

Synthesis, characterisation and antimicrobial activity of copper(II) and iron(II) complexes with some Schiff bases

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ABSTRACT

Metal chelates of bivalent transition metal ions, Cu(II) and Fe(II) of composition $[\text{Cu}(\text{L})_2]$ and $[\text{Fe}(\text{L})_2(\text{H}_2\text{O})_2]$ where L=Schiff base, have been synthesized and characterized on the basis of their elemental analysis, conductance measurement and spectral and magnetic studies. The chelates have 1:2 metal:ligand stoichiometry and all chelates are non electrolyte nature. The Schiff bases and their metal complexes were screened for their biological activity against bacteria *Escherichia coli*, *Salmonella typhi*. The copper(II) chelates were found to be much active as compared to their Schiff base ligands. The Fe(II) chelates show poor activity against these bacteria.

Key words: Synthesis, antimicrobial activity copper(II), iron(II) complexes, Schiff bases.

INTRODUCTION

Schiff bases are significant type of ligands which provide a class of compounds having pronounced biological activities¹⁻³. Most of the bidentate or tridentate Schiff bases have structures quite suitable for chelation with metal ion and studies on the chelation tendency of various organic compounds have supported the hypothesis that formation of strain free chelate rings, enhances the biological activity. In recent years, immense work has been carried out on metal complexes with various Schiff bases.

We describe here the preparation and characterization of Cu(II) & Fe(II) complexes with Schiff bases. The Schiff bases were prepared by refluxing salicylaldehyde and 2-hydroxy-1-naphthaldehyde with different 1o-amines in 1:1 molar ratio. The characterization of metal complexes was done on the basis of elemental analyses molar conductance melting point determination, IR spectral, and magnetic studies. The Fe(II) chelates were subjected to Thermogravimetric analytical studies. The Schiff base & their complexes were screened for the biological activity against bacteria *E.coli* & *S.typhi*. The chelates were found to be more active bactericidal as compared to their Schiff bases.

EXPERIMENTAL

Chemicals used were of Analar grade (BDH, Aldrich or Fluka) and purified before use. The metal(II) salts used were in their hydrated form, melting points were recorded by capillary tube method (using Toshniwal melting points apparatus). The elemental analysis and IR spectra of Schiff bases & complexes were recorded at C.D.R.I Lucknow. The Purity of samples was tested by TLC.

Synthesis of Ligand (Schiff Base)

An equimolar mixture of aldehyde and 1o amine in ethanol was refluxed for about 6 hr. on a water bath. The reaction mixture was cooled to room temperature. The Schiff base was separated and collected by filtration it was recrystallized from absolute ethanol.

The respective aldehyde used were -

1. Salicylaldehyde
2. 2-hydroxy-1-naphthaldehyde

The various amines used were:-

1. 4-amino-2-nitro toluene
2. 4-chloro aniline
3. 4-chloro-2-nitro aniline
4. m-nitroaniline
5. p-nitro aniline.

Preparation of Cu(II) and Fe(II) complexes with schiff bases

All the chelates were prepared by following general method. The hot & concentrated solution of ligand in ethanol 30 ml was added a hot ethanolic solution (10 ml) of respective metal(II) chloride (0.002 mol) the reaction mixture was refluxed on a steam bath for 12 hr. The resulting solid coloured complexes were separated by filtration and washed with ethanol and then dried in vacuum over anhydrous calcium chloride in a desiccator.

RESULTS AND DISCUSSION

The analytical data and magnetic moments of complexes are presented in table 1. The elemental analyses for carbon, hydrogen, nitrogen chlorine and gravimetric percentage estimation of metal, indicated that all chelates possess 1:2 metal:ligand stoichiometry.

The molar conductance values (6.0 to $9.0 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) of 10^{-3} M solutions of metal complexes in DMSO indicate that all the complexes are non electrolyte in nature^{4,5} in DMSO. The magnetic moment of the Cu(II) complexes are 1.85 to 1.95 B.M. corresponding to one unpaired electron of d9 system⁶ of square planar geometry Fe(II) complexes magnetic moment values 5.12 to 5.62 B.M. correspond to the high spin octahedral complexes⁷

IR spectrum of the ligand shows a medium band at $2800\text{-}2895 \text{ cm}^{-1}$ due to intramolecular hydrogen bonded OH group. This band is absent in the spectra of the complexes, indicating the dissociation of the phenolic proton on complexation and involvement of phenolic anionic oxygen in coordination.

Moreover, the strong band at $1280\text{-}1285 \text{ cm}^{-1}$ due to C-O (phenolic) in the ligand has been shifted to the $1291\text{-}1320 \text{ cm}^{-1}$ in the spectra of complexes.

The band due to C=N 8,9 is observed in the schiff bases at $1596\text{-}1629 \text{ cm}^{-1}$ shows a negative shift $39\text{-}74 \text{ cm}^{-1}$ and appeared in the region $1522\text{-}1590 \text{ cm}^{-1}$ in all the complexes indicating the coordination through azomethine nitrogen atom¹⁰.

Thus the ligand schiff base functions as bidentate one coordinating with the metal ion through phenolic oxygen 11 and azomethine nitrogen atom. The new bands in the complexes at $406\text{-}429 \text{ cm}^{-1}$ and $460\text{-}508 \text{ cm}^{-1}$ have been assigned to M-O 12-13 and M-N respectively

In all chelate of iron(II) with schiff bases, there appear some new bands in spectrum of complexes. These broad bands appear at $3000\text{-}3400 \text{ cm}^{-1}$ which may be attributed to $\nu(\text{OH})$ of coordinated water molecules^{14,15} presence of two coordinated water molecules have also been confirmed by TGA.

Zone of Inhibition (mm)				
S. No.	Compd	<i>S. aureus</i> ppm	<i>B. subtilis</i> ppm	<i>E. coli</i> ppm
1	C ₁₉ H ₁₄ O ₂	06	04	06
2	C ₁₉ H ₁₃ O ₂ Br	12	10	11
3	C ₁₉ H ₁₃ O ₂ Cl	22	15	16
4	C ₂₁ H ₁₆ O ₂	17	12	14
5	C ₁₆ H ₁₂ ON ₂	07	10	11
6	C ₁₆ H ₁₁ ON ₂ Br	17	10	12
7	C ₁₆ H ₁₁ ON ₂ Cl	08	02	00
8	C ₁₈ H ₁₄ ON ₂	22	12	13

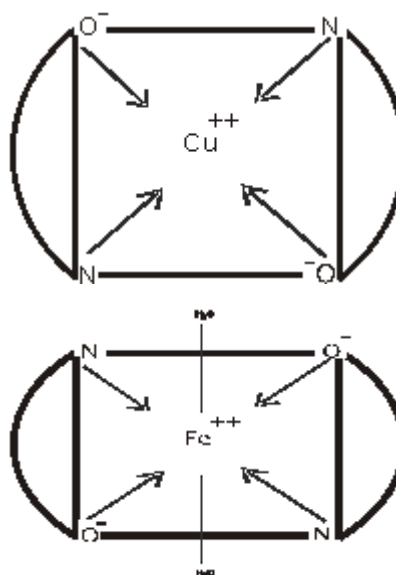


Table 1: Analytical, magnetic and molar conductance of the Schiff bases and their complexes

S. No.	Compound Mol.wt.	Colour	Decomposition temp °C	Molar Cond. $\Omega\text{m cm}^2\text{ mol}^{-1}$	μ_{eff} (B.M)	% Elemental Analyses				
						Metals	C	H	N	Cl
1	L_I ($C_{14}H_{12}N_2O_3$) 256	Lightyellow	110	-	-	-	64.86 (65.63)	3.98 (4.69)	10.12 (10.94)	-
a	$[Cu(L_I)_2]$ 573.48	Blackish	165	8.3	1.85	10.88 (11.06)	58.11 (58.58)	3.09 (3.83)	9.12 (9.76)	-
b	$[Fe(L_I)_2(H_2O)_2]$ 602	RedishYellow	>200	9.0	5.13	8.81 (9.30)	55.12 (55.81)	3.98 (4.32)	8.89 (9.30)	-
2	L_{II} ($C_{13}H_{10}NOCl$) 231.5	Orange	185	-	-	-	66.56 (67.38)	4.11 (4.31)	5.92 (6.04)	14.98 (15.33)
a	$[Cu(L_{II})_2]$ 524.48	Purplebrown	>200	6.0	1.95	11.92 (12.10)	58.98 (59.48)	3.11 (3.43)	4.96 (5.33)	13.06 (13.53)
b	$[Fe(L_{II})_2(H_2O)_2]$ 553	Redishbrown	190	8.0	5.18	9.79 (10.12)	55.99 (56.41)	3.66 (3.98)	4.56 (5.06)	12.22 (12.83)
3	L_{III} ($C_{13}H_9N_2O_3Cl$) 276.5	Brown	115	-	-	-	55.88 (56.41)	3.12 (3.25)	9.96 (10.12)	12.11 (12.84)
a	$[Cu(L_{III})_2]$ 614.48	Darkbrown	160	8.0	1.85	9.86 (10.33)	50.11 (50.77)	2.11 (2.60)	8.88 (9.11)	10.98 (11.55)
b	$[Fe(L_{III})_2(H_2O)_2]$ 643	Red	195	9.0	5.21	8.10 (8.70)	48.06 (48.52)	2.93 (3.11)	8.22 (8.70)	10.68 (11.04)
4	L_{IV} ($C_{13}H_{10}N_2O_3$) 242	Darkbrown	124	-	-	-	63.12 (64.46)	4.02 (4.13)	10.86 (11.57)	-
a	$[Cu(L_{IV})_2]$ 545.48	Yellow	170	8.0	1.91	11.09 (11.63)	56.94 (57.19)	2.92 (3.29)	9.83 (10.26)	-

Table 1. Continue

b	$[\text{Fe}(\text{L}_{\text{vi}})_2(\text{H}_2\text{O})_2]$ 574	RedishYellow	190	7.0	5.15	9.12 (9.75)	53.93 (54.35)	2.93 (3.83)	9.12 (9.75)	-
5	$\text{L}_{\text{v}}(\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_3)$ 242	Brown	130	-	-	-	63.12 (64.46)	4.02 (4.13)	10.98 (11.57)	-
a	$[\text{Cu}(\text{L}_{\text{v}})_2]$ 545,48	Darkpurple	165	6.0	1.86	11.04 (11.63)	57.20 (57.19)	2.86 (3.29)	9.56 (10.26)	-
b	$[\text{Fe}(\text{L}_{\text{v}})_2(\text{H}_2\text{O})_2]$ 574	Darkred	180	8.0	5.22	9.22 (9.75)	53.85 (54.35)	2.98 (3.83)	9.00 (9.75)	-
6	$\text{L}_{\text{vi}}(\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3)$ 292	Yellowbrown	145	-	-	-	68.56 (69.86)	3.98 (4.11)	9.16 (9.59)	-
a	$[\text{Cu}(\text{L}_{\text{v}})_2]$ 645,48	Goldenyellow	185	6.0	1.93	9.58 (9.83)	62.99 (63.20)	2.92 (3.40)	8.40 (8.67)	-
b	$[\text{Fe}(\text{L}_{\text{vi}})_2(\text{H}_2\text{O})_2]$ 674	Darkbrown	190	9.0	5.62	8.11 (8.30)	60.21 (60.53)	3.46 (3.86)	8.21 (8.30)	-

L_1 = Salicylaldehyde-4-amino-2-nitro toluene ($\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_3$)

L_{iii} = Salicylaldehyde-4-chloro-2-nitro anilene ($\text{C}_{13}\text{H}_9\text{N}_2\text{O}_3\text{Cl}$)

L_{v} = Salicylaldehyde-4-nitro anilene ($\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_3$)

L_{ii} = Salicylaldehyde-4-chloro anilene ($\text{C}_{13}\text{H}_{10}\text{NOCl}$)

L_{iv} = Salicylaldehyde-3-nitro anilene ($\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_3$)

L_{vi} = 2-hydroxy-1-naphthaldehyde-3-nitro anilene ($\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3$)

The melting points of the chalcones and their amino derivatives were determined. These were characterised by the elemental analyses and recording of IR and NMR spectra (Table 1 & 2).

Biological evaluation

The antibacterial activity was evaluated by Cup Plate method against *staphylococcus aureus*, *Bacillus subtilis* and *Escherichia coli* at a concentration of 100 g/ml in agar medium. Norfloxin was used as standard reference drug.

Antimicrobial activity

The in vitro biological screening effect of the investigated compounds were tested against bacteria *Salmonella typhi* and *E.coli* by the disc diffusion method using agar nutrient as medium and utilising streptomycin as control. The stock solutions were prepared by dissolving the compounds in DMF and all blank disc assays. Paper (6mm) containing the compounds placed on the surface of the nutrient agar plates previously spread with 0.1 ml of overnight culture of micro organisms after 36 hr. of incubation

Table 2: IR Spectra data (cm⁻¹)

S. No.	Compound Mol.wt.	v(OH)	v(C=N)	(OH)H. bonded	C-O phenolic	v(M-O)	v(M-N)
1	L _i (C ₁₄ H ₁₂ N ₂ O ₃) 256		1600.5	2895	1280	-	-
a	[Cu(L _i) ₂] 573.48		1590	-	1297	429	460
b	[Fe(L _i) ₂ (H ₂ O) ₂] 602	3300	1580	-	1291	420	464
2	L _{ii} (C ₁₃ H ₁₀ NOCl) 231.5		1596	2800	1281	-	-
a	[Cu(L _{ii}) ₂] 524.48		1522	-	1298	417	465
b	[Fe(L _{ii}) ₂ (H ₂ O) ₂] 553	3000	1590	-	1300	420	491
3	L _{iii} (C ₁₃ H ₉ N ₂ O ₃ Cl) 276.5		1620	2890	1285	-	-
a	[Cu(L _{iii}) ₂] 614.48		1585	-	1320	417	508
b	[Fe(L _{iii}) ₂ (H ₂ O) ₂] 643	3400	1522	-	1298	429	465
4	L _{iv} (C ₁₃ H ₁₀ N ₂ O ₃) 242		1629	2895	1280	-	-
a	[Cu(L _{iv}) ₂] 545.48		1524	-	1297	420	460
b	[Fe(L _{iv}) ₂ (H ₂ O) ₂] 574	3300	1580	-	1300	406	464
5	L _v (C ₁₃ H ₁₀ N ₂ O ₃) 242		1620	2800	1280	-	-
a	[Cu(L _v) ₂] 545.48		1572	-	1291	419	460
b	[Fe(L _v) ₂ (H ₂ O) ₂] 574	3400	1570	-	1297	420	466
6	L _{vi} (C ₁₇ H ₁₂ N ₂ O ₃) 292		1620	2895	1281	-	-
a	[Cu(L _{vi}) ₂] 645.48		1580	-	1300	420	491
b	[Fe(L _{vi}) ₂ (H ₂ O) ₂] 674	3000	1531	-	1320	429	508

Table 3: Zone of Inhibition (mm)

S. no.	Compounds	<i>S.typhi</i>	<i>E.coli</i>
	Standard	22	20
1	L _i (C ₁₄ H ₁₂ N ₂ O ₃) 256	08	10
a	[Cu(L _i) ₂] 573.48	15	12
b	[Fe(L _i) ₂ (H ₂ O) ₂] 602	10	09
2	L _{ii} (C ₁₃ H ₁₀ NOCl) 231.5	06	08
a	[Cu(L _{ii}) ₂] 524.48	14	16
b	[Fe(L _{ii}) ₂ (H ₂ O) ₂] 553	12	10
3	L _{iii} (C ₁₃ H ₉ N ₂ O ₃ Cl) 276.5	07	09
a	[Cu(L _{iii}) ₂] 614.48	16	18
b	[Fe(L _{iii}) ₂ (H ₂ O) ₂] 643	11	13
	Standard	22	20
4	L _{iv} (C ₁₃ H ₁₀ N ₂ O ₃) 242	08	07
a	[Cu(L _{iv}) ₂] 545.48	12	14
b	[Fe(L _{iv}) ₂ (H ₂ O) ₂] 574	03	0
5	L _v (C ₁₃ H ₁₀ N ₂ O ₃) 242	09	06
a	[Cu(L _v) ₂] 545.48	13	15
b	[Fe(L _v) ₂ (H ₂ O) ₂] 574	04	0
6	L _{vi} (C ₁₇ H ₁₂ N ₂ O ₃) 292	08	08
a	[Cu(L _{vi}) ₂] 645.48	15	18
b	[Fe(L _{vi}) ₂ (H ₂ O) ₂] 674	11	18

at 37°C the diameter of inhibition zones was measured and is listed in table-3

Most of the complexes have higher antimicrobial activity than the free ligands. Such increased activity of the metal chelates¹⁶ can be explained on the basis of chelation theory

CONCLUSION

On the basis of elemental analysis, magnetic moments & IR spectral analysis we report tetrahedral geometry for Cu(II) complexes and an octahedral geometry for Fe(II) complexes. The ligand behaves as bidentate, chelating agent coordinating through the deprotonated hydroxyl group and azomethine nitrogen. All the complexes showed enhanced antimicrobial activity as compared to their ligand.

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