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Study of the transition metal complexes with novel Schiff bases and their biological activity

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Abstract

The Synthesis of novel Schiff base from substituted aminothiazole i.e. 5-methyl 2-4 Diamino thiazole and substituted hydroxy aldehyde i.e. R=H, and 5-CH₃ and transition metal ion Co^{II}, Ni^{II}, Cu^{II} & Zn^{II}. Etc. their characterization were made by elemental analysis i.e. uv visible and IR spectra, magnetic susceptibility and conductivity measurement. The complexes are monomeric as well as dimeric in nature. The ligand coordinate through oxygenatom of phenolic – OH group and ring nitrogen with azomethine group (–C=N–) the complexes are non-electrolyte in nature. The Schiff bases and transition metal complexes are screen for antimicrobial, fungicidal and pesticidal activity.

Keywords: Schiff base, transition metal complexes, microbial activity

1. Introduction

Metal complexes of Schiff bases have been studies extensively [1-3] because of their interesting structural and spectral properties of Schiff bases derived from heterocyclic amines and their metal complexes exhibit a wide variety of biological activities 4-5. Literature survey reveals that no reports are available on transition metal complexes of Schiff bases derived from 2-4 Diamino-5-methyl thiazole. In present communication we report synthesis characterization and microbial activities of Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} complexes of Schiff base derived from 2-4 Diamino-5-methyl thiazole and hydroxyaldehyde. (R = H, 5-CH₃)

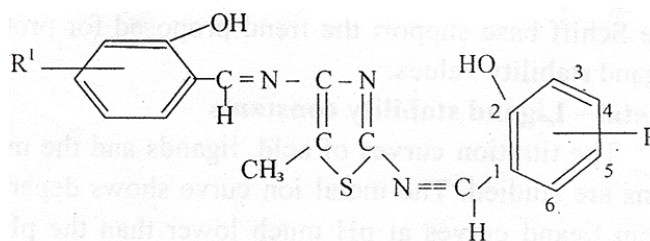
2. Materials and Methods

2.1 Synthesis of Schiff Base

2-4 Diamino-5-Methylthiazole (0.1 mole) and salicylaldehyde (0.2 mole, 22.4ml) were dissolved in absolute ethanol and the mixture was heated under reflux for two hours on water bath. The Schiff base is obtained as yellow coloured crystalline fibrous mass and after cooling filtered off. The crude product was dissolved in minimum quantity of hot ethanol and recrystallized the product. The purity of product checked by thin layer chromatography their melting point and elemental analysis data listed in table no.1.

Table 1: Elemental analysis of ligand. L₁-L₂

S. No	Ligand	Molecular formula	Molecular Weight	C% found (cal.)	H% found (cal.)	N% Found (cal.)	S% found (cal.)	M.P.C°
1.	L ₁	C ₁₈ H ₁₇ N ₃ SO ₂	338 (339)	63.50 (63.71)	4.90 (5.01)	12.40 (12.38)	9.50 (9.43)	157C°
2.	L ₂	C ₂₀ H ₂₁ N ₃ SO ₂	368(367)	63.20 (65.39)	4.95 (5.07)	11.30 (11.44)	8.80 (8.71)	182C°



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S. No	Schiff base	R-R ¹	Ligand
I	(Sal) ₂ DMT	H	L ₁
II	(5MS) ₂ DMT	5-CH ₃	L ₂

- I. [N-bis (salicidene) 2-4 diamino – 5 – methylthiazole]: (Sal)₂ DMT
- II. [N-bis (5- methyl salicidene) 2-4 diamino – 5 – methylthiazole]: (5MS)₂DMT.

3. Preparation of Metal Complexes

3.1 Cobalt Complex: In 100ml capacity round bottom flask, ethanoic solution of anhydrous cobalt chloride (0.01M) was added to the solution of Schiff base (0.01M) in minimum quantity of ethanol. The reaction mixture was then refluxed for two hours using condenser fitted with calcium chloride guard tube. The solvent was then distilled off. The product obtained was then dissolved in methanol and the solution was refluxed for one hour and then cooled. On standing for overnight, a fine crystalline complex obtained which was then filtered and washed with dry ether and then dried under reduced pressure, Same way the Ni-complexes were prepared.

3.2 Copper Complex: An ethanoic solution of anhydrous

copper chloride (0.01M) was added to the solution of Schiff base (0.01M) in 100ml Capacity round bottom flask fitted with condenser and calcium guard tube. The reaction mixture was then refluxed for 30min on water bath and the solvent was then distilled off the obtain gray colored residue. The residue was then refluxed for 30 min. the recrystallied product was obtained on slow cooling as long monoclinic, dirty gray. The fibrous product was filtered off, washed with very small quantity of absolute alcohol and was dried under vacuum. Similarly Zn-complexes were synthesized. The molecular weight of the complexes determined by Rast's method. The Electronic spectra were recorded in chloroform solution on Hitachi spectrophotometer. IR-Spectra were recorded in KBr pullets on Perkin Elmer spectrophotometer in the range 4000-250cm⁻¹. Electrical conductivity of the complexes were measured in nitrobenzene using Philips Conductivity Bridge. Magnetic susceptibility measurements were carried out by Gouy method at room temperature. Diamagnetic correlations were applied using pascal's constants. Elemental analyses were carried out by the usual micro analytical technique. The elemental analysis, molecular weight and magnetic movement (BM) listed in table 2.

Table 2: Elemental Analysis of metal complexes and their magnetic movements. (B.M.)

Metal Complexes	Nature	Colour	Molecular weight found (cal.)	μ_{eff} (BM)	Elemental Analysis			
					Metalion% found (cal.)	C% found (cal.)	N% found (cal.)	S% found (cal.)
CoL ₁	Crystalline	Blue	397.90 (393.50)	4.5	14.30(14.24)	55.08 (54.96)	10.75 (10.68)	8.20(8.14)
NiL ₁	Crystalline	Ochre Yellow	398.40 (393.50)	Diamagnetic	14.35(14.25)	55.10 (55.96)	10.74 (10.68)	8.19 (8.14)
Cu L ₁	Crystalline	Dirty gray	399.99 (398.40)	1.9	15.90(15.82)	54.35 (54.27)	10.62 (10.55)	7.92 (8.04)
Zn L ₁	Crystalline	Creamy Yellow	405.40 (400.15)	Diamagnetic	16.32(16.25)	54.20 (54.00)	10.62 (10.55)	7.95 (8.00)
CoL ₂	Crystalline	Blue	428(425)	4.6	13.70(13.64)	56.55 (56.47)	10.00 (9.80)	7.63 (7.56)
NiL ₂	Crystalline	Ochre Yellow	425(430)	Diamagnetic	13.72(13.65)	56.58 (56.48)	10.01 (9.88)	7.65 (7.57)
Cu L ₂	Crystalline	Dirty gray	435(430)	2.0	14.72(14.65)	55.90 (55.81)	9.90 (9.76)	7.54 (7.47)
Zn L ₂	Crystalline	Creamy Yellow	438(432)	Diamagnetic	15.610 (15.04)	55.65 (55.55)	9.80 (9.72)	7.51 (7.41)

4. Result and Discussion

The complexes are crystalline solid do not show sharp melting points and are soluble in common organic solvents. The elemental analysis data suggest that the complexes possess 1:1 stoichiometry. The molecular weight determination data shows that the complexes are monomeric and dimeric in nature. The very low conductance values of complexes in nitrobenzene solution indicates that the complexes are non-electrolytic in nature, Elemental analysis data given in table-2.

4.1 Electronic Spectra: The electronic spectra of Co^{II} complex exhibits prominent two transition band at -6620 (v₂), ~1500 (v₃) cm⁻¹ corresponding to transition 4T₁ (P) ←4A₂ (v₂), 4T₁ (F) ←4A₂ (v₃) respectively. Occurrence of these transition bands suggests a tetrahedral geometry for complexes [6]. Magnetic moment values of complexes (4.5, 4.6 BM) support the tetrahedral geometry proposed for the complexes (7). The electronic spectra of Ni^{II} complexes exhibits three bands at ~9000, ~13400 and ~22000 cm⁻¹. Three

bands attributed to v₁ v₂ and v₃ 1 B₁ ←1A_{1g} (v₁), 1A_{2g} ← A_{1g} (v₂) and 1E_g, ← 1A_{1g} (v₃) There bands are observed in the reflectance mode and its solution spectra shows band at 14000 and 16000cm⁻¹. Occurrence of these transition band suggests square-planar geometry [8-10]. The Ni^{II} complexes are diamagnetic in character [11]. Electronic spectra of Cu^{II} complexes exhibits a broad band at ~7400 cm⁻¹ suggesting a square-planar geometry [12]. The magnetic moment values of complexes (1.9, 2.0 BM) supports the square-planar geometry proposed for the complexes [13], Electronic spectra of Zn^{II} complexes exhibits an electronic absorption band at ~17000 cm⁻¹, hence be assigned four coordinated square-planar structure the complexes are diamagnetic.

4.2 Infrared Spectra: Infrared spectrum of Schiff bases exhibits a broad and weak band at ~2900 cm⁻¹ instead of strong band at -3100 cm⁻¹ (expected due to phenolic - OH group) This may be due to intermolecular hydrogen bonding between hydroxyl hydrogen and nitrogen of the azomethine group forming a stable six membered ring. The absence of v-

OH mode in the complexes suggest the formation of metal oxygen bond. The ν_{C-O} and $\nu_{C=N}$ modes occur at around 1230, and 1630 cm^{-1} respectively in the ligands and are in agreement with the earlier reported data. The complexes exhibit ν_{C-O} and $\nu_{C=N}$ modes at ~ 1330 and ~ 1580 cm^{-1} . The shifting of $\nu_{C=N}$ towards lower frequency and to ν_{C-O} towards higher frequency in the complexes indicates the formation of metal-oxygen and metal-nitrogen bonds. Infrared spectral data given in table-3. Cobalt complexes show broad

and weak bonds at 1120 cm^{-1} $\sim 470 \text{ cm}^{-1}$ and may be due to Co-O and Co-N modes [14, 15]. Copper complexes exhibit a broad band at 1015, 1110 cm^{-1} and may be assigned to Cu-O and Cu-N modes [16]. In Nickel complexes a broad band ~ 1110 , 1115 cm^{-1} and $\sim 475 \text{ cm}^{-1}$ due to metal nitrogen metal oxygen vibrations. In case of Zn complexes also broad band at ~ 1108 , 1110 cm^{-1} and $\sim 420 \text{ cm}^{-1}$ and may be due to Zn-O or Zn-N modes [14-16].

Table 3: IR Spectral data of ligand and metal complexes

S. No	Compound	$\nu(\text{O-H})$	$\nu(\text{C-O})$	$\nu(\text{C=N})$	Phenyl ring	$\nu(\text{M-O})$	$\nu(\text{M-N})$
1	L ₁	2900	-	1630	1465,1430	-	-
2	L ₂	2950	-	1625	1487,1450	-	-
3	CoL ₁	-	1380	1610	1560,1505	470	1120
4	NiL ₁	-	1386	1610	1575,1510	475	1115
5	Cu L ₁	-	1385	1600	1555,1510	480	1095
6	Zn L ₁	-	1386	1600	1555,1515	420	1110
7	CoL ₂	-	1390	1595	1560,1540	470	1122
8	NiL ₂	-	1395	1610	1565,1560	475	1110
9	Cu L ₂	-	1390	1605	1575,1567	480	1105
10	Zn L ₂	-	1392	1608	1565,1560	420	1108

4.3 Antimicrobial Activity

The antibacterial activity of ligand and their metal complexes were tested *in vitro* against bacteria. Staphylococcus aureas and Escheria coli by paper disc method [17]. The compounds were tested at 250 and 500 ppm. Concentration in DMF and compared with know antibiotics *viz* ciprofloxacin. The 10mm diameter whatman no.1 paper discs were soaked in different solutions of compounds dried and then placed on the lawn culture on nutrient agar plate. The plates were incubated for 24 hr's at 37 °C and the inhibition zone around each disc was measured. The result obtained were compared with known antibiotics ciprofloxacin. For antimicrobial activity, compounds were against Aspergillums Niger and Trichoderma by mycelia dry weight method [18] with glucose nitrate media. The compounds were tested at the concentration 250 to 500 ppm in DMF and compared with control. The metal complexes exhibit enhanced inhibitory effect than the free ligands against the same organism under identical conditions. Increasing activity of metal chelate can

be explained on the basis of chelation Theory. Thus killing of more organism than ligands due to suspected that factors such as stability, dipole moment and bond length between the metal and ligand and also cell permeability mechanism influence by the presence of metal ion may be the possible reason for increasing the activity of Schiff bases [19] Cu^{II} complexes have higher antibacterial activity due their higher stability than other complexes. Except Ni^{II} and Zn^{II} complexes. The activity increase with increasing concentration of complexes due to the effect of metal ions on normal portion of cell. The toxicity of metal chelation follow order Cu^{II}> Co^{II}> Ni^{II}>Zn^{II}. This shows that antibacterial activity is not accordance with stability order of metal ion. The antifungal activity of the ligand and metal complexes are more fungi toxic than ligands. Antifungal activity of metal complexes is found to be increased as the stability of complexes increased which is same at the order of stability constant Cu^{II}> Co^{II}> Ni^{II}>Zn^{II} [20].

Table 4: Antibacterial and antifungal activity in mg (% inhibition zone) schiffbase and their metal complexes. (Diameter of inhibition zone in mm)

Compounds	Antibacterial activity				Antifungal Activity			
	Escheia Coli		Staphylo cocuus		Aspergillus Niger		Trichoderma	
	250 ppm	500 ppm	250 ppm	500 ppm	250 ppm	500 ppm	250 ppm	500 ppm
L ₁	15	18	11	13	61	57	44	35
L ₂	14	16	15	17	62	58	45	30
CoL ₁	23	25	19	21	43	18	35	22
NiL ₁	11	14	14	16	45	15	30	20
Cu L ₁	28	32	27	29	41	11	32	21
Zn L ₁	12	16	10	12	42	14	35	21
CoL ₂	22	25	20	23	44	17	34	22
NiL ₂	10	15	13	16	41	15	32	21
Cu L ₂	27	31	26	29	40	13	31	19
Zn L ₂	10	13	11	15	35	10	28	18
Ciprofloxacin (Control)	29	32	30	32	70	68	65	62

4.4 Pesticidal activity

The insecticide and pesticide activity of Schiff base were tested against some sessional edible plants chilli. (*Capsicum annum* L) Okra (*Abelmoschus esculents* (L) moench) Lay's Finger or Bhendi, Tomato. Pesticidal and insecticidal

activities of Schiff bases and their Cu^{II} complexes shows much more activity on poisoning [21-24] In present report Schiff bases and Cu^{II} and Zn^{II} complexes shows pesticidal and insecticidal activities. The rate of poisoning is lower than commercial pesticide and insecticide.

4.5 Effect of decomposition on Composé Manure

Schiff bases and their metal complexes are used for compost purpose on treatment of Schiff bases and metal complexes the effects are observed it is found that the rate of decomposition of compost material is i.e. leaves, Steami and roots of Jawar, Maize, Sugar cane and other fodder crops is very low after in six months.

5. Conclusion

In this report we are described complex chemistry of a Schiff bases and their transition metal complexes. The Schiff bases derived from 2-4 Diamino-5-methylthiazole and hydroxyaldehyde-(R = H, 5CH₃). I.e. N-bis (Salicylidene)-2-4diamino-5-methylthiazole and N-bis (5-methylsalicylidene)-24-diamino -5-methylthiazole with transition metal ion. Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}. The Schiff bases and their metal complexes were synthesized and characterized on the basis of physico chemical and spectral data discussed above. The IR data reveals that coordinated through phenolic Oxygen ring nitrogen with azomethine nitrogen. The electronic data and dipole moment suggest that complexes are tetrahedral and square planar geometry to Co^{II}, Cu^{II} and Ni^{II} Zn^{II} respectively. The complexes are nonelectrolyte in nature. Metal complexes show antibacterial, antifungal and pesticidal activities higher than free ligand.

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