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Biologically active Co (II), Ni (II), Cu (II) and Mn(II) Complexes of Schiff Bases derived from Vinyl aniline and Heterocyclic Aldehydes

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Abstract : Co (II), Ni (II), Cu (II) and Mn(II) complexes of Schiff bases have been prepared and characterized by their physical, spectral and analytical data. The newly synthesized metal complexes having a composition [M $(LX)_2Y_2$] where M=Co (II), Ni (II), Cu (II) and Mn (II), LX=bidentate ligand (derived from pyridine-2 aldehyde, furfuraldehyde or thiophene-2 carboxy aldehyde with vinyl aniline) Y=Cl shows an octahedral geometry. In order to evaluate the biological activity of Schiff bases and their metal complexes, the Schiff-bases and their new metal complexes have been screened for their antibacterial and antifungal activity against bacterial species like- *Escherichia coli, Staphylococcus aureus, Klebsiella* and *Psuedomonas* and as well as fungal species like- *Candida albicans or Candida krusei.*
Key words: Schiff Bases, Vinyl aniline ,Heterocyclic Aldehydes

Introduction

Compounds containing imines bases have not only found extensive application in organic synthesis, but several of these molecules display significant biological activity[1-4]. In the last decade Schiff base ligands have received more attention mainly because of their wide application in the field of catalysis and due to their antimicrobial[5], anti-tuberculosis[6], and antitumour activity[7]. They easily form stable complexes with most transition metal ions.

Schiff base complexes (derived from heterocyclic compounds) have increased the interest in the development of the field of bioinorganic chemistry[8]. Heterocyclic compounds such as pyridine, 2, 2'-bipyridine and related molecules are good ligands due to the presence of at least one ring nitrogen atom with a localized pair of electrons. The successful application has led to the formation of series of novel compounds with a wide range of physical, chemical and biological properties[9-12], spanning a broad spectrum of reactivity and stability. Keeping in view of the pronounced biological activity of the metal complexes of Schiff bases derived from heterocyclic compounds, it was thought of worthwhile to synthesize and characterize some new metal ligand complexes of Co (II), Ni (II), Cu (II) and Mn (II) with Schiff base (derived from pyridine-2 aldehyde, furfuraldehyde or thiophene-2 carboxy aldehyde with vinyl aniline). Interesting biological properties of theses NX ($X=L_1=N$, $L_2=O$, $L_3=S$) donor Schiff base complexes (having the composition [M $(LX)_2Y_2$], where Y=Cl), compelled to prepare and report on the proceeding paper, which describe the biological role against bacterial and fungal strains like- *Escherichia coli, Staphylococcus aureus, Klebsiella* and *Psuedomonas* and *Candida albicans* or *Candida krusei*.

Experimental

Material and Methods

All chemicals and solvents used were of analytical grade. All metal (II) salts were used as chlorides. UV-VIS spectra were obtained on a Perkins- Elmer λ-15 UV/VIS spectrophotometer in the 200-900nm range in methanol. IR spectra were recorded using KBr discs on a FT-IR spectrophotometer, Shimadzu 8201PC in the range of 4000-400cm^{-1}. ^{1}HNMR spectra were recorded in DMSO-d_6 at room temperature using TMS as internal standard on a Bruker Advance 400 MHz FT NMR.Elemental analysis were carried out on a Vario EL III Elementar Carlo- Erba 1108. Conductance measurements of 10^{-3} M solutions of the complexes in DMF were carried out on an Equiptronics model no Eq-660A. Melting points of the ligands and their metal complexes were determined by open capillary method using Sunsim electric melting point apparatus and uncorrected. Molecular weight of ligands and their metal complexes were determined by Rast camphor method.

*[L_1 (derived from pyridine-2 aldehyde and vinyl aniline), L_2 (derived from furfuraldehyde and vinyl aniline), L_3 (deived from thiophene -2 carboxaldehyde and vinyl aniline)]

Synthesis of the organic ligands (L_1-L_3)*

The aldehydes (pyridine-2 aldehyde, furfuraldehyde or thiophene-2 carboxy aldehyde) (1m mol 1.46ml, 1.36ml, 1.22ml) were dissolved in absolute ethanol (10ml) was added to the vinyl aniline (1m mol 1.22ml) dissolved in absolute ethanol (10ml.). The mixture was refluxed for 4 hrs. After complete refluxation, the mixture was allowed to cool for 4hrs. Yellow precipitates were filtered by Buckner funnel on vacuum pump and washed with absolute ethanol (5ml) and recrystallized from ethanol to give the ligand (80% yield, mp 120^0C, yellow solid, 77% yield mp 130^0C, yellow solid, 75% yield mp 140^0C, yellow solid).

Synthesis of metal complexes

Warm ethanol solutions (20ml) of the respective Schiff base (0.002M) were added to a magnetically stirred solution of the metal (II) salts (0.001M) in ethanol (25ml). The mixture was refluxed for 1hr and cooled to room temperature. On cooling, precipitates of metal complexes were formed, which were filtered from Buckner funnel, washed with ethanol and dried. Recrystallization in aqueous ethanol (30:70) gave the pure metal complexes. All other metal complexes were prepared respectively following the same method (scheme-1). The analytical data of ligands and their metal complexes are given in table-1.

Antibacterial studies

The synthesized metal complexes and Schiff base ligands were screened for their antibacterial and antifungal activity against pathogenic bacterial species, like- *Escherichia coli, Staphylococcus aureus, Klebsiella* and *Psuedomonas* or fungal species like- *Candida albicans* and *Candida krusei.* The paper disc diffusion method[13-15]was adopted for the determination of antibacterial and antifungal activity.

Result and Discussion

Physical Properties

These complexes are air and moisture stable, intensely coloured, amorphous solids which decomposes above 140^0C. They are insoluble in common organic solvents like chloroform, acetone and ether but soluble in ethanol, DMSO and DMF. The molar conductance of the complexes (dissolved in DMF) fall into the range (4-10ohm^{-1}cm^{2}mol^{-1}) indicating their non electrolytic nature.

I.R. spectra

The IR spectra of the Schiff bases indicated that stretching vibrations due to the ν(C=O) and ν(NH_2) functions at 1735cm^{-1} and 3420cm^{-1}, which were found to be in parent compounds (pyridine-2 aldehyde, furfuraldehyde or thiophene-2 carboxy aldehyde and vinyl aniline), disappeared in the spectra of Schiff bases and, instead a strong new band appeared at1590, 1600 and 1614 cm^{-1} assigned to the azomethine ν(CH=N) linkage. It however, suggested that the amino and aldehyde moieties of the starting reagents were no more existed and converted into the Schiff bases showing, the azomethine linkage ν(CH=N) (fig.1 and 2).

The comparison of the IR spectra of the Schiff base and its metal complexes (table-2) further indicated that the Schiff bases were coordinated to the metal atom from mainly two donor sites hence, acting as a bidentate ligand. The band originally appearing at 1590 ,1600 and 1614cm^{-1} in the spectra of ligand L_1, L_2 and L_3 respectively due to the azomethine shifted to lower frequency by 10-15cm^{-1}suggesting[16] the participation of the azomethine nitrogen in complexation. A further evidence of the coordination of the Schiff base with the metal atom was shown by the appearance of a new weak frequency bands at 570-635cm^{-1} assigned[17] to the metal-nitrogen ν(M-N). These new bands were observed only in the spectra of the metal complexes and not in Schiff bases which confirmed the participation of the donor groups (nitrogen of the vinyl aniline moiety).

Magnetic moment, NMR and UV-Visible spectra-

The nature of the ligand field around the metal ion and the geometry of the complexes have been deduced from the NMR and UV-VIS spectra and magnetic moment data. The magnetic moment (at room temperature) of the solid Cobalt (II) complexes was found to lie in the range of (4.3-5.2BM) indicative of four unpaired electrons per Co (II) ion in an octahedral environment. The Cu (II),Ni(II) and Mn (II) complexes showed μ_{eff} values 1.93,3.8 and 5.85BM corresponding to one, three and five unpaired electrons respectively in a octahedral configuration.

The UV–VIS spectrum of the solid ligands L_1, L_2 and L_3 (table-2) showed two bands at 280-320 nm and 360-380 nm respectively. The first band would be assigned to π- π* transition within the aromatic ring. The second band would be due to n-π* transition within the –C= N group.

The ^{1}HNMR spectrum (table-2) of the ligands L_1, L_2 and L_3 in deuterated DMSO-d_6 showed signal at 7.54, 7.61 and 7.68 ppm corresponding to the -CH=N group respectively. Like IR spectra, the ^{1}HNMR spectra of the metal complexes of ligands L_1, L_2 and L_3 shows coordination via the nitrogen atom of azomethine group (table2).

On the basis of the above observations, it is tentatively suggested that Co (II), Ni (II), Cu (II) and Mn(II) complexes show a octahedral geometry in which the Schiff bases act as bidentate ligand and possibly accommodate themselves around the metal atom in such a way that a stable chelate ring of the complex is formed hence, giving a following stable structure of the complex (Fig-3&4).

Antibacterial activity

Schiff bases and their Co (II), Ni (II), Cu (II) and Mn(II) metal chelates were evaluated for their antibacterial and antifungal activity against bacterial species like- *Escherichia coli, Staphylococcus aureus, Klebsiella* and *Psuedomonas* and as well as fungal species like- *Candida albicans* and *Candida krusei*. The compounds were tested at a two different concentration of 50ppm and 100ppm in DMF solution using the paper disc diffusion method[18-20]. The susceptibility zones measured in diameter (mm) were the zones around the discs killing the active bacteria and fungi (table-3&4).

The Schiff bases and their complexes individually exhibited varying degrees of inhibitory effects on the growth of the tested bacterial and fungal species (Fig-5-10).

The antimicrobial results evidently show that the activity of the Schiff bases became more pronounced when coordinated to the metal ions.

The results of antimicrobial studies clearly show that the process of chelation dominantly affects the overall biological behaviour of the compounds, which are potent against bacterial and fungal strains.

Table-1: Micro analytical data of the ligands and their metal complexes

Compounds (Colour)	Elemental analysis Found (Calc.)						μ_{eff}	M.P	Λ_m	Molecular Weight
	Carbon % Found (Calc)	Hydrogen% Found (Calc)	Nitrogen % Found (Calc)	Metal Found (Calc) %	Oxygen % Found (Calc)	Sulphur Found (Calc) %	BM	^0C	$Ohm^{-1} cm^2 mol^{-1}$	Found (Calc.)
L_1 (Yellow solid)	79.10 (80.0)	5.62 (5.64)	14.28 (14.35)	-	-	-	-	120^0	4.02	192 (195)
L_2 (Yellow solid)	79.09 (79.18)	5.48 (5.58)	7.04 (7.10)	-	11.80 (8.12)	-	-	130^0	4.15	194 (197)
L_3 (Yellow solid)	73.80 (73.93)	5.11 (5.21)	6.55 (6.63)	-	-	21.10 (15.1)	-	140^0	4.18	205 (211)
L_1-Cu^{+2} (Brown solid)	69.50 (69.64)	4.88 (4.91)	12.43 (12.5)	12.87 (12.9)	-	-	1.75	150^0	4.89	440 (448)
L_1-Ni^{+2} (Black solid)	69.85 (69.95)	4.88 (4.93)	12.48 (12.55)	12.45 (12.5)	-	-	-	160^0	5.12	442 (446)
L_1-Co^{+2} (Brown solid)	70.20 (70.27)	4.91 (4.95)	12.57 (12.61)	11.98 (12.1)	-	-	3.12	165^0	5.17	441 (444)
L_1-Mn^{+2} (Black solid)	70.85 (70.9)	4.80 (5.00)	12.69 (12.72)	11.25 (11.3)	-	-	5.83	170^0	5.22	438 (440)
L_2-Cu^{+2} (yellow solid)	68.95 (69.02)	4.83 (4.86)	6.09 (6.19)	12.74 (12.8)	6.92 (7.07)	-	1.76	175^0	5.35	449 (452)
L_2-Ni^{+2} (Brown solid)	69.29 (69.33)	4.84 (4.88)	6.13 (6.22)	12.33 (12.4)	7.07 (7.11)	-	-	180^0	5.42	448 (450)
L_2-Co^{+2} (Black solid)	69.58 (69.64)	4.88 (4.91)	6.18 (6.25)	11.88 (12.0)	7.12 (7.14)	-	3.13	190^0	5.47	446 (448)
L_2-Mn^{+2} (Brown solid)	70.17 (70.27)	4.91 (4.95)	6.24 (6.30)	11.16 (11.2)	7.15 (7.20)	-	5.87	205^0	5.13	442 (444)
L_3-Cu^{+2} (Black solid)	64.90 (65.0)	4.53 (4.58)	5.79 (5.83)	11.97 (12.0)	-	13.27 (13.3)	1.77	210^0	5.25	355 (480)
L_3-Ni^{+2} (Brown solid)	65.17 (65.27)	4.57 (4.60)	5.79 (5.85)	11.67 (11.7)	-	13. 26 (13.38)	-	220^0	5.37	475 (478)
L_3-Co^{+2} (Black solid)	65.49 (65.54)	4.51 (4.62)	5.82 (5.88)	11.25 (11.3)	-	13.38 (13.44)	3.14	225^0	5.42	472 (476)
L_3-Mn^{+2} (Brown solid)	66.03 (66.10)	4.57 (4.66)	5.88 (5.93)	9.44 (10.5)	-	13.47 (13.55)	5.85	230^0	5.69	470 (472)

Table-2 : Characteristic IR and ^{1}HNMR spectral data of the ligands and their metal complexes

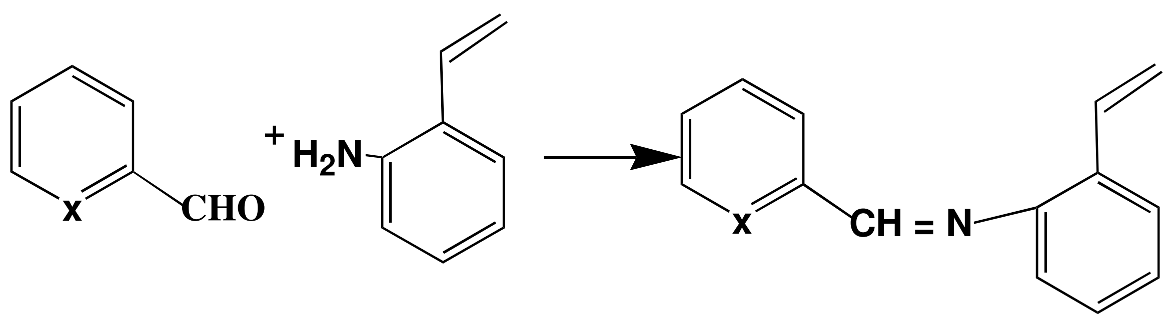
Compounds	I.R. spectra cm^{-1}			^{1}H.N.M.R. spectra ppm		U.V. spectra nm	
	ν(C=N)	ν(M-N) [(X-M)]	ν(C-X-C)	δ(-CH=CH)	δ(HC=N)	-C=C-	(-C=N)
L_1	1590	-	1534	5.27	7.68	280	360
L_2	1600	-	1239	5.17	7.61	300	370
L_3	1614	-	834	5.02	7.54	320	380
L_1-Cu^{+2}	1588	570[420]	1540	4.92	7.58	280	355
L_1-Ni^{+2}	1580	579[427]	1545	4.85	7.45	280	350
L_1-Co^{+2}	1572	570[433]	1554	4.80	7.32	280	345
L_1-Mn^{+2}	1565	563[442]	1560	4.60	7.28	280	340
L_2-Cu^{+2}	1594	552[455]	1241	4.45	7.22	300	365
L_2-Ni^{+2}	1586	547[463]	1245	4.32	7.18	300	360
L_2-Co^{+2}	1576	536[470]	1252	4.28	7.08	300	358
L_2-Mn^{+2}	1570	542[478]	1263	4.17	7.99	300	344
L_3-Cu^{+2}	1604	656[465]	837	4.09	7.47	320	372
L_3-Ni^{+2}	1600	600[472]	844	3.97	7.39	320	366
L_3-Co^{+2}	1590	620[481]	854	3.86	7.26	320	350
L_3-Mn^{+2}	1584	635[486]	863	3.67	7.18	320	348

Table-3: Antibacterial activity of the Schiff base ligands and their metal complexes, Showing diameter of inhibition zone

Compounds	**Micro-organisms**							
	Staphylococus aureu mm		***Klebsiella*** mm		***Enterococci*** mm		***E.coli*** mm	
	Concentration							
	50ppm	**100ppm**	**50ppm**	**100ppm**	**50ppm**	**100ppm**	**50ppm**	**100ppm**
L_1	14	15	12	14	13	15	14	16
L_2	12	14	14	17	14	16	15	17
L_3	14	16	14	16	15	17	13	15
L_1-Cu^{+2}	18	22	18	21	18	20	19	20
L_1-Ni^{+2}	18	19	17	18	17	19	18	21
L_1-Co^{+2}	17	19	18	20	20	22	22	23
L_1-Mn^{+2}	22	23	18	19	18	20	21	22
L_2-Cu^{+2}	18	20	17	19	20	22	21	23
L_2-Ni^{+2}	21	22	22	23	21	22	23	24
L_2-Co^{+2}	19	22	18	20	22	23	20	21
L_2-Mn^{+2}	20	22	19	22	22	24	22	23
L_3-Cu^{+2}	19	20	20	21	18	20	20	21
L_3-Ni^{+2}	21	24	20	22	21	22	21	24
L_3-Co^{+2}	19	21	22	24	19	20	19	22
L_3-Mn^{+2}	20	21	19	21	20	21	20	24

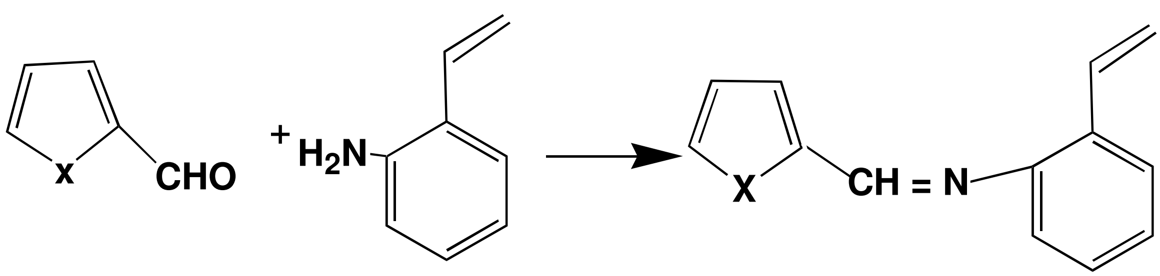
Table-4: Antifungal activity of the Schiff base ligands and their metal complexes,showing diameter of inhibition zone

Compounds	Microorganisms			
	***Candida albicans*mm**		***Candida krusei*mm**	
	Concentration			
	50ppm	**100ppm**	**50ppm**	**100ppm**
L_1	15	17	14	16
L_2	16	18	17	19
L_3	17	19	18	19
L_1-Cu^{+2}	19	21	20	23
L_1-Ni^{+2}	22	23	22	24
L_1-Co^{+2}	18	20	22	23
L_1-Mn^{+2}	18	24	21	23
L_2-Cu^{+2}	21	23	20	23
L_2-Ni^{+2}	20	22	20	22
L_2-Co^{+2}	19	20	21	25
L_2-Mn^{+2}	21	22	20	23
L_3-Cu^{+2}	20	21	21	23
L_3-Ni^{+2}	19	21	22	23
L_3-Co^{+2}	22	24	20	22
L_3-Mn^{+2}	23	24	20	24



X = L_1 = N

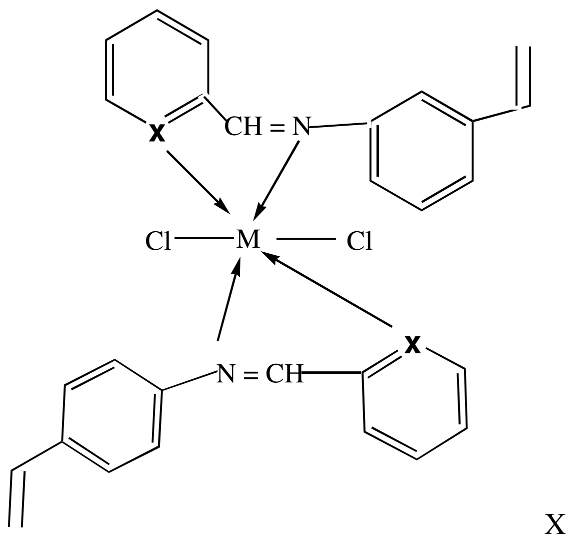
FIG- 1 SYNTHESIS OF LIGAND L_1



X = L_2 = O

X = L_3 = S

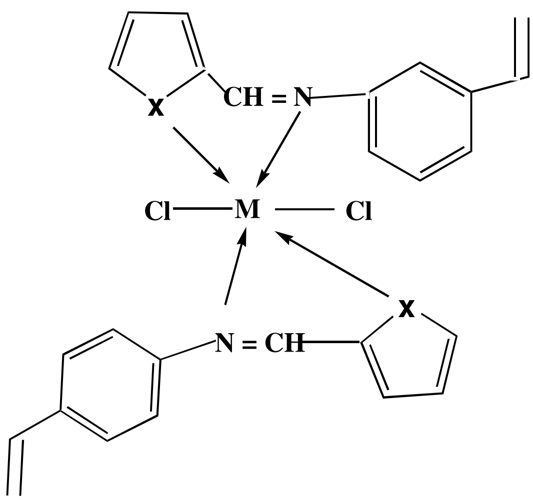
FIG- 2 SYNTHESIS OF LIGANDS (L_2&L_3)



X =

$X_{1} = L_{1} = N$

FIG: 3 METAL COMPLEXES OF PYRIDINE -2ALDEHYDE –VINYL ANILINE



$X = X_{2} = L_{1} = O$ $X = X_{3} = L_{1} = S$

FIG: 4 METAL COMPLEXES OF FURFURALDEHYDE AND THIOPHENE-2 CARBOXYALDEHYDE –VINYL ANILINE

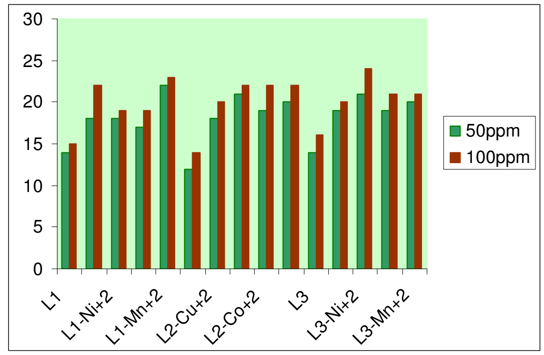


FIG: 5 INHIBITION ZONE OF S.AUREUS

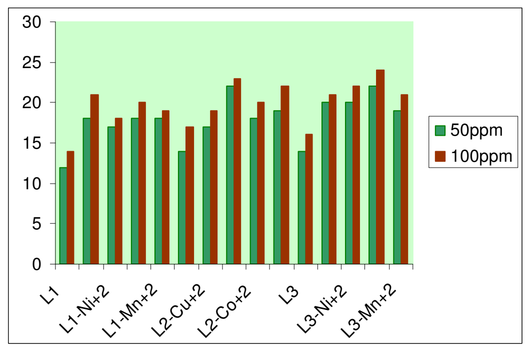


FIG: 6 INHIBITION ZONE OF KLEBSIELLA

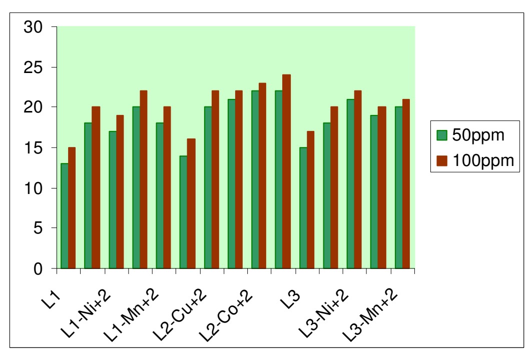


FIG: 7 INHIBITION ZONES OF ENTEROCOCCI

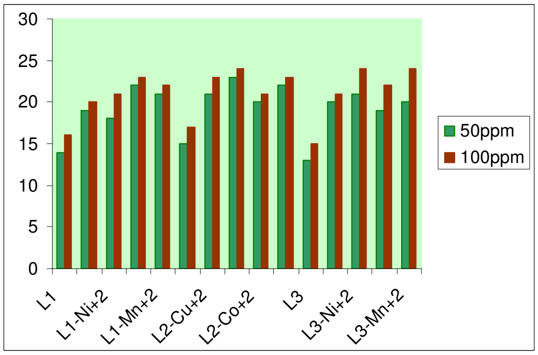


FIG: 8 INHIBITION ZONE OF E.COLI

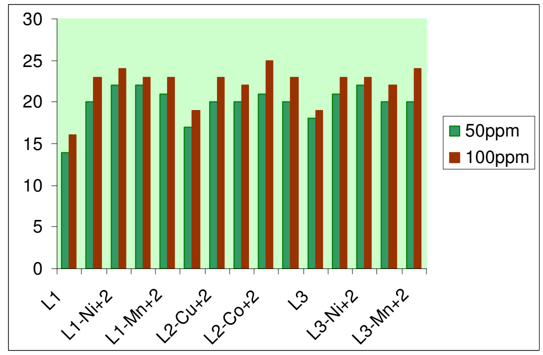


FIG: 10 INHIBITION ZONE OF CANDIDA KRUSEI

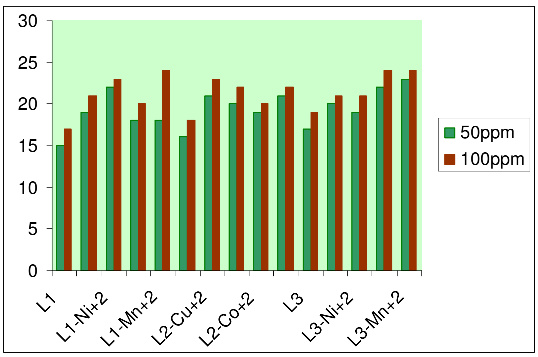


FIG: 9 INHIBITION ZONE OF CANDIDA ALBICANS

M = Co (II), Ni (II), Cu (II) and Mn(II)

Y= Cl

$X = X_1 = L_1 = N$

$X = X_2 = L_2 = O$

$X = X_3 = L_3 = S$

(Scheme 1)

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