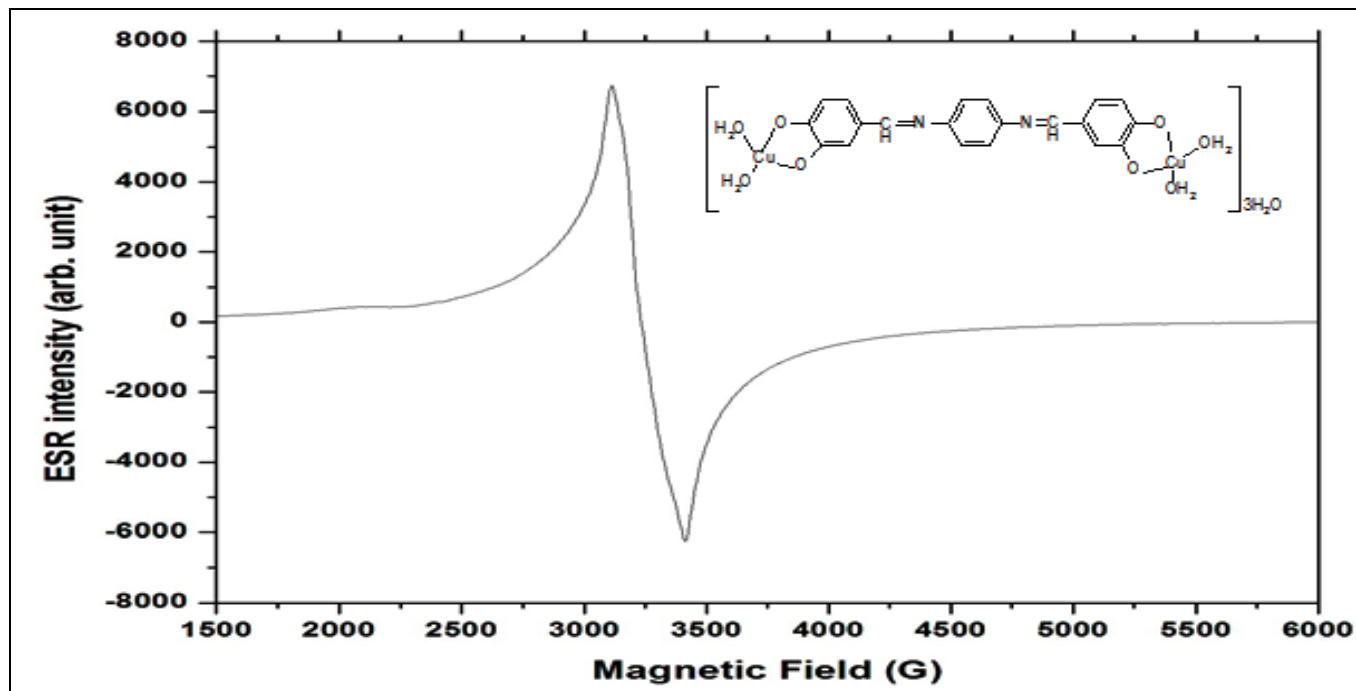


FIG. 9: ESR SPECTRUM OF COMPLEX 5

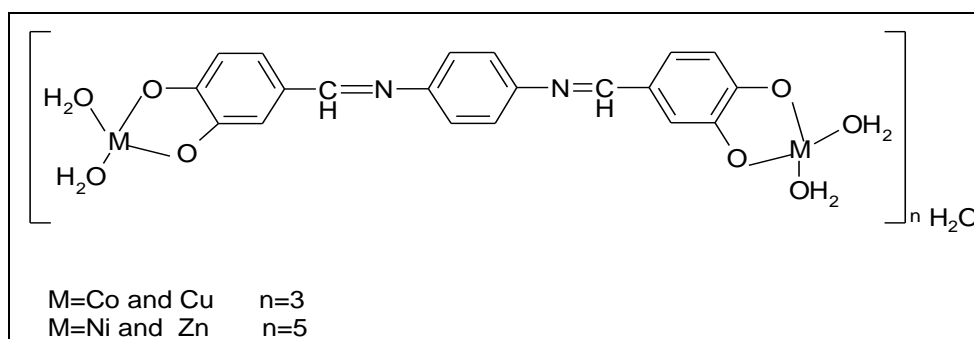


FIG. 10: PROPOSED STRUCTURE OF COMPLEXES 3, 4, 5 AND 6

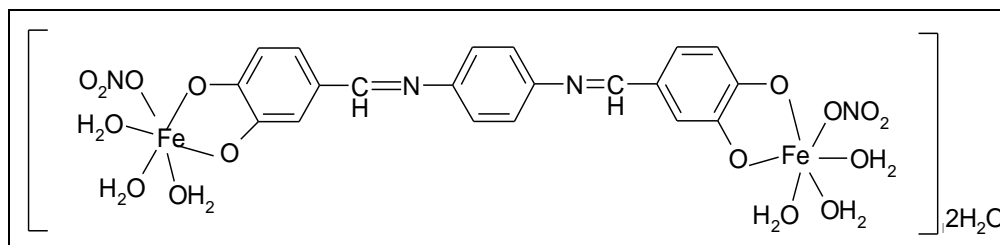


FIG. 11: PROPOSED STRUCTURE OF COMPLEX (2)

Antimicrobial Activity: Screening for the antimicrobial activity of the ligand H₄L and its complexes was tested. The testing was carried out using the classical agar diffusion method (Cooper, 1972). Antimicrobial disk diffusion was performed as described by the National Committee for Clinical Laboratory Standard^{23,24}.

The data in **table 3** show that all tested compounds have an appropriate activity against Gram-positive bacteria represented by *Bacillus subtilis*, the most active of them was compound number **1** (recorded 23.0 mm inhibition zone) and the compounds **3** & **5**

showed activity against *Staphylococcus aureus* and were recorded (21.5mm). Also, the compounds showed activity against Gram-negative bacteria represented by *Escherichia coli* (the most active compound **3** which record (21.0mm) and *Pseudomonas aeruginosa* (the most active compound **5** was record 20.0 mm inhibition zone). In turn, compound **3** have a good and highest activity against unicellular fungi represented by *Candida albicans* (compound **3** recorded 26.0 mm zone diameter) and filamentous fungi represented by *Aspergillus niger*

(compounds **5**, **1**, **6** and **3** showed a good activity and recorded 30, 27.0, 26.5 and 25.0 mm zone diameter respectively). In sum, the most active compound among the six tested compounds against the six tested microorganisms was compound **3** due to its wide spectrum of activity and good activity against bacteria and fungi (See Fig. 12).

Also, the minimum inhibitory concentration values of the compounds against the growth of microorganisms were determined by means of standard dilution method and summarized in **table 4**.

TABLE 3: THE ANTIMICROBIAL ACTIVITY OF THE COMPOUNDS (1-6)

Comp. No.	Recorded zone diameter (mm) for each test microorganism					
	Bacteria				Fungi	
	Gram +ve		Gram -ve		Unicellular	Filamentous
	<i>B. subtilis</i>	<i>S. aureus</i>	<i>E. coli</i>	<i>P. aeruginosa</i>	<i>C. albicans</i>	<i>A. niger</i>
1	23.00	19.00	17.00	15.50	17.50	27.00
2	18.50	16.00	15.50	15.00	14.00	20.00
3	18.50	21.50	21.00	19.50	26.00	25.00
4	14.50	15.50	15.00	16.00	20.00	20.00
5	21.00	21.50	13.50	20.00	21.00	30.00
6	18.00	15.50	15.00	13.50	18.00	26.5
St.	29.00	31.00	34.00	32.00	25.00	00.00

St. = Standard antibiotic (Amikacin)

TABLE (4): THE MIC (IN MICROGRAMS PER MILLILITER) = MINIMUM INHIBITORY CONCENTRATION. I.E., THE LOWEST CONCENTRATION OF DRUG WHICH COMPLETELY INHIBITS BACTERIAL AND FUNGAL GROWTH FOR COMPOUNDS (1-6)

Comp. No.	Recorded zone diameter (mm) for each test microorganism					
	Bacteria				Fungi	
	Gram +ve		Gram -ve		Unicellular	Filamentous
	<i>B. subtilis</i> NCTC 10400	<i>S. aureus</i> NCTC 7447	<i>E. coli</i> NCTC 10416	<i>P. aeruginosa</i> ATCC 10145	<i>C. albicans</i> MRU3669	<i>A. niger</i> LIV131
1	2.5	5	5	5	5	1.25
2	5	5	1.25	5	2.5	2.5
3	5	2.5	1.25	1.25	1.25	1.25
4	1.25	2.5	5	5	2.5	2.5
5	1.25	1.25	1.25	2.5	5	0.625
6	1.25	5	1.25	5	1.25	2.5
St.	0.0195	0.0097	0.0195	0.00976	0.039	-

St. = Standard antibiotic (Amikacin)

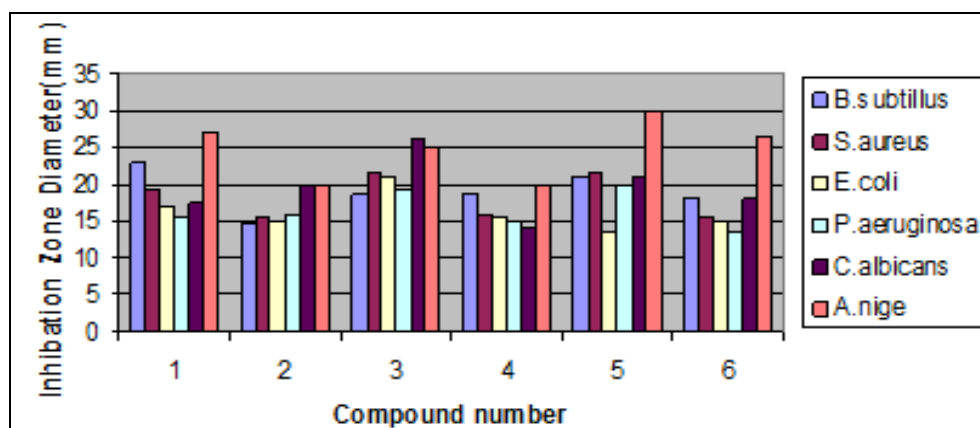


FIGURE 12: BIOLOGICAL EVALUATION OF (H₄L; 1) AND ITS COMPLEXES

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