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Synthesis, Spectral Characterization, Magnetic Properties and Biological Activity Studies of Mn (II), Co (II), Cu (II) and Ni (II) Complexes of Azo Dye Schiff Base Ligand

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ABSTRACT

A new azo dye Schiff base ligand, namely N, N′-bis (5-(4-nitrophenyl) diazenyl)-2-hydroxybenzylideneamino) ethylenediimine (NDHBDED) has been synthesized and characterized by analytical techniques. And transition metal complexes of Mn (II), Co (II), Cu (II) and Ni (II) were synthesized by the derived azo dye Schiff base. The complexes were characterized for the elemental analysis, molecular weight determination, electronic spectra, spectral analysis, pH metric method, conductance measurement, magnetic moment measurement at room temperature. Analytical data reveal that Mn (II), Co (II), Cu (II) and Ni (II) complexes posses 1:1 metal-ligand ratios. Schiff base and synthesized complexes were screened for antibacterial and antifungal activities. Co (II) and Cu (II) complexes have been found to be more effective for antimicrobial activity.

Keywords: Azo dye Schiff base, Metal complexes, Characterization, Spectral analyses, Antimicrobial activity.

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INTRODUCTION

Azo dye Schiff base ligands play an important role in coordination chemistry because they form stable complexes with most of the transition metal ions[1-3]. Depending on the nature of their donor sites in the ligand, a large number of complexes with different transition metal ions are reported[4-5]. Azo dye Schiff base complexes consist both azo and azomethine groups[6-7]. The azomethine group has excellent donor properties and can form stable complexes with transition metal ions[8-10]. Out of azo and azomethine groups in azo dye Schiff base ligand, only azomethine group participate in coordination while the azo group is left free in coordination[11-12]. Some reported Schiff base ligands are [(bis [N(4-chlorophenyl) salicyldehydeneiminato], 5-bromo-3-hydrazonoindolin-2-one with 5,5-dimethylcyclohexane-1,3-dione, N,N-(3,3-dipropylamine) bis (3-methoxysalicylideneiminato) form complexes by the coordination of a N_3O_2-donor site[12-16]. Based on the afore-mentioned properties of Schiff bases, we report herein the synthesis of an azo dye Schiff base derived from salicyldehyde and ethylenediamine which is coupled with diazoniumchloride of p-nitroaniline. The synthesized azo dye Schiff base coordinated to the transition metal ions as: Mn (II), Co (II), Cu (II) and Ni (II). The complexes of these metal ions with the derived azo dye Schiff base ligand exhibits adverse microbial activities viz: antibacterial and antifungal. The Mn (II), Co (II), Cu (II) and Ni (II) complexes derived from the azo-linked salicyladimine were prepared. The product here also been characterized by elemental analysis, Mass spectra, IR Spectra, UV-Vis spectroscopy, electronic spectra, conductitvity measurements, molecular weight determination, magnetic moment measurements and pH metric method. Based upon the above study results, the structure of metal ion-ligand complex is proposed and analytical application is on progress.

MATERIALS AND METHOD

All Chemicals and solvents were of analytical grade reagent from E. Merck, Germany and other metal salts from BDG, India were of analytical grade reagent. Ethylenediamine was from Sigma and Aldrich. The UV-Vis spectra were recorded in the mixture of ethanol-methanol using Shimadzu UV-Vis spectrophotometer (UV-1800) fitted with 1 cm quartz cell. The IR spectra were recorded in KBr pellets with Shimadzu Corporation (Class-I Laser Product, 220V/230/240V, V50-60Hz, 240V). The magnetic measurements were carried out by Gouy method, conductivity measurements and pH measurements were carried out by a Labtronic pH meter (Model No-23) equipped with a combined glass calomel electrode.

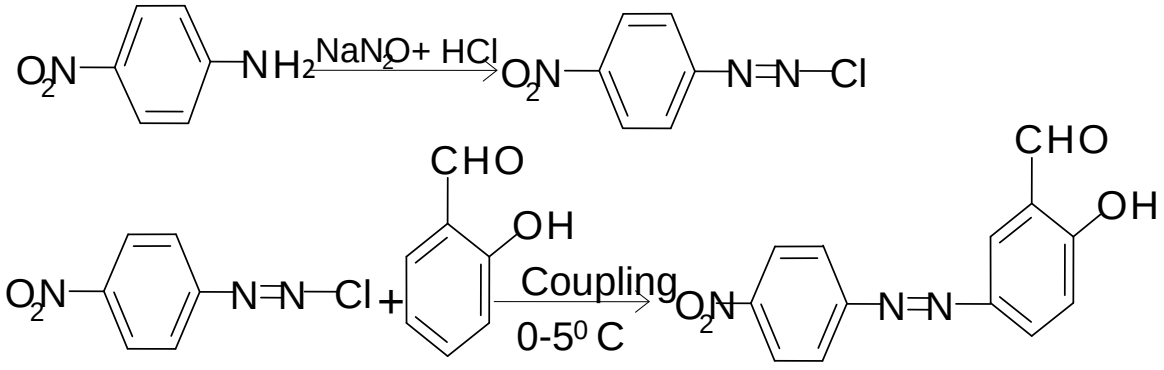
Synthesis of the Azo Dye Schiff Base Ligand

(a) Azo coupling of salicyldehyde

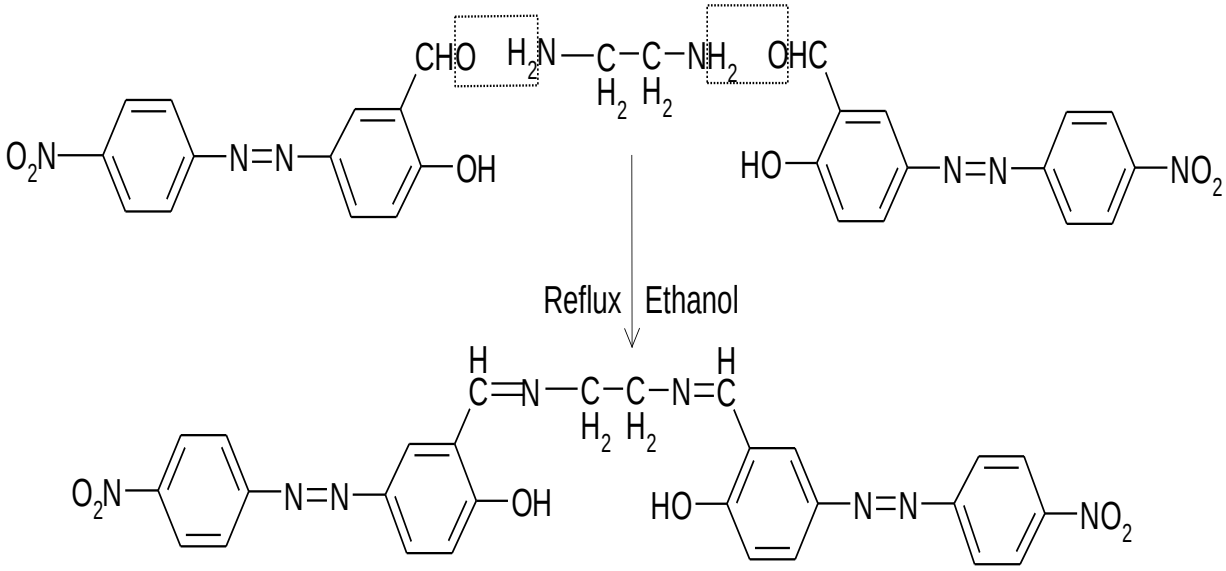
Our proposed diazo compound was synthesized by a reported method[17-18]. A suspension of p-nitroaniline (2.50 g, 20 mmol) in 30 ml HCl and 10 ml of water was heated from 60-70^0 C until complete dissolution. The clear solution was poured into ice water and was diazotized at 0-5^0 C with $NaNO_2$ (2.5 g) dissolved in water (10 ml). The cold diazonium solution was added over the course of 40 minutes at 0^0 C to a solution of salicyldehyde (4.25 ml, 40 mmol) in 50 ml water containing NaOH (1.5 g) and Na_2CO_3 (10 g). The reaction mixture was stirred during the process. The product was collected and washed with NaCl solution (100ml, 10%). Coupling of the diazonium reagent to the salicyldehyde occurred at the para position to the hydroxyl group. The diazo compound was recrystallized many times from ethyl alcohol and finally dried at 60-70^0 C for at least 3 hours. Yellow solid, yield 91 %, m.p.165-170^0 C, Anal. Calcd. For $C_{13}H_9N_3O_4$; C:57.56, H:3.32, N:15.49, O:23.61%, Found: C:57.60, H:3.31, N:15.45, O:23.6 %. FTIR (KBr cm^{-1}): 1285 (phenolic C-O), 1665 (-CHO group), 1448 (N=N), 1345 (-NO_2 group) cm^{-1} UV-Vis: λ_{max}=390, 545 nm.

(b) Synthesis of the Azo Dye Schiff Base Ligand (NDHBDED)

For the ligand,N,N′-bis (5-(4-nitrophenyl) diazenyl)-2-hydroxybenzylideneamino) ethylenediimine (NDHBDED), a mixture of 0.02 mol ethylenediamine and 0.04 mol of the prepared azo dye were dissolved in absolute alcohol (80 ml) with a few drops of glacial acetic acid as a catalyst[19-20]. The resulting mixture was allowed to stare under reflux for 3 hours. The product was collected and washed with small amount of ethanol and it was soluble in solvents such as ethanol, methanol, DMF and DMSO. The yellow yield was 86 % m.p. 165-170^0 C. Anal. Calcd. $C_{28}H_{22}N_8O_6$, C:59.36, H:3.88, N:19.78, O:16.96 %, Found: C:59.50, H:3.91, N:19.81, O:17.00 %. FTIR (KBr cm^{-1}): 3055 (C-H, aromatic), 2890, 2842 (C-H, aliphatic), 1645 (C=N), 1605 (C=C, aromatic), 1420 (N=N), 1275 (C-O, phenolic) cm^{-1}. UV-Vis: λ_{max}= 275,390,460,545 nm.



Scheme 1: The reaction scheme of the Azo Coupling of salicyldehyde.



N, N′-bis (5-(4-nitrophenyl)diazenyl)-2-hydroxybenzylideneamino)ethylenediimine(NDHBDED)

Scheme 2: The reaction scheme of synthesis of the Azo Dye Schiff Base Ligand

Synthesis of the Metal Complexes

To a stirred suspension of manganese chlorides (5 mmol) in 20 ml alcoholic solution, an appropriate amount of the azo dye Schiff base ligand (NDHBDED) (5 mmol) was added and then 20 ml boiling methanol solution was finally added. The reaction mixture was allowed to reflux for ~4 hrs, during which time the colour of the solution becomes brownish. The extra solvent was removed by distillation and dried product was washed with a small amount of ethanol. The brown yield: 82 % (2.528 g). Similar procedure was adopted to synthesize Co (II), Cu (II) and Ni (II) complexes with an appropriate amount of the azo dye Schiff base ligand in ethanol-methanol mixture.

Complex [N, N′-bis (5- (4-nitrophenyl) diazenyl) – 2 - hydroxybenzylideneamino) ethylenediimino Mn(II) chloride] **1:** Brown; yield 82 %,

Anal. Calcd. for $C_{28}H_{20}N_8O_6Cl_2Mn$(II): C:48.69, H:2.89, N:16.23, O:13.91, Cl:10.28, Mn (II):7.97 %, Found: C:48.68, H:2.90, N:16.25, O:13.97, Cl:10.30, Mn (II):8.0 %.

Complex [N, N′-bis(5-(4-nitrophenyl)diazenyl)-2-hydroxybenzylideneamino) ethylenediimino Co(II) chloride] **2:** Redish Brown, yield 80 %, Anal. Calcd. for $C_{28}H_{20}N_8O_6Cl_2Co$(II): C:48.41, H:2.88, N:16.13, O:13.83, Cl:10.23, Co (II):8.5 %, Found: C:48.45, H:2.87, N:16.15, O:13.85, Cl:10.26, Co (II):8.52 %.

Complex [N, N′-bis (5-(4-nitrophenyl)diazenyl)-2-hydroxybenzylideneamino) ethylenediimino Cu(II) chloride] **3:** Orange, yield 76 %, Anal. Calcd. for $C_{28}H_{20}N_8O_6Cl_2Cu$(II): C:48.1, H:2.86,

N:16.03, O:13.74, Cl:10.16, Cu (II):9.09 %, Found: C:48.12, H:2.86, N:16.05, O:13.73, Cl:10.17++, Co (II):9.1 %.

Complex [N, N′-bis(5-(4-nitrophenyl)diazenyl)-2-hydroxybenzylideneamino) ethylenediimino Ni(II) chloride] **4:** Brown, yield 78 %, Anal. Calcd. for $C_{28}H_{20}N_8O_6Cl_2Ni$(II): C:48.43, H:2.88, N:16.14, O:13.83, Cl:10.23, Ni (II):8.46 %, Found: C:48.42, H:2.87, N:16.15, O:13.84, Cl:10.25, Ni (II):8.47 %.

RESULTS AND DISCUSSION

Mass Spectra

Mass spectroscopy is an important technique in coordination chemistry for structural characterization of the ligand (NDHBDED) and its metal complexes. The mass spectra of the azo dye Schiff base ligand and its complexes were recorded at room temperature, these are used to analyse the stoichiometry of the composition. Mass spectrum of the azo dye Schiff base ligand shows molecular ion peak at m/z 566 [M^+], isotopic ion peak at m/z 568 [M+2], fragment ion peaks appeared at m/z 241, 174,136,102, 93, 88, 56,46. The mass spectra of Mn (II) complex shows molecular ion peaks m/z 690, isotopic ion peaks at m/z 692 [M+2], fragment ion peaks at m/z 519, 448, 365,309,296,160, 146, 91,46. The above spectra of Mn (II) complex confirmed a structure of stoichiometry of 1:1 for ligand to Mn (II) ion. The mass spectral data of the transition metal complexes and isotopic peaks from chlorine atom which are found at the mass spectra confirms the stoichiometries of the complexes are as [ML].

IR Spectra

The IR stretching frequencies of the ligand and its metal complexes are given in Table 2. The IR spectra of the free ligand and the metal complexes were determined over a spectral range of 4000-300 cm^{-1}. The IR spectra of the complexes showed absence of absorption band in the region 3350-3443 cm^{-1} with respect to azo dye Schiff base 3441 cm^{-1} due to $\nu_{(O-H)}$ stretching band, indicating the deprotonation of phenolic proton in complex formation. Such interaction is further supported by upward shifting of the $\nu_{(C-O)}$ phenolic band at 1490-1520 cm^{-1} and appearance of band at 545-535 cm^{-1} due to M←O stretching vibration. Azo dye Schiff base showed an intense band at 1626 cm^{-1} due to $\nu_{(C=N)}$ were assigned to the stretching vibration of the azomethine group of the ligand. This band was shifted to lower frequency by ~15 cm^{-1} in the complexes, indicating participation of azomethine nitrogene in the interaction with metal ions. The bands in the range 458-460 cm^{-1} are ascribed to $\nu_{(M\leftarrow N)}$ stretching vibration. The sharp band appeared at 1495 cm^{-1} is assigned to the stretching vibration of the diazo group of the ligand and the IR spectra of the complexes did not

show any frequency shifting of the -N=N- band, which may be considered by nonparticipation in complex formation.

UV-Vis Spectroscopy (Electronic Spectra)

The absorption spectra of the ligand in the UV-Vis ranges were carried out in ethanol-methanol mixture. The spectra exhibiting two bands at 280-256 and 260-265 nm regions and the band at 280-256 nm is attributed to the $\pi \rightarrow \pi^*$ transitions of C=N group which is overlapped. These two bands are shifted to lower energies after complexation ~265-225 nm. These bands are assigned due to charge transfer transition from the 'N' and 'O' to an empty d-orbital of the metal ions. The spectra of Mn (II) complex three absorption bands are expected corresponding to $^2B_{1g} \rightarrow {}^2A_{1g}$; $^2B_{1g} \rightarrow {}^2B_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$. But only two absorption bands are obtained at λ_{max} 630 nm & 765 nm and these are attributed to the transition $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2B_{2g}$ respectively, because $^2B_{1g} \rightarrow {}^2A_{1g}$ band would have overlapped with $^2B_{1g} \rightarrow {}^2B_{2g}$ band and so it could be seen in the spectra. The above data support the Mn (II) complex is distorted octahedral in nature. And the resemblance of these above observations it is concluded that the other metal ion complexes are also distorted octahedral in geometry. The electronic absorption spectra of the ligand and its complexes with Mn (II), Co (II), Cu (II) and Ni (II) metal ions were recorded in the mixture of ethanol-methanol at normal temperature. The absorption spectra of the ligand show strong peaks at 25200 cm^{-1} and 29109 cm^{-1} which are assigned to the –N=N- azo group and –CH=N- groups of the azo dye Schiff base ligand, respectively. The electronic spectrum of the Mn (II) complex exhibited two bands at 17650 and 25382 cm^{-1}. These two bands are assigned to $^3A_{2g}$ (F) → $^3T_{1g}$ (F) (ν_2) and $^3A_{2g}$ (F) → $^3T_{1g}$ (P) (ν_3) transitions respectively in an octahedral geometry. The electronic spectra of Co (II) complex exhibited two bands at 15782 and 20593 cm^{-1}. These two bands are assigned to $^4T_{1g}$ (F) → $^4A_{1g}$ (F) (ν_2) and $^4T_{1g}$ (F) → $^4T_{2g}$ (P) (ν_3) transitions respectively in octahedral geometry. The Cu (II) complex exhibited low intensity single broad asymmetric absorption band in the region 14653-17193 cm^{-1}. This broadness of the band indicates the three transitions $^2B_{1g} \rightarrow {}^2A_{2g}$ (ν_1), $^2B_{1g} \rightarrow {}^2E_g$ (ν_2) and $^2B_{1g} \rightarrow {}^2B_{2g}$ (ν_3), which are similar in energy and gives rise to only one broad absorption band. The broadness of the band may be due to John-Teller distortion band. All these data support a distorted octahedral geometry around the Cu (II) ion. The Ni (II) complex exhibited three bands at 11135, 16565 and 25873 cm^{-1}. These three bands are assigned to $^3A_{2g}$ (F) → $^3T_{2g}$ (F) (ν_1), $^3A_{2g}$ (F) → $^3T_{1g}$ (F) (ν_2) and $^3A_{2g}$ (F) → $^3T_{1g}$ (P) (ν_3) transitions respectively in an octahedral geometry of the complex.

pH metric method

During the determination of stepwise stability constant by a Labtronic pH meter at room temperature, three sets of acid, acid + ligand, acid + ligand + metal ion solutions were prepared. In all the sets, the total volume was made up to 50 ml by adding required amount of distilled water. The ionic strength was maintained by adding an appropriate amount of KCl (0.01M). The formation of the metal ion complexes was good in the pH range of 5-7 which was adjusted by adding hydrochloric acid and NaOH solution. But at lower pH, the magnitude of stability constant was found to decrease. So, basic medium was chosen for the metal ion complex formation which gives good yield for each metal ion.

Molar Conductance

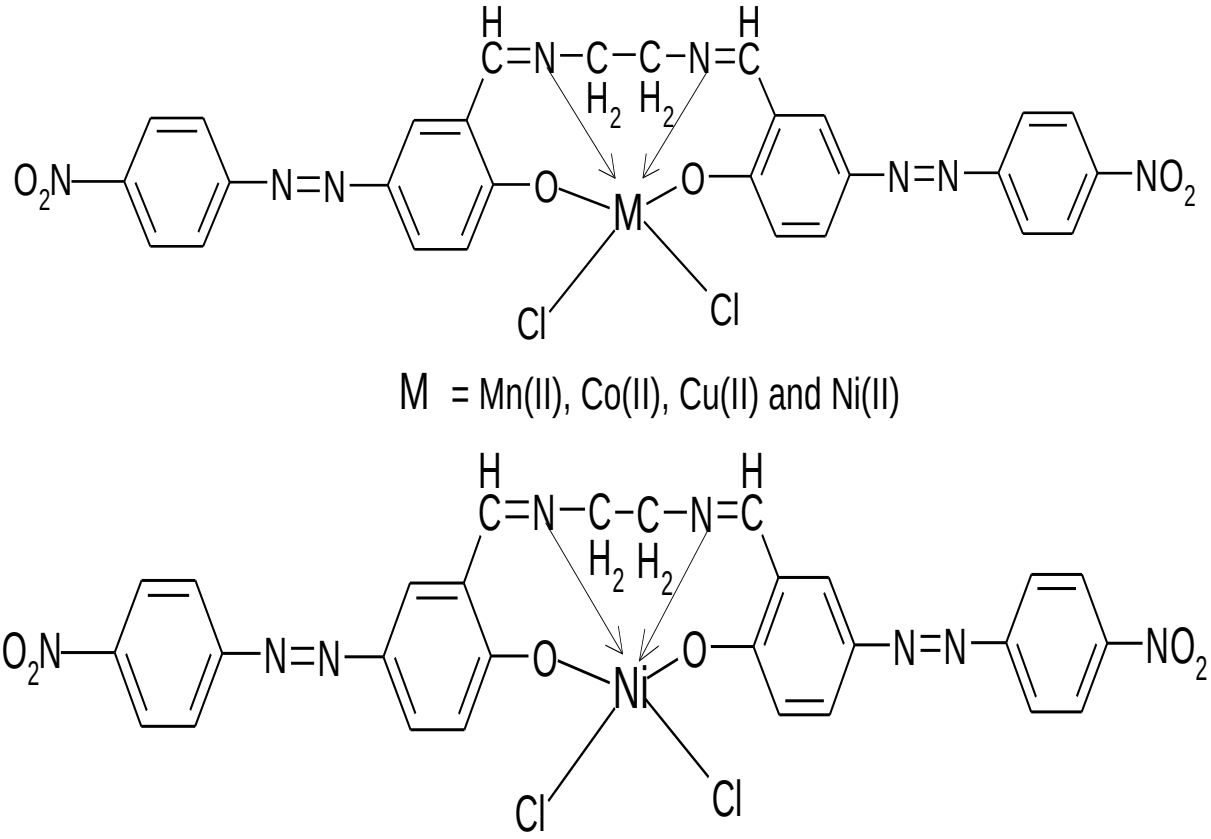
The molar conductivity (Λ_M) values of all the azo dye Schiff base ligands complexes were measured in ethanol-methanol mixture and their values lie in the range of 90-103 ohm^{-1} cm^2 mol^{-1} indicating their electrolytic nature.

Magnetic Moment Measurements

The effective magnetic moments (μ_{eff}) were measured using a Gouy balance at room temperature. The effective magnetic moments (μ_{eff}) of the complexes in this study to be found 5.28, 3.81, 1.73 and 2.85 BM for Mn (II), Co (II), Cu (II) and Ni (II) complexes respectively. The magnetic moments values of the complexes corresponding to five, three, one and two electron systems of the $3d^5$, $3d^7$, $3d^9$ and $3d^8$ systems of distorted octahedral geometry.

Biological Activities

The biological activities viz: Antibacterial and antifungal activities of the synthesized azo dye Schiff base ligand and its Mn (II), Co (II), Cu (II) and Ni (II) complexes were carried out by the agar diffusion method in DMSO solvent against *E.coli, S. aureus* and *S. typhi, A. nigar, C. albicans* respectively. The micro-organisms were individually introduced on the surface of the agar plates. The standard solution of the test compounds was prepared at the concentration of 1mg/ml of DMSO. The standard solution was diluted with sterilized distilled water. The standard drugs gentamycin and flucanozole were also tested for their antibacterial and antifungal activities under similar conditions for comparison. The antimicrobial activity was measured by measuring the diameter of the inhibited zone in millimetre and the results of the screened compounds are given in the Table 3. The data show that the Co (II) and Cu (II) complexes are more effective antibacterial agents in comparison to the Mn (II) and Ni (II) complexes. It is also shows that the antibacterial and antifungal activities of the ligand were enhanced on complexation which can be explained by Chelation theory.



Proposed structure of the Metal ions-Ligand complexes

Table 1: Physical and analytical data of the ligand and its metal (II) Complexes

Compounds	Molecular Formula	Yield (%)	Found (Calculated) %					Ω ($Ω^{-1}$ cm^2 mol^{-1})	μeff (BM)
			C	H	N	M	Cl		
Ligand	$C_{28}H_{20}N_8O_6$	88	58.50 (59.57)	35.50 (35.46)	19.81 (19.85)	_	_	_	_
$MnLCl_2$	$MnC_{28}H_{18}N_8O_6Cl_2$	82	48.75 (48.84)	2.60 (2.61)	16.25 (16.28)	8 (7.9)	10.30 (10.32)	92	5.28
$CoLCl_2$	$CoC_{28}H_{18}N_8O_6Cl_2$	80	48.5 (48.54)	2.61 (2.60)	16.20 (16.18)	8.52 (8.5)	10.25 (10.26)	94	3.81
$CuLCl_2$	$CuC_{28}H_{18}N_8O_6Cl_2$	76	48.25 (48.28)	2.55 (2.58)	16.05 (16.07)	9.1 (9.12)	10.20 (10.19)	93	1.73
$NiLCl_2$	$NiC_{28}H_{18}N_8O_6Cl_2$	78	48.55 (48.57)	2.61 (2.60)	16.18 (16.19)	8.47 (8.48)	10.25 (10.26)	102	2.85

Table 2: IR spectral data of the ligand and its metal complexes (cm^{-1})

Frequency assignments	Lignad $C_{28}H_{20}N_8O_6$	$MnC_{28}H_{18}N_8O_6Cl_2$	$CoC_{28}H_{18}N_8O_6Cl_2$	$CuC_{28}H_{18}N_8O_6Cl_2$	$NiC_{28}H_{18}N_8O_6Cl_2$
Azo dye ring	3441	3441	3441	3441	3441
ν(C-O)	1505	1525	1520	1528	1526
ν(C=N)	1626	1605	1610	1602	1612
ν(M←O)	_	530	535	540	535
ν (M←N)	_	455	460	459	465

Table 3: Antimicrobial activity of the ligand and its metal (II) Complexes (mg/ml)

Compounds	Antibacterial Acativity		Antifungal Activity		
	E. coli	S. aureus	A. niger	S. typhi	C. albicans
Lignad $C_{28}H_{20}N_8O_6$	5	5.5	6	5	5.23
$MnC_{28}H_{18}N_8O_6Cl_2$	7.5	7.2	6.9	6	7.12
$CoC_{28}H_{18}N_8O_6Cl_2$	8	7.5	7.55	8.25	8.52
$CuC_{28}H_{18}N_8O_6Cl_2$	9.1	10.25	9.55	8.25	8.52
$NiC_{28}H_{18}N_8O_6Cl_2$	8.1	7	7.2	7.25	6.9
Gnt	15.1	14.8	-	-	-
Fnz	-	-	14.59	15.2	13.28

CONCLUSION

In this study, we have synthesized a new azo dye Schiff base ligand containing-N_2O_2 donor site and its Mn (II), Co (II), Cu (II), Ni (II) complexes. The composition of the complexes have been established by elemental analyses such as mass spectra which revealed molecular ion peak and its fragmental ion peaks, IR spectra shows that the azomethine moiety is the basic site in addition to the phenolic O-donor site for the metal ions complexation, UV-Vis, electronic spectra, magnetic moment measurements provided the distorted octahedral geometrical structure and electronic nature of the metal ions complexes. The biological activity results showed that Co (II) and Cu (II) complexes are found to be more effective compared to Mn (II) and Ni (II) complexes.

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