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Synthesis and Characterization of Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}. Schiff Base Complexes and Their Microbial Activities

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Abstract

A newly synthesized Schiff bases N-bis-(salicylidene)-2-4-diamino-5-chlorothiazole and N-bis-(5-methylsalicylidene)-2-4 diamino-5-chloro-thiazole and metal ion Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}, their metal complexes have been reported. The complexes are characterized by elemental analysis, UV-visible and infrared spectra, magnetic susceptibility and conductivity measurement. The Schiff base act as monomeric as well as dimeric to Co^{II}, Cu^{II} and Ni^{II}, Zn^{II} respectively. The ligand coordinate through oxygen atom of phenolic OH group and the nitrogen atom of azomethine group. The complexes are non-electrolytic in nature.

The Schiff bases and their metal complexes were screened for antibacterial fungicidal and pesticidal activity.

Keywords: Schiff base, transition metal complexes, microbial activity.

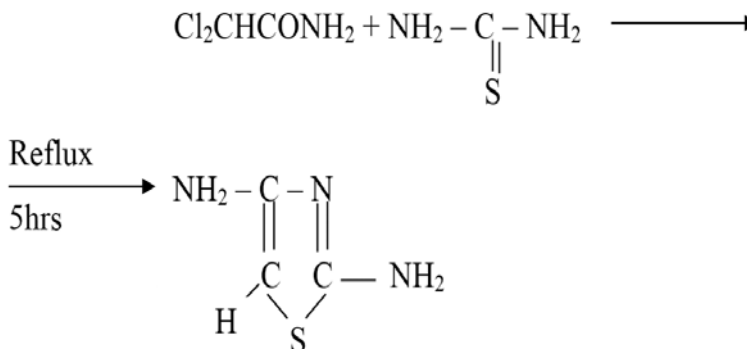
1. Introduction

Metal complexes of Schiff bases have been studied 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-chloro 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-chloro thiazole and hydroxyaldehyde. (R = H, 5-CH₃)

2. Materials and Methods

Synthesis of 2-4 Diamino-5-chlorothiazole (DCT) Dichloro acetamide (0.1 mole, 12.8g) was dissolved in minimum quantity of absolute ethanol and thiourea (0.1 mole, 7.6g) dissolved in hot ethanol was added and heated under reflux for five hours on water bath. The resulting material was poured in an evaporating dish and evaporation was allowed at room temperature, when crude product obtained as brownish solid. The crude product dissolved in boiling ethanol and treated with activated charcoal on filtration slow crystallization was allowed to give light weight, white needle (112g). Melting point 127 °C and yield 75%. Elemental analysis in Table No.1.

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2.1 Synthesis of Schiff Base

2-4 Diamino-5-chlorothiazole (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 on cooling it was filtered off. The crude product was dissolved in minimum quantity of hot ethanol and

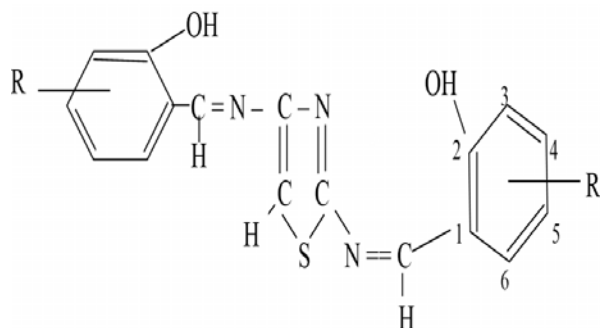
recrystallized product was obtained on slow cooling as long monoclinic, yellow crystals. The fibrous product was filtered off, washed with very small quantity of absolute alcohol by rapid Suction and was dried under vacuum. The melting point and elemental analysis listed in table-1.

Similarly Schiff base from 5-methyl salicylaldehyde was prepared. The molecular weight determined by Rast's method.

Table 1: Analytical data of 2, 4 Diamino-5-chloro thiazole (DCT) and Schiff bases.
(Sal)₂ DCT and (5MSal)₂ DCT

Sr. No.	Ligand	Molecular Formula	Molecular Weight	Elemental Analysis				
				C% (Found) (Cal)	H% (Found) (Cal)	N% (Found) (Cal)	Cl% (Found) (Cal)	3% (Found) (Cal)
1.	DCT	C ₃ H ₄ N ₃ SCl	146 (149)	24.10 (24.16)	2.60 (2.68)	28.09 (28.18)	23.40 (23.48)	21.39 (21.47)
2.	(Sal) ₂ DCT	C ₁₇ H ₁₂ N ₃ O ₂ SCl	355 (357)	57.01 (57.14)	3.27 (3.36)	11.74 (11.76)	9.73 (9.80)	8.89 (8.96)
3.	(5MS) ₂ DCT	C ₁₉ H ₁₃ N ₃ O ₂ SCl	380 (395)	59.10 (59.22)	4.03 (4.15)	10.81 (10.90)	8.98 (9.09)	8.19 (8.31)

Structure of Schiff bases.
The structure I and II.



Sr. No.	Ligand	R
I.	(Sal) ₂ DCT	H
II.	(5MS) ₂ DCT	5-CH ₃
	1. N-bis (Salicylidene)-2-4 Diamino-5-chlorothiazole.	
	2. N-bis (5-methyl Salicylidene)-2-4 Diamino-5-chlorothiazole.	

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, washed with dry ether and then dried under reduced pressure. Same way the Ni-complex 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 to obtain gray colored residue. The residue was then refluxed for 30 min

and then cooled to room temperature on standing over night; greenish gray coloured crystal of complex separated out. The complex was then filtered and dried under reduced pressure similarly the Zn-complex were prepared.

Electronic spectra were recorded in chloroform solution a 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 having dip type cell. 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. Molecular weights were determined by Rast method.

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-electrical 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 ~6600 (ν₂), ~1500 (ν₃) 0m⁻¹ corresponding to transition 4T₁ (P) ← 4A₂ (ν₂), 4T₁ (F) ← 4A₂ (ν₃) 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 ν₁, ν₂ and ν₃.

1B₁ ← 1A_{1g} (ν₁), 1A_{2g} ← 1A_{1g} (ν₂) and 1E_g ← 1A_{1g} (ν₃) 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 a electronic absorption band at ~17000 cm⁻¹, hence be assigned four coordinated square-planar structure the complexes are diamagnetic.

Table 2: Elemental analytical data of Schiff base and the metal complexes.

Sr. No.	Formula of complex	Nature	Colour	Elemental analysis					Molecular weight	Neff (B.M.)
				C% Found (Cal)	H% Found (Cal)	N% Found (Cal)	S% Found (Cal)	Cl% Found (Cal)		
1	[Co(Sal) ₂ DCT]	Crystalline	Blue	49.22 (49.28)	2.35 (2.41)	10.05 (10.14)	7.70 (7.79)	8.35 (8.45)	407 (413.94)	4.5
2.	[Ni(Sal) ₂ DCT]	Crystalline	Ochre Yellow	49.20 (49.31)	2.30 (2.41)	10.05 (10.15)	7.69 (7.73)	8.41 (8.46)	408 (413.69)	Diamagnetic
3.	[Cu(Sal) ₂ DCT]	Crystalline	Dirty gray	48.55 (48.73)	2.34 (2.38)	9.95 (10.03)	7.59 (7.64)	8.22 (8.36)	410 (418.57)	1.9
4.	[Zn(Sal) ₂ DCT]	Crystalline	Cream Yellow	48.44 (48.52)	2.33 (2.37)	9.81 (9.99)	7.57 (7.61)	8.25 (8.32)	409 (420.38)	Diamagnetic
5.	[Co(5ms) ₂ DCT]	Crystalline	Blue	51.48 (51.59)	3.06 (3.16)	9.45 (9.50)	7.17 (7.24)	7.88 (7.91)	438 (441.94)	4.6
6.	[Ni(5MS) ₂ DCT]	Crystalline	Ochre Yellow	51.49 (51.61)	3.07 (3.16)	9.41 (9.50)	7.18 (7.24)	7.89 (7.42)	437 (441.69)	Diamagnetic
7.	[Cu(Sal) ₂ DCT]	Crystalline	Dirty gray	50.90 (51.05)	3.03 (3.13)	9.34 (9.40)	7.08 (7.16)	7.77 (7.83)	442 (446.57)	2.0
8.	[Zn(Sal) ₂ DCT]	Crystalline	Cream Yellow	50.77 (50.84)	3.08 (3.12)	9.31 (9.36)	7.04 (7.13)	7.74 (7.80)	443 (448.38)	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 ν-OH mode in the complexes suggest the formation of metal oxygen bond.

The ν-C-O and ν-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 ν-C=N modes at ~1330 and ~1580 cm⁻¹. The shifting of ν-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 bands at ν1120 cm⁻¹ ~470 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 ~475 cm⁻¹ due to metal nitrogen oxygen vibrations. In case of Zn complexes also broad band at ~1108, 1110 cm⁻¹ and ~420 cm⁻¹ and may be due to Zn-O or Zn-N modes [14-16].

Table 3: Infrared spectral data and magnetic moment (BM).

Compound	ν(O-H)	ν(C-O)	ν(C=N)	ν(C-Cl)	Phenyl ring	ν(M-O)	ν(M-N)
(Sal) ₂ DCT	2900	-	1630	52	1465, 1430	-	-
(5MS) ₂ DCT	2950	-	1625	1110	1487, 1450	-	-
[Co(Sal) ₂ DCT]	-	1380	1610	1093	1560, 1505	470	1120
[Ni(Sal) ₂ DCT]	-	1386	1610	1090	1575, 1510	475	1115
[Cu(Sal) ₂ DCT]	-	1385	1600	1090	1555, 1510	480	1095
[Zn(Sal) ₂ DCT]	-	1386	1600	1090	1555, 1515	420	1110
[Co(5MS) ₂ DCT]	-	1390	1595	1085	1560, 1540	470	1122
[Ni(5MS) ₂ DCT]	-	1395	1610	1087	1565, 1560	475	1110
[Cu(5MS) ₂ DCT]	-	1390	1605	1085	1575, 1567	480	1105
[Zn(5MS) ₂ DCT]	-	1392	1608	1088	1565, 1560	420	1108

4.3 Antimicrobial Activity

The antibacterial activity of ligand and their metal complexes were tested in vitro against bacteria. Staphylococcus aureus and Escheria coli by paper disc method [17]. The compounds were tested at 250 and 500 ppm. Concentration in DMF and compared with known 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 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. Expect Ni^{II} and Zn^{II} complexes. The activity increase with increasing concentration of complexes due to the effect of metal ions on normal procen of cell. The toxicity of metal chelalies follow order Cu^{II} > Co^{II}

> Ni^{II} > Zn^{II}. This shows that antibacterial activity is not accordance with stability order of metal ions.

The antifungal activity of the ligands and metal complexes reveals that all metal complexes are more fungi toxic than ligands. Antifungal activity of metal complexes in found to be increased as the stability of the complexes increased which is same at the order of stability constant Cu>Ni>Co>Zn [20].

Table 4: Antibacterial activity of compounds and antifungal activity weight in mg (% inhibition zone) Schiff bases and their 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
1. [(Sal) ₂ DCT]	15	18	11	13	61	57	44	35
2. [(5MS) ₂ DCT]	14	16	15	17	62	58	45	30
3. [Co(Sal) ₂ DCT]	23	25	19	21	43	18	35	22
4. [Ni(Sal) ₂ DCT]	11	14	14	16	45	15	30	20
5. [Cu(Sal) ₂ DCT]	28	32	27	29	41	11	32	21
6. [Zn(Sal) ₂ DCT]	12	16	10	12	42	14	35	21
7. [Co(5MS) ₂ DCT]	22	25	20	23	44	17	34	22
8. [Ni(5MS) ₂ DCT]	10	15	13	16	41	15	32	21
9. [Cu(5MS) ₂ DCT]	27	31	26	29	40	13	31	19
10. [Zn(5MS) ₂ DCT]	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} shows complexes shows pesticidal and insecticidal activities. The rate of poisoning is lower than commercial pesticide and insecticide.

4.5 Effect of decomposition on Compost 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. Steam 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-chlorothiazole and hydroxyaldehyde-(R = H, 5CH₃). I.e. N-bis (Salicylidene)-2-4-diamino-5-chlorothiazole and N-bis (5-methylsalicylidene)-2-4-diamino -5-chlorothiazole 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 dat reveals that coordinated through phenolic oxygen and 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 non-electrolyte in nature. Metal complexes show antibacterial, antifungal and pesticidal activities higher than free ligand.

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