



**SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF NOVEL
Co (II), Ni (II) AND Fe (III) COMPLEXES OF HETEROATOM
BEARING LIGANDS**

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ABSTRACT

Schiff bases of 2-Amino, 4, 7-dimethyl benzothiazole with different heterocyclic aldehydes and their metal complexes of Co (II), Ni (II) and Fe (II) have been synthesized. The synthesized Schiff bases and the corresponding complexes have been characterized by spectral analysis viz IR, ¹H NMR, Electronic, XRD, solution conductivity and their magnetic moment. The spectral studies indicate octahedral geometry for Co (II), Ni (II) and Fe (II) complexes. From XRD study, monoclinic, 'p' type crystal structure can be assigned to the synthesized complexes. The complexes were also screened for antifungal and antibacterial activities. The antimicrobial screening shows that the metal complexes show the enhanced activity than their corresponding ligands.

Key words: Schiff bases, Metal complexes, Spectral analysis, Antimicrobial activity.

INTRODUCTION

Coordination compounds exhibit different characteristic properties, which depend on the metal ion to which they are bound, its nature as well as the type of ligand etc. These metal complexes have found extensive applications in various fields of human interest. Schiff bases derived from aromatic amines and aromatic aldehydes have a wide variety of applications in many fields, e.g., biological, inorganic and analytical chemistry^{1,2}. Some Schiff bases were tested for fungicidal activity, which is related to their chemical structure³. Metal complexes of Schiff bases are extensively studied due to synthetic flexibility, selectivity and sensitivity towards a variety of metal atoms⁴. They are found useful in catalysis, in medicine as antibiotics and anti-inflammatory agents and in the industry as anticorrosive substance⁵⁻¹¹. The present paper aims to prepare, characterize the chemical structure and to study the antimicrobial activity of the prepared Schiff base complex derived from 2-amino, 4, 7-dimethyl benzothiazole with different heterocyclic aldehydes.

EXPERIMENTAL

All the chemicals used for the synthetic work were of A. R. grade procured from Lancaster and Aldrich. The solvents used were purified by standard methods. 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 pre-coated sheets of silica gel-G.

General procedure for the synthesis of Schiff bases

Schiff bases were synthesized by taking equimolar ethanolic solutions of heterocyclic amine and respective hydroxyl aldehyde/ketone in 50 mL ethanol and refluxing the reaction mixture for 3-4 hrs. Progress of the reaction was monitored by TLC. The reaction mixture was poured on crushed-ice or cold water and the separated solid was then filtered, washed with distilled water, dried and recrystallised from ethanol.

General procedure for the synthesis of metal complexes

For the synthesis of Cu (II), Ni (II) and Fe (III) complexes, the metal acetates were used. Ethanolic solutions of Schiff bases and respective metal acetate solutions were refluxed in the stoichiometric ratio. After cooling, the solutions were precipitated by the drop wise addition of alcoholic ammonia solution so as to raise the pH up to 5. Then the precipitated solid complexes were filtered, washed to remove excess base and then dried over fused CaCl₂ in vacuum desiccators.

Magnetic moment

Co(II) complexes show magnetic moment in the range 4.85-5.18 B.M. at room temperature pointing towards the octahedral geometry¹². Ni(II) complexes of ligand L₅-L₇ show magnetic moment values in the range of 2.78-3.12 B.M. at room temperature which are tabulated in Table 1. In view of above discussion, it may possess octahedral geometry^{13,14}.

Table 1: Physical and analytical data of the synthesised metal complexes

S. No.	Mol. formula	Mol. Wt.	M.P. (°C)	Colour	Elemental analysis (%)				Mol. cond. Mhos cm ² mol ⁻¹	μ _{eff} B.M.
					C Found (cal)	H Found (cal)	N Found (cal)	Metal found (cal)		
1	Co(C ₁₆ H ₁₁ SN ₂ Br ₂ O) ₂ .2H ₂ O	1034	210	Leafy green	37.12 (36.19)	2.51 (1.88)	5.41 (4.44)	5.69 (4.93)	131	5.18
2	Co(C ₁₆ H ₁₄ SN ₂ O ₂ I) ₂ .2H ₂ O	1130	150	Dirty green	36.09 (35.78)	2.83 (1.92)	4.95 (3.78)	5.21 (4.49)	122	4.98
3	Co(C ₁₅ H ₁₂ SN ₃) ₂ .2H ₂ O	688	199	Dark brown	52.29 (50.55)	4.06 (2.98)	12.20 (11.57)	8.56 (7.37)	118	4.85
4	Ni(C ₁₆ H ₁₁ SN ₂ Br ₂ O) ₂ .2H ₂ O	971	290	Brown	39.54 (38.12)	2.67 (1.49)	5.76 (4.36)	6.07 (5.72)	133	3.12
5	Ni(C ₁₇ H ₁₄ SN ₂ O ₂ I) ₂ .2H ₂ O	1067	130	Green	38.23 (37.50)	2.99 (1.79)	5.24 (4.19)	5.52 (4.38)	124	2.99
6	Ni(C ₁₅ H ₁₂ SN ₃) ₂ .2H ₂ O	625	270	Dark brown	57.60 (56.82)	4.48 (3.67)	13.44 (12.42)	9.44 (8.30)	120	2.78
7	Fe(C ₁₆ H ₁₁ SN ₂ Br ₂ O) ₂ .2H ₂ O	968	200	Dark brown	39.66 (38.51)	2.68 (1.53)	5.78 (4.87)	5.78 (4.39)	124	--
8	Fe(C ₁₇ H ₁₄ SN ₂ O ₂ I) ₂ .2H ₂ O	1064	198	Dark brown	39.66 (38.73)	3.00 (2.91)	5.26 (4.68)	5.26 (4.41)	126	--
9	Fe(C ₁₅ H ₁₂ SN ₃) ₂ .2H ₂ O	622	261	Brown	50.42 (49.00)	3.92 (2.18)	11.76 (10.27)	7.84 (6.58)	120	--

IR Spectra

In the IR spectra of all complexes, medium to strong intensity bands appeared in the region 1598-1636 cm^{-1} , which can be assigned to characteristic azomethine group that is (-C=N) present in almost all ligands. The bands at 837-892 cm^{-1} and 679-742 cm^{-1} in almost all metal complexes can be assigned due to C-S-C thiazole vibrations.

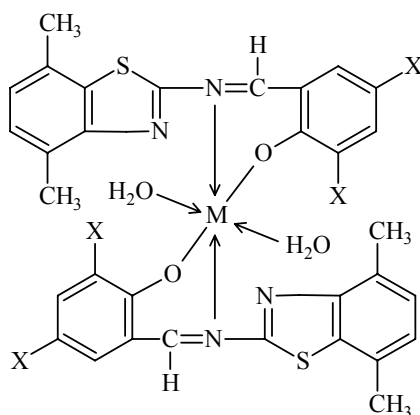
The appearance of non-ligand band at 447-455 cm^{-1} can be attributed to M-O band. The appearance of the band in the region of 3300-3600 cm^{-1} for Co (II), Ni(II) and Fe(III) complexes can be assigned for coordinated water molecules.

^1H NMR Spectra

^1H NMR spectra of synthesized metal complexes were recorded in DMSO. The ^1H NMR spectra of complexes show broad signals due to presence of metal ion and the confirmation of each signal in the aromatic region is difficult due to complex pattern of splitting.

Thermal analysis

The thermograms of complexes show the coordination of two moles of hydrated water. Hence from TGA, it is clear that the complex under study contains two water molecules, which are coordinated to central metal ion^{15,16}.



(X = I/Br)

M = Ni (II), Co (II) and Fe (III)

Antimicrobial activity

The antibacterial activity of the compounds was determined by agar diffusion method against various bacteria like *E. coli*, *S. typhi*, *S. aureus* and *B. subtilis* at various concentrations such as 20, 50 and 100 $\mu\text{g/mL}$. The zone of inhibition was measured in mm and DMSO was used as solvent. Sterile nutrient agar was seeded with test organism and layered in sterile petri plate. After solidification, agar cups were prepared with cork borer. 0.1 mL of the compound solution was added to the cup with the help of micropipettes. One cup in the plates was filled with solvent. Standard penicillin (10 v/mL) was used as reference drug. The plates were kept at low temperature (4°C) for 20 min to allow diffusion of the compound. Then the plates were incubated at 37°C for 24 hr. After proper incubation, the plates were observed for zone of no growth (zone of inhibition) around the cup. Similarly, the same compounds were screened for the antifungal activity against different organisms like *P. chrysogenum*, *A. niger*, *F.*

moniliformae and *A. Flavus* by using poison plate method. The compound was mixed with sterile potato dextrose agar medium so as to get final concentration 2%. It was then poured in sterile petri plate and allowed to solidify. Spots of test organisms were placed on the agar surface. A plate without compound was prepared for control. The plates were incubated at room temperature for 48 hr. After proper incubation, plates were observed for growth of the test organisms. The growth indicates that the compound is not antifungal while inhibition of growth of test organism indicates antifungal activity. The antifungal activities of the compounds were compared with standard grysofulvin.

Table 2: Antimicrobial activity of synthesized complexes

S. No.	Complex	Bacterial strain				Fungal strain			
		Ec	St	Sa	Bs	An	Pc	Fm	Af
1	Co-L ₅	12	-ve	22	20	+ve	-ve	-ve	+ve
2	Co-L ₆	-ve	-ve	20	22	-ve	-ve	-ve	-ve
3	Co-L ₇	12	13	15	18	-ve	-ve	-ve	RG
5	Ni-L ₅	-ve	-ve	12	15	RG	-ve	-ve	RG
6	Ni-L ₆	16	-ve	14	29	RG	-ve	-ve	-ve
7	Ni-L ₇	-ve	-ve	16	14	RG	-ve	-ve	-ve
9	Fe-L ₅	-ve	11	15	18	RG	-ve	-ve	RG
10	Fe-L ₆	14	12	-ve	-ve	-ve	-ve	-ve	-ve
11	Fe-L ₇	13	-ve	15	15	-ve	-ve	-ve	-ve
	Penicillin	13	18	36	18	NA	NA	NA	NA
	Grysofulvin	NA	NA	NA	NA	-ve	-ve	-ve	-ve

Ec-E.coli, St-S.typhi, Sa- S.aureus, Bs-B.subtilis; An-A.niger, Pc-P.chrysogenum, Fm -F.moneliformae, Ca-C.albicans; -ve: No growth of fungi, +ve; Growth of fungi, RG-Reduced growth, NA-Not Applicable, Zone of inhibition was measured in mm

CONCLUSION

The analytical data show 1:2 metal to ligand stoichiometry and the electronic spectral data suggest that all the synthesised complexes have octahedral geometry. The molar conductivity data show the non-electrolytic nature of the complexes. The antimicrobial studies show that the complexes of the corresponding Schiff bases show more potent activity than their corresponding ligand.

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