

Electrical Conductivity of Cr(III), Mn(III) And Fe(III) Metal Complexes of 2-Hydroxy-5-Methyl-3-Nitroacetophenone Thiazole Schiff Base

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ABSTRACT

The newly coordinating metal complexes of Cr(III), Mn(III) and Fe(III) have been synthesized using 2-hydroxy-5-methyl-3-nitro acetophenone thiazole Schiff base ligand was derived from the condensation of 2-hydroxy-5-methyl-3-nitro acetophenone and thiazole. The Schiff bases behaved as charge bidentate ligand. The ligand was characterized by elemental analysis and spectral methods. Metal complexes characterized by elemental analysis, conductance measurements, molecular weight determinations and spectral studies. The synthesized products are coloured solids, soluble in DMF, DMSO and THF. The Schiff base and their metal complexes have been studied by electrical conductivity

Keywords: Schiff Base, Magnetic Susceptibility, Electrical Conductivity

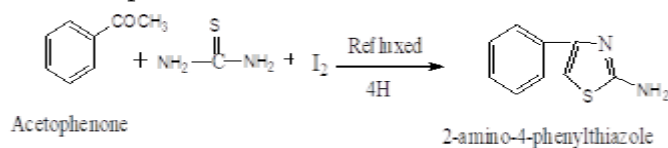
I. INTRODUCTION

The chemical studies of metal complexes with heterocyclic Schiff base ligands containing nitrogen, sulfur, and oxygen has attracted increasing attention. It is well known that these heterocyclic compounds can exhibit bacterial, fungicidal, herbicidal and insecticidal activities in addition to their application as potential drugs. Such heterocyclic ligands, when complexed with metal ions, exhibit enhanced microbiological activities^{1,2}. In the study of comparative reactivity of ambidentate ligand systems two or more potential donor centre of amino heterocycles plays an important role³. In the chemistry of organic and inorganic compound the number of Schiff base ligand and metal complexes are of substantial sake and attention because of their biological activity including anti-tumor, antibacterial, fungicidal and anti-carcinogenic properties^{4,5}. Due to biological potency, pharmacological properties and

synthetic flexibility of thiazole Schiff bases. The aim of present investigation is to synthesize various transition metal complexes of Schiff base derived from 2-hydroxy-5-methyl-3-nitro acetophenone and 2-amino-4-phenylthiazole.

II. METHODS AND MATERIAL

All the chemicals were of A.R. grade and used as received. 2-hydroxy-5-methyl-3-nitro acetophenone (HMNA) and 2-amino-4-phenylthiazole was prepared by known methods⁶⁻⁹. The solvents were purified by standard methods¹⁰. Synthesis of 2-amino-4-phenylthiazole: The Synthesis of 2-amino-4-phenylthiazole prepared by known method⁷⁻⁹. Yield: (75%); m.p.: 148-150°C



Synthesis of 2-hydroxy-5-methyl-3-nitroacetophenone 4-phenyl-2 imino thiazole [HMNAT]:

A solution of 4-phenyl-2 imino thiazole (0.02M) in 25ml of ethanol was added to an ethanolic solution(25ml) of 2-hydroxy-5-methyl-3-nitroacetophenone (0.02M) and the reaction mixture was refluxed on a water bath for 4-6h. After cooling a pale yellow coloured crystalline solid was separated out. It was filtered and washed with ethanol, crystallized from DMF and dried under reduced pressure at ambient temperature. The purity of ligand was checked by elemental analysis and m.p. It was also characterized by IR and ^1H NMR spectral studies. Yield:70%; m.p. 310°C

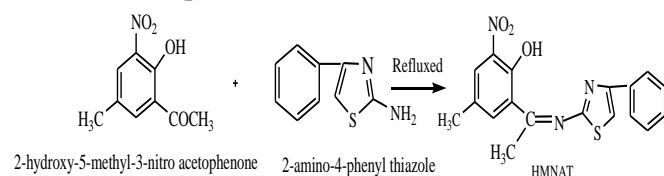


Table1. Analytical data of the Ligands.

| Ligand | Molecular Formula | Formula Weight | Colour and nature | Elemental Analysis | | |
|--------|--|----------------|--------------------|--------------------|-----------------|-----------------|
| | | | | C% found (Cal.) | H% Found (Cal.) | S% Found (Cal.) |
| HMNAT | $\text{C}_{18}\text{H}_{15}\text{N}_3\text{O}_3\text{S}$ | 353.1 | Yellow Crystalline | 60.42 (61.17) | 04.04 (04.24) | 08.84 (09.06) |

Preparation of complexes: All the metal complexes were prepared in a similar way by following method. To a hot solution of ligand HMNAT (0.02M) in 25ml of ethanol a suspension of respective metal salts was added drop wise with constant stirring. The reaction mixture was refluxed on a water bath for 3-5 h. The precipitated complexes were filtered, washed with ethanol followed by ether and dried over fused calcium chloride. Yield : 55-60%

The complexes are soluble in DMSO and DMF but insoluble in water and common organic solvents. The metal chloride content of complexes were analyzed by standard methods^{11,12} The ^1H NMR spectra of ligand was recorded and obtained from RSIC Chandigarh. IR spectra of the compounds were recorded on Perkin Elmer 842 spectrophotometer in the region 400-4000 cm^{-1} , Carbon, Hydrogen and Nitrogen analysis were carried out at RSIC, Punjab University, Chandigarh. The molar conductance of the complexes at 10^{-3} M dilution in DMF were determined using equiptronic digital conductivity meter EQ-660 with a cell constant 1.00 cm^{-1} at room temperature. The magnetic moment measurement were made on a Gouy balance at room temperature using $[\text{HgCo}(\text{SCN})_4]$ as the calibrant. The molecular weights of the complexes were determined by Rast method.

Table 2. Analytical data and molar conductance of the compounds.

| Ligand | Formula weight | Colour | Elemental Analysis Found (Calcd.) | | | μ_{eff} (B.M) | Λ_{M} ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) |
|---|----------------|--------|-----------------------------------|---------------|-------------|--------------------------|--|
| | | | M% | C% | H% | | |
| $[\text{CrL}_2(\text{H}_2\text{O})\text{Cl}]\text{H}_2\text{O}$ | 827.7 | Green | 6.12 (6.28) | 51.69 (52.19) | 3.34 (3.86) | 3.6 | 16.6 |
| $[\text{MnL}_2(\text{OAc})]\text{H}_2\text{O}$ | 854.1 | Brown | 6.28 (6.42) | 53.18 (53.38) | 4.15 (4.21) | 4.2 | 17.4 |
| $[\text{FeL}_2(\text{H}_2\text{O})\text{Cl}]\text{H}_2\text{O}$ | 831.6 | Black | 6.40 (6.70) | 51.05 (51.19) | 4.03 (4.08) | 5.6 | 20.2 |

III. RESULTS AND DISCUSSION

The Schiff base HMNAT and its complexes have been characterized on the basis of ^1H NMR, IR spectral data, elemental analysis, molar conductance, magnetic susceptibility measurements and thermogravimetric analysis data. All these values and analytical data is consistent with proposed molecular formula of ligand. All the compounds are coloured solid and stable in air. They are insoluble in water but soluble in coordinating solvents like DMF and DMSO. The molar conductance values in DMF(10^{-3} M) solution at room temperature (Table 2) shows all the complexes are non electrolytes.

The ^1H NMR spectra of ligand HMNAT shows signals at δ 12.24, (1H, s phenolic OH), δ 7.60, 7.74, 7.63 and 7.72 (4H, m, phenyl) δ 6.87, 6.88, and 6.72 (3H, s Phenyl), 6.78 (1H s thiophene), and 2.66 (3H, s, methyl) ^{11,13-15}.

IR spectra of ligand and metal complexes shows $\nu(\text{C}=\text{N})$ peaks at 1626 cm^{-1} and absence of $\text{C}=\text{O}$ peak at around $1700 - 1740\text{ cm}^{-1}$ indicates the Schiff base formation ¹⁶⁻¹⁹.

Table 3. IR spectra of ligand and metal complexes

| Compound | $\nu(\text{O}-\text{H})$ hydrogen bonded | $\nu(\text{C}=\text{N})$ imine | $\nu(\text{C}-\text{O})$ phenolic | $\nu(\text{M}-\text{O})$) | $\nu(\text{M}-\text{N})$) | $\nu(\text{C}-\text{S})$) |
|---|--|-----------------------------------|--------------------------------------|-------------------------------|-------------------------------|-------------------------------|
| HMNAT | 3085 | 1626 | 1520 | -- | -- | 1128 |
| $[\text{CrL}_2(\text{H}_2\text{O})\text{Cl}]$ H_2O | -- | 1596 | 1508 | 475 | 409 | 1116 |
| $[\text{MnL}_2(\text{OAc})]$ $2\text{H}_2\text{O}$ | -- | 1566 | 1466 | 498 | 420 | 1091 |
| $[\text{FeL}_2(\text{H}_2\text{O})\text{Cl}]$ H_2O | -- | 1606 | 1502 | 512 | 440 | 1082 |

Electrical Conductivity: The electrical resistivity of the different metal chelates can be measured either with a.c. or d.c. methods. However, in the present work the d.c. method is used for resistivity

measurements, over a wide range of temperature. The electrical conductivity of metal complexes varies with their nature and temperature ¹⁹⁻²³. The variation of electrical conductivity of the metal complexes with temperature is the basis of their classification as semiconductors or metallic conductors. The electrical conductivity of metallic conductors decreases with increasing temperature (i.e. temperature coefficient is negative) and their resistivity ranges from 10^{-6} to $10^{-3}\ \Omega$.

The electrical conductivity and activation energy of HMNAT complexes are cited in Table 4

1. Electrical conductivity of the complexes lies in the range of 1.89×10^{-8} to $4.24 \times 10^{-7}\ \Omega^{-1}\text{cm}^{-1}$ at 373 K.
2. The electrical conductivity of these complexes at 373 K follows the order $\text{Fe} > \text{Mn} > \text{Cr}$.
3. The activation energy of electrical conduction of the complexes has been found to increase in the order $\text{Mn} < \text{Cr} < \text{Fe}$.

Table 4. Electrical Conductivity (σ) at 373 K and Activation Energy (E_a) of the complexes

| Metal | | Cr(III), | Mn(III) | Fe(III) |
|----------|--------------------------------------|-----------------------|-----------------------|-----------------------|
| HCA T | $\sigma (\Omega^{-1}\text{cm}^{-1})$ | 4.89×10^{-8} | 1.89×10^{-8} | 4.24×10^{-7} |
| | E_a (eV) | 0.0188 | 0.0124 | 0.1636 |

IV. CONCLUSION

The D.C. Electrical conductivity of the synthesized complexes were measured in the temperature range 298-423 K. All the complexes indicating their semiconducting behaviour

V. REFERENCES

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