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Study of Metal Complexes with Schiff Base Derived from 2-Amino-4, 6-dimethylbenzothiazole and Pyrrole-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 O,N 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

I. INTRODUCTION

Ketones and amines are very reactive organic compounds due to presence of C=O and NH_2 groups respectively. The nucleophilic addition reaction of these compounds results in an important class of compounds known as Schiff bases having the general structure $-\text{R}-\text{C}=\text{N}-$. They are formed by the condensation of a primary amine with an active carbonyl compound.

Now a days the transition metal complexes of the Schiff bases are the study of interest for many young scientist because of the wide variety of possible structure for the ligands, depending upon the carbonyl compounds and amines used and also due to their varied industrial and biological applications. The various biological applications of the Schiff bases are anticancer, antidiabetic, antimicrobial, antitubercular. Many transition metal complexes show fluorescence properties used in DNA binding studies, diuretic studies. Keeping all the varied applications of Schiff base metal complexes in mind we synthesized a series of heterocyclic Schiff bases and all the synthesized Schiff bases are analyzed using different physical and analytical tools such as IR, UV, ^1H -NMR, Mass Spectra etc. 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_1)

II. 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.

A. Synthesis of 2-Amino - 4, 6 dimethylbenzothiazole

Synthesis of 2-amino-4, 6-dimethylbenzothiazole was carried out by the standard method. (0.1M) 2,4- Xylidine (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.

0.1 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 group.

B. Synthesis of Schiff Base ligand

Schiff base was synthesized by taking equimolar ethanolic solution of the L₁(pyrole-2-aldehyde) and 2-amino-4,6-dimethylbenzothiazole and were refluxed for 4-5 hours on water-bath. The reaction progress was monitored by TLC. After confirming the completion of the reaction by TLC, the reaction mixture was poured on ice cold water and the separated solid was collected by filtration, washing and drying, recrystallized from ethanol, melting point was recorded.

C. 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 wererefluxed 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 CaCl₂ in vacuum desiccators.

Table.1 Analytical data of complex

S.No.	Mol. Formula	Mol. wt	Colour	M.P./ D.P. °C	Elemental analysis, %			Metal (Cal) Found	Mol. Cond. mhos cm ² Mol ⁻¹	μ eff. B. M.
					C (Cal) Found	H (Cal) Found	N (Cal) found			
1	C ₁₄ H ₁₃ N ₃ S	267	Yellow	115	65.88/64.14	5.09/4.89	16.47/16.04	-	-	-
2	Mn(C ₁₄ H ₁₃ SN ₃) ₂ 2H ₂ O	595	Grey	262	(56.47) 56.03	(4.70) 4.63	(14.11) 12.98	(8.56) 8.14	121	5.92
3	Cu(C ₁₄ H ₁₃ SN ₃) ₂	597	Hena	190	(58.64) 57.78	(4.20) 3.46	(14.71) 15.06	(11.03) 11.97	128	1.76
4	Co(C ₁₄ H ₁₃ SN ₃) ₂ 2H ₂ O	603	Vannilla	>280	(55.72) 54.13	(4.64) 5.57	(13.93) 14.48	(9.77) 9.21	129	4.84
5	Ni(C ₁₄ H ₁₃ SN ₃) ₂ 2H ₂ O	602	Blue	>280	(55.81) 55.45	(4.67) 3.89	(13.95) 13.23	(9.74) 8.31	130	2.84
6	Fe(C ₁₄ H ₁₃ SN ₃) ₂ 2H ₂ O	599	Brown	>280	(56.09) 57.17	(4.67) 4.11	(14.02) 14.67	(9.32) 9.13	128	
7	Cr(C ₁₄ H ₁₃ SN ₃) ₂ 2H ₂ O	596	Grey	>280	(56.37) 55.67	(4.69) 4.76	(14.09) 13.56	(8.72) 8.97	130	

III. RESULTS AND DISCUSSION

A. Magnetic susceptibility measurement of complexes

The magnetic susceptibility values of transition metal complexes were calculated by Guoy balance method. Magnetic susceptibility of Cu(II) complexes at room temperature exhibit magnetic moment in the range 1.75-1.84 B.M which is characteristic of spin values for Cu(II) complexes, magnetic moment of Co(II) complexes derived from L₁ show magnetic moment in the range 4.82-5.18 B.M at room temperature showing the Octahedral geometry.

Ni(II) complexes of ligand L₁ show magnetic moment values in the range of 2.72 - 3.18

B.M at room temperature showing octahedral geometry. Magnetic moment of Fe(III) complexes derived from ligands L₁ shows magnetic moment in the range 5.38-5.79 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 showing octahedral geometry. Cr(II) complexes showed magnetic moment in the range 4.90 B.M at room temperature pointing towards the octahedral geometry

B. Electronic spectral analysis

The absorption spectra of transition metal complexes can be very well interpreted using ligand field theory. 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 22250 cm⁻¹ to 41750 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) complexes. 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 transitions. 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 geometry.

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	ν_1 cm ⁻¹	ν_2 cm ⁻¹	ν_2/ν_1	B^1/B	LFSE (Kcal/mole)
Mn - L ₁	37453	43103	1.15	0.572	106.74
Co - L ₁	37453	43478	1.16	0.542	106.7
Ni - L ₁	36764	39062	1.10	0.484	104.77
Fe - L ₁	37593	43668	1.16	0.524	107.14
Cr - L ₁	37453	43478	1.16	0.651	106.7

C. IR Spectroscopy

In the complexes of ligand the characteristic band at 3186 cm⁻¹ for N-H vibration of pyrrole ring. Five membered 2-substituted aromatic C-N stretch ring vibrations occurs in the range of 1460-1490 Cm⁻¹ Thus the ligand L₁ is coordinating through thiazole ring nitrogen and pyrrole ring nitrogen. 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. The appearance of non-ligand band at 555- 600 cm⁻¹ can be attributed to M-N band where as the non-ligand band at 462-491 cm⁻¹ can be attributed to M-O band. 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. This was evidenced by the formation of new bands in the range 1125-1185 cm⁻¹ corresponding to δ (-OH) of the coordination water 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). Again the thermograms and thermo analytical data supports this very fact strongly.

D. 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.

E. 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 (L₁)₂] complex shows isotropy. The ESR spectrum of Mn(II) complexes of ligands [Mn(L₁)₂], shows single line resulting in the interaction of unpaired electron present in Mn(II) nucleus. The 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 complexes.

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

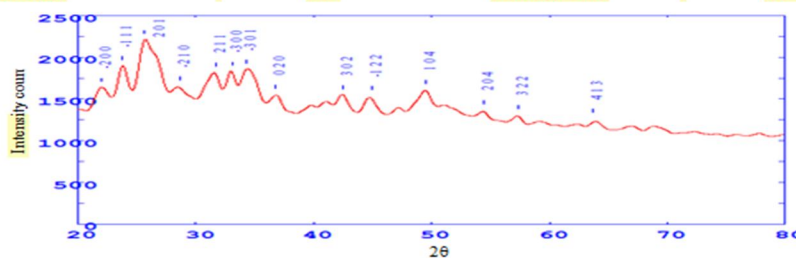
Complex code	g_{\parallel}	g_{\perp}	g_{av}	G Axial symmetry parameter	m_{eff} BM from Gouy Balance
Cu(L ₁) ₂	1.857	1.857	1.857	1	1.73
Mn(L ₁) ₂	1.698	1.851	1.749	0.486	5.92

F. X-Ray crystallography

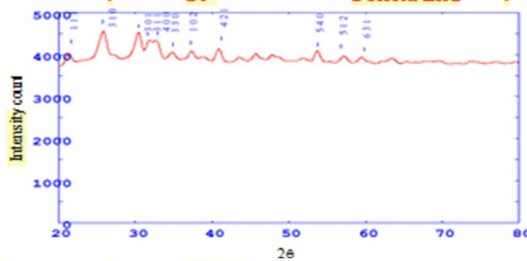
X-ray diffractograms of the metal complexes under investigation show good intense peaks indicating high crystallinity. The results obtained from computational data gave lattice parameter values as Lattice parameter values as $a = b \neq c$ and $\alpha = \beta = \gamma$ which suggest Orthorhombic crystal structure of P type lattice for Nickel complex of ligand L₁.

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 L₁

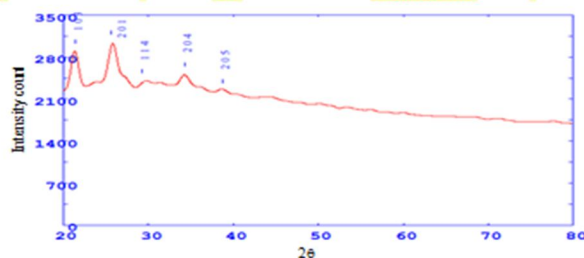
Sample Name	Cu- L₁	Crystal system	Orthorhombic	Lattice Type	P
Lattice Parameter	a= 5.27	b= 4.26	c	c= 9.38	γ
Radiation	Cu	Wave Length	1.540598(Å)	2Theta start	20°
2Theta End	80°				

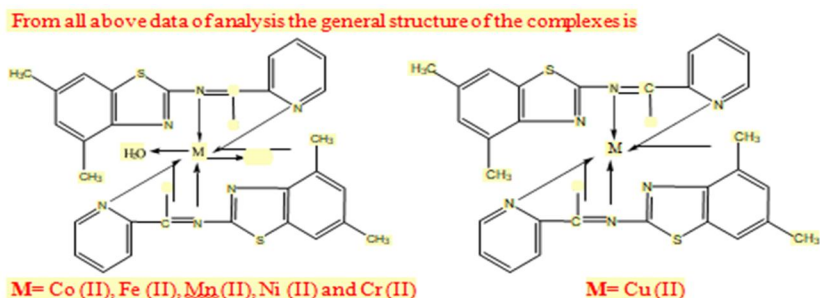


Sample Name	Co- L₁	Crystal system	Orthorhombic	Lattice Type	P
Lattice Parameter	a= 16.23	b= 7.53	c	c= 4.80	γ
Radiation	Cu	Wave Length	1.540598(Å)	2Theta start	20°
2Theta End	80°				



Sample Name	Ni- L₁	Crystal system	Orthorhombic	Lattice Type	P
Lattice Parameter	a= 14.32	b= 13.11	c	c= 2.63	γ
Radiation	Cu	Wave Length	1.540598(Å)	2Theta start	20°
2Theta End	80°				





G. 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 from 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.

H. 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).

Table 4. Antibacterial activity of ligand and complexes

S.No.	Compound	Zone of inhabitation in mm			
		<i>E.coli</i>	<i>S.typhi</i>	<i>S.Aureus</i>	<i>B.Subtilis</i>
1	L ₁	-Ve	-Ve	-Ve	-Ve
2	Cu-L ₁	22	21	25	26
3	Co-L ₁	21	20	34	30
4	Ni-L ₁	19	18	21	26
5	Fe-L ₁	19	22	23	20
6	Mn-L ₁	18	13	25	22
7	Cr-L ₁	13	17	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>Aspergillusniger</i>	<i>Penicillium chrysogenum</i>	<i>Fusariummone liforme</i>	<i>Aspergillus flavus</i>
1	L ₁	+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 ₁	-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, **RG – Restricted**

IV. 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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