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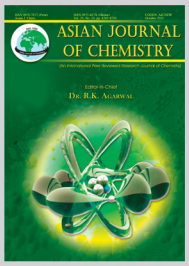

# Synthesis, Characterization and Biological Studies of Mn(III), Co(II), Ni(II) and Cu(II) Chelates of Polystyrene Schiff Base

K. SANKAR[1,*] and A. NAZEERA BEEVI[2]

[1]Department of Chemistry, Mahatma Gandhi College, Thiruvananthapuram-695 004, India
[2]Department of Chemistry, Government College, Kariyavattom, Thiruvananthapuram-695 581, India

*Corresponding author: E-mail: sankarkponmana@gmail.com

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The Schiff base of polystyrene with indole-3-acetic acid have been synthesized and complexed with Co(II), Ni(II), Cu(II) and Mn(III). They are characterized by elemental analysis, magnetic susceptibility, IR, UV-visible spectral methods and thermal studies. The electronic spectra along with the magnetic studies suggest octahedral or distorted octahedral geometry for all the chelates. The ligand and its metal complexes were screened for their antimicrobial activity using *S. aureus* and *E. coli* microorganisms and found to be moderately active. All these complexes catalyze the decomposition of $H_2O_2$, Cu(II) complex being the most active.

**Key Words: Merrifield resin, Polystyrene, Indole-3-acetic acid, Antimicrobial activity.**

## INTRODUCTION

Among the different polymer supported metal complexes, Schiff base polymer metal complexes[1,2] are important. Apart from their novel structural features, unusual magnetic properties and role in biological processes, the polymer supported Schiff base metal complexes are important in preconcentration[3,4] of metal ion, catalysis[5,6], *etc*. Synthesis of polymer complexes using *bis*-bidentate Schiff base ligands were studied and their structural elucidation are done already[7,8]. A number of polymer Schiff base ligand has been synthesized for their ion-selective properties[9,10].

The present work deals with synthesis and characterization of polymeric copper(II), nickel(II), cobalt(II) and manganese(III) complexes of Schiff base derived by condensation of Merrifield resin with indole-3-acetic acid. The complex has been characterised by various physico chemical methods. The catalytic activity of the complexes was also studied. The antimicrobial activity of the ligand and its metal chelates against *S. aureus* and *E.coli* has also been studied.

## EXPERIMENTAL

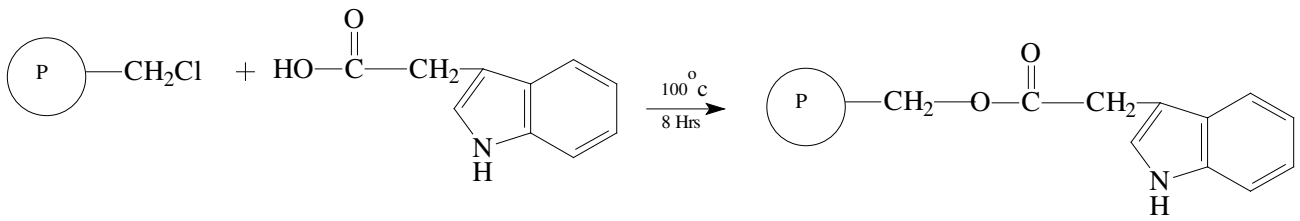
All the chemicals used were of AR grade. Merrifield resin (Fluka) and indole-3-acetic acid (Fluka) were used as such. Metal salt solutions were prepared in doubly distilled water.

The resin and metal complexes were characterized by analytical and spectral methods. The spectral methods employed were IR and UV-VIS spectroscopy. The IR spectra were taken on a Perkin-Elmer FTIR Paragon 1000 spectrophotometer (4000-400 $cm^{-1}$). UV-Visible spectra were recorded on a Schimadzu 2100 UV-visible spectrophotometer. Magnetic susceptibility was measured on a Gouy balance using $Hg[Co(NCS)_4]$ as the calibrant. Thermal analysis was done on a Dupont 2000 thermo balance in air, at a heating rate of 10 ºC/min. Standard volumetric methods were employed to determine metal ion concentration.

**Preparation of the Schiff base ligand:** The Schiff base was obtained by the condensation of Merrifield resin (0.7 mmol Cl/g, 3 g) with indole-3-acetic acid (3.5 mmol, 0.68 g). Indole-3-acetic acid was refluxed with Merrifield resin in THF (15 mL) in the presence of pyridine (7 mmol) for about 8 h to get the Schiff base. The product was then filtered, repeatedly washed with distilled water and then finally with ethanol and then dried. The reaction is represented in **Scheme-I**.

**Preparation of complexes:** 0.02M solution of copper(II) acetate, nickel(II) acetate, cobalt (II) acetate and manganese(III) acetate were prepared. A fixed quantity was pipetted out and shaken with the Schiff base (0.5 g) for 24 h. The initial and final concentration of metal solution were determined volumetrically.

**Antimicrobial screening:** Antimicrobial activity of the ligand and its metal chelates has been studied by disc diffusion method[11]. The activity of the compound was assessed by measuring the diameter of inhibited zone in millimeter (mm). The culture of *E. coli* bacteria and *S. aureus* bacteria were used as test organism, which were grown on nutrient agar




**Scheme-I**

medium and gentamycin as control. DMSO was used as solvent for making test solution of all compounds studied. The paper disc (6 mm) containing the compound (100 µg/disc) was placed on the surface of the nutrient agar plate previously spread with 0.1 mL of sterilized culture of micro organism. After incubating this at 37 ºC for 36 h, the diameter of inhibition zone around paper disc was measured.

## RESULTS AND DISCUSSION

**IR spectra:** The Important bands of the ligand and its complexes and their assignments are presented in Table-1. The band at 1640 $cm^{-1}$ assigned to the ν(C=O) undergoes a downward shift in the complex showing the participation of carbonyl group in co-ordination[12]. The band at 3400 $cm^{-1}$ assigned to ν(N-H) of the ligand is absent in the complex, confirming the co-ordination of N atom of $NH_2$ group after deprotonation. The ν(M-O) frequencies are observed at around 590 $cm^{-1}$ and the ν(M-N) frequencies observed at around 570, support the above observation[13].

TABLE-1
IMPORTANT IR SPECTRAL BANDS AND THEIR ASSIGNMENTS

| | C=O ($cm^{-1}$) | N-H ($cm^{-1}$) | M-O ($cm^{-1}$) | M-N ($cm^{-1}$) |
|---|---|---|---|---|
| Ligand | 1640 | 3400 | – | – |
| Copper (II) complex | 1632 | | 590 | 571 |
| Cobalt (II) complex | 1635 | | 593 | 573 |
| Nickel (II) complex | 1638 | | 591 | 572 |
| Manganese (III) complex | 1645 | | 595 | 570 |

The solid state electronic spectra exhibit a single band around 20406 $cm^{-1}$ for copper(II) complex, 20404 $cm^{-1}$ for cobalt(II) complex, 20400 $cm^{-1}$ for nickel(II) complex and 20408 $cm^{-1}$ for manganese(III) complex. The spectral data suggests octahedral geometry for all the complexes. The copper(II), cobalt(II), nickel(II) and manganese(III) complexes shows magnetic moment values 1.53, 3.67, 2.78 and 4.78 BM, respectively. The values agree with the expected values[14].

**Phenomenological data of thermal decomposition of Merrifield resin supported Schiff base complexes:** All the complexes have only one stage of decomposition. The $T_i$, $T_f$ and $T_s$ values for the above mentioned complexes are given in Table-2. The MF-IA copper(II) complex was found to be stable up to 633 K ($T_i$), the decomposition takes place from 633-833 K ($T_f$) and $T_s$ occurs at 683 K. Likewise the $T_i$, $T_f$ and $T_s$ values for all the complexes are given in the Table-2. Of these copper(II) complex shows the maximum $T_i$ and $T_f$ values.

**Kinetic data of the thermal decomposition of Merrifield resin supported Schiff base chelates:** The kinetic parameters were evaluated using Coats-Redfern equation and the values of E, -log A and -ΔS are shown in Table-3. The negative value of ΔS for the complexes indicates that the activated complex has a more ordered structure than the reactants[15].

TABLE-2
PHENOMENOLOGICAL DATA OF THERMAL DECOMPOSITION

| Metal Schiff base complexes | Decomposition temperature range in TG (K) | | Peak temp. DTG (K) $T_s$ |
|---|---|---|---|
| | $T_i$ | $T_f$ | |
| Cu(II) | 633 | 833 | 683 |
| Co(II) | 583 | 781 | 708 |
| Ni(II) | 573 | 773 | 688 |
| Mn(III) | 513 | 773 | 723 |

TABLE-3
KINETIC DATA OF THERMAL DECOMPOSITION

| Metal ion of Schiff base complex of MF-IA ligand | E (kJ $mol^{-1}$) | -log A | -ΔS (J $K^{-1}$ $mol^{-1}$) |
|---|---|---|---|
| Cu(II) | 29.79 | 0.89 | 268.64 |
| Co(II) | 37.09 | 0.79 | 253.71 |
| Ni(II) | 28.73 | 0.98 | 270.66 |
| Mn(III) | 30.05 | 0.81 | 260.12 |

**Influence of $H_2O_2$ concentration on the rate of decomposition of Schiff base complexes:** A definite amount of catalyst (100 mg) was subjected to decomposition reaction by varying the concentration of $H_2O_2$ (1.8-3.0 g/L). The result for different complexes is given in Table-4. The rate of reaction is found to increase with increase in concentration of $H_2O_2$. Of these copper(II) complex, is the most active.

TABLE-4
INFLUENCE OF $H_2O_2$ CONCENTRATION ON THE RATE OF DECOMPOSITION

| Concentration of $H_2O_2$ (g/L) | Amount of catalyst 100 mg | | | |
|---|---|---|---|---|
| | Rate constant $10^3$ (k $min^{-1}$) | | | |
| | Cu(II) | Co(II) | Ni(II) | Mn(III) |
| 1.8 | 4.32 | 3.98 | 4.12 | 4.01 |
| 2.4 | 5.38 | 4.52 | 4.92 | 4.81 |
| 3.0 | 6.20 | 5.01 | 5.28 | 5.73 |

**Influence of varying amount of catalyst in the Schiff base complexes of Merrifield resin:** The effect of varying amount of catalyst on the decomposition reaction shows first order dependence. For a definite concentration of $H_2O_2$ (1.8 g/L) varying amounts of catalyst (50, 100, 150 and 200 mg) are subjected to decomposition reaction. The rate of reaction increased with increase in amount of catalyst. The values are given in Table-5.

TABLE-5
INFLUENCE OF VARYING AMOUND OF CATALYST ON THE RATE OF DECOMPOSITION

| Concentration of $H_2O_2$ = 1.8 g/L | | | | |
|---|---|---|---|---|
| Amount of catalyst (mg) | Rate constant $10^3$ (k $min^{-1}$) | | | |
| | Cu(II) | Co(II) | Ni(II) | Mn(III) |
| 50 | 3.1 | 2.98 | 3.12 | 3.01 |
| 100 | 4.31 | 3.92 | 4.2 | 4.30 |
| 150 | 5.01 | 4.02 | 5.01 | 5.0 |
| 200 | 6.04 | 5.8 | 5.98 | 6.01 |

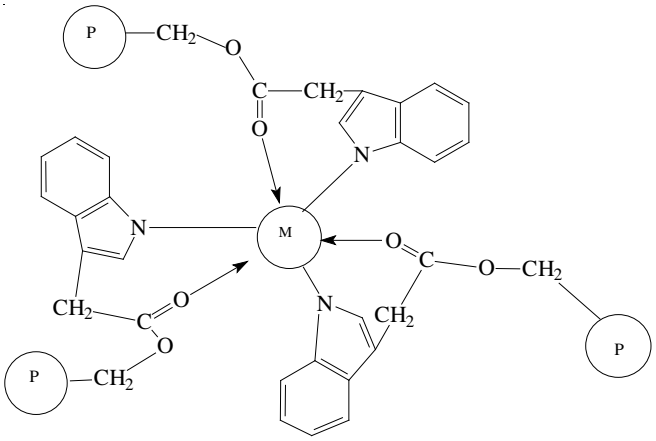
**Antibacterial activity of the ligand and complex by disc diffusion method:** Antimicrobial activity of the ligand and its metal complexes have been investigated by disc diffusion method. Gentamycine was used as control. The complexes are more active than the ligand. The Copper(II) complex has the highest activity against *S. aureus* and *E. coli*. The results are given in Table-6.

TABLE-6
ANTIMICROBIAL ACTIVITY OF THE LIGAND AND COMPLEXES

| Compound | *S. aureus* (zone formation in mm) | *E. coli* (zone formation in mm) |
|---|---|---|
| Control | 24 | 16 |
| MF-IA ligand | 13 | 11 |
| Ni(II) complex | 16 | 12 |
| Co(II) complex | 17 | 13 |
| Cu(II) complex | 20 | 15 |
| Mn(III) complex | 18 | 14 |

## Conclusion

The IR spectral studies of the complexes reveals that the co-ordination of the ligand through oxygen of the carbonyl group and the nitrogen of the indole ring. The reflectance spectra of the complexes show an octahedral or distorted octahedral symmetry for the complexes. The metal and ligand ratio for the complexes is 1:3. It can be inferred that three ligands get attached to the metal[16]. A tentative structure of the complexes is represented in Fig. 1. The synthesized complexes were evaluated for their antimicrobial and catalytic activities. The antimicrobial activities of the complexes revealed that copper(II) complex has the highest activity against *S. aureus* and *E. coli*. The catalytic activities of all Schiff base complexes were studied using $H_2O_2$ solution. In the case of varying concentration of $H_2O_2$ the catalytic activity increases by increasing the concentration $H_2O_2$. The catalytic activity of the complex was also checked by varying the amount of catalyst. Here also the catalytic activity increases by increasing the amount of catalyst.




M= Cu(II), Co(II), Ni (II)

Fig. 1.

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