



The template synthesis, spectral and antibacterial investigation of new N₂O₂ donor Schiff base Cu(II), Ni(II), Co(II), Mn(II) and VO(IV) complexes derived from 2-Hydroxy acetophenone with 4-chloro-2,6-diaminopyrimidine

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ABSTRACT

A novel tetradentate Schiff base ligand 2,2'-(1E,1'E)-1,1'-(6-chloropyrimidine-2,4-diyl)bis(azan-1-yl-1-ylidene)bis(ethan-1-yl-1-ylidene)diphenol (L) was synthesized by the reaction of 2-hydroxy acetophenone and 4-chloro-2,6-diaminopyrimidine. The structure of the ligand was elucidated by elemental analysis IR, ¹H NMR and electronic spectra. Then, its Cu(II), Ni(II), Co(II), Mn(II) and VO(IV) complexes were synthesized by the template effect of 2-Hydroxy acetophenone, 4-chloro-2,6-diaminopyrimidine and (CH₃COO)₂Cu.H₂O, (CH₃COO)₂Ni.4H₂O, (CH₃COO)₂Co.4H₂O, (CH₃COO)₂Mn.4H₂O and VO₂.5H₂O respectively. The structure of the newly prepared complexes were identified by elemental analyses, molar conductance, infrared, electronic, magnetic susceptibility and electrochemical studies. The bonding sites are the azomethine nitrogen atoms and phenolic oxygen atoms. The schiff base ligand and its metal complexes were tested against four pathogenic bacteria (*Staphylococcus aureus*, *Bacillus subtilis*) as Gram-positive bacteria, and (*Escherichia coli*, *Klebsiella pneumonia*) as Gram-negative bacteria. All the metal complexes exhibit higher antibacterial activity than the free ligand. Cobalt(II) complexes have higher bacterial activity and Nickel(II) than the other complexes.

Keywords: Schiff base, 4-chloro-2, 6-diaminopyrimidine, Electrochemical studies, Antibacterial studies.

INTRODUCTION

Schiff base ligands have been studied extensively due to synthetic flexibilities, selectivity as well as sensitivity towards the transition metal ions. The architectural beauty of these coordination complexes arises due to the interesting ligand systems containing different donor sites in heterocyclic rings. In the last decades, Schiff base have received much great interest, mainly because of their wide application in the field of synthesis and catalysis [1, 2]. Similarly heterocyclic ligands containing nitrogen atoms are drawing a great deal of attention in Coordination chemistry and homogeneous Catalysis [3-5]. Two or more potential donor centre of amino heterocycles plays an important role in the study of comparative reactivity of ambidentate ligand systems [6]. Furthermore, transition metal complexes containing pyrimidine ligands are commonly found in biological studies and play important roles in processes, such as catalysis of drug interaction with biomolecules [7-9]. A tumid number of Schiff base ligand and metal complexes are of substantial sake and attention because of their biological activity including anti-tumor, antibacterial, fungicidal and anti-carcinogenic properties [10, 11]. Several complexes coordinated through the Schiff base ONNO donors have been studied as oxygen carrier and they are useful models for bioinorganic processes [12]. The cobalt(II) and manganese(II) complexes with tetradentate Schiff base which coordinate through N₂O₂ donor atoms have been extensively studies as oxygen carriers and also as catalysts for water-splitting systems[13].

In this paper, we report the recent research on template reaction of 2-Hydroxy acetophenone, with 4-chloro-2, 6-diaminopyrimidine in the presence of copper(II), nickel(II), manganese(II), cobalt(II) and oxovanadium(IV) ions a result of (2+1+1) Schiff base condensation complexes. The obtained new mononuclear complexes were characterized by some physico-chemical techniques and some biological applications

EXPERIMENTAL SECTION

Reagents

All the chemicals used were of reagent grade and the solvents were distilled before use according to the standard procedure. 2-Hydroxyacetophenone, 4-Chloro-2,6-diamino-pyrimidine, $(\text{CH}_3\text{COO})_2\text{Cu} \cdot \text{H}_2\text{O}$, $(\text{CH}_3\text{COO})_2\text{Ni} \cdot 4\text{H}_2\text{O}$, $(\text{CH}_3\text{COO})_2\text{Co} \cdot 4\text{H}_2\text{O}$, $(\text{CH}_3\text{COO})_2\text{Mn} \cdot 4\text{H}_2\text{O}$ and $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ were obtained from Aldrich, Acros organics and Merck products. For voltammetric experiments, tetrabutylammonium perchlorate (TBAP) used as supporting electrolyte was purchased from sigma.

Physical measurements

The metal content of the complexes were determined by titration with EDTA. Elemental analyses were carried out on a model 240 Perkin Elmer elemental analyzer. The melting point of the compounds determined on a melting point apparatus. The molar conductance measurements were made on Systronics Conductivity Bridge with a cell having cell constant of 1.1. The magnetic measurements were made by Gouy's method at room temperature by using $\text{Hg}[\text{Co}(\text{SCN})_6]$ as calibrant. The electronic absorption spectra were recorded using a UV/Vis Jasco 550 double beam, spectrophotometer in DMSO solvent at 300k. The IR spectra were recorded by FT-IR spectrophotometer (Jasco FT-IR-410) in the range $4000\text{-}400\text{cm}^{-1}$, potassium bromide disc method was employed for sample preparation. Electrochemical measurements were performed with a digital CHI760C recorder with three electrode system of a glassy carbon electrode as the working electrode, a platinum electrode as auxiliary electrode and Ag/AgCl as the reference electrode. Tetrabutylammoniumperchlorate (0.1M) was used as supporting electrolyte.

Synthesis of Ligand:

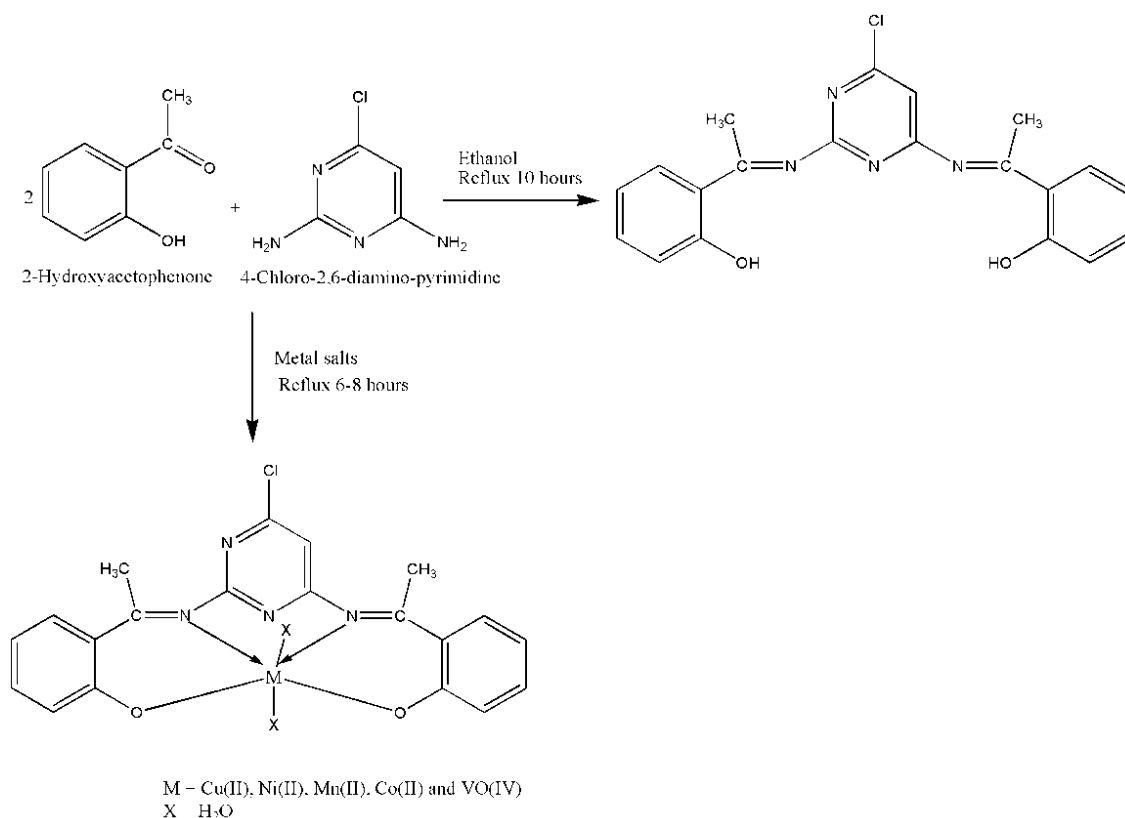
A solution of 4-Chloro-2, 6-diamino-pyrimidine (0.1 g, 0.69 mmole) in ethanol (10 ml) was added drop wise to a solution of 2-hydroxyacetophenone (0.166 ml, 1.37 mmole) in ethanol (10 ml) and few drops of glacial acetic acid were added, and then refluxed for 10 hours. The reaction mixture was condensed to 10 ml and the white color precipitate was then filtered off, washed with cold ethanol then with diethyl ether and dried under vacuum over anhydrous calcium chloride.

Synthesis of Schiff base metal complexes:

2-hydroxyacetophenone (0.166 ml, 1.37 mmole) was dissolved in 10 ml of ethanol and a solution of 4-Chloro-2, 6-diamino-pyrimidine (0.1 g, 0.69 mmole) was added drop wise with constant stirring and few drops of glacial acetic acid was added. To this a solution of a metal salt (0.69 mmole) in 10 ml ethanol was added drop wise with constant stirring and the mixture was boiled under reflux for 6-8 hours. Then, the volume of the reaction mixture was reduced to 10 ml. The precipitated complexes were filtered off, washed with ethanol then with diethyl ether and dried under vacuum over anhydrous calcium chloride.

Biological activities

The synthesized Schiff base and their corresponding Cu(II), Ni(II), Co(II), Mn(II) and VO(IV) complexes were screened for their biological activities by using four bacteria namely *Staphylococcus aureus*, *Bacillus subtilis*, *Escherichia coli* and *Klebsiella pneumonia* by the reported method [14]. The bacteria were subcultured in agar medium. The Petri dishes were incubated for 24 hours at 37°C . The standard antibacterial drug was also screened under similar conditions for comparison. The wells were dug in the agar media using sterile metallic borer. Activity was determined by measuring the diameter of the zone showing complete inhibition (mm). Growth inhibition was compared with standard drugs. In order to clarify any effect of solvent DMSO on the biological screening, separate studies were carried out with solvent DMSO only and it showed no activity against any microbial strains.



Scheme 1: Synthesis of ligand and Schiff base metal complexes

RESULTS AND DISCUSSION

Schiff base ligand was easily obtained by condensation of 1:2 molar ratio of 4-chloro-2,6-diaminopyrimidine and 2-hydroxyacetophenone. The mononuclear Schiff base metal complexes were prepared by template method using 2:1:1 ratio of 4-chloro-2,6-diaminopyrimidine, 2-hydroxyacetophenone and metal salts, respectively. All the metal complexes are intense colored and thermodynamically stable at room temperature, non hygroscopic, insoluble in water, but soluble only in DMSO, DMF and THF. The elemental analysis (C, H, N, M) data of the metal chelates showed that they may be represented by the formula $[\text{ML}(\text{H}_2\text{O})_2]$, $M = \text{Cu(II), Ni(II), Co(II), Mn(II)}$ and $[\text{ML}(\text{H}_2\text{O})]$ for VO(IV) . The elemental analysis data (Table 1) of the ligand and its metal complexes are consistent with the calculated results from the empirical formula of each compound. The purity of the Schiff base and its metal complexes was confirmed by TLC.

Table 1. Elemental analysis of the ligand and metal complexes

Compounds	Molecular formula	Molecular weight	Color	Yield	M.p (°C)	Calcd. (found) %			
						C	H	N	M
Ligand	$\text{C}_{20}\text{H}_{17}\text{ClN}_4\text{O}_2$	380.45	White	85	>250	63.08 (63.05)	4.46 (4.40)	14.71 (14.68)	-
$[\text{CuL}(\text{H}_2\text{O})_2]$	$\text{C}_{20}\text{H}_{19}\text{ClN}_4\text{O}_4\text{Cu}$	477.99	Green	83	>250	50.20 (49.15)	3.97 (3.95)	11.71 (11.69)	13.29 (13.26)
$[\text{NiL}(\text{H}_2\text{O})_2]$	$\text{C}_{20}\text{H}_{19}\text{ClN}_4\text{O}_4\text{Ni}$	473.14	Pale green	78	>250	50.72 (50.69)	4.01 (3.97)	11.83 (11.80)	12.40 (12.36)
$[\text{CoL}(\text{H}_2\text{O})_2]$	$\text{C}_{20}\text{H}_{19}\text{ClN}_4\text{O}_4\text{Co}$	473.38	Pale pink	82	>250	50.69 (50.64)	4.01 (3.96)	11.82 (11.79)	12.44 (12.42)
$[\text{MnL}(\text{H}_2\text{O})_2]$	$\text{C}_{20}\text{H}_{19}\text{ClN}_4\text{O}_4\text{Mn}$	469.43	Dirty white	80	>250	51.12 (51.11)	4.04 (4.05)	11.92 (11.86)	11.71 (11.76)
$[\text{VOL}(\text{H}_2\text{O})]$	$\text{C}_{20}\text{H}_{17}\text{ClN}_4\text{O}_4\text{V}$	463.77	Green	75	>250	51.80 (51.77)	3.69 (3.65)	12.08 (12.10)	10.98 (10.95)

Molar conductance

The molar conductivity measurements, recorded for 10^{-3} M solutions at 25°C of the Schiff base metal complexes in DMSO. The molar conductivity was applied to help in the investigation of the geometrical structures of the complexes. The conductance values of the complexes are given in the Table 2. All complexes are non-conducting and the measured molar conductance ranged from $1 - 11 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ indicating their neutrality and the divalent metal cations replaced by the phenolic protons [15, 16].

Table 2. Molar conductivity ($\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$) and Magnetic moment value (BM) of the complexes

Compounds	Solvent	Molar conductance Λ_m ($\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$)	Magnetic moment μ_{eff} B.M
[CuL(H ₂ O) ₂]	DMSO	2.98	1.80
[NiL(H ₂ O) ₂]	DMSO	1.73	3.10
[CoL(H ₂ O) ₂]	DMSO	1.45	4.70
[MnL(H ₂ O) ₂]	DMSO	10.12	5.80
[VOL(H ₂ O)]	DMSO	6.20	1.69

Infrared spectra

The infrared spectrum provides valuable information regarding the nature of the functional group attached to the metal atom. In all the complexes, no peaks corresponding to unreacted primary amines or carbonyl groups were present. The most relevant IR absorption bands from the spectra of the complexes, along with their assignments are given in the Table 3. The appearance of a broad strong band in the IR spectra of the ligand and complexes at $3470 - 3200 \text{ cm}^{-1}$ may be due to ν (-OH) of water and phenolic -OH group, water molecules are coordinated confirmed by occurrence of additional strong and sharp band at $890 - 740 \text{ cm}^{-1}$ arising due to -OH rocking vibration [17, 18]. The FT-IR spectrum of ligand exhibits a strong band of the azomethine (C=N) at 1645 cm^{-1} . This band shifted to the $1637-1630 \text{ cm}^{-1}$ confirming the azomethine-metal coordination as was expected [19, 20]. The characteristic ring vibration of pyrimidine moiety appearing at $1546 - 1570 \text{ cm}^{-1}$ & $\sim 975 \text{ cm}^{-1}$ [21]. In the spectra of all the complexes shows the band near at $\sim 1140-1151 \text{ cm}^{-1}$ may be due to ν (C-O) stretching frequency. It indicates the coordination of ν (C-O) oxygen to the metal ion via deprotonation. The aromatic ν (C=C) stretching frequency [22] occurs at $1450 - 1420 \text{ cm}^{-1}$. The strongest absorption band for vanadium complex corresponds to ν (V=O) vibrations in a range of 972 cm^{-1} [23, 24].

New bands in the range of $590 - 540 \text{ cm}^{-1}$ and $470 - 410 \text{ cm}^{-1}$ which are not present in the free Schiff base are due to ν (M-O) and ν (M-N) vibration [25] and the appearance of the vibrations support the involvement of the nitrogen and oxygen atoms of the azomethine and C-O groups complexation with the metal ions under investigations.

Table 3. Infrared spectra (cm^{-1}) of ligand and metal complexes

Compounds	ν (-OH)	ν (C=N)	ν (C=N)Pyr	ν (C=C)	ν (C-O)	ν (M-O)	ν (M-N)
Ligand	3453	1645	1566	1450	1145	-	-
[CuL(H ₂ O) ₂]	3319	1630	1570	1437	1150	568	466
[NiL(H ₂ O) ₂]	3376	1632	1546	1421	1151	552	412
[CoL(H ₂ O) ₂]	3314	1630	1562	1414	1146	539	416
[MnL(H ₂ O) ₂]	3318	1639	1568	1423	1149	554	415
[VOL(H ₂ O)]	3325	1637	1565	1415	1148	560	418

Electronic spectral studies

The electronic absorption spectra values are often very helpful in the evaluation of results provided by other methods of structural investigation. The study of the electronic spectral in the ultraviolet and visible ranges for ligand and their metal complexes were carried out in DMSO solution at 300 K. The absorption region and the proposed geometry of the complexes are given in Table 4 (Fig 1). The ligand exhibit the band at 222 and 273 nm. The band at 222 nm can be assigned to intra ligand $\pi \rightarrow \pi^*$ transition. The band almost unchanged in spectra of all the complexes. The band at 273 nm on low energy side is due to $n \rightarrow \pi^*$ transition associated with the azomethine linkage. The band experience red shift in all the complexes [26, 27]. The bands at around 343-383 nm are attributed to the ligand to metal charge transfer transition. The electronic spectra of all the complexes display the electronic spectral band at 410-430 nm assignable to the corresponding transitions, respectively, characteristic of octahedral geometry [28].

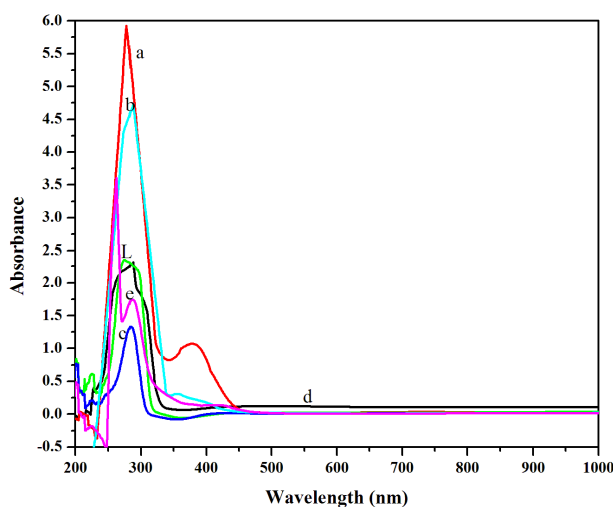


Fig 1. UV-Vis spectra of (L) Ligand (a) [CuL(H₂O)₂] (b) [NiL(H₂O)₂] (c) [MnL(H₂O)₂] (d) [CoL(H₂O)₂] (e) [VOL(H₂O)]

Table 4. Electronic spectral data (nm) of the metal complexes

Compounds	$\pi \rightarrow \pi^*$ (nm)	$n \rightarrow \pi^*$ (nm)	LMCT & d-d transition (nm)	Geometry
Ligand	222	273	-	-
[CuL(H ₂ O) ₂]	223	277	383	Octahedral
[NiL(H ₂ O) ₂]	225	286	356, 401	Octahedral
[CoL(H ₂ O) ₂]	229	282	406	Octahedral
[MnL(H ₂ O) ₂]	229	291	304, 419	Octahedral
[VOL(H ₂ O)]	223	282	343, 423	Octahedral

Magnetic studies

The magnetic moment was recorded at room temperature and is shown in Table 2. Magnetic studies also help to look into the structure of the complexes. The copper(II) complex has magnetic moment value of 1.73 BM which indicates the octahedral geometry. The μ_{eff} value of cobalt complex is found to be 4.44 BM suggesting the octahedral geometry [29]. Similarly nickel(II) and manganese(II) complexes have magnetic moment value of 2.95 and 5.48 BM. The effective magnetic moment (μ_{eff}) of the VO(IV) complex is in the normal range (1.69 μ_{B}). These values are expected for the spin only μ_{s} of the d^1 system when the orbital contribution is completely quenched [30]. These magnetic moment value consistent with those predicted for six coordinate VO(IV) complexes, whose structures are octahedral in C_{4v} symmetry [31, 32].

Table 5. Electrochemical data of binuclear Schiff base metal complexes

Complexes	Negative potential				Positive potential			
	E_{pc} (V)	E_{pa} (V)	$E_{1/2}$ (V)	ΔE_{p} (mV)	E_{pc} (V)	E_{pa} (V)	$E_{1/2}$ (V)	ΔE_{p} (mV)
[CuL(H ₂ O) ₂]	-1.31	-1.01	-1.16	300	0.76	1.02	0.89	260
[NiL(H ₂ O) ₂]	-0.98	-0.62	-0.80	360	0.16	0.38	0.27	220
[CoL(H ₂ O) ₂]	-1.22	-1.0	-1.11	220	0.8	0.97	0.88	170
[MnL(H ₂ O) ₂]	-1.34	-1.0	-1.17	340	0.88	1.20	1.04	320
[VOL(H ₂ O)]	-1.40	-1.25	-1.32	150	0.60	0.45	0.52	150

Electrochemical studies

The cyclic voltammetry of the Cu(II), Ni(II), Co(II), Mn(II) and VO(IV) complexes were commemorated in DMSO solution containing 0.1 M TBAP as supporting electrolyte at a glassy carbon working electrode was studied the room temperature. The electrochemical behaviors of metal complexes in the potential range from +2.0 to -2.0 V and 0.1Vs⁻¹ scan rate. The obtained data from the electrochemical properties of the metal complexes were given in the Table 5. The M(II) complexes (M = Cu, Ni, Co, Mn) exhibit a one electron quasi-reversible oxidation and reduction process. At negative and positive potential, the anodic peak at $E_{\text{pa}} = -1.01$ to -0.62 V & 1.20 to 0.38 V and associated cathodic peak at $E_{\text{pc}} = -1.34$ to -0.98 V & 0.88 to 0.16 V, the complexes exhibit quasi-reversible

behavior indicated by the peak separation, ΔE_p value of greater than 59 mV. The anodic process is attributed to quasi-reversible one electron oxidation of M(II) to M(III) process while cathodic process is attributed to quasi-reversible one electron reduction M(II) to M(I) process, similar to that of VO(IV) to VO(V) in anodic process (E_{pa} - 1.25 & 0.45 V) and VO(IV) to VO(III) in cathodic process (E_{pc} -1.40 & 0.60 V) [33].

Antibacterial activities

The in vitro antibacterial activity of the synthesized Schiff base ligands and their corresponding metal complexes were tested against the selected bacteria *Staphylococcus aureus*, *Bacillus subtilis*, *Escherichia coli* and *Klebsiella pneumonia*. The compounds were tested at concentration 2 mg/ml using the agar well diffusion method. The growth inhibition zones were measured in diameter (mm) and the results are listed in Table 6. All the tested compounds showed good biological activity against microorganism. From this study, all the metal complexes exhibit higher anti microbial activity than the free ligand. Cobalt(II) complexes have higher bacterial activity and Nickel(II) than the other complexes. The bioactivity of the ligand and its complexes is found to be order Co(II) > Ni(II) > Cu(II) ~ Mn(II) > L. The observed higher antimicrobial activities of the complexes can be explained on the basis of Tweedy's chelation theory [34].

The lipid membrane that surrounds the cell favors the passage of only lipid soluble materials due to which lipophilicity is an important factor which controls the antimicrobial activity. On chelation, the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with the donor groups. Further, it increases the delocalization of p-electrons over the whole chelate ring and hence enhances the liposolubility of the complexes. This increased liposolubility enhances the penetration of the complexes into the lipid membrane; the lipophilic group to drive the compound through the semipermeable membrane of the cell; and blocks the metal binding sites in the enzymes of the microorganisms.

Table 6. Antimicrobial activity of the Schiff base ligand and its complexes

Compounds	Zone of inhibition (mm)			
	<i>Staphylococcus aureus</i>	<i>Bacillus subtilis</i>	<i>Escherichia coli</i>	<i>Klebsiella pneumonia</i>
DMSO (Control)	-	-	-	-
Ligand	2	1	2	3
[CuL(H ₂ O) ₂]	16	14	5	6
[NiL(H ₂ O) ₂]	15	13	12	12
[CoL(H ₂ O) ₂]	18	14	16	14
[MnL(H ₂ O) ₂]	3	16	5	10
[VOL(H ₂ O)]	8	12	11	7

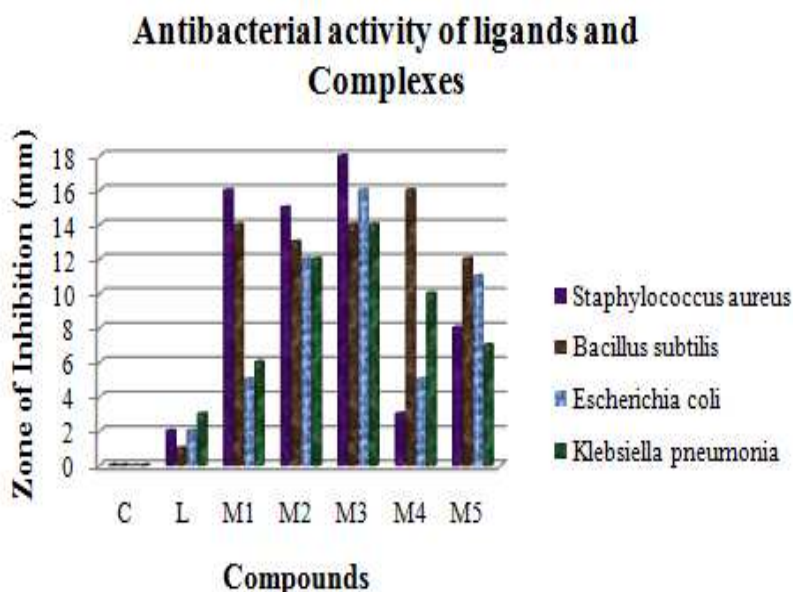


Fig 2. Antimicrobial activity of ligands and its metal complexes, (C) DMSO, (L) Ligand, (M1) [CuL(H₂O)₂], (M2) [NiL(H₂O)₂], (M3) [MnL(H₂O)₂], (M4) [CoL(H₂O)₂], (M5) [VOL(H₂O)]

CONCLUSION

From the analytical and spectral data, it has been observed that the ligand (L) act as potential tetradentate N_2O_2 , being coordinated through the azomethine nitrogen and phenolic oxygen. The water molecules also coordinated to the metal atom indicated by infrared spectra, while electronic spectra and magnetic studies are consistent with an octahedral geometry for all complexes. The cyclic voltammetry study indicates all the metal complexes are quasi-reversible in nature. The complexes show good antimicrobial activity compared to the ligand.

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