

## Biologically active Co(II), Ni(II), Cu(II) and Mn(II) complexes of Schiff bases derived from allyl amine and vinyl aniline

V. UMA\* and PRATIBHA MITTAL

P.G. Department of Chemistry Faculty of Science, Government College, Ajmer (India).

(Received: July 11, 2008; Accepted: September 16, 2008)

### 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  $[M(L)_2X_2]$ , where M=Co (II), Ni (II), Cu (II) and Mn (II), Where, L=monodentate ligand (derived from p-chloro benzaldehyde, p-nitro benzaldehyde or p-methoxy benzaldehyde with vinyl aniline or allyl amine) X=Cl shows a square planar 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:** Metal complexes, Schiff bases, physical, spectral and analytical data.

### INTRODUCTION

Compounds containing imines bases have not only found extensive application in organic synthesis, but several of these molecules display significant biological activity<sup>1-4</sup>. 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<sup>5</sup>, anti-tuberculosis<sup>6</sup>, and antitumour activity<sup>7</sup>. They easily form stable complexes with most transition metal ions. The development of the field of bioinorganic chemistry has increased the interest in Schiff base complexes, since it has been recognized that many of these complexes may serve as models for biologically important species<sup>8-12</sup>. Therefore, some biologically active new metal complexes of the type  $[M(L)_2X_2]$  where M=Co (II), Ni (II), Cu (II) and Mn (II), L= Schiff base (derived from p-chloro benzaldehyde, p-nitro benzaldehyde or p-methoxy benzaldehyde with vinyl aniline or allyl amine),

X= Cl, have been synthesized. Interesting biological properties of these N donor Schiff base ligands compelled to prepare and report on the proceeding paper these new metal complexes 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 Method

All chemicals and solvents used were of analytical grade. All metal (II) salts were used as chlorides. Copper was estimated using ammonium thiocyanate; nickel by dimethyl glyoxime gravimetrically. Cobalt and manganese were estimated by ammonium thiocyanate, mercuric chloride and diammonium hydrogen phosphate respectively. UV-VIS spectra were obtained on a Perkins- Elmer  $\lambda$ -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<sup>-1</sup>. <sup>1</sup>HNMR spectra were recorded in CDCl<sub>3</sub> 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<sup>-3</sup> M solutions of the complexes in DMF were carried out on an Equiptronics model no Eq-660A. Melting points of the ligand and its metal complexes were determined by open capillary method using Sunsim electric melting point apparatus. Molecular Weights were determined by Rast camphor method. Purity of Compounds were checked by TLC using Hexane – water medium.

#### Synthesis of the organic ligand (L<sub>1</sub>-L<sub>3</sub>)

The aldehydes (p-Chloro Benzaldehyde, p-nitro benzaldehyde and p-methoxy benzaldehyde) (1m mol 1.40g, 1.1g, 1.36mL) were dissolved in

absolute ethanol (10mL) was added to the allyl amines (1m mol 1.32mL) dissolved in absolute ethanol (10mL). The mixture was refluxed for 4 h. After 2 h a golden yellow precipitate started to precipitate. After the refluxation, the mixture was allowed to cool for 4h Yellow precipitates were filtered by Buckner funnel on vacuum pump and washed with absolute ethanol (5mL) and re-crystallized from ethanol to give the ligand (table 1).

#### Synthesis of Organic ligand (L<sub>4</sub>-L<sub>6</sub>)

The aldehydes (p-Chloro Benzaldehyde, p-nitro benzaldehyde and p-methoxy benzaldehyde) (1m mol 1.40g, 1.1g, 1.36mL) were dissolved in absolute ethanol (10mL). To this solution vinyl aniline (1m mol 1.22mL) was added. The reaction mixture was refluxed for 4hrs. After cooling, the formed yellow precipitates were collected, filtered by Buckner funnel on vacuum pump and finally washed with absolute ethanol (10mL) and purified by recrystallization from ethanol (Table 2).

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

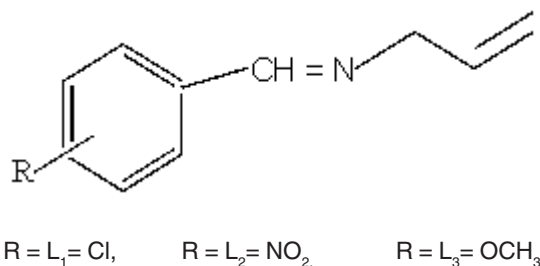
Comp.	Elemental analysis					M.P. (°C)	Condu-ctivity ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>	Mag Mom BM	Molecular weight (Calc.)
	Carbon % (Calc.) Found	Hydrogen % (Calc.) Found	Nitrogen % (Calc.) Found	Metal % (Calc.) Found	Oxygen % (Calc.) Found				
L <sub>1</sub>	(67.03) 66.98	(5.58) 5.52	(7.82) 7.77	-	-	120°C	-	-	(179) 171
L <sub>1</sub> -Cu <sup>+2</sup>	(57.55) 57.49	(4.79) 4.73	(6.71) 6.68	(13.90) 13.87	-	130°C	2.12	1.73	(417) 410
L <sub>1</sub> -Ni <sup>+2</sup>	(57.83) 57.79	(4.81) 4.77	(6.74) 6.69	(13.49) 13.42	-	135°C	2.32	-	(415) 409
L <sub>1</sub> -Co <sup>+2</sup>	(58.11) 58.04	(4.84) 4.81	(6.77) 6.71	(13.07) 12.98	-	140°C	2.09	3.05	(413) 407
L <sub>1</sub> -Mn <sup>+2</sup>	(58.67) 58.60	(4.88) 4.83	(6.84) 6.81	(12.22) 12.20	-	150°C	2.15	5.34	(409) 400
L <sub>2</sub>	(63.15) 63.12	(5.26) 5.21	(14.73) 14.68	-	(16.84) 16.79	110°C	-	-	(190) 185
L <sub>2</sub> -Cu <sup>+2</sup>	(54.79) 54.72	(4.56) 4.53	(12.78) 12.71	(13.24) 13.20	(14.61) 14.58	120°C	2.07	1.73	(438) 432
L <sub>2</sub> -Ni <sup>+2</sup>	(55.04) 54.99	(4.58) 4.54	(12.84) 12.79	(12.84) 12.80	(14.67) 14.60	145°C	2.22	-	(436) 432
L <sub>2</sub> -Co <sup>+2</sup>	(55.29) 55.21	(4.60) 4.55	(12.90) 12.86	(12.44) 12.40	(14.74) 14.69	160°C	2.50	3.07	(434) 430
L <sub>2</sub> -Mn <sup>+2</sup>	(55.81) 55.77	(4.65) 4.60	(13.02) 12.98	(11.62) 11.59	(14.88) 14.82	170°C	2.45	5.35	(430) 427

L <sub>3</sub>	(75.42)	(7.42)	(8.00)	-	(9.14)	130°C	-	-	(175)
	75.39	7.38	7.95		9.06				170
L <sub>3</sub> -Cu <sup>+2</sup>	(64.70)	(6.37)	(6.86)	(14.21)	(7.84)	150°C	2.16	1.73	(408)
	64.62	6.30	6.81	14.19	7.79				399
L <sub>3</sub> -Ni <sup>+2</sup>	(65.02)	(6.40)	(6.89)	(13.79)	(7.88)	170°C	2.37	-	(406)
	64.99	6.34	6.82	13.71	7.81				398
L <sub>3</sub> -Co <sup>+2</sup>	(65.34)	(6.43)	(6.93)	(13.36)	(7.92)	180°C	2.43	3.09	(404)
	65.29	6.39	6.89	13.30	7.88				396
L <sub>3</sub> -Mn <sup>+2</sup>	(66.00)	(6.50)	(7.00)	(12.50)	(8.00)	190°C	2.56	5.32	(400)
	65.98	6.44	6.92	12.42	7.93				395
L <sub>4</sub>	(74.68)	(4.97)	(5.80)	-	-	130°	-	-	(241)
	74.60	4.88	5.78						238
L <sub>4</sub> -Cu <sup>+2</sup>	(66.54)	(4.43)	(5.17)	(10.7)	-	140°	2.45	1.73	(541)
	66.42	4.38	5.07	10.65					533
L <sub>4</sub> -Ni <sup>+2</sup>	(66.79)	(4.45)	(5.19)	(10.3)	-	150°	2.28	-	(539)
	66.72	4.39	5.10	10.26					533
L <sub>4</sub> -Co <sup>+2</sup>	(67.03)	(4.47)	(5.21)	(10.0)	-	160°	2.09	3.06	(537)
	66.98	4.41	5.17	9.94					531
L <sub>4</sub> -Mn <sup>+2</sup>	(67.54)	(4.50)	(5.25)	(9.38)	-	180°	3.92	5.31	(533)
	67.49	4.42	5.17	9.32					529
L <sub>5</sub>	(71.42)	(4.76)	(11.11)	-	(12.69)	140°	-	-	(252)
	71.39	4.70	11.06		12.60				249
L <sub>5</sub> -Cu <sup>+2</sup>	(64.05)	(4.27)	(9.96)	(10.3)	(11.38)	170°	3.52	1.75	(562)
	63.99	4.21	9.88	10.27	11.32				558
L <sub>5</sub> -Ni <sup>+2</sup>	(64.28)	(4.28)	(10.00)	(10.00)	(11.42)	190°	3.43	-	(560)
	64.19	4.22	9.95	10.96	11.37				553
L <sub>5</sub> -Co <sup>+2</sup>	(64.51)	(4.30)	(10.03)	(9.67)	(11.46)	200°	3.38	3.24	(558)
	64.47	4.25	9.94	9.61	11.43				552
L <sub>5</sub> -Mn <sup>+2</sup>	(64.98)	(4.33)	(10.10)	(9.02)	(11.55)	210°	3.29	5.30	(554)
	64.91	4.29	10.01	8.99	11.49				550
L <sub>6</sub>	(81.01)	(6.32)	(5.90)	-	(6.75)	150°	-	-	(237)
	79.09	6.28	5.87		6.71				230
L <sub>6</sub> -Cu <sup>+2</sup>	(72.18)	(5.63)	(5.26)	(10.9)	(6.01)	175°	3.78	1.73	(532)
	72.08	5.59	5.21	10.87	5.99				529
L <sub>6</sub> -Ni <sup>+2</sup>	(72.45)	(5.66)	(5.28)	(10.56)	(6.03)	185°	2.95	-	(530)
	72.40	5.62	5.20	10.52	5.96				528
L <sub>6</sub> -Co <sup>+2</sup>	(72.72)	(5.68)	(5.30)	(10.22)	(6.06)	215°	3.22	3.09	(528)
	72.66	5.63	5.25	10.19	5.94				522
L <sub>6</sub> -Mn <sup>+2</sup>	(73.28)	(5.72)	(5.34)	(9.54)	(6.10)	220°	3.34	5.33	(524)
	73.22	5.68	5.30	9.49	6.01				519

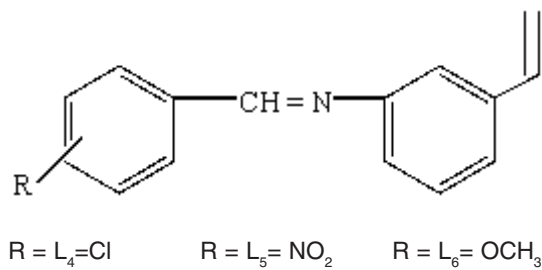
### Synthesis of metal complexes

Warm ethanol solutions (20mL) of the respective Schiff bases (L<sub>1</sub>-L<sub>6</sub>) (0.002M) were added to a magnetically stirred solution of the metal (II) salts (0.001M) in ethanol (25mL). At pH 6.0 the mixture was refluxed for 1h and cooled to room temperature. On cooling, precipitates of metal

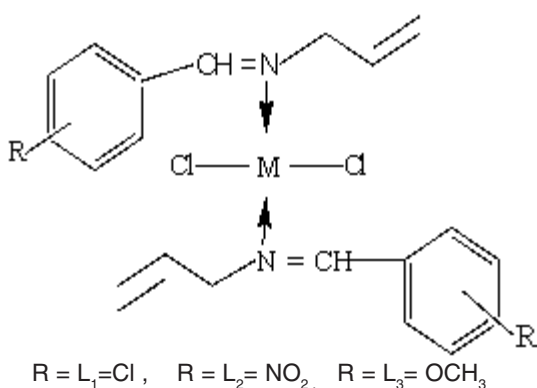
complexes were formed, which were filtered from Buckner funnel, washed with ethanol and dried. Recrystallization in aqueous ethanol (30:70) gave the metal complex. All other metal complexes (scheme-1) were prepared respectively following the same method. Analytical data of Schiff bases and their metal complexes are given in Table 1 & 2.



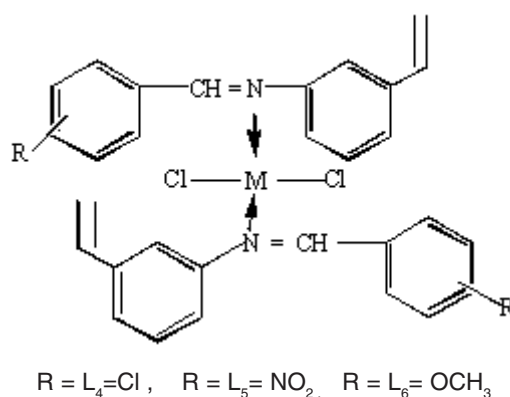
**Fig. 1: Structure of the Schiff bases ( $L_1$ - $L_3$ )**



**Fig. 2: Structure of the Schiff bases ( $L_4$ - $L_6$ )**



**Fig. 3: Metal complexes of schiff bases derived from substituted benzaldehyde & allyl amine**



**Fig. 4: Metal complexes of schiff bases derived from substituted Benzaldehyde & vinyl aniline**

### Antibacterial studies

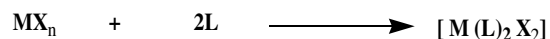
The synthesized metal complexes and Schiff base ligands were screened for their antibacterial and antifungal activity against pathogenic bacterial species, like- *Escherichia coli*, *Staphylococcus aureus*, *Klebsiella* and *Pseudomonas* and fungal species like-*Candida albicans* and *Candida krusei*.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

## RESULTS AND DISCUSSION

### Physical properties

These complexes are air and moisture stable, intensely coloured, amorphous solids which decomposes above 130°C. 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 (2-5ohm<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>) indicating their non electrolytic nature<sup>16</sup>.



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

L =  $L_1$  -  $L_6$

X = Cl

### I.R. spectra

The IR spectra of the Schiff bases indicated that stretching vibrations due to the  $\nu(\text{C}=\text{O})$  and  $\nu(\text{NH}_2)$  functions at 1735cm<sup>-1</sup> and 3420cm<sup>-1</sup>, which were found to be in parent compounds (p-chloro benzaldehyde, p-nitro benzaldehyde and p-methoxy benzaldehyde, or allyl amine and vinyl aniline), disappeared in the spectra of Schiff bases and, instead strong new bands appeared at 1575-1625cm<sup>-1</sup> assigned to the azomethine  $\nu(\text{CH}=\text{N})$  linkage. It however, suggested

that the amino and aldehyde moieties of the starting reagents no more existed and converted into the Schiff base compounds showing, in turn, the azomethine linkage  $\nu(\text{CH}=\text{N})$  (fig.1 and 2).

The comparison of the IR spectra of the Schiff bases and their metal complexes (table-3,4) further indicated that the Schiff bases were coordinated to the metal atom from mainly one donor sites hence, acting in a monodentate manner. The band originally appearing at  $1575\text{-}1625\text{cm}^{-1}$  in the spectra of ligand  $L_1\text{-}L_6$  respectively due to the

azomethine shifted to lower frequency by  $10\text{-}15\text{cm}^{-1}$  suggesting<sup>17</sup> the participation of the azomethine nitrogen in complexation. A further evidence of the coordination of the Schiff bases with the metal atom was shown by the appearance of weak low frequency new bands at  $545\text{-}655\text{cm}^{-1}$  assigned<sup>18</sup> to the metal-nitrogen  $\nu(\text{M-N})$ . 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 and allyl amine moieties).

**Table 2 : Characteristic IR and <sup>1</sup>H-NMR spectral data of the ligands (derived from allyl amine) and their metal complexes**

Compounds	I.R. spectracm <sup>-1</sup>			<sup>1</sup> H-NMR. spectrappm			U.V. spectranm	
	$\nu(\text{M-N})$	$\nu(\text{C=N})$	$\nu(\text{Ar-H})$	$\delta(\text{-CH=CH})$	$\delta(\text{Ar-H})$	$\delta(\text{HC=N})$	-C=C-	(-C=N)
L <sub>1</sub>	-	1595	3005	5.27	6.18 -7.2	7.64	280	360
L <sub>1</sub> -Cu <sup>+2</sup>	560	1589	2989	5.17	6.55 -7.0	6.60	280	355
L <sub>1</sub> -Ni <sup>+2</sup>	545	1577	2980	5.02	6.52-6.9	6.58	280	345
L <sub>1</sub> -Co <sup>+2</sup>	535	1568	2972	4.92	6.45 -6.8	6.45	280	342
L <sub>1</sub> -Mn <sup>+2</sup>	532	1565	2965	4.85	6.35 -6.7	6.32	280	340
L <sub>2</sub>	-	1590	3002	5.20	6.10-7.2	7.60	290	370
L <sub>2</sub> -Cu <sup>+2</sup>	558	1588	2996	5.17	6.25-7.0	6.89	290	368
L <sub>2</sub> -Ni <sup>+2</sup>	568	1578	2985	5.11	6.22-6.9	6.83	290	363
L <sub>2</sub> -Co <sup>+2</sup>	562	1560	2888	5.08	6.27-6.8	6.77	290	355
L <sub>2</sub> -Mn <sup>+2</sup>	532	1500	2882	5.02	6.32-6.9	6.68	290	350
L <sub>3</sub>	-	1592	2998	5.22	6.2-7.01	7.62	295	365
L <sub>3</sub> -Cu <sup>+2</sup>	553	1575	2991	5.18	6.34-6.8	6.95	295	360
L <sub>3</sub> -Ni <sup>+2</sup>	560	1566	2983	5.07	6.42-6.7	6.88	295	358
L <sub>3</sub> -Co <sup>+2</sup>	565	1555	2977	5.01	6.44-6.7	6.80	295	349
L <sub>3</sub> -Mn <sup>+2</sup>	570	1549	2970	4.99	6.5-6.68	6.75	295	344
L <sub>4</sub>	-	1622	3015	5.80	6.58-7.3	7.71	300	378
L <sub>4</sub> -Cu <sup>+2</sup>	570	1620	3002	5.60	6.52-7.1	6.68	300	370
L <sub>4</sub> -Ni <sup>+2</sup>	565	1618	2899	5.45	6.48-7.0	6.58	300	365
L <sub>4</sub> -Co <sup>+2</sup>	555	1614	2878	5.32	6.38-6.9	6.48	300	360
L <sub>4</sub> -Mn <sup>+2</sup>	545	1600	2871	5.28	6.35-6.8	6.38	300	358
L <sub>5</sub>	-	1612	3010	5.76	6.68-7.3	7.75	320	380
L <sub>5</sub> -Cu <sup>+2</sup>	578	1610	3005	5.72	6.62-7.1	6.88	320	378
L <sub>5</sub> -Ni <sup>+2</sup>	570	1598	2998	5.65	6.58-7.0	6.80	320	370
L <sub>5</sub> -Co <sup>+2</sup>	565	1593	2992	5.63	6.52-7.1	6.78	320	368
L <sub>5</sub> -Mn <sup>+2</sup>	563	1590	2989	5.60	6.49-6.9	6.68	320	360
L <sub>6</sub>	-	1625	3008	5.74	6.60-7.0	7.73	320	380
L <sub>6</sub> -Cu <sup>+2</sup>	580	1617	2990	5.68	6.55-6.9	6.99	340	376
L <sub>6</sub> -Ni <sup>+2</sup>	576	1606	2988	5.64	6.5-6.98	6.87	340	372
L <sub>6</sub> -Co <sup>+2</sup>	573	1589	2983	5.60	6.45-6.9	6.84	340	366
L <sub>6</sub> -Mn <sup>+2</sup>	570	1582	2978	5.58	6.4-6.88	6.77	340	364

**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 (3.1-3.3BM) indicative of three unpaired electrons per Co (II) ion in a square planar environment<sup>19</sup>. The Cu (II) and Mn (II) complexes showed  $\mu_{\text{eff}}$  values

1.73 and 5.31BM corresponding to one and five unpaired electrons respectively in a square planar configuration.

The UV-VIS spectrum of the solid ligands  $L_1$ -  $L_6$  (table-3, 4) showed two bands at 270-300 nm and 350-380 nm respectively. The first band would be assigned to  $\pi$ -  $\pi^*$  transition within the aromatic ring. The second band would be due to  $n$ - $\pi^*$  transition within the  $-C=N$  group.

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

Compounds	Micro-organisms							
	<i>Staphylococcus aureus</i>		<i>Klebsiella</i>		<i>Enterococci</i>		<i>E.coli</i>	
	50ppm	100ppm	50ppm	100ppm	50ppm	100ppm	50ppm	100ppm
$L_1$	16	18	17	19	16	18	17	19
$L_1$ -Cu <sup>+2</sup>	18	22	18	21	19	25	19	22
$L_1$ -Ni <sup>+2</sup>	18	21	17	24	19	24	19	23
$L_1$ -Mn <sup>+2</sup>	19	22	16	23	20	26	22	26
$L_1$ -Co <sup>+2</sup>	22	23	17	25	19	23	19	23
$L_2$	17	19	16	18	18	20	17	19
$L_2$ -Cu <sup>+2</sup>	16	22	22	23	21	22	23	24
$L_2$ -Ni <sup>+2</sup>	17	23	19	25	22	23	20	21
$L_2$ -Co <sup>+2</sup>	18	25	19	24	22	24	22	23
$L_2$ -Mn <sup>+2</sup>	19	24	18	20	20	27	20	24
$L_3$	18	19	16	19	17	20	16	20
$L_3$ -Cu <sup>+2</sup>	19	21	19	23	19	23	19	23
$L_3$ -Ni <sup>+2</sup>	20	22	18	24	19	25	20	21
$L_3$ -Co <sup>+2</sup>	21	23	19	25	19	22	21	22
$L_3$ -Mn <sup>+2</sup>	22	25	19	22	18	25	22	23
$L_4$	15	19	15	17	17	20	15	19
$L_4$ -Cu <sup>+2</sup>	20	22	19	22	19	22	18	21
$L_4$ -Ni <sup>+2</sup>	19	23	18	21	20	23	19	22
$L_4$ -Co <sup>+2</sup>	19	24	19	24	20	24	22	25
$L_4$ -Mn <sup>+2</sup>	19	22	20	25	21	26	19	26
$L_5$	16	19	16	19	18	19	16	20
$L_5$ -Cu <sup>+2</sup>	18	20	19	23	19	20	18	21
$L_5$ -Ni <sup>+2</sup>	19	22	20	24	19	24	21	22
$L_5$ -Co <sup>+2</sup>	20	21	20	23	20	23	20	26
$L_5$ -Mn <sup>+2</sup>	19	22	19	25	21	23	19	24
$L_6$	17	19	17	19	16	19	17	20
$L_6$ -Cu <sup>+2</sup>	19	22	19	23	20	27	19	23
$L_6$ -Ni <sup>+2</sup>	20	23	20	24	19	21	21	27
$L_6$ -Co <sup>+2</sup>	19	22	21	25	22	24	19	24
$L_6$ -Mn <sup>+2</sup>	20	23	19	24	22	25	20	25
*Impinam	-	-	16	25	-	-	17	26
*Linezolid	17	25	-	-	18	27	-	-

\* Standard controls

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

Comps	Microorganisms			
	<i>Candida albicans</i>		<i>Candida krusei</i>	
	50ppm	100ppm	50ppm	100ppm
L <sub>1</sub>	18	19	16	19
L <sub>1</sub> -Cu <sup>+2</sup>	18	22	18	21
L <sub>1</sub> -Ni <sup>+2</sup>	19	20	21	22
L <sub>1</sub> -Mn <sup>+2</sup>	17	19	20	23
L <sub>1</sub> -Co <sup>+2</sup>	22	26	22	26
L <sub>2</sub>	16	18	17	19
L <sub>2</sub> -Cu <sup>+2</sup>	18	24	22	23
L <sub>2</sub> -Ni <sup>+2</sup>	21	23	19	25
L <sub>2</sub> -Co <sup>+2</sup>	20	22	20	22
L <sub>2</sub> -Mn <sup>+2</sup>	19	20	21	24
L <sub>3</sub>	13	15	14	15
L <sub>3</sub> -Cu <sup>+2</sup>	17	19	18	20
L <sub>3</sub> -Ni <sup>+2</sup>	18	25	19	22
L <sub>3</sub> -Co <sup>+2</sup>	21	26	18	23
L <sub>3</sub> -Mn <sup>+2</sup>	18	24	17	25
L <sub>4</sub>	13	14	15	17
L <sub>4</sub> -Cu <sup>+2</sup>	16	20	19	20
L <sub>4</sub> -Ni <sup>+2</sup>	17	19	18	21
L <sub>4</sub> -Co <sup>+2</sup>	20	22	22	23
L <sub>4</sub> -Mn <sup>+2</sup>	18	20	17	20
L <sub>5</sub>	15	16	14	18
L <sub>5</sub> -Cu <sup>+2</sup>	21	22	23	24
L <sub>5</sub> -Ni <sup>+2</sup>	22	23	20	21
L <sub>5</sub> -Co <sup>+2</sup>	22	24	22	23
L <sub>5</sub> -Mn <sup>+2</sup>	17	19	20	21
L <sub>6</sub>	13	15	11	15
L <sub>6</sub> -Cu <sup>+2</sup>	15	18	16	19
L <sub>6</sub> -Ni <sup>+2</sup>	19	20	20	21
L <sub>6</sub> -Co <sup>+2</sup>	19	21	21	22
L <sub>6</sub> -Mn <sup>+2</sup>	18	20	22	23
*Ampho- tericin-B	19	22	19	23
*Fluconazole20		27	22	28
*Clotrinazole17		26	21	27

The <sup>1</sup>H NMR spectrum (Table 3 & 4) of the ligands L<sub>1</sub>-L<sub>6</sub> in deuterated DMSO-d<sub>6</sub> showed signal at 7.64 and 7.71 ppm corresponding to the -CH=N group respectively. Like IR spectra, the <sup>1</sup>H NMR spectra of the metal complexes of ligands L<sub>1</sub>-L<sub>6</sub> differ from the spectra of Schiff bases due to coordination via the nitrogen atom of azomethine group (Table 3 & 4).

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

#### Antibacterial activity

The title Schiff bases and their Co (II), Ni (II), Cu (II) and Mn (II) metal complexes were evaluated for their antibacterial and antifungal activity against bacterial species like- *Escherichia coli*, *Staphylococcus aureus*, *Klebsiella* and *Pseudomonas* 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<sup>18-20</sup>. 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. 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 complexation dominantly affects the overall biological behaviour of the compounds, which are potent against bacterial and fungal strains.

#### ACKNOWLEDGEMENTS

We are grateful to Principal, Head Department of Chemistry, Government College, Ajmer for encouragement. We also thank the Regional Sophisticated Instrumentation Centre (RSIC), Central Drug Research Institute (CDRI) Lucknow, for providing Spectral Analysis, and micro analytical data. We are also grateful to Microbiology department of J.L.N. Medical College, Ajmer for providing all facilities and support in biological activity.

## REFERENCES

- Miyaura, N.; Suzuki, A. *Chem. Rev.* **95**: 2457 (1995).
- Baleizno, C.; Gigante, B; Garcia, H; Corma, A. *J.Catal.* **221**: 77 (2004).
- M.Bandini, P.G. Cozzi and A.Umani-Ronichi, *Chem. comun.* 919 (2002).
- L.Canali and D.C. Sherrington, *Chem. Soc. Rev.* **28**, 85 (1999).
- Chohan, Z.H.; Sheazi, S.K.A. synthesis and characterization of some Co (II) and Ni(II) complexes with nicolinyl hydrazine derivatives and their biological role of metal and anions ( $\text{SO}_4^{-2}$ ,  $\text{NO}_3$ ,  $\text{C}_2\text{O}_4^{-2}$  and  $\text{CH}_3\text{CO}_2$ ) on the antibacterial properties. *Synth. React. Inorg. Met.-Org. Chem* **29**: 105 (1999).
- Jayabalakrishnan, C.; Natarajan. K. synthesis, characterization and biological activities of ruthenium (II) carbonyl complexes containing bifunctional tridentate Schiff bases. *Synth.react. inorg.met.-org. chem* **30**: 1023 (1999).
- Jeeworth, T.; Wah, H. L.K.; bhoen, M.G.; Ghoorhoo. D.; Babooram, K. synthesis and antibacterial/ catalytic properties of Schiff bases and Schiff base metal complexes derived from 2, 3-diaminopyridine. *Synth. React. Inorg. Met.-org chem.* **30**: 1023 (2000).
- Dharmraj, N.; Viswanathamurti, P.; Natarajan.K Ruthenium (II) complexes containing bidentate Schiff bases and their antifungal activity. *Transit. Metal Chem.* **26**: 105 (2001).
- Colins, C.H.; Lyne, P.M. In *Microbial methods*; university Park Press; Baltimore, (1970).
- Savanini, L; Chiasserini, L; Gaeta, A.; C. Pellerno. Synthesis and anti- tubercular evaluation of 4-quinolyhydrazones. *Bioorg. Med. Chem* **10**: 2193 (2002).
- Tarcerro, J.M.; Matilla, A.; Sanjuan, M.A.; Moreno, C.F.; Martin, J.D.; Walmsley, J.A. *Inorg. Chem. Acta* **342**: 77(2003).
- Milvoic, N.M.; Dutca, L.M.; Kostic, N.M. *Inorg. Chem.* **42**: 4036 (2003).
- A.I. Vogel "practical organic chemistry including Quantitative org. analysis" 3<sup>rd</sup> Ed. P.854. Longmans London. (1956).
- A.I. Vogel "A text book of Quantitative inorg analysis" Longmans London.(1971).
- Singh, Agarwal, R.K.; L.; Sharma, D.K.; Singh, R. Synthesis, Spectral and thermal investigations of some oxovanadium (IV) complexes of isonicotinic acid hydrazide. *Turk J. Chem.* **29**: 309 (2005).
- Mane V.G, Patange V.N, Arbad B.R, Synth, structure and thermal characterization and antifungal study of Mn (II), Fe (III), Co (II) and Cu(II) complexes of N,O donor ligands, *J. Ind. Chem. Soc.*, **84**: 1091 (2007).
- M. Yongxiang, Z. Zhengzhi, M. Yun and Z. Gang, *Inorg. Chem. Acta*, **165**: 185 (1989).
- K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", 2<sup>nd</sup> Ed, Wiley Interscience, New York, (1970).
- Ferrari, M.B. Capacchi, S.; Pelosi, G.; Reffo, G.; Tarasconi, P.; Alberlini, R.; Pinelli, S.; Lunghi, P. Synthesis, Structural characterization and biological activity of helicon thiosemicarbazone monohydrate and a copper (II) complex of salicaldehyde thiosemicarbazone. *Inorg. Chem. Acta* **286**: 134 (1999).
- Raman N, Dhaweethu Raja J and Saktivel A, Synth, spectral characterization of Schiff base transition metal complexes: DNA cleavage and antimicrobial activity studies, *J. Chem Sci.*, **119**(4): 303-310 (2007).
- Elo, H.; Sunila, L.; Lumne, P. Studies on the acute toxicity of antineoplastic metal chelate. Trans-bis (salicyldoximate) copper (II) in rats. *Inorg. Chem. Acta* **136**: 61 (1987).
- Ali, M.A.; Kabir, M.H.; Mazimuddin. M.; Majumdar, S.M.H.; Tarafdar, M.T.H.; Akhir, M. Synthesis, characterization and antifungal properties of some four-coordinate nickel (II) and four and five co-ordinate copper (II) complexes containing tridentate thiosemicarbazone and heterocyclic bases. *Indian J. Chem.* **27A**: 1064 (1988).