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Environmentally Benign Studies of Bivalent Transition Metal Complexes of Tridentate (NNO donor) Schiff Base Ligands

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ABSTRACT

A rapid, efficient, clean and environmentally benign exclusive synthesis of Schiff bases as new ligands has been developed using condensation of 2-aminonicotinic acid with salicyldehyde, 5-nitrosalicyldehyde, 5-bromosalicyldehyde and 5-methoxysalicyldehyde efficiently in a water suspension medium using acid catalyst with excellent yields under microwaves irradiation. The results are compared with conventional methods. All the Schiff bases were tridentate (NNO donor) ligands that were used for complexation with Co^{2+}, Ni^{2+} and Zn^{2+} ions. All the ecofriendly synthesized Schiff bases and their metal complexes were characterized by analytical and spectral methods. The synthesized Schiff bases and their transition metal complexes were evaluated for their in vitro antibacterial activity against four gram-negative and two gram-positive bacterial stains by the agar-well diffusion method. Schiff bases were found to exhibit either no or low to moderate activity but all the complexes exhibited varied vigorous activity against different bacteria. Schiff bases which were inactive before complexation became active and less active became more active upon coordination with mentioned bivalent transition metal ions.

Keywords: Microwave irradiation, Schiff bases, Coordination compounds, Antibacterial activity.

INTRODUCTION

Schiff bases and their biologically active complexes have been studied extensively over the past decade [1]. Day by day Schiff bases are more frequently applied for the betterment of human welfare. The importance of the Schiff base is due its versatile nature. Literature survey shows that many Schiff bases exhibit biological activities [1-4] such as antifungal, antibacterial, antitumor, anti-inflammatory and antipyretic among others. Some of them have been used as complexing agents [5, 6] and powerful corrosion inhibitors [7]. The chemistry of metal complexes with Schiff base ligands and their application have aroused considerable attention, mainly because of preparative accessibility, diversity and structural variability [2]. Schiff bases belong to a widely used group of organic intermediates important for production of specialty chemicals, e.g. pharmaceuticals, or rubber additives [8] and as amino protective groups in organic synthesis [9-13]. They also have uses as liquid crystals [14] and in analytical [15], medicinal [16] and polymer chemistry [17].

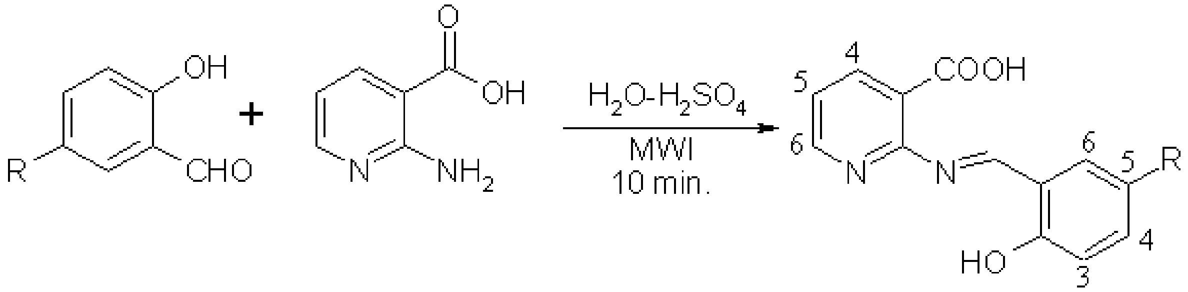
A big challenge facing academia and industry is the relationship of modern societies to the environment that requires reinventing the manufacture and use of materials. Synthetic methodologies nowadays should be designed to use and generate substances that possess little or no toxicity to human health and the environment. Conventionally Schiff bases have been prepared by refluxing mixtures of the amine and the carbonyl compound in an organic solvent, for example, ethanol or methanol [18], but variations are known. In general, ketones react more slowly than aldehydes and higher temperatures and longer reaction times are often required as a result. In addition, the equilibrium must often be shifted, usually by removal of the water, either azeotropically by distillation or with suitable drying agents [19-20]. In recent years, environmentally benign synthetic methods have received considerable attention and some solvent-free protocols have been developed [21]. Catalyzed synthesis of imines under solvent-free conditions using microwave irradiation has been reported [22, 33]. Based on these facts, we decided to synthesize some new Schiff bases of 2-aminonicotinic acid and salicyldehydes in water suspension medium using acid catalyst under microwave irradiation without using any non-ecofriendly organic solvent and the products were isolated simply by filtration. We report the ecofriendly synthesis, structural characterization and antibacterial activities of synthesized new ligands and their complexes with Co(II), Ni(II), and Zn(II) ions respectively in this research paper.

MATERIALS AND METHODS

All starting reagents were purchased from commercial sources and used without further purification. Melting points were determined on a Mel-Temp melting point apparatus and are uncorrected. Infrared spectra were recorded on Nicolet Impact-410 FTIR spectrophotometer. NMR spectra were recorded on a Brucker Varian-300 MHz NMR spectrometer in DMSO-d_6 as solvent and TMS as an internal standard. All compounds were analysed satisfactorily for C, H and N using Carl-Ebra 1106 elemental analyser in micro analytical laboratory. Thin layer chromatography (TLC) was carried out on silica gel plates (Fluka-Kieselgel, 0.2 mm thickness) and the plates were scanned under 254 nm ultraviolet light. Ultra-violet spectra were recorded on a Hitachi U-2000 double-beam spectrophotometer. Magnetic susceptibility measurements of the metal complexes in the solid state were determined by a Gouy balance at room temperature.

2.1: Synthesis of Ligands

A reaction mixture of 0.01 mol of 2-aminonicotinic acid in water, 0.01 mol of the appropriate aldehydes and 2 drops of concentrated sulphuric acid was kept inside a microwave oven (BPL make-model, BMO: 700T) operating at 160 W for about ten minutes (**Scheme 1**). After completion of the reaction the product was poured in water and then allowed to cool to room temperature. The resulting solid was recrystallized from hot ethanol. The progress of the reaction was monitored by TLC after every 3 minutes. TLC showed complete conversion after 10 minutes.



1. R = H
2. R = 5-Br
3. R = 5-NO_2
4. R = 5-OCH_3

SCHEME- I

2.2: Synthesis of Complexes

All the metal complexes were prepared by the stoichiometric reaction of the corresponding metal (II) chlorides with the Schiff base ligands in a molar ratio (M: L) of 1:2. A mixture of ethanolic solution of appropriate ligand (0.02mol) and metal(II) chloride (0.01mol) was microwave irradiated for about 10 minutes and the solid formed upon cooling was collected by suction filtration and then crystallisation from aqueous ethanol purified products were obtained**(scheme-2).**

$$MCl_2 + 2LH \xrightarrow[\text{10-15 minutes}]{\text{MWI}} ML_2$$

SCHEME-2

All the metal complexes were intensely coloured and amorphous solids except that of zinc complexes which were light yellow in colour and decompose above 190^0C without melting. They were insoluble in common organic solvents viz. ethanol, methanol, chloroform, acetone etc. but fairly soluble in DMSO and DMF.

2.3: Biological Evaluation

The synthesized ligands (1-4) and their corresponding metal (II) complexes were screened in vitro for their antibacterial activity against four Gram-positive (*E.coli, P.aeruginosa, S.typhi & S.flexeneri*) and two Gram-positive (*B.subtilis & S.aureus*) bacterial strains by the agar-well diffusion method[23]. The minimum inhibitory concentration was determined using the disc diffusion technique [24].

RESULTS AND DISCUSSION

3.1: Chemistry of Ligands

The purity of the synthesized Schiff bases was checked on TLC plates and the spots were visualized under ultraviolet light at 254-366 nm and by spraying with iodine vapour. The structures of all synthesized ligands were established through elemental analyses and spectroscopic data (IR & ^{1}H-NMR). The **table-1** presents the comparative data of methods applied for the synthesis of the ligands under investigation.

Table-1: Microwave irradiated and Traditional methods of synthesis of ligands

Compound			MW Method		Traditional Methods	
No.	Formula & Colour	m.p.(K)	*Time(min.)*	*Yield (%)*	*Time(Hr.)*	*Yield (%)*
1	$C_{13}H_{10}N_2O_3$ (Yellow)	305-307	04	93	0.2	75
2	$C_{13}H_9N_2O_3Br$ (Yellow)	407-409	05	89	0.5	70
3	$C_{13}H_9N_3O_5$ (Dark Yellow)	413-415	07	87	0.8	68
4	$C_{13}H_{12}N_2O_4$ (Yellow)	409-411	09	83	1.0	65

The structures of all the synthesized Schiff bases were established through IR and 1H-NMR spectral data. Further support for their structures was derived from elemental analyses (**Table-2**).

Table-2*: Analytical data of Ligands*

Schiff Base Ligands	Mol. Mass (g/mol)	Analytical Data Expt. (cal.) %			
		C	H	N	O
$C_{13}H_{10}N_2O_3$ L^1H	242.2	64.8 (64.5)	4.5 (4.3)	11.5 (11.6)	19.2 (19.6)
$C_{13}H_9N_2O_3Br$ L^2H	321.1	48.8 (48.6)	3.2 (3.1)	8.8 (8.7)	14.4(14.7)
$C_{13}H_9N_3O_5$ L^3H	287.2	54.8 (54.4)	3.5 (3.2)	14.5 (14.6)	27.2 (27.8)
$C_{13}H_{12}N_2O_4$ L^4H	272.3	62.1 (61.8)	4.3 (4.2)	10.4 (10.5)	23.2 (23.5)

IR Spectral studies:

The IR spectra of Schiff base ligands (**L^1H to L^4H**) showed bands resulting from the OH stretchings of phenol and carboxyl function in the 3420-3425 and 3530-3540 cm^{-1} regions respectively, whereas the carboxyl (C=O) stretchings were observed in the 1680-1685 cm^{-1} regions.

The azomethine (HC=N) stretchings were observed in the 1630-1635 cm^{-1} region, whereas the pyridine (C=N) stretchings appeared at 1610 cm^{-1} in all the cases.

^{1}H-NMR Spectral studies:

The ^{1}H-NMR spectrum of **L^1H** displayed OH proton of the phenyl moiety at δ=10.22 and the carboxyl OH proton at δ=11.32 as singlets. In the rest Schiff bases (**L^2H-L^4H**), the ^{1}H-NMR spectra exhibited the OH protons of the phenol moieties at δ=10.21-10.45 and the carboxyl OH protons at δ=11.31-11.42 as three separate singlets. The azomethine (HC=N) protons of all the Schiff bases appeared as singlets at δ=8.66-8.93.The ^{1}H-NMR spectrum of **L^1H** demonstrated the phenyl C_5-H and C_4-H as a doublet of double doublet at δ=6.96 and δ=7.21, respectively. The phenyl C_3-H and C_6-H however, appeared as double doublet at δ=7.11 and δ=7.85 respectively. The ^{1}H-NMR spectra of **L^2H** and **L^4H** displayed phenyl C_3-H as a doublet at δ=7.15 and δ=7.16 respectively. The phenyl C_6-H experiencing a deshielding effect due to the inductive effect of HC=N function, resonated as a doublet at δ=7.89 and δ=7.86 respectively. The phenyl C_4-H appeared as a double doublet at δ=7.25 and δ=7.21 respectively. In addition, the methoxy protons in the case of **L^4H** appeared as a singlet at δ=3.59. In the case of **L^3H**, the ^{1}H-NMR spectrum exhibited the phenyl C_3-H as a doublet at δ=7.00. The phenyl C_4-H, experiencing a deshielding effect due to the electron attracting effect of the nitro group, appeared as a double doublet at δ=8.41. The phenyl C_6-H, being deshielded due to inductive effect of the (HC=N) function and the electron attracting effect of the nitro function at 5-position, appeared further downfield as doublet at δ=8.68. As far as exhibition of the different pyridine protons in all the Schiff bases by the ^{1}H-NMR spectra is concerned, a very small difference in the δ values was observed. The pyridine C_4-H and C_6-H appeared as a doublet at δ=8.31- 8.75, respectively, whereas C_5-H resonated as a doublet at δ=7.38 – 7.41.

3.2: Chemistry of Metal Complexes:

All the metal complexes (**1-12**) were air stable and prepared by the stoichiometric reaction of the corresponding metal (II) chlorides with the Schiff base ligands in a molar ratio (M:L) of 1:2. All the metal complexes are intensely coloured and amorphous solids except that of zinc complexes which were light yellow in colour and decompose above 190^0C without melting. They were insoluble in common organic solvents viz. ethanol, methanol, chloroform, acetone etc. but fairly soluble in DMSO and DMF. Their solubility behavior and elemental analysis data suggested that they are monomers. The molar conductance of the soluble complexes in DMF (10^{-3}M solution at 298K) indicated that they all are non-electrolytic in nature [25]. The elemental analysis was also found to be in agreement with the proposed formulae for the ligands and also confirmed the $M(L)_2$ composition of the metal (II) complexes. The **Table-3 & 4** present the comparative data of methods applied for the synthesis of the metal complexes and characteristic data of the complexes under investigation respectively.

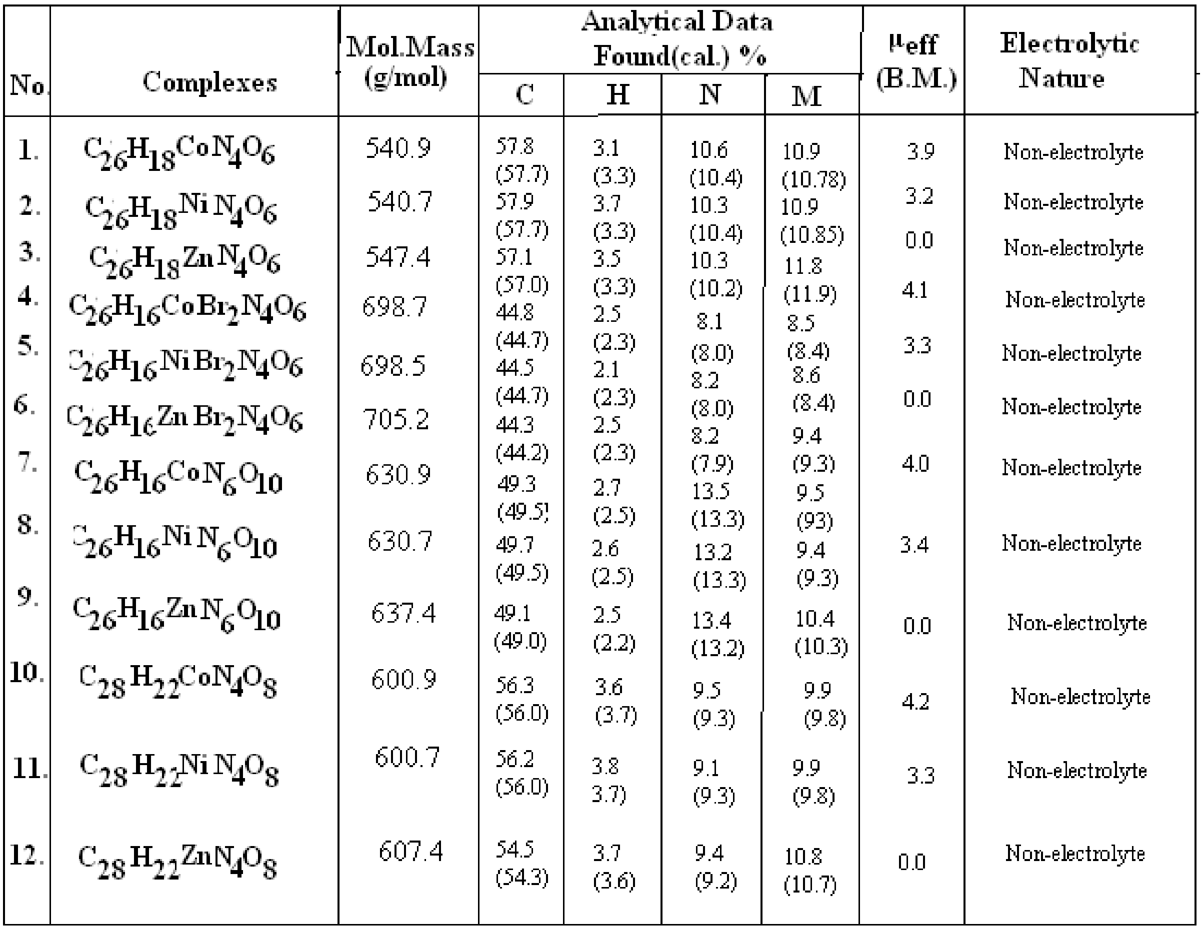
Table-3: **Microwave irradiated and Traditional methods for synthesis of complexes**

Metal Complexes			MW method		Traditional methods	
No.	Formula	Colour	Time(min)	Yield (%)	Time(hour)	Yield (%)
1.	$C_{26}H_{18}CoN_4O_6$	Light Pink	3	95	1.5	69
2.	$C_{26}H_{18}NiN_4O_6$	Light Green	6	93	1.2	65
3.	$C_{26}H_{18}ZnN_4O_6$	Pale Yellow	3	95	1.0	68
4.	$C_{26}H_{16}CoBr_2N_4O_6$	Pink	5	93	1.7	67
5.	$C_{26}H_{16}NiBr_2N_4O_6$	Bright Green	7	89	1.75	65
6.	$C_{26}H_{16}ZnBr_2N_4O_6$	Light Yellow	4	96	0.85	69
7.	$C_{26}H_{16}CoN_6O_{10}$	Red	7	88	1.50	65
8.	$C_{26}H_{16}NiN_6O_{10}$	Light Green	3	95	1.00	68
9.	$C_{26}H_{16}ZnN_6O_{10}$	Pale Yellow	5	91	1.25	69
10.	$C_{28}H_{22}CoN_4O_8$	Red	8	89	1.87	65
11.	$C_{28}H_{22}NiN_4O_8$	Yellow Green	6	91	1.54	68
12.	$C_{28}H_{22}ZnN_4O_8$	White	3	94	1.15	66

IR Spectral studies:

The comparision of the IR spectra of Schiff bases (**L^1H to L^4H**) and their metal complexes (**1-12)** indicated that the ligands are principally coordinated to the metal ions in three ways, thus acting as tridentate ligands. The bands appearing at ~ 1630 – 1635 cm^{-1}due to azomethine linkage in the ligands is shifted to lower frequency by ~ 5 – 15 cm^{-1} in the complexes, indicating the participation of the azomethine nitrogen in interaction with the metal ion. The band at ~ 1610 cm^{-1}, assigned to the nitrogen of the pyridine ring (C=N), is also shifted to lower frequency by ~ 5 cm^{-1}, which was indicative of the involvement of the pyridine ring N in the coordination with metal ions. A broad band, appearing at ~ 3420 – 3425 cm^{-1} assigned to OH in the Schiff bases, was no longer found in the spectra of the investigated metal complexes and instead, appearance of a new band at ~ 1380 – 1385 cm^{-1} due to (C-O) stretching vibrations, indicated deprotonation and coordination of the hydroxyl oxygen to the metal ion. Further conclusive evidence of coordination of these Schiff bases with the metal ions was shown by the appearance of weak low frequency new bands at 525 – 530 and 455 – 460 cm^{-1}. These were assigned [26-27] to the metal-nitrogen (M – N) and metal-oxygen (M – O) vibrations, respectively, and were observed in the spectra of the investigated metal complexes and not in the spectra of the uncomplexed Schiff bases, thus confirming participation of the O & N atoms in the coordination.

Table-4: Analytical & Physical Data of Complexes



No.	Complexes	Mol.Mass (g/mol)	Analytical Data Found(cal.) %				μ_{eff} (B.M.)	Electrolytic Nature
			C	H	N	M		
1.	$C_{26}H_{18}CoN_4O_6$	540.9	57.8 (57.7)	3.1 (3.3)	10.6 (10.4)	10.9 (10.78)	3.9	Non-electrolyte
2.	$C_{26}H_{18}Ni N_4O_6$	540.7	57.9 (57.7)	3.7 (3.3)	10.3 (10.4)	10.9 (10.85)	3.2	Non-electrolyte
3.	$C_{26}H_{18}Zn N_4O_6$	547.4	57.1 (57.0)	3.5 (3.3)	10.3 (10.2)	11.8 (11.9)	0.0	Non-electrolyte
4.	$C_{26}H_{16}CoBr_2N_4O_6$	698.7	44.8 (44.7)	2.5 (2.3)	8.1 (8.0)	8.5 (8.4)	4.1	Non-electrolyte
5.	$C_{26}H_{16}NiBr_2N_4O_6$	698.5	44.5 (44.7)	2.1 (2.3)	8.2 (8.0)	8.6 (8.4)	3.3	Non-electrolyte
6.	$C_{26}H_{16}Zn Br_2N_4O_6$	705.2	44.3 (44.2)	2.5 (2.3)	8.2 (7.9)	9.4 (9.3)	0.0	Non-electrolyte
7.	$C_{26}H_{16}CoN_6O_{10}$	630.9	49.3 (49.5]	2.7 (2.5)	13.5 (13.3)	9.5 (93)	4.0	Non-electrolyte
8.	$C_{26}H_{16}Ni N_6O_{10}$	630.7	49.7 (49.5)	2.6 (2.5)	13.2 (13.3)	9.4 (9.3)	3.4	Non-electrolyte
9.	$C_{26}H_{16}Zn N_6O_{10}$	637.4	49.1 (49.0)	2.5 (2.2)	13.4 (13.2)	10.4 (10.3)	0.0	Non-electrolyte
10.	$C_{28}H_{22}CoN_4O_8$	600.9	56.3 (56.0)	3.6 (3.7)	9.5 (9.3)	9.9 (9.8)	4.2	Non-electrolyte
11.	$C_{28}H_{22}Ni N_4O_8$	600.7	56.2 (56.0)	3.8 3.7)	9.1 (9.3)	9.9 (9.8)	3.3	Non-electrolyte
12.	$C_{28}H_{22}ZnN_4O_8$	607.4	54.5 (54.3)	3.7 (3.6)	9.4 (9.2)	10.8 (10.7)	0.0	Non-electrolyte

Magnetic Moment studies:

The room temperature magnetic moments of the solid cobalt (II) complexes were found at 3.9 – 4.2 B.M., indicative of three unpaired electrons per Co(II) ion in an octahedral environment [28]. The Ni(II) complexes showed μ_{eff} values 3.2 – 3.4 B.M. corresponding to two unpaired electrons per Ni(II) ion for their ideal six-coordinated configuration [28]. All the zinc (II) complexes were diamagnetic in nature.

Electronic Spectral studies:

The electronic spectra of Co(II) complexes (**1**), (**4**), (**7**) and (**10**) showed three bands at 8780 – 8810, 17475 – 17775 and 30235 – 30270 cm^{-1}, which may be assigned to

$$\begin{gathered} {}^4T_{1g} \rightarrow {}^4T_{2g}\ (F), \\ {}^4T_{1g} \rightarrow {}^4T_{2g}\ (P)\ \text{and} \\ {}^4T_{1g} \rightarrow {}^3A_{2g}\ (F) \end{gathered}$$

transitions respectively, and suggested octahedral geometry [28-29] around the Co(II) ions.

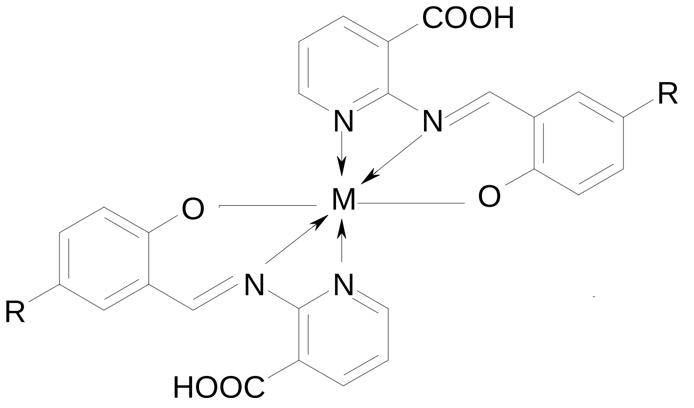
The Ni(II) complexes (**2**), (**5**), (**8**) and (**11**) exhibited three bands at 9960 – 10165, 15850 – 16155 and 29940 – 29985 cm^{-1} assignable [27-28] respectively to the transitions

$$\mathbf{^3A_{2g}\,(F) \rightarrow {}^3T_{2g}\,(F)(\nu_1),}$$
$$\mathbf{^3A_{2g}\,(F) \rightarrow {}^3T_{1g}(F)\,)(\nu_2)\ and}$$
$$\mathbf{^3A_{2g}\,(F) \rightarrow {}^3T_{2g}(P)(\,\nu_3)}$$

which are characteristic of Ni(II) in octahedral geometry.

The diamagnetic Zn(II) complexes (**3**), (**6**), (**9**) and (**12**) did not show ant d-d bands and their spectra were dominated by the charge transfer bands at 28850 – 28975 cm^{-1}.

On the basis of the above observations, it is tentatively suggested that Co(II), Ni(II) and Zn(II) investigated complexes show an octahedral geometry [**Figure-1**] in which the Schiff bases act as tridentate ligands.



Where R = H, 5-Br, 5-NO_2 & 5-OCH_3 and M = Co(II), Ni(II) or Zn(II)

Figure – 1: Proposed octahedral structural formulae of the investigated Metal Complexes

3.3: *Antibacterial studies of the Schiff base ligands and their Metal complexes*

The antibacterial activity of the synthesized Schiff bases (**L^1H to L^4H**) and their corresponding metal complexes (**1 – 12**) was determined against four Gram-negative (*Escherichia coli, Pseudomonas aeruginosa, Salmonella typhi & Shigella flexneri*) and two Gram-positive (*Bacillus subtilis & Staphylococcus aureus*) bacterial stains. The synthesized Schiff bases and their corresponding metal (II) complexes either exhibited no or varying degree of inhibitory effects (low to moderate) on growth of different tested strains (**Table-5**).

The compound L^3H was found to be active against all the Gram-positive and Gram-negative bacteria. The compound L^4H was found to be inactive against the Gram-negative species, *Escherichia coli, Pseudomonas aeruginosa & Salmonella typhi* and the Gram-positive species, *Bacillus subtilis*. The compound **L^1H** showed no inhibitory action against the Gram-negative species, *Salmonella typhi & Shigella flexneri*, and the Gram-positive species, *Bacillus subtilis*.

The Schiff base, **L^{2}H** was found to be inactive against the Gram-negative species, *Pseudomonas aeruginosa & Shigella flexneri.*

In contrast, the growth of all the Gram-negative and Gram-positive species was inhibited by all the metal complexes under investigation. These results substantiate our findings and the findings of some other workers [30-31] that biologically inactive compounds become active and less biologically active compounds become more active upon coordination. The higher activity of the metal complexes may be owing to the effect of metal ions on the normal cell membrane. This can be well ascribed to Tweedy's Chelation Theory [32].

Table-5: Primary screening of the synthesized Schiff bases and their metal (II) complexes for antibacterial activity

Schiff base / Complexes	**Gram-positive Bacteria**				**Gram-negative Bacteria**	
	E. coli	*P. aeruginosa*	*S.typhi*	*S.flexeneri*	*B.subtilis*	*S.aureus*
L^{1}H	08	08	00	00	00	05
L^{2}H	08	00	06	00	07	09
L^{3}H	09	09	07	06	06	08
L^{4}H	00	00	00	09	00	08
1	14	11	09	07	11	14
2	18	15	11	05	13	17
3	14	11	14	08	10	15
4	13	10	10	09	13	17
5	12	12	10	10	11	15
6	19	11	11	08	16	18
7	13	14	13	12	10	13
8	15	16	15	15	11	13
9	18	16	14	12	13	17
10	12	07	08	13	08	12
11	12	07	08	13	08	12
12	10	08	07	13	09	15

00: absence of measurable inhibitory action; 9 <: weak; 9 – 16: moderate and > 16: significant

CONCLUSION

Based on various physiochemical and structural investigations, it was concluded that the ligands act as tridentate (NOO donor) forming octahedral complexes with Co(II), Ni(II) and Zn(II) ions.

Furthermore, the current study strongly demonstrates that these complexes are more effective antibacterial agents that the parent ligands.

In the present protocol, we observed better yields in a shorter period compared to the reactions carried out in the non-aqueous medium. The compounds have been characterized by comparing their melting points and by the spectral and analytical data (provided in the experimental part). In conclusion, we have described here an efficient and environmentally benign synthesis of Schiff base ligands and their corresponding metal (II) complexes under microwave irradiation using water and ethanol as solvents and acid as green catalyst. Further, this method is simple, mild and ecofriendly from green chemistry point of view.

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