

Studies of Fe(II), Mn(II), Cr(II), Ni(II), Co(II) and Cu(II) Complexes with Schiff Base Derived from 2-Amino-4,6-dimethylbenzothiazole and Pyridine-2-aldehyde

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Abstract: As it is proved that the transition metal complexes have drug activities, hence we have synthesized heterocyclic Schiff bases. Six complexes of Co(II), Ni(II), Fe(III), Mn(II), Cr(II) and Cu(II) Schiff bases have been prepared. All ligands and its metal complexes the structures of the complexes have been proposed by analytical data, conductivity measurement, magnetic moment, IR, ¹H NMR spectra and thermal studies. Analytical data confirmed 1:2 (metal:ligand) stoichiometry and the spectral data suggest that all Fe(III), Mn(II), Cr(II), Ni(II) and Co(II) complexes have octahedral geometry where as the Cu(II) metal complex shows the square planar geometry. The molar conductance values of metal complexes suggest their non electrolytic nature. The IR spectral data reveals that the ligand behaves as bidentate with ON donor atoms sequence towards central metal ion. Antibacterial and antifungal activities of ligands and its metal complexes were performed *in vitro* against *E.coli*, *S. typhi*, *S. aureus*, *B. subtilis* and against various fungi like *P.chrysogenum*, *A. niger*, *F. moniliformae*, and *A.Flavus*. The complexes show more activity compare to the ligand.

Keywords: Substituted benzothiazole Schiff bases, Transition metal complexes, Spectral analysis, Antimicrobial activity

Introduction

Hetero donar groups like N, O containing metal complexes of Schiff bases gained importance for more than two decades because of their biological activities¹⁻³, as antibacterial⁴, antifungal⁵, antitumour⁶ and anti-inflammatory activities⁷.

Now a days it is a center of interest that is Schiff bases containing heterocyclic ring as they possesses biological, clinical, medicinal, analytical and pharmacological fields⁸⁻¹⁰. The activity of the benzothiazole Schiff bases enhances by combining with the metal ions. All these review encourages the study of the metal chelates of the substituted benzothiazole transition metal complexes.

Following all these observations of studies and a part of our research we report here the synthesis and structural studies on the transition metal complexes of Co(II), Ni(II), Fe(III), Mn(II), Cr(II) and Cu(II) with Schiff base of benzothiazole (L_3)

Experimental

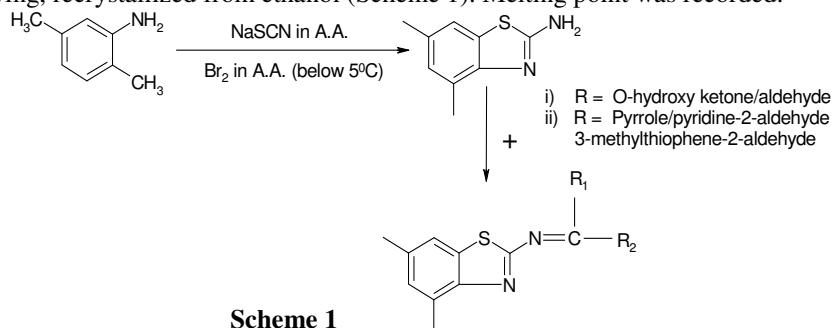
All the melting points were determined in an open capillary tube and are uncorrected completion of the reaction was monitored by thin layer chromatography on precoated sheets of silica gel G. All the reagents used were chemically pure and are of AR grade.

Synthesis of 2-amino-4, 6 dimethylbenzothiazole


Synthesis of 2-amino-4, 6-dimethylbenzothiazole was carried out by the standard method. 0.1 M 2,4-xylylidine(2,4-dimethylaniline) and sodium thiocyanate (0.2 M) in 100 mL glacial acetic acid were mixed together and reaction mixture was cooled to 0 °C temperature. 0.2 M bromine in acetic acid (25 mL) was added to the above solution drop wise and the mixture was stirred till the complete addition of bromine maintaining temperature below 5 °C throughout addition. Stirring was kept continued maintaining temperature below 5 °C for half an hour after addition of bromine is made. The solid thus obtained after complete addition of bromine was filtered on vacuum and then dissolved in hot water. The solution was then treated with very dilute alkali like NaOH for the separation of free amine. The free amine thus obtained was filtered, washed and dried and was recrystallized from ethanol. Observed melting point is 140 °C, yield 80%. It was tested for free NH_2 group.

Synthesis of Schiff Base ligand

Equimolar ethanolic solution of the L_3 (pyridine-2-aldehyde) and 2-amino-4,6-dimethylbenzothiazole were refluxed for 4-5 hours on water-bath and the reaction mixture was poured on ice cold water and the separated solid was collected by filtration, washing and drying, recrystallized from ethanol (Scheme 1). Melting point was recorded.



Scheme 1

S.No.	Compound	Substituents	
		R_1	R_2
1	L_3	H	

Preparation of metal complexes

For the synthesis of all Cu(II), Co(II), Ni(II), Fe(III), Mn(II) and Cr(II) complexes, the respective metal chlorides were used. Ethanolic solutions of Schiff base and respective metal chloride were refluxed in the stoichiometric ratio 1:2. After cooling, the solutions were treated with 10% alcoholic ammonia solution so as to raise the pH up to 5. Then the solid complexes separated in solution were filtered, washed to dry over fused $CaCl_2$ in vacuum desiccators.

Table 1. Analytical data of complexes

S. No.	Mol. Formula	Mol. wt	Colour	M.P./ D.P. °C	Elemental analysis, %				Mol. Cond. mhos cm ² Mol ⁻¹	μ eff. B. M.
					C (Cal) Found	H (Cal) Found	N (Cal) found	Metal (Cal) Found		
1	C ₁₅ H ₁₃ N ₃ S	267	Brown	110	67.41/67.05	4.86/3.96	15.73/14.84	-	-	-
2	Mn(C ₁₅ H ₁₃ SN ₃) ₂ . 2H ₂ O	621	Dull Yellow	>280	(57.97) 57.32	(4.83) 5.24	(13.52) 12.67	(8.20) 8.68	124	5.88
3	Cu(C ₁₅ H ₁₃ SN ₃) ₂	597	Parrot Green	274	(60.30) 59.16	(4.35) 4.56	(14.07) 13.24	(10.63) 9.47	130	1.81
4	Co(C ₁₅ H ₁₃ SN ₃) ₂ . 2H ₂ O	629	Green	272	(57.23) 56.36	(4.76) 4.34	(13.35) 12.23	(9.36) 8.73	118	5.16
5	Ni(C ₁₅ H ₁₃ SN ₃) ₂ . 2H ₂ O	628	Brown	254	(57.32) 56.78	(4.77) 4.98	(13.37) 12.67	(9.34) 9.67	120	3.06
6	Fe(C ₁₅ H ₁₃ SN ₃) ₂ . 2H ₂ O	625	Grey	182	(57.60) 56.34	(4.80) 3.78	(13.44) 13.68	(8.93) 9.12	134	
7	Cr(C ₁₅ H ₁₃ SN ₃) ₂ . 2H ₂ O	622	Green	>280	(57.87) 56.32	(4.82) 4.22	(13.50) 12.79	(8.35) 7.97	122	

Results and Discussion

Magnetic susceptibility measurement of complexes

The magnetic susceptibility values of transition metal complexes were calculated by Guoy balance method results of the magnetic moment of Co(II) complexes are given in Table 1. Co(II) complexes derived from ligand L₃ show magnetic moment in the range 4.82-5.18 B.M at room temperature showing the Octahedral geometry¹¹.

Ni(II) complexes of ligand L₃ show magnetic moment values in the range of 2.72 - 3.18 B.M at room temperature which is given in Table 1 showing octahedral geometry^{12,13}. Magnetic moment of Fe(III) complexes derived from ligands L₃ shows magnetic moment in the range 5.39-5.78 B.M at room temperature showing the octahedral geometry. Mn(II) complexes of the corresponding ligand shows magnetic moment values in the range of 5.92 B.M. at room temperature which is tabulated in table showing octahedral geometry. Cr(II) complexes showed magnetic moment in the range 4.90 B.M at room temperature pointing towards the octahedral geometry

Electronic spectral analysis

The absorption spectra of transition metal complexes can be very well interpreted using ligand field theory (Table 2). The spectra of transition metal complexes have one or more weak absorption due to d-d transition. Electronic spectra of ligand exhibited maxima in the range of 230 nm to 420 nm respectively which can be assigned to n→ π^* transitions of azomethine group. These bands showed blue shift in the complexes of Cu(II), Co(II), Ni(II), Fe(III), Mn(II) and Cr(II) respectively.

For Cu(II) complexes the electronic spectra showed bands in the range 22200 cm⁻¹ to 41700 cm⁻¹ i.e these spectral bands are observed near and above 3500 cm⁻¹ can be assigned to charge transfer transitions. The bands at 34400 cm⁻¹ to 37037 cm⁻¹ are typically characteristic for square-planar geometry for Cu(II) complexes¹⁴⁻¹⁷. The electronic absorption spectra of Co(II) complexes displays the absorption bands in the range of 30,000 to 42,000 cm⁻¹ which can be assigned due to charge transfer transitions¹⁸. The ligand field

parameters like ligand splitting energy ($10Dq$) cm^{-1} , ligand field stabilization energy (LFSE) in K.cal/mole and v_2/v_1 are consistent with the octahedral geometry¹⁹.

The octahedral geometry of Ni(II) complexes shows the absorption bands at 28,000 to 42,000 cm^{-1} which are due to ligand to metal charge transfer to Ni(II) complexes. The spectral features of Fe(III) ions in octahedral surroundings are in accordance with theoretical considerations. Fe(III) complexes showed absorption peaks in the range of 28,000 to 43,000 cm^{-1} which can be again assigned due to charge transfer transitions.

For Mn(II) complexes the electronic spectral bands are observed in the range of 29,000 cm^{-1} to 43,000 cm^{-1} which can be assigned due to charge transfer transitions, whereas for Cr(II) complexes the electronic spectral bands are observed in the range of 30,000 cm^{-1} to 42,000 cm^{-1} which can be assigned due to charge transfer transitions. The medium intensity bands in the range of 34500 cm^{-1} to 43500 cm^{-1} due to Π to Π^* transitions in the ligands remained unchanged in the spectra of most of the complexes.

Table 2. Electronic spectral data of the complexes

Complex code	$\mu_1 \text{cm}^{-1}$	$\mu_2 \text{cm}^{-1}$	μ_2/μ_1	$\beta = \frac{B^1}{B}$	LFSE (Kcal/mole)
Mn – L ₃	37878	43290	1.14	0.547	107.95
Co – L ₃	29416	38753	1.13	0.906	83.8
Ni – L ₃	37735	43290	1.15	0.461	107.5
Fe – L ₃	37878	43478	1.14	0.480	107.95
Cr – L ₃	37735	43103	1.14	0.576	107.5

IR Spectroscopy

In the complexes of ligand²⁷ the characteristic band at 3143 cm^{-1} for 2-pyridyl nucleus shows considerable downward shift in the band value there by showing the pyridine nitrogen's involvement in the coordination. Thus the ligand L₃ is coordinating through thiazole ring nitrogen and pyridine ring nitrogen²⁰⁻²².

The bands at 825-840 cm^{-1} and 740-756 cm^{-1} in almost all metal complexes can be assigned due to C-S-C thiazole vibrations^{23,24}. The appearance of non-ligand band at 555-600 cm^{-1} can be attributed to M-N band²⁵⁻²⁷ where as the non-ligand band at 462-491 cm^{-1} can be attributed to M-O band³⁸. The appearance of these new bands of M-N and M-O vibrations supports the involvement of N and O atoms in complexation with metal ions.

The band in the region of 3400-3550 cm^{-1} for Co(II), Ni(II), Fe(III), Mn(II) and Cr(II) complexes can be assigned for coordinated water molecules^{20,29}. This was evidenced by the formation of new bonds in the range 1120-1180 cm^{-1} corresponding to $\delta(\text{-OH})$ of the coordination water³⁰ reinforcing the presence of two coordinated water molecules in the compound, which is well supported by the thermo analytical data of these complexes which show appreciable thermal stability. In case of Cu(II) complexes the band appears nearly in the same region but it is supported to be because of surface water (hydrated water)^{29,31-34}. Again the thermograms and thermo analytical data supports this very fact strongly.

¹H NMR Spectra

¹H NMR spectra of the transition complexes were recorded, unfortunately, however due to the presence of a metal ion, proton resonance was not affected and one could observe only broad peaks indicating the formation of the complex.

ESR Spectroscopy

It is observed from ESR spectrum Cu(II) complexes that there is a single line resulting in the interaction of unpaired electron present in Cu(II) nucleus. The Table 3 reveals that the ' g_{av} ' values less than 2.3 which suggest the existence of sufficient covalent nature of metal ligand bond. Also the 'G' values less than 4 indicate that the Cu(II) complexes are strong field ligands. [Cu (L₃)₂] complex shows anisotropy.

The ESR spectrum of Mn(II) complexes of ligands [Mn(L₃)₂], shows single line resulting in the interaction of unpaired electron present in Mn(II) nucleus. Table 3 reveals that the g_{av} values are less than 2.3 which suggest the existence of sufficient covalent nature of metal ligand bond. Also the 'G' values less than 4 indicates that the Mn(II) complexes are strong field ligands. All the complexes show anisotropy.

The hyperfine splitting in positive amplitude and negative amplitude at respective magnetic field for each spectrum gave rise to two 'g' values which are less than 2.3 suggests the covalent nature of complexes³⁵.

Table 3. ESR spectral values of Cu(II) and Mn(II) complexes

Complex code	$g_{ }$	g_{\perp}	g_{av}	G Axial symmetry parameter	m_{eff} BM from Gouy Balance
Cu(L ₃) ₂	1.870	1.821	1.837	0.72	1.74
Mn(L ₃) ₂	1.669	1.747	1.747	0.765	5.88

X-Ray crystallography

X-ray diffractograms of the metal complexes under investigation show good intense peaks indicating high crystallinity. The results obtained from computational data gave lattice parameter values as Lattice parameter values as $a = b \neq c$ and $\alpha = \beta = \gamma$ which suggest tetragonal crystal structure of P type lattice for copper complex of ligand L₄ and cobalt complex of ligand L₃.

Lattice parameter values as $a \neq b \neq c$ and $\alpha = \gamma \neq \beta$ which suggest monoclinic crystal structure of P type lattice for copper complex of ligand L₃ and chromium complex of ligand.

Sample Name	:	Cu- L₃		
Crystal system	:	Monoclinic	Lattice Type	: P
Lattice Parameter	:	a= 8.12	b= 4.88	c= 7.72
Lattice Parameter	:	α = 90	β = 94.63	γ = 90
Radiation	:	Cu	Wave Length	: 1.540598(Å)
2Theta start	:	20°	2Theta End	: 80°

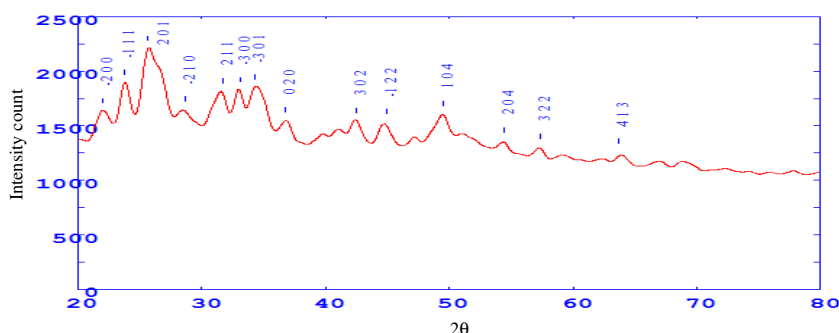


Figure 1. XRD of Copper complex

Sample Name	:	Co- L₃		
Crystal system	:	Tetragonal	Lattice Type	: P
Lattice Parameter	:	a= 10.96	b= 10.96	c= 4.97
Lattice Parameter	:	α = 90	β = 90	γ =90
Radiation	:	Cu	Wave Length	: 1.540598(Å)
2Theta start	:	20°	2Theta End	: 80°

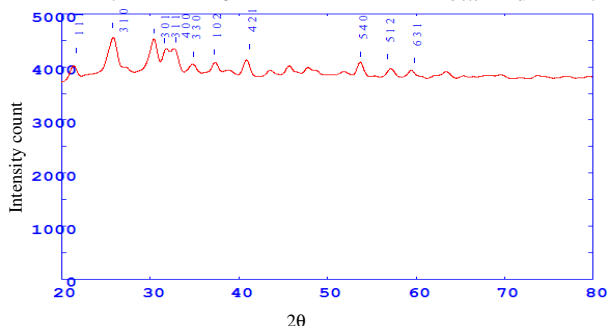


Figure 2. XRD of Cobalt complex

Sample Name	:	Ni- L₃		
Crystal system	:	Tetragonal	Lattice Type	: P
Lattice Parameter	:	a= 7.13	b= 7.13	c= 15.32
Lattice Parameter	:	α = 90	β = 90	γ =90
Radiation	:	Cu	Wave Length	: 1.540598(Å)
2Theta start	:	20°	2Theta End	: 80°

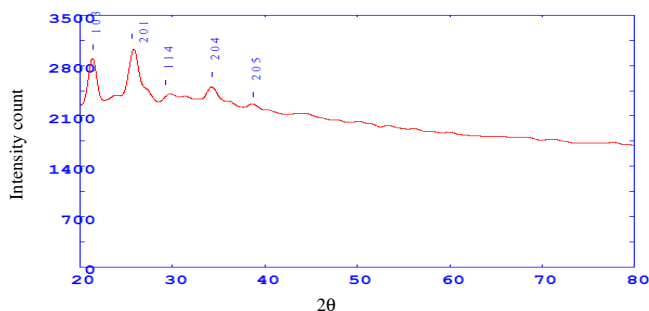


Figure 3. XRD of Nickel complex

From all above data of analysis the general structure of the complexes is

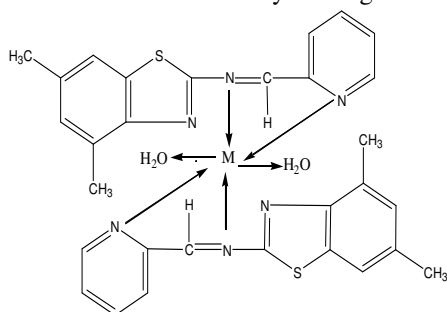


Figure 4. Structure of Complexes (Where M= Co(II), Fe(II), Mn(II), Ni(II) and Cr(II))

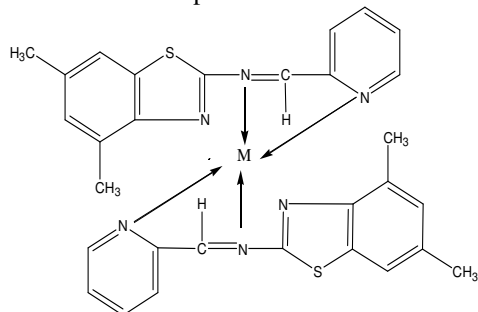


Figure 5. Structure of Complex (Where M= Cu(II))

Antibacterial activity

The antibacterial activity was measured by agar cup method. Nutrient agar (Himedia) was prepared and sterilized at 15 Psi for 15 minutes in the autoclave. It was allowed to cool below 45 °C and seeded with turbid suspension of test bacteria separately, prepared from²⁴ hours old slant cultures. 3% Inocula were used every time. The bacterial cultures selected were, two gram negative cultures viz. *Escherichia coli*, *salmonella typhi* and two Gram positive cultures viz. *Staphylococcus aureus*, *Bacillus subtilis*. This seeded preparation was then poured in sterile petri plate under aseptic condition and allowed it to solidify cups of 10 mm diameter were bored in the agar plate with sterile cork borer. 100 µL of compound solution prepared in the cup under aseptic condition with the help of micropipette 100 µL of DMSO was also placed in one of the cup as blank (negative control). A standard antibiotic disk impregnated with 10 units of penicillin was also placed on the seeded nutrient agar surface as standard reference antibiotic (positive control).

The plates were kept in refrigerator for 15 minutes to allow diffusion of the compound from agar cup into the medium. Then the plates were shifted to incubator at 37 °C and incubated for 24 h. After incubation plates were observed for the zone of inhibition of bacterial growth around the agar cup. Results were recorded by measuring the zone of inhibition in millimeter (mm) using zone reader. Antibacterial Activity of the synthesized metal complexes is given in Table 4.

Antifungal activity

Antifungal activity was performed by poison plate method. The medium used was Potato Dextrose Agar (Himedia). The medium was prepared and sterilized at 10 Psi in autoclave for 15 minutes. Then the compound to be tested is added to the sterile medium in aseptic condition so as to get final concentration as 1%. *Gresiofulvin* was prepared as standard reference plate (positive control) *Aspergillus niger*, *penicillium chrysogenum*, *Fusarium moneliforme*, *Aspergillus flavus* were selected as test fungal cultures.

They were allowed to grow on slant for 48 hours so as to get profuse sporulation. 5 mL of 1:100 aqueous solution of Tween 80 was added to the slant and spores were scraped with the help of nicrome wire loop to form suspension.

The fungal suspension was spot inoculated on the plate's prepared using compound with the help of nicrome wire loop. The plates were incubated at room temperature for 48 hours. After incubation plates were observed for the growth of inoculated fungi. Results were recorded as growth of fungi (no antifungal activity) reduced growth of fungi (moderate antifungal activity) and no growth of inoculated fungi (antifungal activity). Antifungal Activity of the synthesized metal complexes is given in Table 5.

Table 4. Antibacterial activity of ligands and complexes

S.No.	Compound	Zone of inhibition in mm			
		<i>E.coli</i>	<i>S. Typhi</i>	<i>S. Aureus</i>	<i>B. Subtilis</i>
1	L ₃	-ve	19	22	22
2	Cu - L ₃	28	24	31	37
3	Co - L ₃	18	20	28	39
4	Ni - L ₃	-ve	23	28	37
5	Fe - L ₃	22	23	27	23
6	Mn- L ₃	18	17	31	30
7	Cr- L ₃	18	16	18	15
8	DMSO	-ve	-ve	-ve	-ve
9	Penicillin	13	18	36	18

Table 5. Antifungal activity of ligand and complexes

S.No.	Compound	Zone of inhibition in mm			
		<i>Aspergillus niger</i>	<i>Penicillium chrysogenum</i>	<i>Fusarium moniliforme</i>	<i>Aspergillus flavus</i>
1	L ₃	-ve	-ve	-ve	-ve
2	Cu - L ₃	-ve	-ve	-ve	-ve
3	Co - L ₃	-ve	-ve	-ve	+ve
4	Ni - L ₃	-ve	-ve	-ve	-ve
5	Fe - L ₃	-ve	-ve	-ve	-ve
6	Mn- L ₃	-ve	-ve	-ve	-ve
7	Cr - L ₃	-ve	-ve	-ve	-ve
8	+ve control (blank)	+ve	+ve	+ve	+ve
9	(Griseofulvin)	-ve	-ve	-ve	-ve

Legends :-ve – No antibacterial activity

Conclusion

The Cu(II), Ni(II), Mn(II), Fe(III), Cr(II) and Co(II) complexes are coloured, insoluble in most of the organic solvent but soluble in DMF and DMSO. The stoichiometry of the metal complexes obtained has been found to be 1:2. The infrared spectral data indicate that all the ligands act as mononegative bidentate species towards all the complexes. All the synthesized metal complexes gave satisfactory spectral and analytical data. The screening of antimicrobial data revealed that the all complexes show good antimicrobial activity.

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