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 Co²⁺, Ni²⁺, Cu²⁺ & Zn²⁺, 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 oxygen atom 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 screened for antimicrobial, 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-methyl thiazole. In present communication we report synthesis characterization and microbial activities of Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺ 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.

| S. No | Ligand | Molecular formula | Molecular Weight | C% found (cal.) | H% found (cal.) | N% found (cal.) | S% found (cal.) | M.P.°C |
|-------|--------|-------------------|------------------|----------------|----------------|----------------|----------------|--------|
| 1.    | L₁     | C₈H₇N₃SO₂         | 338 (339)        | 63.50 (63.71)  | 4.90 (5.01)    | 12.40 (12.38)  | 9.50 (9.43)    | 157°C  |
| 2.    | L₂     | C₂₀H₂₁N₃SO₂       | 368(367)         | 63.20 (65.39)  | 4.95 (5.07)    | 11.30 (11.44)  | 8.80 (8.71)    | 182°C  |

Table 1: Elemental analysis of ligand. L₁-L₂
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 recrystallized product was obtained on slow cooling as long mononclinc, 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.

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 recrystallized product was obtained on slow cooling as long mononclinc, 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.

| S. No | Schiff base | R-R¹ | Ligand |
|-------|-------------|------|--------|
| I     | (Sal)₂DMT   | H    | L₁     |
| II    | (5MS)₂DMT   | 5-CH₃| L₂     |

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 recrystallized product was obtained on slow cooling as long mononclinc, 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. 

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 dimesric 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 CoIl complex exhibits prominent two transition band at -6620 (ν₂), ~1500 (ν₃) cm⁻¹ corresponding to transition 4T₁g (P) ←4A2 (ν₂), 4T₁g, (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 NiIl complexes exhibits three bands at ~9000, ~13400 and ~22000 cm⁻¹. Three bands attributed to v₁ v₂ and v₃ 1 B₁g←1A₁g (v₁), 1A₂g ← A₁g (v₂) and 1E₂g ← 1A₁g (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 NiIl complexes are diamagnetic in character [11]. Electronic spectra of CuIl complexes exhibits a board 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 ZnIlcomplexes exhibits a 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 phenolie - OH group) This may be due to intermolecular hydrogen bonding between hydroxyl hydrogen and nitrogen of the azomethine group forming a stable membered ring. The absence of v-
OH mode in the complexes suggest the formation of metal oxygen bond. The νc-o and νc = 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 νc-o and νc = N modes at ~1330 and ~1580 cm⁻¹. The shifting of νc = N towards lower frequency and to νc - 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 1120 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 metal 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].

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 Aspergillus 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] CuII complexes have higher antibacterial activity due their higher stability than other complexes. Except NiII and ZnII 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 CuII> CoII> NiII>ZnII. This shows that antibacterial activity is not accordance with stability order of metal ion. The antibacterial 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 CuII> CoII> NiII>ZnII [20].

4.4 Pesticidal activity
The insecticide and pesticide activity of Schiff base were tested against some sessional edible plants chili. (Capsicum annum L) Okra (Abelmoschus esculents (L) moench) Lay’s Finger or Bhendi, Tomato. Pesticidal and insecticidal activities of Schiff bases and their CuII complexes shows much more activity on poisoning [21-24] In present report Schiff bases and CuII and ZnII complexes shows pesticidal and insecticidal activities. The rate of poisoning is lower than commercial pesticide and insecticide.

Table 3: IR Spectral data of ligand and metal complexes

| S. No | Compound | ν(O-H) | ν(C=O) | ν(C=N) | Phenyl ring | ν(M-O) | ν(M-N) |
|-------|----------|--------|--------|--------|------------|--------|--------|
| 1     | L₁       | 2900   | -      | 1630   | 1465,1430  | -      | -      |
| 2     | L₂       | 2950   | -      | 1625   | 1487,1450  | -      | -      |
| 3     | CoL₁     | -      | 1380   | 1610   | 1560,1505  | 470    | 1120   |
| 4     | NiL₁     | -      | 1386   | 1610   | 1575,1510  | 475    | 1115   |
| 5     | CuL₁     | -      | 1385   | 1600   | 1555,1510  | 480    | 1095   |
| 6     | ZnL₁     | -      | 1386   | 1600   | 1555,1515  | 420    | 1110   |
| 7     | CoL₂     | -      | 1390   | 1595   | 1560,1540  | 470    | 1120   |
| 8     | NiL₂     | -      | 1395   | 1610   | 1565,1560  | 475    | 1110   |
| 9     | CuL₂     | -      | 1390   | 1605   | 1575,1567  | 480    | 1105   |
| 10    | ZnL₂     | -      | 1392   | 1608   | 1565,1560  | 420    | 1108   |

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 | Staphylococcus | Aspergillus Niger | Trichoderma |
|           | 250 ppm | 500 ppm | 250 ppm | 500 ppm | 250 ppm | 500 ppm | 250 ppm | 500 ppm |
| L₁       | 15       | 18       | 11     | 13     | 61     | 57     | 44     | 35     |
| L₂       | 14       | 16       | 15     | 17     | 62     | 58     | 45     | 30     |
| CoL₁     | 23       | 25       | 19     | 21     | 43     | 18     | 35     | 22     |
| NiL₁     | 11       | 14       | 14     | 16     | 45     | 15     | 30     | 20     |
| CuL₁     | 28       | 32       | 27     | 29     | 41     | 11     | 32     | 21     |
| ZnL₁     | 12       | 16       | 10     | 12     | 42     | 14     | 35     | 21     |
| CoL₂     | 22       | 25       | 20     | 23     | 44     | 17     | 34     | 22     |
| NiL₂     | 10       | 15       | 13     | 16     | 41     | 15     | 32     | 21     |
| CuL₂     | 27       | 31       | 26     | 29     | 40     | 13     | 31     | 19     |
| ZnL₂     | 10       | 13       | 11     | 15     | 35     | 10     | 28     | 18     |
| Ciprofloxacin (Control) | 29       | 32       | 30     | 32     | 70     | 68     | 65     | 62     |
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. 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 compiex chemistry of a Schiff bases and their transition metal complexes. The Schiff bases derived from 2-4 Diamino-5-methylthiazole and hydroxaldehyde-(R = H, 5CH$_3$). 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 nonelectrolite in nature. Metal complexes show antibacterial, antifungal and pesticidal activities higher than free ligand.

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6. References

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