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Research Article

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Synthesis, Characterization, Spectroscopy and Bactericidal Properties of Polydentate Schiff Bases Derived from Salicylaldehyde and Anilines and their Complexes

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ABSTRACT

Three Schiff base, 2-(4-dimethylamino)phenyliminomethyl phenol (L_1), (2-hydroxy-benzylidene-amino)benzoic acid (L_2), and 2,2-((4-nitrobenzene-1,2-iyl)bis(nitrilomethyl-yildene)diphenol (L_3), has been synthesized from salicylaldehyde and N,N-dimethyl p-phenylene diamine, 2-amino benzoic acid, and 3-Nitro-o-phenylenediamine. The chemical structures of the Schiff-base ligand and their metal complexes were confirmed by various spectroscopic and physical techniques viz. UV-vis., FT-IR, ^{1}H NMR, ^{13}C NMR, ESI-mass spectra, elemental analysis, flame atomic absorption spectroscopy (FAAS), molar conductance, and magnetic susceptibility measurements. Metal complexes of the Schiff base were prepared from chloride salts of Co(II), Mn(II), Cu(II) and Zn(II) in an alcoholic medium. On the basis of elemental and spectral studies, six-coordinated geometry was assigned to these complexes. In the light of these results, it is suggested that these ligand acts as neutral and polydentate ligands, hence coordinates to metal atom through azomethine nitrogen and oxygen atoms of phenol groups, as well as the carboxyl group of 2-amino benzoic acid. The proposed geometry for these complexes were suggested according UV-visible and FT-IR spectrophotometry, molar variation method, and molar conductivity measurement: (1) $[M(L_1)(H_2O)_3Cl]$ for Mn(II) and Cu(II), (2) $[Co(L_1)_2].2H_2O$ for Co(II) and Zn(II), (3) $[M(L_2)_2].2H_2O$ for Co(II), (4) $[Mn(L_2)(H_2O)_2Cl][Et_3N]$ for Mn(II), (5) $[M(L_2)(H_2O)]$ for Cu(II), (6) $[M(L_2)(H_2O)_3]$ for Zn(II), (7) $[Mn(L_3)]$ for Mn(II), (8) $[Co(L_3)(H_2O)_2]$ for Co(II) and Cu(II), and (9) $[Zn_2(L_3)Cl_2(H_2O)_2]$ for Zn(II). The free Schiff base and their complexes have been tested for their antibacterial activity against Escherichia Coli (G-), Staphylococcus aureus (G+), and Pseudomonas aeruginosa (G-) by using Agar well diffusion and the results were discussed.

Keywords: Schiff base; 3-ethoxy salicylaldehyde; 2-amino benzoic acid; UV-vis.; FT-IR; ^{1}H NMR; ^{13}C NMR; ESI-mass spectra; Metal complexes; Antibacterial activity

INTRODUCTION

In recent years a considerable amount of work has been done on Schiff bases and their transition metal complexes. They found use in various fields, such as in medicine as radiopharmaceuticals for cancer targeting [1-3], and as model systems for biological macromolecules [4-5] such as bactericides and fungicides [6–7]. The growth inhibitory potential of the Schiff base and the metal complexes of cobalt, nickel and copper ions with Schiff base derived from 5-bromosalicylaldehyde and o-phenylenediamine against some clinically important bacteria, namely *Staphylococcus aureus* (ATCC 25923), *Escherichia coli* (ATCC 25922), *Enterococcus feacalis* (ATCC 29212) and *Salmonella typhi* show that the metal complexes are more potent than the parent Schiff base ligand against all tested bacterial strains [8].

Oxovanadium Complexes have been found strongly active, against some type of Leukemia [9]. Metal complexes of Schiff bases are specifically of interest in bioinorganic chemistry because many of these complexes provide biological models for use in understanding the structure of biomolecules and biological processes. They have found applications in agriculture, analytical chemistry [10], and in industry as catalysts for organic synthesis [11]. Chiral Schiff base complexes are more selective in various reactions such as oxidation, hydroxylation, aldol condensation and epoxidation [12]. The high thermal and moisture stabilities of many Schiff base complexes were useful attributes for their application as catalysts in reactions involving at high temperature.

Schiff base ligands containing nitrogen and oxygen donor may act as bidentate *N*,*O*-, tridentate NO_2, NON, NOS, tetradentate N_2O_2, and hexadentate $N_2O_2S_2$-donor ligands [13-14]. Schiff base complexes of transition metals containing ligands with N_2O_2 donors are known to exhibit interesting electrochemical and electronic properties [15–17].

The aim of the present work is to synthesize a Schiff bases from salicylaldehyde and *N*,*N*-dimethyl *p*-phenylene diamine, 2-amino benzoic acid, and 3-Nitro-*o*-phenylenediamine. Preparing their transition metal complexes with Co(II), Mn(II), Cu(II) and Zn(II), characterize their geometrical structures and study various spectroscopic, physical and magnetic behaviors, as well as their bactericidal activities.

EXPERIMENTAL SECTION

Chemicals and Instruments

All chemicals used in this work were analytical grade and used without further purification. Metal salts: $CoCl_2.6H_2O$, $CuCl_2.2H_2O$, $MnCl_2.4H_2O$, $ZnCl_2$, *o*-amino benzoic acid, *N*,*N*-dimethyl-1,4-phenylene diamine, 3-Nitro-*o*-phenylenediamine, Absolute ethanol, *N*,*N*-dimethylformamide (DMF), and dimethyl sulphoxides (DMSO), are obtained from BDH, England. The rest of the chemical viz. 3-nitro-*o*-phenylenediamine, salicylaldehyde, and triethyl amine (TEA) were obtained from Fluka, Switzerland.

Instruments

Melting points were determined with Stuart Scientific SMP_1, England melting point apparatus. Molar conductance measurements were carried out in DMSO (10^{-3} M) using WTWF56 conductivity meter having platinum electrode with a cell constant of 1.01 cm and calibrated with KCl. The electronic absorption spectra of the compounds were investigated in *N*,*N*-dimethylformamide (DMF) and 1,4-dioxane and recorded on a Varian 100 Conc. UV-visible Spectrophotometer using 1.0 cm quartz cell immediately after preparing the solutions in the range 200-800 nm. Infrared spectra of the ligand and its complexes were carried out by using KBr pellets in the range (200-4000 cm^{-1}) on Fourier transform Infrared spectrophotometer-Shimadzu model 8300. The ^1H and ^{13}C NMR spectra were recorded on 300 MHz Bruker DMK-500 NMR Spectrophotometer) Spectrometer by employing TMS as internal standard. The high resolution Mass spectra were recorded by Bruker Daltonics Data. Elemental analysis of C, H, and N of complexes were determined by using micro analytical methods on was carried by Carlo-Erba microanalyser. The percentage of the metals in the complexes was measured with Shimadzu Corporation Model 6809 Flame Atomic Absorption.

General procedure for schiff bases synthesis

The Schiff bases were prepared by condensation of freshly distilled salicylaldehyde (1.22 g, 10.0 mmol) [or 3-nitro-*o*-phenylenediamine (0.765 g, 5.0 mMol)], with *N*-dimethyl-1,4-phenylene diamine (1.36 g, 10.0 mMol), or *o*-amino benzoic acid (1.53 g, 10.0 mmol), or 3-nitro-*o*-phenylenediamine, or (1.53 g, 10.0 mMol) in ethanol (30 mL) and the mixture was refluxed for 6 hours. The resulting solution was evaporated under vacuum to remove the solvent. The product was collected by filtration, washed several times with ethanol and recrystallized from hot ethanol and dried in vacuum desiccators at 60°C. Physical and spectroscopic properties of the resulting Schiff base ligands (L_1, L_2, and L_3) were presented in Table -1, Table-2, and Table-3.

General procedure for the preparation of the metal complexes

A mixture of the Schiff base L_1, L_2 (1.0 mMol), and L_3 (0.5 mMol) under investigation in 10 ml ethanol and the same molar amount of metal salt (1.0 mmol), [MX_2 = $CoCl_2.6H_2O$, $CuCl_2.2H_2O$, $MnCl_2.4H_2O$, or $ZnCl_2$] was refluxed for an hour. The pH of the solution was adjusted to 6.0 with TEA buffer solution. The reaction mixture was refluxed for additional 2 hours. On cooling, colored solid product was collected by filtration and then washed several times with hot ethanol (5 ml portions) until the washing becomes colorless. The product was recrystallized from ethanol, and the crystals formed were dried at 60° C for 5 hours under vacuum. Physical and spectroscopic properties of the resulting ligands Mn(II), Co(II), Cu(II), and Zn(II) complexes were presented in Tables-1, and Table-3.

Antimicrobial activity measurement

The *in vitro* antimicrobial screenings of effects of the investigated compounds were tested against *Escherichia Coli, Staphylococcus aureus, and Pseudomonas aeruginosa*, using agar nutrient as the medium. The solvent, free ligands, transition metal salts, and their new complexes were tested for their effect on certain human pathogenic bacteria and fungus by Agar well diffusion method [18-19]. In a typical procedure a wells were made on the agar medium which is inoculated 100 µL of the microorganisms inoculants. The wells were filled with the test solution of varying concentrations with the aid of a micropipette (100 µL), then the plate was incubated, 24 hour for each bacteria at 35°C. During this period, the test solution diffused and the growth of the inoculated microorganisms was affected. The inhibition zone (measured in mm) was developed, at which the concentration was noted. The inhibition zone of the Schiff base ligands (L_1, $L_{2,}$ and L_3) and their complexes by Well Diffusion method measured in mm (% Inhibition) against *E. Coli S. aureus* and *P. aerugenosa* were presented in Table-5.

RESULT AND DISCUSSION

Ligands were prepared by condensation of salisaldehyde with anilines under reflux for specified time interval and solvent, as shown in the equations of Figure-1. They were characterized by the available analytical techniques viz. nuclear magnetic resonance ^{1}H-NMR, in which they showed a single peak for the 2-{4-dimethylamino)phenylimino}methyl phenol (L_1) at 8.85 ppm as shown in Figure-3, while its ^{13}C-NMR spectrum showed a peak at 158.0 ppm as shown in Figure-4, and both peaks stands for the azomethin group (HC=N) formation [20]. Its mass spectrum showed a signal of *m/q* at 241 amu shown in Figure-9, which match the molecular weight of the expected reaction product. Other spectrohotometric absorption spectra include UV-visible, which gave three absorption maxima (λmax) at 202, 224, and 245 nm, while FT-IR showed strong peak for the azomethin group (HC=N) at 1612 cm-1 as shown in Figure-2.

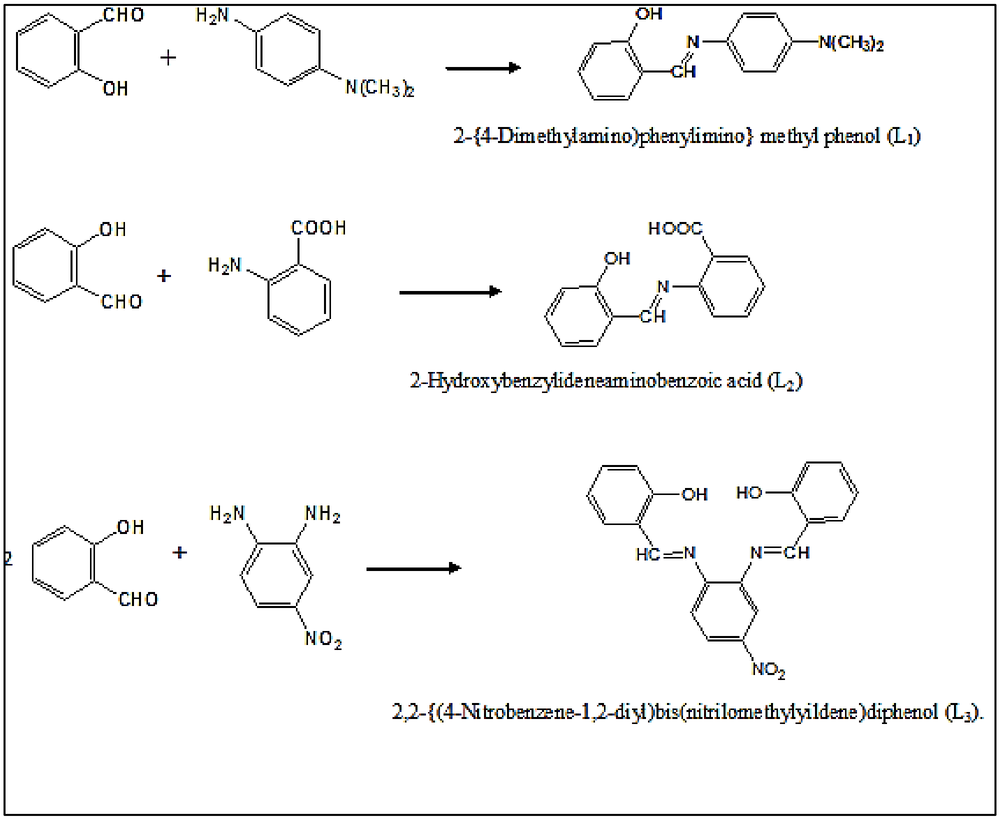

Figure 1: Ligands were prepared by condensation of salisaldehyde with the amines under reflux for specified time interval and solvent.

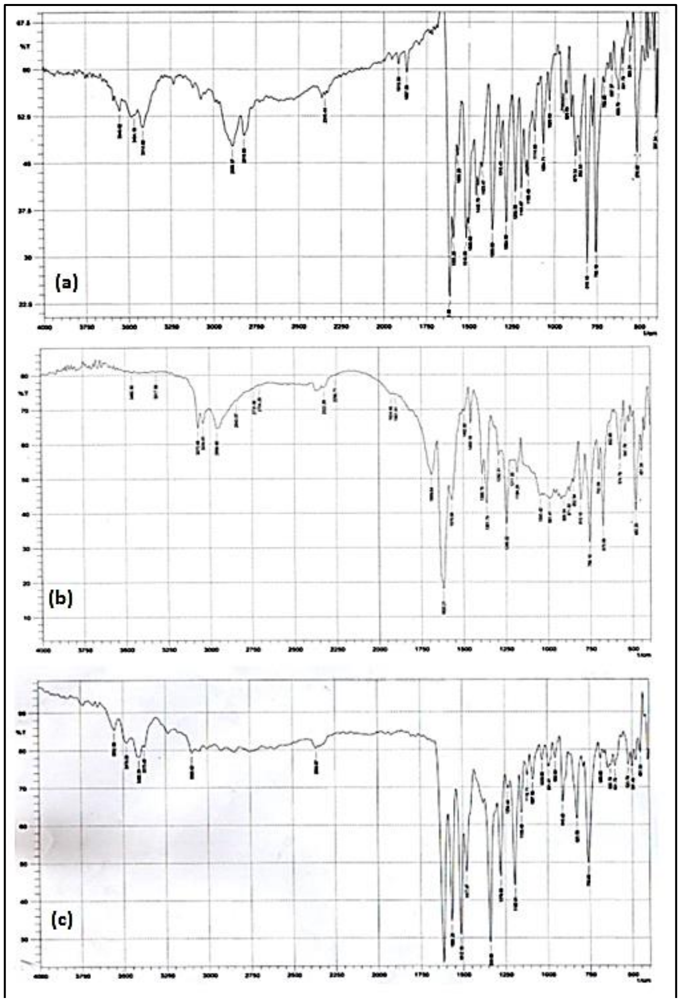

Figure 2: FT-IR of the Schiff base ligand (a) 2-[4-dimethylamino)phenylimino]methyl phenol, (L1), and (b) 2-Hydroxybenzylideneaminobenzoic acid (L2), and (c) 2,2-{(4-Nitrobenzene-1,2-diyl)bis- (nitrilomethylyildene)diphenol (L3)

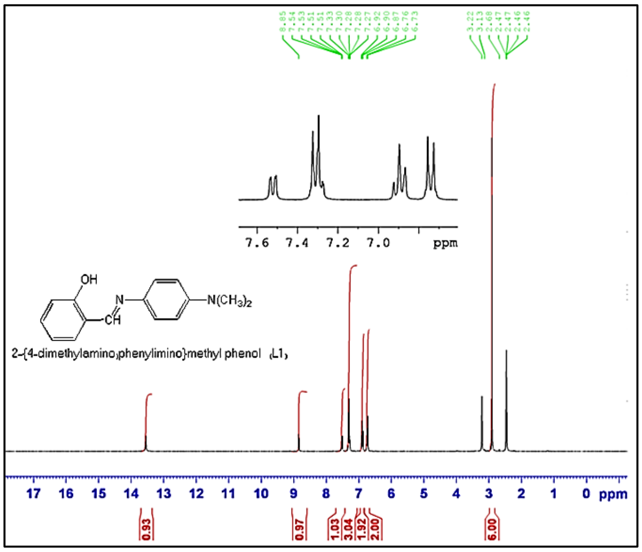

Figure 3: ^{1}H NMR of 2-[4-dimethylamino)phenylimino]methyl phenol, (L$_1$)

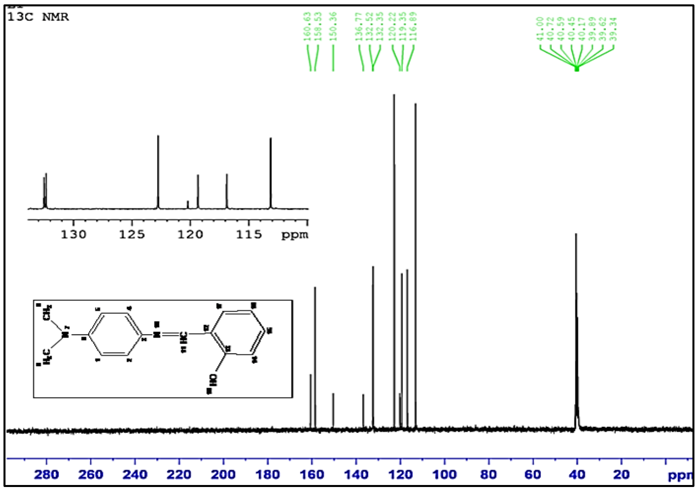

Figure 4: ^{13}C NMR of 2-Hydroxybenzylideneaminobenzoic acid, (L$_1$)

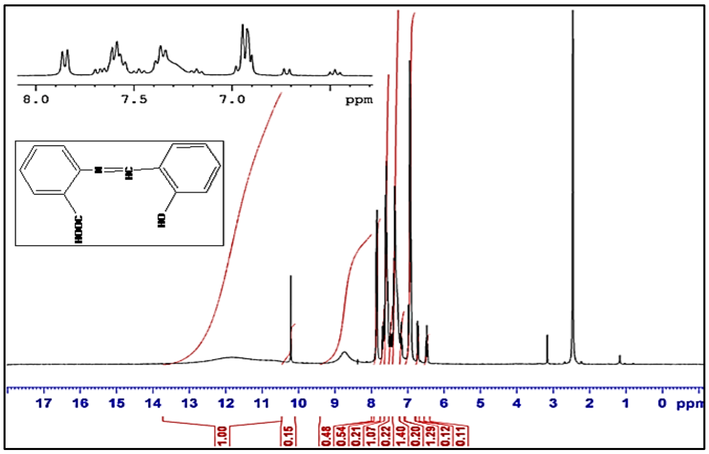

Figure-5: 1H NMR of 2-Hydroxybenzylideneaminobenzoic acid, (L2)

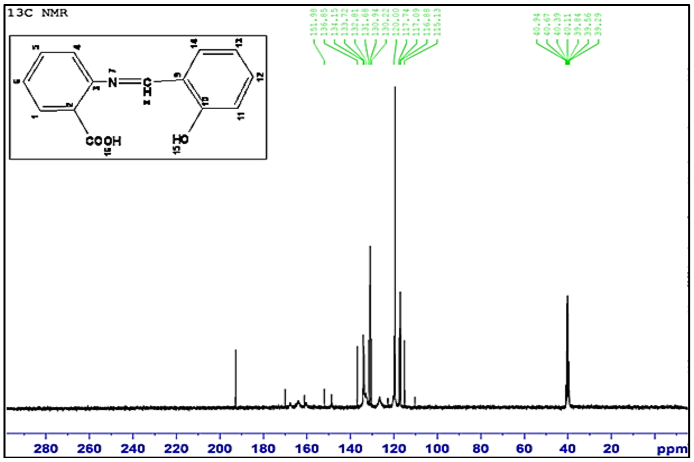

Figure-6: 13C NMR of 2-[4-dimethylamino)phenylimino]methyl phenol, (L2)

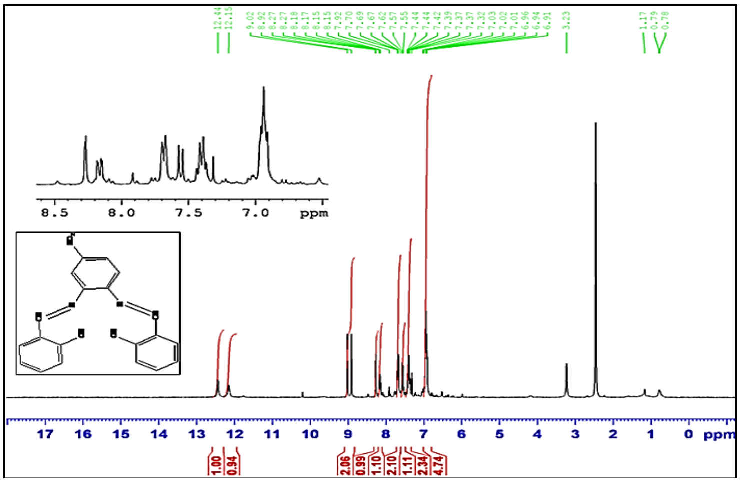

Figure-7: 1H NMR of 2,2-{(4-Nitrobenzene-1,2-diyl)bis(nitrilomethylyildene)diphenol, (L3)

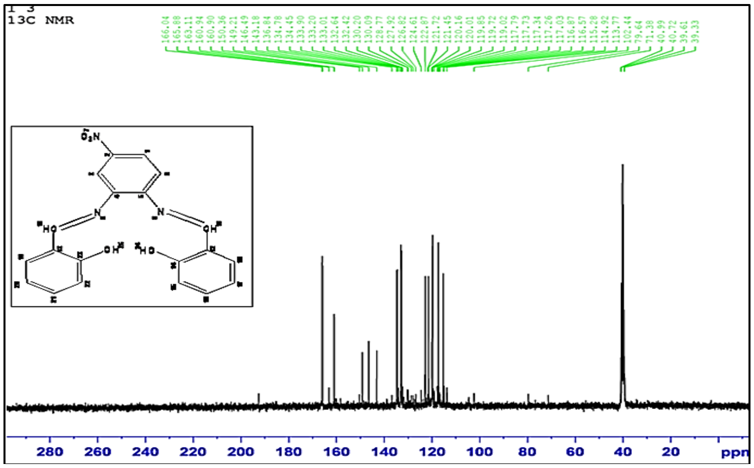

Figure-8: 13C NMR of 2,2-{(4-Nitrobenzene-1,2-diyl)bis(nitrilomethylyildene)diphenol, (L3)

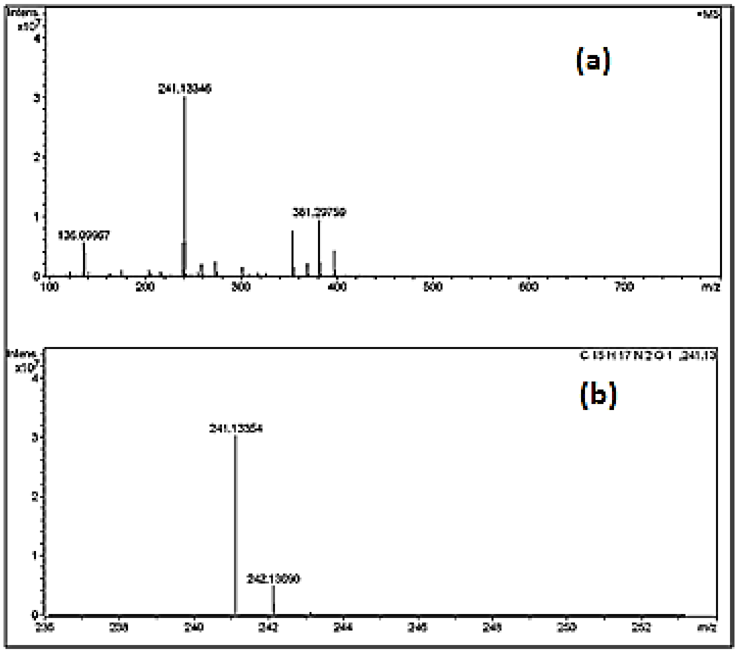

Figure 9: (a) The measured high resolution mass spectrum of the ligand C15H16N2O, (L1), [M + H]+ molecular ion at m/q = 241.13354, and (b) the calculated [M + H]+ at m/q = 241.13411 with % RD of 2.3 × 10-4 (Manura, J. J., and Manura, D. J., "Isotope Distribution Calculator and Mass Spec Plotter", Scientific Instrument Services, 2009, Ringoes, NJ)

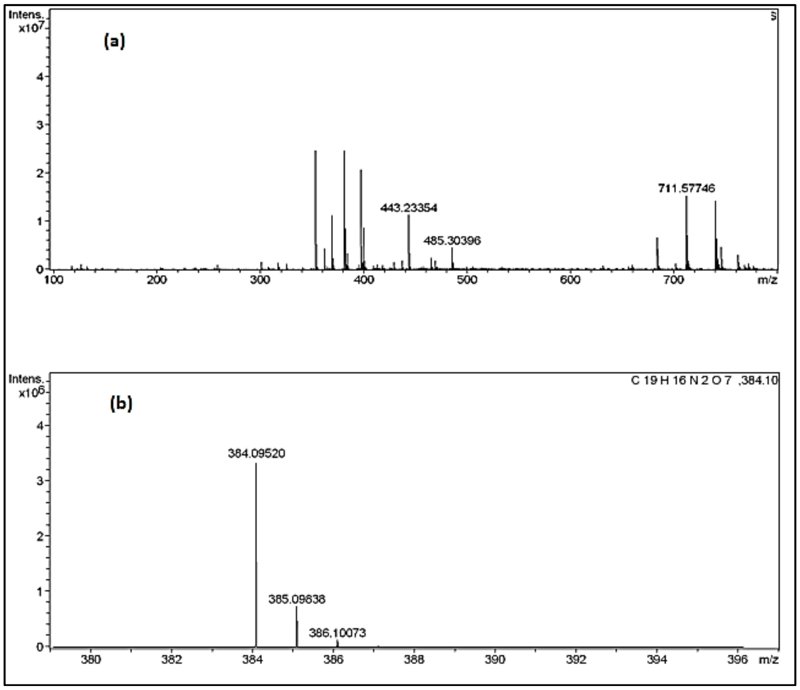

Figure 10: (a) The measured high resolution mass spectrum of the ligand C15H16N2O, (L1), [M + H]+ molecular ion at m/q = 242.08117, and (b) the calculated [M + H]+ at m/q = 241.08173 with % RD of 22.3 × 10-6 (Manura, J. J., and Manura, D. J., "Isotope Distribution Calculator and Mass Spec Plotter", Scientific Instrument Services, 2009, Ringoes, NJ)

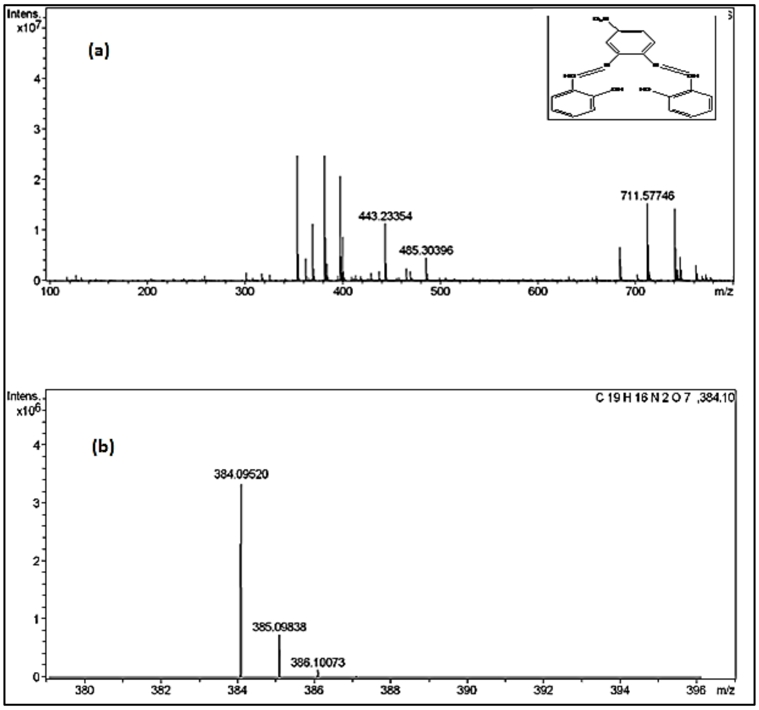

Figure 11: (a) The measured high resolution mass spectrum of the ligand $C_{20}H_{15}N_3O_4$, (L_3), $[M + H]^+$ molecular ion at m/q = 362.11353, and (b) the calculated $[M + H]^+$ at m/q = 362.1141 with % RD of 5.85×10^{-5} (Manura, J. J., and Manura, D. J., "Isotope Distribution Calculator and Mass Spec Plotter", *Scientific Instrument Services*, 2009, Ringoes, NJ)

Table-1: Physical properties of the Schiff base ligands (L_1, L_2, and L_3), and their Mn(II), Co(II), Cu(II), and Zn(II) complexes

Compound	Empirical formula	M. wt (Calc.)	M. pt °C	Color	Yield %	Element analysis found (Calculated)			
						C	H	N	M*
L_1	$C_{15}H_{16}N_2O$	240.3	141-143	Bright orange	84	74.23	6.87	-11.34	-
						-74.97	-6.71	-11.66	
[Mn(L_1)(H_2O)$_3$Cl]	$C_{15}H_{21}ClMnN_2O_4$	383.73	220 (d)	Green	63	47.11	5.45	6.99	14.3
						-46.95	-5.52	-7.3	-14.32
[Co(L_1)$_2$].2H_2O	$C_{30}H_{30}CoN_4O_4$	569.16	208 (d)	Deep green	62	63.18	5.45	9.56	10.26
						-63.27	-5.31	-9.84	10.35))
[Cu (L_1)(H_2O)$_3$Cl]	$C_{15}H_{22}ClCuN_2O_4$	393.35	226 (d)	Brown	70.3	45.93	5.68	7.05	16.08
						-45.8	-5.64	-7.12	-16.27
[Zn(L_1)$_2$].2H_2O	$C_{34}H_{36}N_4O_4Zn$	581.99	216 (d)	Cream color	51.3	63.98	5.74	9.1	11.21
						-64.81	-5.76	-8.89	10.38))
L_2	$C_{14}H_{11}NO_3$	241.24	209-211	Deep orange	73.4	70.1	4.56	5.57	-
						-69.7	-4.6	-5.81	
[Mn(L_2)(H_2O)$_2$Cl][Et_3N]	$C_{20}H_{30}$ $ClMnN_2O_5$	468.85	246 (d)	Yellow	50	-	-	-	12.01
						-51.23	-6.45	-5.97	11.72))
[Co(L_2)].2H_2O	$C_{16}H_{15}CoNO_3$	328.23	260 (d)	Light pink	54.5	58.46	4.45	4.24	17.35
						-58.55	-4.61	-4.27	-16.98
[Cu(L_2)(H_2O)]	$C_{14}H_{13}CuNO_4$	322.8	186 (d)	Green	50	51.88	3.95	4.17	19.62
						-52.09	-4.06	-4.34	-19.69
[Zn(L_2)(H_2O)$_3$]	$C_{14}H_{17}NO_6Zn$	360.68	195 (d)	Cream	50.45	46.72	4.65	3.68	18.01
						-46.62	-4.75	-3.88	-18.13
L_3	$C_{20}H_{15}N_3O_4$	361.35	218-220	Yellow	65.5	66.87	4.08	11.46	-
						-66.48	-4.18	-11.63	
[Mn(L_3)]	$C_{20}H_{15}MnN_3O_4$	416.29	246 (d)	Cream	71	57.83	3.56	9.95	13.25
						-57.7	-3.63	-10.09	-13.2
[Co(L_3)(H_2O)$_2$]	$C_{20}H_{19}CoN_3O_6$	456.31	260 (d)	Brown	54.5	52.45	4.56	8.95	12.72
						-52.64	-4.2	-9.21	12.92))
[Cu(L_3)(H_2O)$_2$]	$C_{20}H_{19}CuN_3O_6$	460.93	186 (d)	Brown	50	52.46	4.45	9.24	13.95
						-52.12	-4.15	-9.12	-13.79
[Zn_2(L_3)Cl_2(H_2O)$_2$]	$C_{20}H_{19}Cl_2N_3O_6Zn_2$	599.07	282 (d)	Cream color	65	40.58	3.31	6.86	21.77
						-40.1	-3.2	-7.01	-21.83

Table 2: 1H and proton decoupled 13C NMR of 2-[4-dimethylamino)phenylimino]methyl phenol, (L1), 2-(2-hydroxybenzylideneamino)-benzoic acid (L2), and 2,2-[(4-nitrobenzene-1,2-diyl)bis(nitrilomethylyildene]diphenol, (L3)

Compound	^{1}H (ppm)					^{13}C(ppm)			
	COOH	OH	HC=N	Ar-H	CH_3	COOH	HC=N	Ar-H	CH_3
$C_{15}H_{16}N_2O$, L_1	-	13.55	8.85	7.54 – 6.73	2.68	-	158	115 - 150	113
$C_{14}H_{11}NO_3$, L_2	12	10.3	8.8	6.50 - 7.90	-	190	151	115 - 139	-
$C_{20}H_{15}N_3O_4$, L_3	-	12.44,	9.02,	6.91 - 8.18	-	-	161,	110 - 151	-
		12.15	8.92				159		

Table 3: The measured high resolution mass spectra of the Schiff base ligands for the ions [M^+] and [M + H]$^+$, and the calculated one 2-[4-dimethylamino)phenylimino] methyl phenol, (L_1), 2-(2-hydroxybenzylideneamino)-benzoic acid (L_2), and 2,2-[(4-nitrobenzene-1,2-diyl)bis(nitrilomethylyildene]diphenol, (L_3), molecular ion at m/q is 241.13354, and (b) the calculated molecular ion for the ligand at [M + H]$^+$ at m/q is 241.13411 with % RD of 2.3 × 10^{-4}

S No	Compound	m/q measured		m/q Calculated*		% RD
		M^+	[M + H]$^+$	M^+	[M + H]$^+$	
1	$C_{15}H_{16}N_2O$, L_1	-	241.13354	240.12627	241.13411	2.3 × 10^{-4}
2	$C_{14}H_{11}NO_3$, L_2	-	242.08117	241.07391	241.08173	2.3 × 10^{-6}
3	$C_{20}H_{15}N_3O_4$, L_3	-	362.11353	361.10628	362.1141	5.85 × 10^{-5}

*(Manura, J. J., and Manura, D. J., "Isotope Distribution Calculator and Mass Spec Plotter", Scientific Instrument Services, 2009, Ringoes, NJ.); % RD = percent relative deviation

The ligand 2-(2-hydroxybenzylideneamino)-benzoic acid (L_2) was obtained as deep orange crystals, its ^{1}H-NMR of the at 8.8 ppm, while ^{13}C-NMR showed a peak at 151 ppm both stand for the formation of azomethin group, as shown in Figure-5 and Figure-6. Its mass spectrum gave a signal of *m/q* at 242 amu, which match the molecular weight of the expected reaction product, as shown in Figure-10. Other spectrohotometric absorption spectra include UV-visible gave the three absorption maxima (λ_{max}) at 219, 250, and 332 nm, while FT-IR showed sharp strong peak for the azomethin group at 1620 cm^{-1} (Table-4). The ligand 2,2-{(4-nitrobenzene-1,2-diyl)bis(nitrilomethylyildene)-diphenol (L_3) was obtained as yellow orange crystals, by the condensation of two equivalent of salisaldehyde with one equivalent of 4-nitro-1,2-diaminobenzene. Its ^1H-NMR showed two peaks for the azomethin group at 8.92 and 9.02 ppm, and two peaks for the phenol hydroxyl group at 12.44, and 12.15 ppm, as shown in Figure-8. The appearance of two signals for azomethin and hydroxyl groups is the possible steric hindrance results from the bulky substitution on the two azomethin groups will make them chemically similar, but magnetically different. However, the ^{13}C-NMR showed a peak at 159 and 161 ppm both for the azomethin group, with similar proposed explanation. The rest of the ^1H-NMR and ^{13}C-NMR signals were in good agreement with expected one, as they are presented in Table-7. The aromatic ring and hydroxyl groups chemical shift are consistent with the chemical shift values for unsubstituted phenyl ring reported in the literature.

High resolution mass spectrum gave a molecular ion signal of *m/q* at 241.13346 (calc. M. wt.: 241.13411), 241.07391 (calc. M. wt.: 241.13411), and 361.10628 (calc. M. wt.: 362.1141) amu, which match the molecular weight of the expected reaction product with very small relative deviation of 2.3×10^{-4}, 2.3×10^{-6} and 5.85×10^{-5} respectively. Other spectrohotometric absorption spectra include UV-visible gave the three absorption maxima (λ_{max}) at 219, 275, and 353 nm, while FT-IR showed sharp strong peak for the azomethin group at 1621 cm^{-1}.

The other physical properties of the Schiff base ligands and their metal complexes with Mn(II), Co(II), Cu(II), and Zn(II) metal ion were presented in Tables-1 and Table-3. The first ligand, 2-{4-dimethylamino)phenylimino}methyl phenol (L_1), was expected to be bidentate ligand through the methane group and phenolic hydroxyl group. The second ligand, 2-(2-hydroxybenzylideneamino)-benzoic acid (L_2), may coordinate as bidentate ligand through the methane group and phenolic hydroxyl group or tridentate if the carboxylic group contribute to the coordinate.

The significant FT-IR absorption bands of the free ligands (L_1, L_2, and L_3) and their metal complexes and their assignments are given in (Table-4). The free ligand showed stretching band, which stand for the azomethine group within the range 1612-1621 cm^{-1}. These bands were shifted due to the formation of metal complexes, and it was the largest red shifted by copper complex, $[Cu(L_2)(H_2O)]$ while manganese complexes, $[Mn(L_2)(H_2O)_2Cl][Et_3N]$ showed largest blue shift. This shift was related with increase in the C=N bond order. The O-H stretching bands of the free ligands appeared at 3406 - 3460 cm^{-1}, due to the hydrogen bridge OH....N=C, while the complexes were at 3144 - 3597 cm^{-1} due to the presence of water molecules [20-24]. The participation of nitrogen atom in through C=N bond to form M-N coordination, was based on data from earlier reports, we could assign the bands at 414 - 490 cm^{-1} and 507 - 555 cm^{-1} to M-N and M-O vibrations, respectively [25-27]. The appearance of M-Cl coordination appeared in four complexes in the region of 243 - 264 cm^{-1}, while coordinated water was within the region 3144 - 3597 cm^{-1}. So, the ligand (L_1) behave as a bidentate ligand and coordinate through nitrogen atom of C=N bond and the phenolic oxygen. So, the ligands behave as a bidentate ligand and coordinate through nitrogen atom of C=N bond and the phenolic oxygen.

By following Molar-Ratio Method for determining the stoichiometric ratio between ligands and metallic ions through UV spectrophotometry, different concentrations for each of the metals and ligands under investigation were prepared [28-30]. An equal concentrations of metallic ions and the ligands (L_1, L_2, and L_3) of 3.0×10^{-3} M were mixed and the absorption at the maximum wavelength of the specified complex was obtained. The graphs obtained by plotting the absorption against the mole ratio of metal:ligand was obtained and the stoichiometric ratio between ligands and metallic ions result from following the preparation procedure of these complexes were presented in Table 4. The molar conductivity Λ_m for the complexes were measured in DMSO as a solvent with a concentration of 1.0×10^{-3} M, and found to be in the range of 6.1 - 32.2 $\Omega^{-1}.cm^2.mole^{-1}$. The conductivity data of these complexes indicate that they were non-electrolyte, and they didn`t react with silver nitrate solution indicating that chlorine atom is inside the coordination sphere (Table 4). The results indicated that molar ratio of metal:ligand (M:L) were 1:1 for Mn(II), Cu(II) and (1:2) Co(II), Zn(II) with the bidentate ligand L_1, while that with tridentate ligand L_2 was 1:1 in all its complexes. The tetradentate ligand L_3 with Mn(II), Cu(II) and Zn(II) gave 1:1 ratio, while Co(II) gave a ratio of M:L of 1:2. These result were in agreement with the measured molar conductivity in dimethyl sulfoxide, DMSO solution given by Refat [31-32]. From the previous results viz. UV-visible and FT-IR spectrophotometry, molar variation method, and molar conductivity measurement, indicated that the geometry of Mn(II) and Cu(II) complexes with L_1 and L_2 were octahedral. The metal ion of Co(II) and Zn(II) with bidentate ligand L_1 form tetrahedral geometry and octahedral with the tridentate ligand L_2. The results of *in vitro* antibacterial activity of the Schiff and their complexes were measured by Well Diffusion method. The inhibition zone were recorded against three pathogenic bacteria viz. *E. Coli*, *S. aureus* and *P. aerugenosa* in mm (% Inhibition), as shown in Table-5. The result revealed that the antibacterial activity of the complexes is one order higher than that of the free ligand L_1. In most cases accept for Co(II) and Cu(II) complexes of L_2 and L_3 they have similar activity against *E. Coli*, while ligand L_2 showed lower activity against *S. aureus* and *P. aerugenosa* than their complexes. Similarly behave the ligand L_3, accept for Co(II) and Cu(II) complexes.

Table 4: The principle absorption bands of UV-visible and FT-IR spectra of the Schiff base ligands their complexes

Compound	λ_{max} (DMSO)		UV-visible Assignment	FT-IR Assignment ν(cm^{-1})							Λ_m	Geometry
	(nm)	(cm^{-1})		O-H	C=N	M-O	M-N	M-Cl	C=O	NO_2	(ohm^{-1},cm^2, $mole^{-1}$)	
$C_{15}H_{16}N_2O$ (L_1)	245	40816	$\pi \rightarrow \pi^*$	3414	1612	-	-	-	1687	-	-	-
	384	26041	$n \rightarrow \pi^*$									
$[Mn(C_{15}H_{16}N_2O)(H_2O)_3Cl]$	325	30769	L.F	3417	1604	522	468	264	-	-	6.6	O.H
	411	24330	C.T									
$[Co(C_{15}H_{16}N_2O)_2].2H_2O$	350	28571	C.T	3560	1633	522	466	-	-	-	6.1	T.H
	390	25641	$^4T_{1(F)} \rightarrow {}^4T_{1(P)}$									
$[Cu\ (C_{15}H_{16}N_2O)(H_2O)_3Cl]$	585	17094	$^2Eg \rightarrow {}^2T_2g$	3144	1606	550	445	243	-	-	12.5	O.H
$[Zn(C_{15}H_{16}N_2O)_2].2H_2O$	383	26109	L.F	3431	1633	507	462	-	-	-	10.5	T.H
	419	23866	C.T									
$C_{14}H_{11}NO_3$, L_2	250	40000	$\pi \rightarrow \pi^*$	3460	1620	-	-	-	1689	-	-	-
	332	30120	$n \rightarrow \pi^*$									
$[Mn(L_2)(H_2O)_2Cl][Et_3N]$	344	25062	L.F	3307	1593	515	420	297	1620	-	32.2	O.H
	399	29069	C.T									
$[Co(C_{14}H_{11}NO_3)].2H_2O$	349	28653	C.T	3308	1614	510	420	-	1620	-	10.3	O.H
	686	14577	$^4T_1g_{(F)} \rightarrow {}^4T_2g_{(F)}$									
	751	13315	$^4T_1g_{(F)} \rightarrow {}^4A_2g_{(F)}$									
	797	12547	$^4T_1g_{(F)} \rightarrow {}^4T_1g_{(P)}$									
$[Cu(C_{14}H_{11}NO_3)(H_2O)]$	380	26315	C.T	3443	1604	508	459	-	1614	-	12.8	T.H
	421	23752	$^2T_2 \rightarrow {}^2E$									
$[Zn(C_{14}H_{11}NO_3)(H_2O)_3]$	345	28985	L.F	3448	1626	515	414	-	1626	-	24.1	O.H
	356	28089	C.T									
$C_{20}H_{15}N_3O_4$, L_3	275	36363	$\pi \rightarrow \pi^*$	3406	1621	555	-	-		1338	-	-
	353	28328	$n \rightarrow \pi^*$									
$[Mn(C_{20}H_{15}N_3O_4)]$	385	25974	C.T	3471	1626	560	441	-		1352	20.3	T.H
	442	22624	$^6A_1g \rightarrow {}^4T_2g(G)$									
	550	18181	$^6A_1g \rightarrow {}^4Eg, A_1g(G)$									
$[Co(C_{20}H_{15}N_3O_4)(H_2O)_2]$	342	29154	C.T	3328	1602-1612	545	490	-		1355	9.3	O.H
	410	24390	$^4T_1g_{(F)} \rightarrow {}^4T_2g_{(F)}$									
	540	18518	$^4T_1g \rightarrow {}^4A_2g_{(F)}$									
$[Cu(C_{20}H_{15}N_3O_4)_2(H_2O)_2]$	316	31645	C.T	3597	1612	545	420	-		1359	20.3	O.H
	510	19607	$^2Eg \rightarrow {}^2T_2g$									
$[Zn_2(C_{20}H_{15}N_3O_4)Cl_2(H_2O)_2]$	356	28089	L.F	3254	1599	555	488	264		1386	9.2	T.H
	482	20746	C.T									

Table 5: The inhibition zone of the Schiff base ligands (L_1, L_2, and L_3)and their complexes by Well Diffusion method measured in mm (% Inhibition) against *E. Coli S. aureus* and *P. aerugenosa*

No.	Compound	*E. Coli*	*S. aureus*	*P. aerugenosa*
1	DMSO	+	+	+
2	$C_{15}H_{16}N_2O$, L_1	+++	++++	++
3	$[Mn(C_{15}H_{16}N_2O)(H_2O)_3Cl]$	+++	+++	+++
4	$[Co(C_{15}H_{16}N_2O)_2].2H_2O$	+++	++	+++
5	$[Cu\ (C_{15}H_{16}N_2O)(H_2O)_3Cl]$	+++	+++	+++
6	$[Zn(C_{15}H_{16}N_2O)_2].2H_2O$	+++	+++	+++
7	$C_{14}H_{11}NO_3$, L_2	+++	++	++
8	$[Mn(L_2)(H_2O)_2Cl][Et_3N]$	+++	++	++
9	$[Co(C_{14}H_{11}NO_3)].2H_2O$	++	+++	++
10	$[Cu(C_{14}H_{11}NO_3)(H_2O)]$	++	+++	+++
11	$[Zn(C_{14}H_{11}NO_3)(H_2O)_3]$	+++	++	+++
12	$C_{20}H_{15}N_3O_4$, L_3	++	+++	+++
13	$[Mn(C_{20}H_{15}N_3O_4)]$	++	+++	+++
14	$[Co(C_{20}H_{15}N_3O_4)(H_2O)_2]$	++	++++	++
15	$[Cu(C_{20}H_{15}N_3O_4)_2(H_2O)_2]$	++	+++	++
16	$[Zn_2(C_{20}H_{15}N_3O_4)Cl_2(H_2O)_2]$	+++	++++	+++

The inhibition zone: (+): 6-10 mm (27 - 45 %); (++): 10-14 mm (45 - 64 %); (+++): 14-18 mm (64 -82 %); (++++): 18 - 22 mm (82 - 100 %)

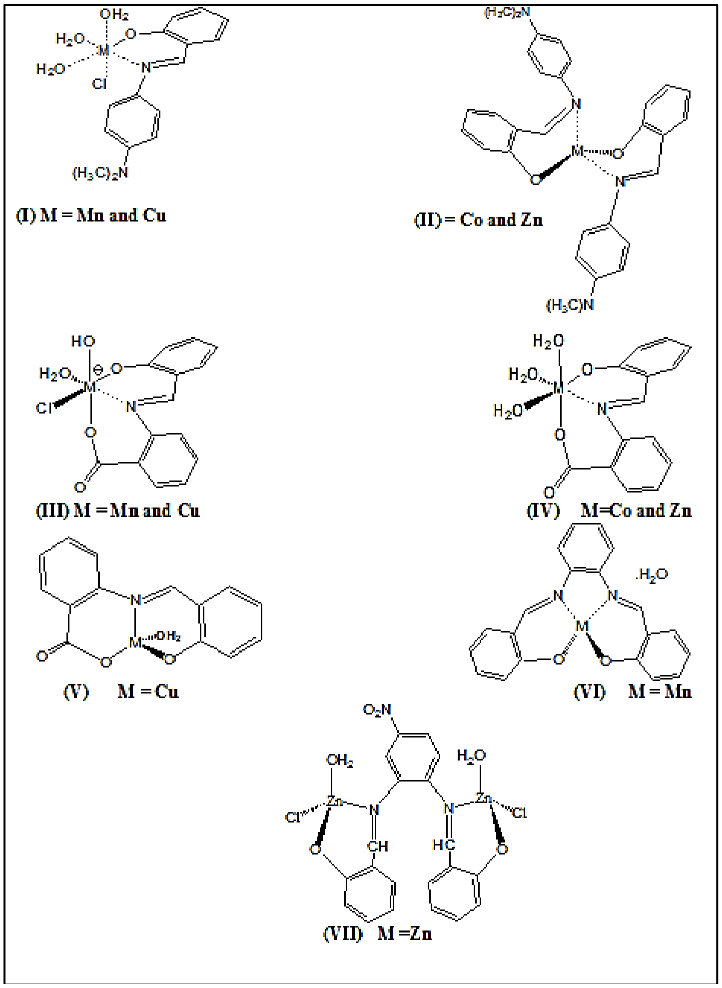

Figure 12: The proposed geometry of the complexes

CONCLUSION

Three Schiff base have been synthesized from salicylaldehyde and *N,N*-dimethyl *p*-phenylene diamine, 2-amino benzoic acid, and 3-Nitro-*o*-phenylenediamine. They were characterized by the available physical and 0spectroscopic methods. Their metal complexes were prepared from the chloride salts of Co(II), Mn(II), Cu(II) and Zn(II) in an alcoholic medium. It was suggested that these ligand acts as neutral and polydentate ligands, hence coordinates to metal atom through azomethine nitrogen and oxygen atoms of phenol groups, as well as the carboxyl group of 2-amino benzoic acid. The geometry for the metal complexes were suggested to have the following: (1) $[M(L_1)(H_2O)_3Cl]$ for Mn(II) and Cu(II), (2) $[Co(L_1)_2].2H_2O$ for Co(II) and Zn(II), (3) $[M(L_2)_2].2H_2O$ for Co(II), (4) $[Mn(L_2)(H_2O)_2Cl][Et_3N]$ for Mn(II), (5) $[M(L_2)(H_2O)]$ for Cu(II), (6) $[M(L_2)(H_2O)_3]$ for Zn(II), (7) $[Mn(L_3)]$ for Mn(II), (8) $[Co(L_3)(H_2O)_2]$ for Co(II) and Cu(II), and (9) $[Zn_2(L_3)Cl_2(H_2O)_2]$ for Zn(II). The free Schiff base and their complexes found to have varying antibacterial activity against *Escherichia Coli* (G-), *Staphylococcus aureus* (G+), *and Pseudomonas aeruginosa* (G-) by using Agar well diffusion and the results were discussed.

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