

Research Article

Synthesis, Spectroscopic Characterization and Biological Evaluation Studies of Mixed ligand Schiff base with Metal (II) Complexes Derived from o-phenylenediamine

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Abstract

In the present study a novel Schiff base mixed ligand chelates of Cu(II), Ni(II), Co(II) and Mn(II) complexes with two newly synthesized Schiff base mixed ligands derived from salicylaldehyde and o-phenylenediamine (H_2L^1), benzaldehyde and o-phenylenediamine (H_2L^2). The ligands and their transition metal complexes were characterized on the basis of various physico-chemical methods including elemental analysis, molar conductance, infrared, electronic spectra, EPR and cyclic voltammetry. The mixed ligand complexes are formed in the 1:1:1 ($L^1:L^2:M$) ratio as found from the elemental analyses and found to have the formulae $[ML^1L^2]$ where $M = Cu(II), Ni(II), Co(II)$ and $Mn(II)$, $L^1 = N, N'$ -Bis-(2-hydroxy-benzylidene)-benzene-1, 2-diamine, $L^2 = N, N'$ -Dibenzylidene-benzene-1, 2-diamine. The molar conductance data reveal that the chelates are non-electrolytes. The IR spectral data suggest the involvement of

azomethine nitrogen in co-ordination to the central metal ion. The electronic spectral results indicate that all the complexes have octahedral geometry. The electrochemical properties of the Schiff base complexes were studied; the observed redox transitions were assigned to specific redox-active sites of the molecule. The 3D molecular modeling and analysis for bond lengths and bond angles have also been carried out for the $[CuL_1L_2]$ complex to substantiate the proposed structure. The ligands and their metal chelates have been screened for their antibacterial activities and the findings have been reported, explained and compared with known antibiotics. Furthermore, the antioxidant activity of the Schiff base complexes was determined by DPPH method *in vitro*.

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Introduction

The preparation of a new Schiff base mixed ligand was a perhaps the most important step in the development of metal complexes which exhibit unique properties and novel reactivity. Since the electron donor and electron acceptor properties of the ligand, structural functional groups and the position of the ligand in the coordination sphere together with the reactivity of coordination compounds may be the factor for different studies [1]. Schiff base compounds are widely studied and used, attracting wide range of applications in organic synthesis and metal ion complexation [2]. They serve as models for biologically important species and find applications in biomimetic catalytic reactions. Chelating ligands containing O and N donor atoms show pronounced biological activity and are of special interest because of the variety of ways in which they are bonded to metal ions [3].

Coordination metal complexes containing Schiff bases as ligand are used as catalyst for many reactions [4]. Many transition metals like copper, nickel, cobalt and manganese containing Schiff bases have more applications in biological activity [5]. Schiff base complexes have been used as drugs and they possess a wide variety of antimicrobial activity against bacteria, fungi and certain type of tumors. Some drugs have increased activity when administrated as metal chelated and inhibit the growth of tumors [6]. We are especially interested in the coordination chemistry of electron rich first row transition metals. In contrast to most metals from the left and center of the transition metal row, which are mostly six coordinate and more or less octahedral, complexes of metals such as Cu, Ni, Co and Mn show a much richer structural diversity. For the Cu(II) ion the d^9 configuration is Jahn-Teller active: a single unpaired d-electron occupies one of the d-orbitals which gives rise to structural flexibility with

coordination numbers varying between 4 and 6 with often severely distorted coordination geometries [7]. Copper is an attractive prospect, being an essential trace element which is required for normal cellular activity as a cofactor for many enzymes. However, role of copper is much more complex because it can also promote nucleic acid cleavage and therefore has been utilized as metallo-drug to cause DNA damage [8]. In Ni(II) no odd unpaired electron is present and its metal complexes are less likely to be distorted, but they still show a diversity of coordination geometries rarely found for other transition metal complexes, with square planar and octahedral being the most common [9].

Therefore, in continuation to our interest in Schiff base ligands and their metal chelates [10], this work deals with the synthesis and characterization of Schiff base ligands; L^1 and L^2 , and their complexes. The coordination behaviour of L^1 and L^2 ligands towards transition metal ions (Cu(II), Ni(II), Co(II) and Mn(II)) is investigated via molar conductance, infrared, electronic spectra, EPR, molecular modeling and cyclic voltammetry. The biological activity of these Schiff bases and their metal chelates are reported.

Experimental

Materials and physical measurements

All the chemicals used were chemically pure and AR grade. Solvents were purified and dried according to standard procedures. Metal salts were purchased from Merck. Salicylaldehyde, o-phenylenediamine and Benzaldehyde were obtained from Aldrich. Ethanol, DMSO and DMF were used as solvents purchased from Merck and Loba Chemie Pvt. Ltd. The purity of metal complexes was tested by TLC.

The elemental analysis were carried out with a Carlo-Erba 1106-model 240 Perkin Elmer analyzer. The solution conductivity measurements were performed to establish the charge type of the complexes. The complexes were dissolved in DMF and molar conductivities of $10^{-3}M$ of their solutions at $29^\circ C$ were measured with ELICO CM 185 conductivity Bridge. Infrared spectra were recorded on the Perkin Elmer FT-IR-8300 model spectrometer using KBr disc and Nujol mull techniques in the range of $4000-400\text{ cm}^{-1}$. Electronic absorption spectra in the UV-Visible range were recorded on Perkin Elmer Lambda-25 between 200-800 nm by using DMF as the solvent.

Synthesis of Schiff base N, N' -Bis-(2-hydroxy-benzylidene)-benzene-1, 2-diamine (H_2L^1)

The Schiff base ligand was prepared according to the literature method. To an ethanolic solution of salicylaldehyde (2 mmol) and ethanolic solution of o-phenylenediamine (1 mmol) was added in drop wise. The reaction mixture was kept on water bath for

refluxion. It was stirred for 2 hours as shown in **Figure 1**. Yellow colour solid was separated and were filtered off, washed with 5 ml of cold ethanol and then dried in air.

Synthesis of Schiff base N, N' -Dibenzylidene-benzene-1, 2-diamine (H_2L^2)

To an ethanolic solution of benzaldehyde (2 mmol) and ethanolic solution of o-phenylenediamine (1 mmol) was added in drop wise. The reaction mixture was kept on water bath for refluxion. It was stirred for 2 hours as shown in **Figure 1**. Brown colour solid was separated and were filtered off, washed with 5 ml of cold ethanol and then dried in air.

Synthesis of metal complexes

All the Schiff base metal complexes were prepared by the same general procedure with stoichiometric amount of ligand and metal salts in a 1:1:1 mole ratio. To an ethanolic solution of Schiff base mixed ligands metal salts was added. The reaction mixture was kept on water bath for refluxing about 5 hrs as shown in **Figure 1**. The separated complexes were collected by filtration, washed with hot methanol and dried under vacuum.

Cyclic voltammetry

All voltammetric experiments were performed with a CHI 760 electrochemical analyzer, in single compartmental cells using tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte. The redox behavior of the complexes has been examined in the scan rate of 0.1 Vs^{-1} in the potential range $+2.0$ to -2.0 V . A three-electrode configuration was used, comprising a glassy carbon electrode as the working electrode, a Pt-wire as the auxiliary electrode and an Ag/AgCl electrode as the reference electrode. The electrochemical data such as cathodic peak potential (Epc) and anodic peak potential (Epa) were measured.

The *in vitro* Antibacterial activity

The *in vitro* antibacterial activity of the ligand and the complexes were tested against the bacteria *E. Coli*, *Bacillus cereus*, *Staphylococcus aureus* and *Pseudomonas aeruginosa* by well diffusion method using nutrient agar as the medium [11]. *Streptomycin* was used as standard component. The stock solution ($10^{-1}\text{ mol L}^{-1}$) was prepared by dissolving the compound in DMF and the solution was serially diluted to find minimum inhibitory concentration (MIC) values. In a typical procedure, a well was made on the agar medium with microorganisms in a petri plate. The well was filled with the test solution and the plate was incubated for 24 h for bacteria at $35^\circ C$. During the period, the test solution diffused and the growth of the inoculated microorganisms was affected. The inhibition zone was developed, at which the concentration was noted.

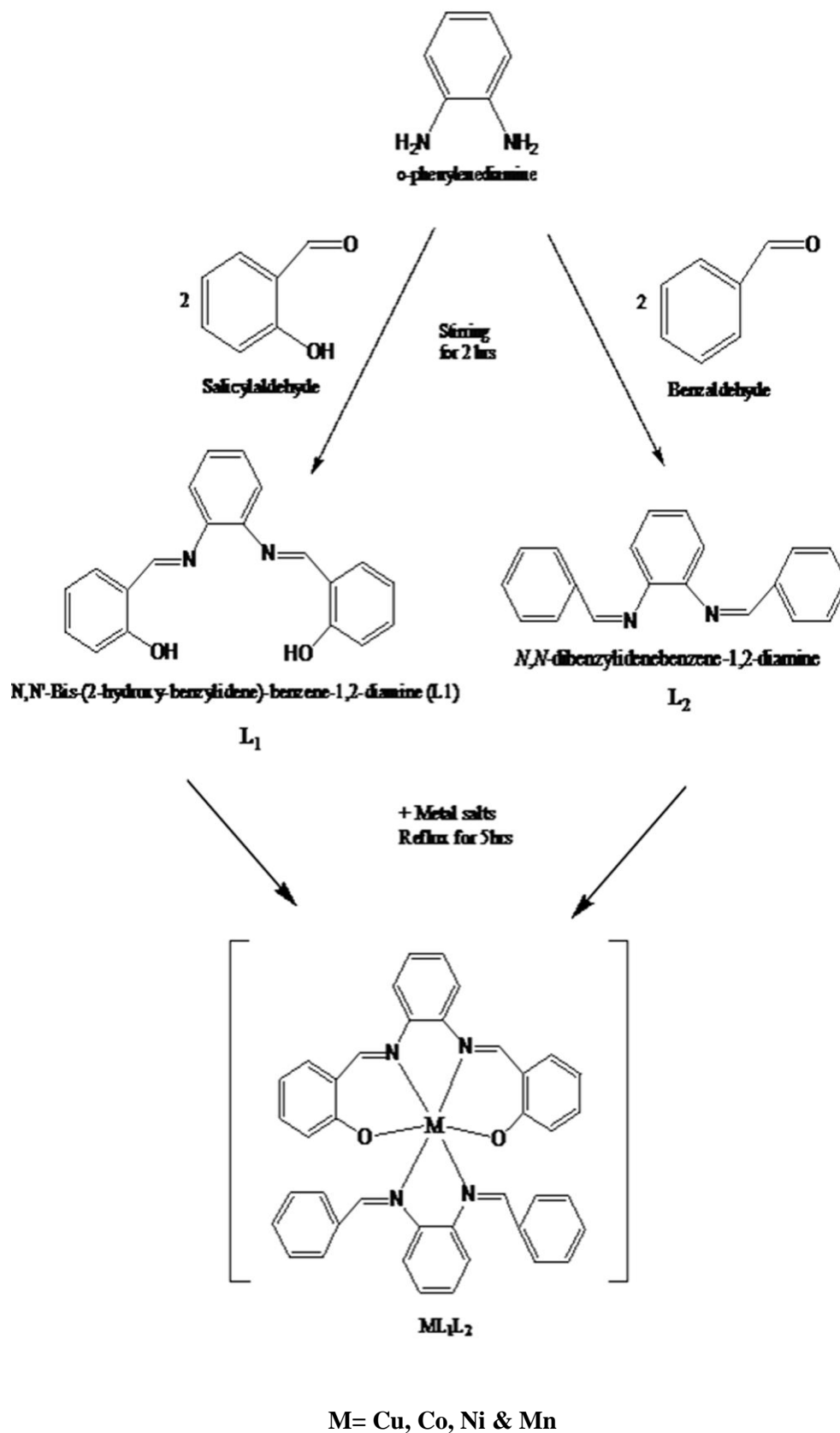
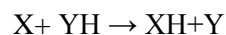


Figure 1 Synthesis of Schiff Base Mixed Ligand Complex [ML₁L₂].

Antioxidant activity

The antioxidant activity assay [12] employed is a technique depending on measuring the consumption of stable free radicals i.e., assess the free radical scavenging activity of the investigated component. The methodology assumes that the consumption of the stable free radical (X) will be determined by reactions as follows:



The rate of the process measured in terms of the decrease in X concentration, would be related to the ability of the added compounds to trap free radicals. The decrease in color intensity of the free-radical solution due to scavenging of the free radical by the antioxidant material is measured. The assay employs the radical cation derived from diphenylpicrylhydrazyl (DPPH) as stable free radical to assess antioxidant and compounds. The capability to scavenge the DPPH radical was calculated using the following equation:

$$\text{DPPH}^\circ \text{ scavenging effect (\%)} = \left[\frac{A_0 - A_1}{A_0} \right] \times 100$$

Where A_0 is the absorbance of the control solution, and A_1 is the absorbance in the presence of sample solutions or standards for positive control.

DPPH free radical scavenging activity

The free radical scavenging activities of metal complexes were measured by the 1,1-diphenyl-2-picrylhydrazyl (DPPH•) compound using the spectrophotometric method. According to this method, 0.1 mM solution of the DPPH• radical in methanol was prepared, and 1 mL of this solution was added to the solutions (3 mL) of the Schiff base ligands in methanol at different concentrations (200, 400, 600, 800, 1000 $\mu\text{g}/\text{mL}$). The mixture was shaken vigorously and allowed to stand at room temperature for 30 min. Then, the absorbance at 517 nm was measured by a spectrophotometer. Lowering of the absorbance of the reaction mixture indicated the higher of the free radical scavenging activity [13].

Results and Discussion

The solubility of the ligand and its complexes were studied in various organic solvents. The ligand was found to be soluble in ethanol, insoluble in water whereas the complexes were soluble in Methanol, Acetonitrile, Acetone, Dichloromethane, DMF and DMSO. The Schiff base metal complexes were characterized by elemental analysis, molar conductivity,

IR, UV, EPR and electrochemical studies are gives satisfactory results.

Elemental analysis

The stoichiometry of the ligand and its complexes were confirmed by their elemental analysis. The metal ligand ratio was found to be 1:1:1 with respect to $L_1:L_2:M$ [where $M = \text{Co(II)}, \text{Cu(II)}, \text{Mn(II)}$ and Ni(II)]. It has been arrived at by estimating the metal and nitrogen contents of the complexes. Elemental analysis show good agreement with the proposed structure of the ligand and its complexes as shown in the **Table 1**.

Molar Conductance

The Conductivity measurements commonly employed in the determination of charge type of the complexes is the determination of the equivalent conductance at infinite dilution of those complexes. The stoichiometry of the metal complexes was confirmed by conductometric measurement [14]. The molar Conductance of the synthesized mixed ligand complexes were measured using 10^{-3}M DMF solvent. The Conductance values are in the range of 4-12 $\text{ohm}^{-1}\text{mol}^{-1}\text{cm}^2$ and the values are listed in **Table 2**. These values are too low to account for any dissociation of the complexes in DMF. Hence these complexes can be regarded as non-electrolyte. The results were compared with the literature values in arriving at this conclusion [15].

Infrared Spectra

The IR- spectra of the complexes were recorded to confirm the binding mode of donor atoms with metal ions. The vibration frequencies and their tentative assignments of the transition metal complexes are listed in **Table 3**. The ligand and metal complexes were characterized mainly using the imine and phenolic bands. A sharp peak at 1568 cm^{-1} is due to $\nu(\text{C}=\text{C})$ stretching mode of vibrations. The band at 1492 and 1456 cm^{-1} are due to the CH deformation mode of vibrations of CH bond [16]. A medium band corresponding to the phenolic oxygen $\nu(\text{C}-\text{O})$ is observed at $1275-1297\text{ cm}^{-1}$ for the free ligands[17]. The IR spectra of the free ligands shows a band in the region 3435 and 3440 cm^{-1} due to $\nu(\text{OH})$ stretching vibration[18]. The band in the range 1616 cm^{-1} are observed due to $\nu(\text{C}=\text{N})$ which has been shifted towards lower region at around $1606-1610\text{ cm}^{-1}$ in the complexes indicating the participation of the azomethine group in the complexes formation[19-20] this shift is also due to reduction of double bond character of carbon-nitrogen bond of azomethine group[21].

In the IR spectra of complexes there is one more additional absorption band appears at $518-566\text{ cm}^{-1}$ range due to $\nu(\text{M}-\text{O})$ band [22]. The appearance of non-ligand bands in the complexes around $451-489\text{ cm}^{-1}$ are due to $(\text{M}-\text{N})$ bond respectively [23].

Table 1 Analytical data of the Schiff base ligands and its complexes

Compounds	Molecular formula	Molecular weight	Color	Yield %	Melting Point (°C)	% of Nitrogen		% of Metal	
						Cal	Exp	Cal	Exp
L ₁	C ₂₀ H ₁₆ N ₂ O ₂	316	Yellow	85	155	4.43	4.42	-	-
L ₂	C ₂₀ H ₁₆ N ₂	284	Brown	70	120	4.92	4.90	-	-
[CuL ₁ L ₂]	Cu[C ₄₀ H ₃₀ N ₄ O ₂]	549	Brown	70	150	2.12	2.11	9.53	9.52
[CoL ₁ L ₂]	Co[C ₄₀ H ₃₀ N ₄ O ₂]	545	Black	80	120	2.13	2.14	8.84	8.83
[NiL ₁ L ₂]	Ni[C ₄₀ H ₃₀ N ₄ O ₂]	545	Green	65	140	2.13	2.12	8.84	8.85
[MnL ₁ L ₂]	Mn[C ₄₀ H ₃₀ N ₄ O ₂]	541	Dark brown	75	103	2.14	2.15	8.28	8.29

Table 2 Molar conductance data of the Schiff base ligands and its complexes

Compounds	Solvent	Molar conductance ohm ⁻¹ cm ² mol ⁻¹	Type of electrolyte
[CuL ₁ L ₂]	DMF	8.8	Non electrolyte
[CoL ₁ L ₂]	DMF	6.3	Non electrolyte
[NiL ₁ L ₂]	DMF	4.6	Non electrolyte
[MnL ₁ L ₂]	DMF	11.6	Non electrolyte

Table 3 Infrared spectroscopic data of the Schiff base ligands and its complexes

Compound	Free-OH	-C=N (cm ⁻¹)	C-O (cm ⁻¹)	M-O (cm ⁻¹)	M-N (cm ⁻¹)
L ₁	3440	1616	1293	-	-
L ₂	3435	1616	1275	-	-
[CuL ₁ L ₂]	-	1608	1292	537	489
[CoL ₁ L ₂]	-	1607	1297	543	458
[NiL ₁ L ₂]	-	1610	1294	518	451
[MnL ₁ L ₂]	-	1606	1294	566	458

Table 4 Electronic Spectral data and Cyclic Voltammetric data of Schiff base mixed ligand metal complexes

Compounds	Electronic spectra (nm)			d-d	Geometry of the complex	CV Data (V)	
	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	L→M			Epc	Epa
L ₁	265	360	-	-	-	-	-
L ₂	269	360	-	-	-	-	-
[CuL ₁ L ₂]	290	365	440	625		1.6	0.7
[CoL ₁ L ₂]	275	370	455	555, 625		1.5	0.7
[NiL ₁ L ₂]	280	390	470	640	Octahedral	1.4	0.6
[MnL ₁ L ₂]	260	375	475	505, 602, 785		1.0	0.7

Electronic Spectra

The electronic spectra of the Schiff base mixed ligand and their Cu(II), Co(II), Ni(II) and Mn(II) complexes have been measured in DMF solution between 200- 800 nm at room temperature. The electronic absorption spectra are often very helpful for structural investigation. The electronic spectral measurements were used for assigning the geometry of metal ions in the complexes based on the positions and number of d-d transition peaks. In the spectra of the Schiff base mixed-ligand L₁ and L₂, the absorption band observed at 260-290 nm were assigned to a $\pi \rightarrow \pi^*$ transition and the band at 360-390 nm were assigned due to $n \rightarrow \pi^*$ transition associated with the azomethine chromophore (-C=N) [24]. The new bands in complexes near 440-475 nm can be assigned to L→M charge transfer band.

Only one broad band is observed at 625 nm in the electronic spectrum of the Cu(II) complex assigned to ${}^2E_g \rightarrow {}^2T_{2g}$ transition which is in conformity with octahedral geometry[25]. Though three transitions are expected in this case, they are very close in energy and often appear in the form of one broad band envelope. The electronic spectra of Co(II) complex showed two spin-allowed transitions at 555 and 625 nm assignable to ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions respectively, are in conformity with octahedral arrangements for Co(II) ion[26]. The appearance of a band at 640 nm due to ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transition favours an octahedral geometry[27] for the Ni(II) complex. The Mn(II) mixed-ligand complexes in an octahedral [28] field should give three transitions corresponding to ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (785 nm), ${}^6A_{1g} \rightarrow {}^4T_{2g}$ (602 nm), and ${}^6A_{1g} \rightarrow {}^4A_{1g}$ (505 nm) in increasing order of energy. The UV spectral data of all the complexes were given in **Table 4**.

Magnetic susceptibility measurements

The magnetic moment value of Cu(II) mixed ligand complex is 1.90 BM which suggests a distorted octahedral geometry[29, 30] around the metal ion. The magnetic moment of Co(II) complex is 4.81 BM which suggests the high spin six-coordinated octahedral geometry [31, 32] of mixed ligand molecules around the metal ion. The Ni(II) complex has magnetic moment value of 2.8 BM indicating a spin-free octahedral [33, 34] configuration. The room temperature magnetic moment value of Mn(II) was found to be 5.71 B.M. These observations suggest a octahedral geometry [35] of the complex.

EPR studies

The EPR-spectra of Copper(II) complexes were measured at X-band frequencies at 9.862117GHZ. The EPR-spectra of Cu(II) complexes provides information about the coordination environment around Cu(II) ion. ESR measurement has been made for copper complex using powder sample at room temperature, which could provide only value of g_{iso} and does not give hint about the individual g perpendicular and g parallel. The g_{iso} value of the complex is 2.157. The value of g_{iso} shows that the copper (II) complex is in octahedral environment.

Cyclic Voltammetry Studies

Electroanalytical techniques are the most efficient and versatile methods available for the mechanistic study of redox systems. The important parameters of a cyclic voltammogram are the magnitudes of the anodic peak potential (Epa) and cathodic peak potential (Epc)[36]. The cyclic voltammogram of the mixed ligand Schiff base contains two peaks. These are due to oxidative nature of organic molecule and reductive nature of azomethine group which is present in Schiff base mixed ligand.

The Copper complex in DMF shows cathodic peak of 1.6 V indicates the one electron reduction of Cu(II)→Cu(I) process and the anodic peak of 0.7 V indicates the oxidation process of Cu(I)→Cu(II)[37, 38]. The copper complexes are redox active and show a cyclic voltammogram response in the potential range 1.6-0.7 V [39-41] assigned to the Cu(II)/Cu(I) couple. The non-equivalent current intensity of cathodic and anodic peaks ($i_c/i_a=0.6$ V) indicates a quasi reversible behavior [42]. It has been shown that the formal redox potential of Cu(II)/Cu(I) couple is dependent on factors such as coordination number, hard/soft nature of the ligands and bulkiness of the ligands[43]. The cobalt complexes exhibit one electron quasi reversible transfer process with a peaks at $E_{pa}=0.7$ V, $E_{pc}=1.5$ V. This gives evidence for quasi reversible Co(II)/Co(I) couple. The cyclic voltammogram of Nickel complexes shows well defined redox process corresponding to the formation of the quasi-reversible Ni(II)/Ni(I) couple. The anodic peak at $E_{pa}=0.6$ V and the associated cathodic peak at $E_{pc}=1.4$ V corresponds to Ni(II)/Ni(I) couple [44]. The one electron

cyclic response for Manganese complexes were observed at $E_{pc}=1.0$ V and $E_{pa}=0.7$ V. This corresponds to Mn(II)/Mn(I). The **Table 4** shows the redox nature of the Schiff base mixed ligand complexes.

3D Molecular modeling

Based on the proposed structure (**Figure 2**), the 3D molecular modeling of $[CuL_1L_2]$ was carried out with the CS Chem 3D Ultra Molecular Modeling and Analysis Program. The details of bond lengths, bond angles as per the 3D structures (**Figure 2**) are given in **Tables 5 and 6** respectively. Except few cases, optimal values of both the bond lengths and the bond angles are given in the Tables along with the actual ones. The missing of some values of standard bond lengths / bond angles may be due to the limitations of the software, which we had already noticed in modelling of other systems (45). In most of the cases, the observed bond lengths and bond angles are close to the optimal values, and thus the proposed structure is octahedral and is acceptable.

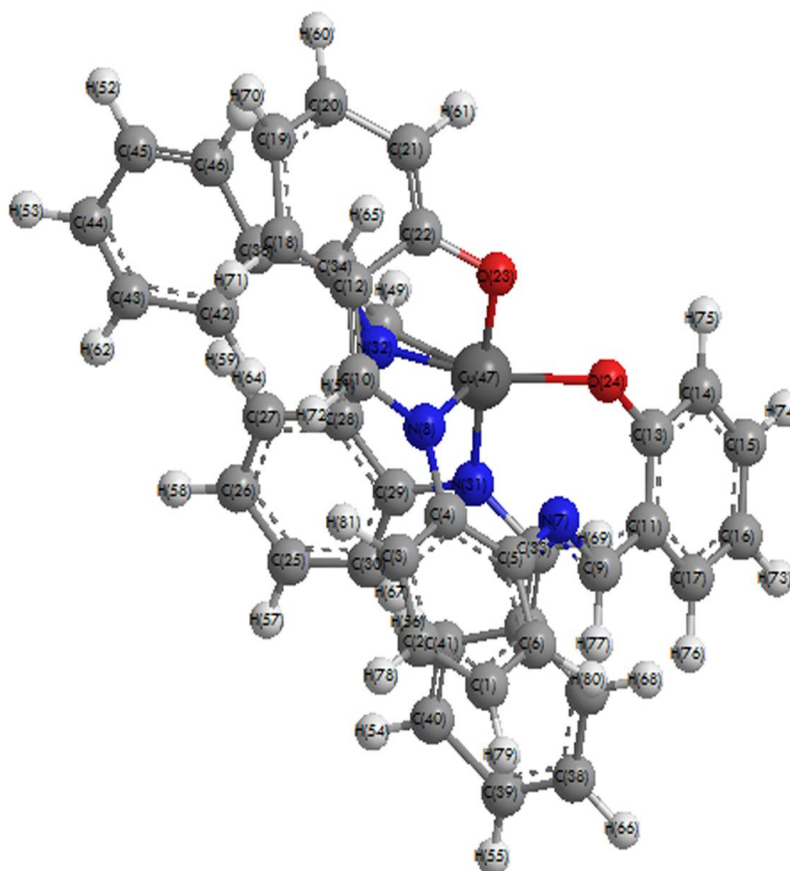


Figure 2 3D structure of compound of $[CuL_1L_2]$

Table 5 Various bond lengths of Schiff base mixed ligand [CuL₁L₂] complex

Atoms	Actual bond length	Optimized bond length	Atoms	Actual bond length	Optimized bond length
C(1)-C(2)	1.420	1.420	C(27)-C(28)	1.420	1.420
C(1)-C(6)	1.420	1.420	C(27)-H(67)	1.100	1.100
C(1)-H(70)	1.100	1.100	C(28)-C(29)	1.422	1.420
C(2)-C(3)	1.420	1.420	C(28)-N(32)	1.462	1.462
C(2)-H(80)	1.100	1.100	C(29)-C(30)	1.420	1.420
C(3)-C(4)	1.420	1.420	C(29)-N(31)	1.462	1.462
C(3)-H(81)	1.100	1.100	C(30)-H(65)	1.100	1.100
C(4)-C(5)	1.420	1.420	N(31)-C(33)	1.462	1.462
C(4)-N(8)	1.462	1.462	N(31)-Cu(47)	1.846	-
C(5)-C(6)	1.420	1.420	N(32)-C(34)	1.462	1.462
C(5)-N(7)	1.358	1.358	N(32)-Cu(47)	1.846	-
C(6)-H(71)	1.100	1.100	C(33)-C(35)	1.420	1.420
N(7)-C(9)	1.214	1.358	C(33)-H(73)	1.100	1.100
N(8)-C(10)	1.462	1.462	C(34)-C(36)	1.420	1.420
N(8)-Cu(47)	1.846	-	C(34)-H(72)	1.100	1.100
C(9)-C(11)	1.420	1.420	C(35)-C(37)	1.420	1.420
C(9)-H(74)	1.100	1.100	C(35)-C(41)	1.503	1.503
C(10)-C(12)	1.420	1.420	C(36)-C(42)	1.420	1.420
C(10)-H(79)	1.100	1.100	C(36)-C(46)	1.503	1.503
C(11)-C(13)	1.420	1.420	C(37)-C(38)	1.503	1.503
C(11)-C(17)	1.420	1.420	C(37)-H(63)	1.100	1.100
C(12)-C(18)	1.420	1.420	C(38)-C(39)	1.337	1.337
C(12)-C(22)	1.503	1.503	C(38)-H(61)	1.100	1.100
C(13)-C(14)	1.420	1.420	C(39)-C(40)	1.586	1.503
C(13)-O(24)	1.355	1.355	C(39)-H(55)	1.100	1.100
C(14)-C(15)	1.420	1.420	C(40)-C(41)	1.337	1.337
C(14)-H(76)	1.100	1.100	C(40)-H(54)	1.100	1.100
C(15)-C(16)	1.420	1.420	C(41)-H(62)	1.100	1.100
C(15)-H(57)	1.100	1.100	C(42)-C(43)	1.503	1.503
C(16)-C(17)	1.420	1.420	C(42)-H(60)	1.100	1.100
C(16)-H(56)	1.100	1.100	C(43)-C(44)	1.337	1.337
C(17)-H(75)	1.100	1.100	C(43)-H(58)	1.100	1.100
C(18)-C(19)	1.503	1.503	C(44)-C(45)	1.586	1.503
C(18)-H(78)	1.100	1.100	C(44)-H(53)	1.100	1.100
C(19)-C(20)	1.505	1.337	C(45)-C(46)	1.337	1.337
C(19)-H(77)	1.100	1.100	C(45)-H(52)	1.100	1.100
C(20)-C(21)	1.503	1.503	C(46)-H(59)	1.100	1.100
C(20)-H(68)	1.100	1.100	Cu(47)-C(48)	1.940	-
C(21)-C(22)	1.337	1.337	C(48)-H(49)	1.113	1.113
C(21)-H(69)	1.100	1.100	C(48)-H(50)	1.113	1.113
C(22)-O(23)	1.335	1.355	C(48)-H(51)	1.113	1.113
O(23)-Cu(47)	1.810	-			
O(24)-Cu(47)	1.810	-			
C(25)-C(26)	1.421	1.420			
C(25)-C(30)	1.420	1.420			
C(25)-H(64)	1.100	1.100			
C(26)-C(27)	1.420	1.420			
C(26)-H(66)	1.100	1.100			

Table 6 Various bond angles of Schiff base mixed ligand [CuL₁L₂] complex

Atoms	Actual bond angle	Optimized bond angle	Atoms	Actual bond angle	Optimized bond angle
C(2)-C(1)-C(6)	120.001	120.000	C(16)-C(17)-H(75)	120.001	120.000
C(2)-C(1)-H(70)	119.998	120.000	C(12)-C(18)-C(19)	120.000	120.000
C(6)-C(1)-H(70)	119.998	120.000	C(12)-C(18)-H(78)	120.000	120.000
C(1)-C(2)-C(3)	120.000	120.000	C(19)-C(18)-H(78)	119.998	120.000
C(1)-C(2)-H(80)	119.998	120.000	C(18)-C(19)-C(20)	112.075	120.000
C(3)-C(2)-H(80)	119.998	120.000	C(18)-C(19)-H(77)	132.598	120.000
C(2)-C(3)-C(4)	120.000	120.000	C(20)-C(19)-H(77)	115.324	120.000
C(2)-C(3)-H(81)	119.998	120.000	C(19)-C(20)-C(21)	117.221	120.000
C(4)-C(3)-H(81)	119.998	120.000	C(19)-C(20)-H(68)	131.089	120.000
C(3)-C(4)-C(5)	119.998	120.000	C(21)-C(20)-H(68)	111.687	120.000
C(3)-C(4)-N(8)	119.998	120.000	C(20)-C(21)-C(22)	119.998	120.000
C(5)-C(4)-N(8)	120.000	120.000	C(20)-C(21)-H(69)	119.998	120.000
C(4)-C(5)-C(6)	120.000	120.000	C(22)-C(21)-H(69)	119.998	120.000
C(4)-C(5)-N(7)	119.998	120.000	C(12)-C(22)-C(21)	119.998	120.000
C(6)-C(5)-N(7)	119.998	120.000	C(12)-C(22)-O(23)	122.311	124.300
C(1)-C(6)-C(5)	120.000	120.000	C(21)-C(22)-O(23)	117.688	124.300
C(1)-C(6)-H(71)	119.998	120.000	C(22)-O(23)-Cu(47)	120.028	-
C(5)-C(6)-H(71)	119.998	120.000	C(13)-O(24)-Cu(47)	109.470	-
C(5)-N(7)-C(9)	81.639	115.000	C(26)-C(25)-C(30)	119.998	120.000
C(4)-N(8)-C(10)	121.998	124.000	C(26)-C(25)-H(64)	120.017	120.000
C(4)-N(8)-Cu(47)	118.001	-	C(30)-C(25)-H(64)	119.984	120.000
C(10)-N(8)-Cu(47)	119.998	-	C(25)-C(26)-C(27)	119.998	120.000
N(7)-C(9)-C(11)	96.599	123.500	C(25)-C(26)-H(66)	120.015	120.000
N(7)-C(9)-H(74)	143.927	116.500	C(27)-C(26)-H(66)	119.982	120.000
C(11)-C(9)-H(74)	119.470	120.000	C(26)-C(27)-C(28)	119.998	120.000
N(8)-C(10)-C(12)	119.001	119.000	C(26)-C(27)-H(67)	120.000	120.000
N(8)-C(10)-H(79)	120.500	113.500	C(28)-C(27)-H(67)	119.998	120.000
C(12)-C(10)-H(79)	120.498	120.000	C(27)-C(28)-C(29)	119.998	120.000
C(9)-C(11)-C(13)	119.998	120.000	C(27)-C(28)-N(32)	126.006	120.000
C(9)-C(11)-C(17)	119.998	120.000	C(29)-C(28)-N(32)	113.992	120.000
C(13)-C(11)-C(17)	120.000	120.000	C(28)-C(29)-C(30)	119.998	120.000
C(10)-C(12)-C(18)	119.998	120.000	C(28)-C(29)-N(31)	113.988	120.000
C(10)-C(12)-C(22)	120.000	120.000	C(30)-C(29)-N(31)	126.008	120.000
C(18)-C(12)-C(22)	119.998	120.000	C(25)-C(30)-C(29)	120.000	120.000
C(11)-C(13)-C(14)	119.998	120.000	C(25)-C(30)-H(65)	119.998	120.000
C(11)-C(13)-O(24)	120.000	124.300	C(29)-C(30)-H(65)	119.998	120.000
C(14)-C(13)-O(24)	119.998	124.300	C(29)-N(31)-C(33)	126.497	124.000
C(13)-C(14)-C(15)	120.000	120.000	C(29)-N(31)-Cu(47)	111.000	-
C(13)-C(14)-H(76)	119.998	120.000	C(33)-N(31)-Cu(47)	122.498	-
C(15)-C(14)-H(76)	120.000	120.000	C(28)-N(32)-C(34)	126.499	124.000
C(14)-C(15)-C(16)	120.001	120.000	C(28)-N(32)-Cu(47)	111.000	-
C(14)-C(15)-H(57)	119.998	120.000	C(34)-N(32)-Cu(47)	122.498	-
C(16)-C(15)-H(57)	119.998	120.000	N(31)-C(33)-C(35)	119.000	119.000
C(15)-C(16)-C(17)	120.000	120.000	N(31)-C(33)-H(73)	120.500	113.500
C(15)-C(16)-H(56)	119.998	120.000	C(35)-C(33)-H(73)	120.500	120.000

C(17)-C(16)-H(56)	119.998	120.000	N(32)-C(34)-C(36)	119.000	119.000
N(32)-C(34)-H(72)	120.500	113.500	O(24)-Cu(47)-C(48)	0.000	-
C(36)-C(34)-H(72)	120.500	120.000	N(31)-Cu(47)-N(32)	90.000	-
C(11)-C(17)-C(16)	120.000	120.000	N(31)-Cu(47)-C(48)	180.000	-
C(11)-C(17)-H(75)	119.998	120.000	N(32)-Cu(47)-C(48)	90.000	-
C(33)-C(35)-C(37)	120.000	120.000	Cu(47)-C(48)-H(49)	109.472	-
C(33)-C(35)-C(41)	119.998	120.000	Cu(47)-C(48)-H(50)	109.470	-
C(37)-C(35)-C(41)	119.998	120.000	Cu(47)-C(48)-H(51)	109.470	-
C(34)-C(36)-C(42)	120.000	120.000	H(49)-C(48)-H(50)	109.000	109.000
C(34)-C(36)-C(46)	119.998	120.000	H(49)-C(48)-H(51)	109.002	109.000
C(42)-C(36)-C(46)	119.998	120.000	H(50)-C(48)-H(51)	110.409	109.000
C(35)-C(37)-C(38)	120.000	120.000			
C(35)-C(37)-H(63)	119.998	120.000			
C(38)-C(37)-H(63)	119.998	120.000			
C(37)-C(38)-C(39)	119.998	120.000			
C(37)-C(38)-H(61)	119.998	120.000			
C(39)-C(38)-H(61)	119.998	120.000			
C(38)-C(39)-C(40)	120.000	120.000			
C(38)-C(39)-H(55)	119.998	120.000			
C(40)-C(39)-H(55)	119.998	120.000			
C(39)-C(40)-C(41)	120.001	120.000			
C(39)-C(40)-H(54)	119.998	120.000			
C(41)-C(40)-H(54)	119.998	120.000			
C(35)-C(41)-C(40)	120.000	120.000			
C(35)-C(41)-H(62)	119.998	120.000			
C(40)-C(41)-H(62)	120.000	120.000			
C(36)-C(42)-C(43)	120.000	120.000			
C(36)-C(42)-H(60)	119.998	120.000			
C(43)-C(42)-H(60)	120.000	120.000			
C(42)-C(43)-C(44)	119.998	120.000			
C(42)-C(43)-H(58)	119.998	120.000			
C(44)-C(43)-H(58)	120.000	120.000			
C(43)-C(44)-C(45)	120.001	120.000			
C(43)-C(44)-H(53)	119.998	120.000			
C(45)-C(44)-H(53)	119.998	120.000			
C(44)-C(45)-C(46)	120.000	120.000			
C(44)-C(45)-H(52)	119.998	120.000			
C(46)-C(45)-H(52)	119.998	120.000			
C(36)-C(46)-C(45)	120.000	120.000			
C(36)-C(46)-H(59)	119.998	120.000			
C(45)-C(46)-H(59)	119.998	120.000			
N(8)-Cu(47)-O(23)	90.000	-			
N(8)-Cu(47)-O(24)	90.000	-			
N(8)-Cu(47)-N(31)	90.000	-			
N(8)-Cu(47)-N(32)	179.451	-			
N(8)-Cu(47)-C(48)	90.000	-			
O(23)-Cu(47)-O(24)	90.000	-			
O(23)-Cu(47)-N(31)	90.000	-			
O(23)-Cu(47)-N(32)	90.572	-			
O(23)-Cu(47)-C(48)	90.000	-			
O(24)-Cu(47)-N(31)	180.000	-			
O(24)-Cu(47)-N(32)	90.00	-			

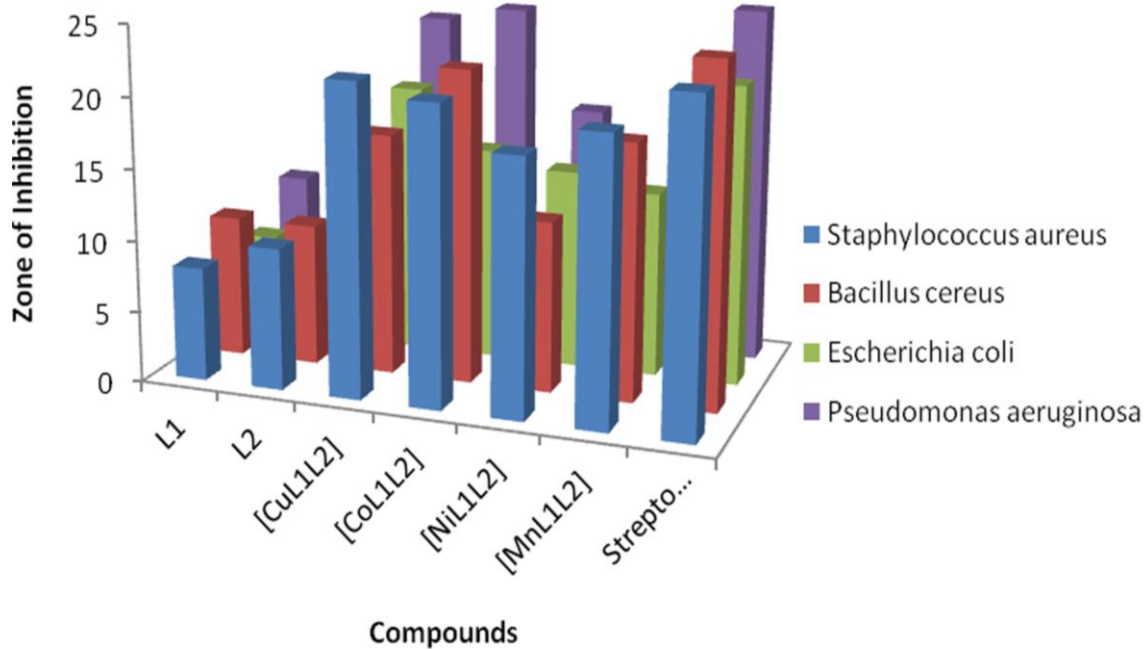


Figure 3 Antibacterial activity of ligand and its complexes.

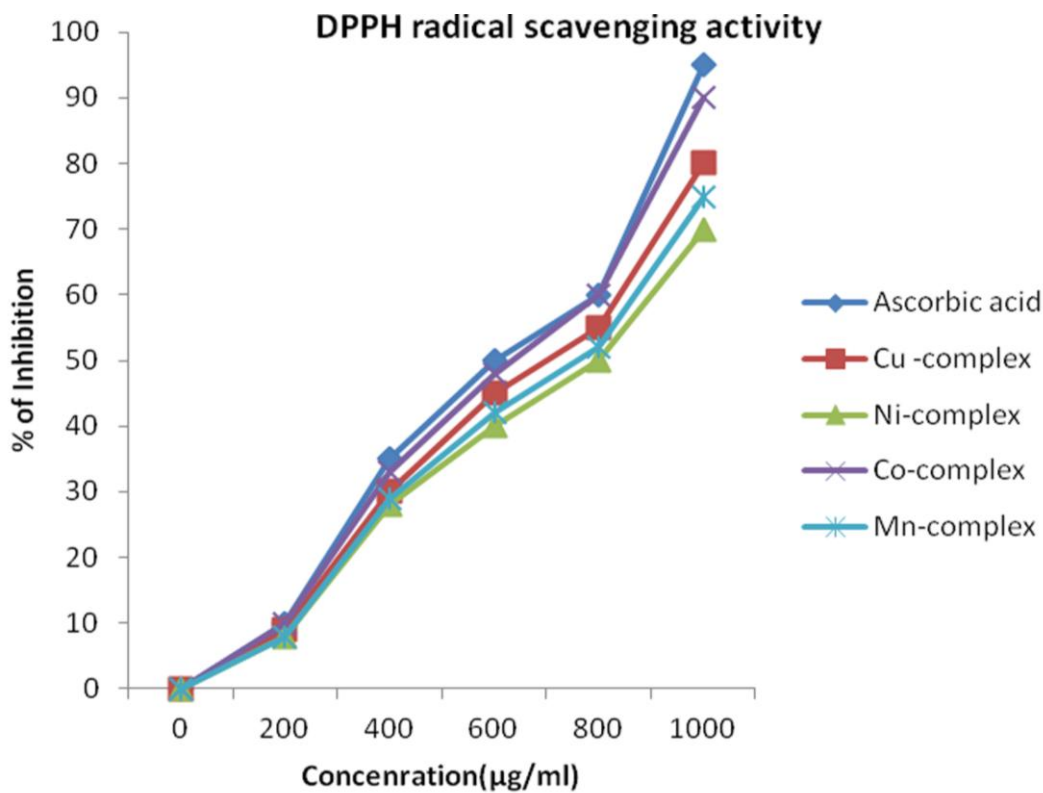


Figure 4 DPPH radical scavenging activity spectrophotometric assays of various concentrations of metal complexes.

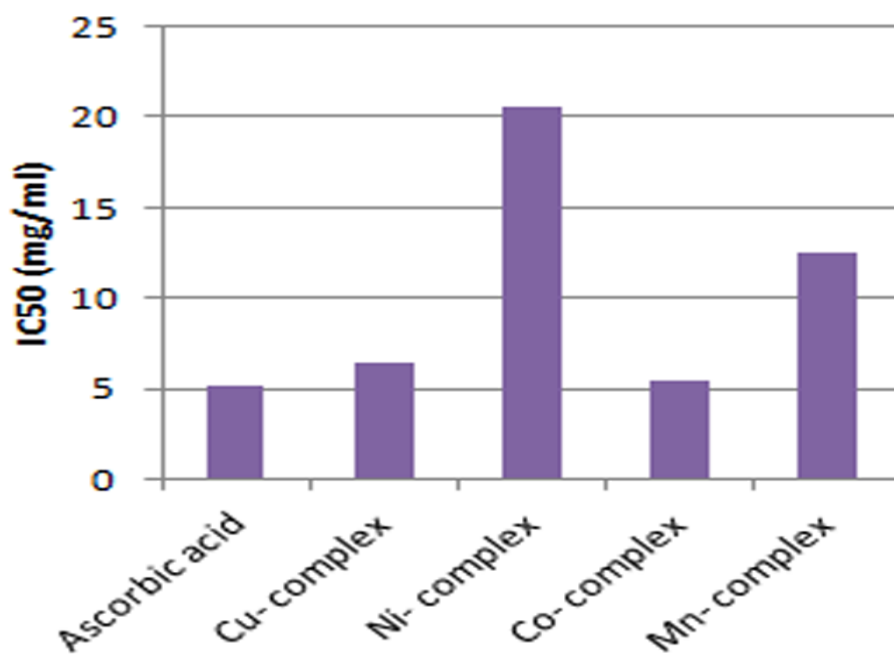


Figure 5 DPPH scavenging capacities (IC₅₀) of metal complexes

Table 7 Antibacterial activities of ligand and its complexes

Compounds	Diameter of inhibition zone (mm)				
	<i>Streptomyces</i>	<i>Staphylococcus aureus</i>	<i>Bacillus cereus</i>	<i>Escherichia coli</i>	<i>Pseudomonas aeruginosa</i>
L ₁	12	8	10	7	10
L ₂	15	10	10	8	12
[CuL ₁ L ₂]	28	22	17	19	23
[CoL ₁ L ₂]	30	21	22	15	24
[NiL ₁ L ₂]	25	18	12	14	17
[MnL ₁ L ₂]	24	20	18	13	11

Table 8 Antioxidant assay for the prepared Schiff base metal complexes

Compounds	IC ₅₀ (mg/ml)
Ascorbic acid	5.2
[CuL ₁ L ₂]	6.42
[NiL ₁ L ₂]	20.5
[CoL ₁ L ₂]	5.46
[MnL ₁ L ₂]	12.5

Antibacterial activity

The antibacterial activities of metal complexes are given in **Table 7**. Antibacterial activity of the complexes arises due to presence of azomethine groups which coordinate with metal ions. Among the complexes Co(II) complexes are highly active against *Bacillus cereus*, *E.coli*, *Pseudomonas aeruginosa* and *staphylococcus aureus* bacteria species. The improved activity of Co(II) complexes can be explained on the basis of chelation theory [46].

Streptomycin was used as standard antibiotics here. On chelation the polarity of the metal ion will subside greater extent due to overlap of ligand orbital and partial sharing of positive charge of the metal ion with donor groups. Further, it increases the delocalization of π -electrons around the whole chelate ring and inhibits the penetration of complexes into lipid membranes. It also blocking metal binding sites in the enzymes of microorganisms and disturb the respiration process of the cell thus block the synthesis of proteins, which restricts further growth of the organisms [47]. The comparison of biological activities of the ligand and its complexes show the results as reported in **Figure 3**.

DPPH free radical scavenging activity

In this antioxidant study, the complexes Co(II) were found to be much better DPPH radical scavenging activity than Cu(II), Mn(II) and Ni(II) complex with IC₅₀ value 5.46, 6.42, 12.5 and 20.50 mg/ mL respectively. Ascorbic acid was used as standard here. The variation of %DPPH radical scavenging activity with concentration of test compounds is represented in **Figure 4**. The IC₅₀ values were determined for all the

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