



Research Article

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**Synthesis, structural characterization, molecular modelling and antimicrobial studies of transition metal complexes of schiff base ligand derived from 5-chlorosalicylaldehyde and 2-(2-aminophenyl) 1H-benzimidazole**

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**ABSTRACT**

*A series of Ni(II), Co(II), Cu(II), and VO(IV) complexes have been synthesized from the Schiff base ligand. The Schiff base ligand is 2-[(Z)-{(2-(1H-Benzimidazole-2-yl)phenyl)imino} methyl] - 4 - Chloro phenol (-BMCP) has been synthesized by the reaction between 2-(2-Aminophenyl)1- H-Benzimidazole and 5- Chloro Salicylaldehyde. The resulting complexes were characterized by elemental analysis, magnetic moment measurements, conductivity measurements, IR, UV-VIS, <sup>1</sup>H NMR, mass spectra, and ESR spectral studies. All the complexes were tested for their antibacterial activity. From the data, an octahedral geometry around the central metal ion has been suggested for all the metal complexes except Cu(II) complex, which has square planar geometry. Antimicrobial activity of the ligand and its metal complexes were studied against two gram negative bacteria: E.Coli, Pseudomonas.flourescence, and two gram positive bacteria: Bacillus.subtilis, Staphylococcus.aureus. The activity data show that the metal complexes are more potent than the free ligand.*

**Keywords:** Schiff base, 5-Chlorosalicylaldehyde, 2-(2-Aminophenyl)1-H- Benzimidazole, Metal complexes, Bacteria.

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**INTRODUCTION**

The chemistry of the carbon-nitrogen double bond plays a vital role in the progress of chemistry science [1]. Schiff base compounds have been used as fine chemicals and medical substrates. In the field of coordination chemistry, Schiff base metal complexes have a curious history [2,3]. Metal ions play vital roles in the vast number of biological processes. Metal complexes with Schiff base ligands have been studied for their application in biological, clinical, analytical and pharmacological areas [4].

Schiff bases derived from the salicylaldehydes are well known as polydentate ligands [5], coordinates in deprotonated or neutral forms.

Benzimidazole and their derivatives were reported to have wide biological activities like antitumor, antiamoebic, antihistaminic, anthelmintic and antihypertensive activity.

Benzimidazoles are very useful intermediates for the development of Molecules of biological interest. Substituted benzimidazole derivatives have found applications in antifungals, anticancers, and antiulcers etc [6-10]. In continuation of our studies on complexes of Schiff bases derived from 2-(2-Aminophenyl)1- H-Benzimidazole and 5- Chloro salicylaldehyde, In this paper efforts were taken for the synthesis, characterization and antimicrobial studies of transition metal Complexes of bidentate nature of the ligand which coordinates through the tertiary Nitrogen of the imidazole ring, the exocyclic imine nitrogen of 2-(2-Aminophenyl)1-H- Benzimidazole.

## EXPERIMENTAL SECTION

**Chemicals:**

All chemicals and solvents used in this work were Analytical grade. 2-(2- Amino phenyl)1-H- Benzimidazole and 5-chloro salicylaldehyde was of Sigma Aldrich chemicals. Vanadyl sulphate, Copper chloride, Nickel chloride, and Cobalt chloride, DMSO, of SD's fine chemicals.

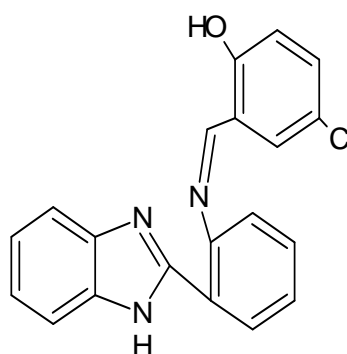
**Instrumentation:**

The percentage compositions of C, H, and N of complexes were determined by using micro analytical methods of PerkinElmer 240 (USA) elemental analyzer. Infrared spectra of ligands and their complexes were recorded on Perkin Elmer Infrared model 337 spectrometer in KBr pellets in the range of (4000-400cm<sup>-1</sup>). The UV-Visible spectra were recorded on a Shimadzu UV spectrometer in the wavelength range 200-1100nm. The mass spectra were recorded by ESI technique on VG AUTOSPEC mass spectrometer instrument. The <sup>1</sup>H NMR spectra was recorded on Varian Gemini Unity Spectrometer by employing TMS as internal standard. Melting points of the ligand and decomposition temperature of complexes were determined on Polmon instrument (model No.MP-96). The Molar conductance measurements were carried out in DMSO (10<sup>-3</sup> M) using Digisun Electronic Digital conductivity meter of model: DI-909 having a dip-type cell calibrated with KCl. The Magnetic susceptibilities of complexes were determined on Gouy balance model 7550 at 23°C. The diamagnetic corrections were made by Pascal's constant and Hg[Co(SCN)<sub>4</sub>] was used as a calibrant. Electro spin resonance spectra of powered Cu(II), complex was recorded on JOEL.TE -3X .X-Band spectrometer.

**Synthesis of Schiff base:**

A mixture of 2-(2-Aminophenyl)1-H-Benzimidazole (2.09g; 0.01 mol) and 5-chloro salicylaldehyde (1.56g; 0.01 mol) and a drop of acetic acid was dissolved in 25ml of ethanol and heated on a steam bath for 45-60 min. The reaction mixture was allowed to stand at room temperature for 24hr, the yellow solid product was separated out and dried under vacuum at room temperature.

Structure of the Schiff base is shown below:



2-[(Z)-[2-(1H-benzimidazol-2-yl)phenyl]imino]methyl-4-chlorophenol

Figure 1 Structure of Schiff Base

**Synthesis of Metal complexes:**

Hot ethanolic solution of ligand (0.005 mol) and ethanolic solution of corresponding metal salts (0.005 mol) (MX<sub>2</sub>, where M= Ni (II), Co (II), Cu (II) and VO(IV) X=Cl/So<sub>4</sub>/acetates ) were stirred constantly. The resulting solution was boiled under reflux for 4-5 hrs and then left to cool. The precipitated complex was filtered off, washed with anhydrous ethanol and dried in vacuum at room temperature.

## RESULTS AND DISCUSSION

**Physical properties:**

All the complexes are stable at room temperature and are non-hygroscopic. On heating, they decompose at high temperatures. The complexes are insoluble in water but are soluble in DMSO. The analytical data and physical properties of the ligand and complexes are summarized in table 1.

**Elemental analysis:**

It is clear from the data that the experimental values shown for each of the compound are in good agreement with the theoretical values calculated for 1:1 ratio. The composition assigned to the ligand and its complexes may, therefore be formulated as presented in Table 1.

**Molar Conductance:** The Molar Conductance of metal complexes were measured using  $10^{-3}$ M DMSO solvent, the obtained values (Table1) suggest the presence of a non-electrolytic nature and that no anions are present outside the coordination sphere.

**Table 1. Analytical data and Physical properties of the Ligand and its Complexes**

| Compound       | Emperical Formula   | Mol. Wt. | M.P (°C) | Yield (%2) | C Found (Calc.) | H Found (Cc.) | N Found (Calc.) | M Found (Calc.) | $\Omega$ Ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> ) |
|----------------|---|----------|----------|------------|-----------------|---------------|-----------------|-----------------|--|
| Ligand (BMCP)  | [C <sub>20</sub> H <sub>14</sub> N <sub>3</sub> OCl]                                | 348      | 175      | 95         | 68.50 (68.96)   | 4.05 (4.02)   | 12.15 (12.06)   | –               | –  |
| Cu(II) Complex | [CuC <sub>20</sub> H <sub>14</sub> N <sub>3</sub> OCl <sub>3</sub> ]                | 482.5    | 186      | 80         | 49.58 (49.74)   | 2.81 (2.90)   | 8.49 (8.70)     | 13.01 (13.16)   | 24   |
| Ni(II) Complex | [NiC <sub>20</sub> H <sub>18</sub> N <sub>3</sub> O <sub>3</sub> Cl <sub>3</sub> ]  | 514      | >300     | 69         | 46.54 (46.69)   | 3.48 (3.50)   | 8.10 (8.17)     | 11.11 (11.47)   | 16   |
| Co(II) Complex | [CoC <sub>20</sub> H <sub>18</sub> N <sub>3</sub> O <sub>3</sub> Cl <sub>3</sub> ]  | 514      | >300     | 85         | 45.99 (46.69)   | 3.35 (3.50)   | 8.00 (8.17)     | 11.00 (11.47)   | 20   |
| VO(IV) Complex | VO[C <sub>20</sub> H <sub>16</sub> N <sub>3</sub> O <sub>3</sub> Cl]SO <sub>4</sub> | 478      | 280      | 90         | 50.11 (50.20)   | 3.15 (3.34)   | 8.58 (8.78)     | 10.52 (10.66)   | 12   |

M.P=Melting Points,  $\Omega$ =Molar Conductance in Ohm<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>

**Table-2 Mass spectra of the schiff base and its complexes**

| Compound  | Calculated mass | Obtained mass | Peak assigned |
|---|-----------------|---------------|---------------|
| [C <sub>20</sub> H <sub>14</sub> N <sub>3</sub> OCl]                                | 348             | 348           | M             |
| [CuC <sub>20</sub> H <sub>14</sub> N <sub>3</sub> OCl <sub>3</sub> ]                | 482.5           | 486.8         | M+4           |
| [NiC <sub>20</sub> H <sub>18</sub> N <sub>3</sub> O <sub>3</sub> Cl <sub>3</sub> ]  | 514             | 537           | M+23          |
| [CoC <sub>20</sub> H <sub>18</sub> N <sub>3</sub> O <sub>3</sub> Cl <sub>3</sub> ]  | 514             | 537           | M+23          |
| VO[C <sub>20</sub> H <sub>16</sub> N <sub>3</sub> O <sub>3</sub> Cl]SO <sub>4</sub> | 478             | 501           | M+23          |

**Infrared Spectra of the Schiff Base and Its Complexes:**

The IR spectra provide valuable information regarding the nature of functional group attached to the metal atom [11]. In order to study the bonding mode of schiff base to the metal complexes, the IR spectrum of the free ligand was compared with the spectra of the complexes. The main IR bands and their assignments are listed in table 2.

- The IR band assignments of all metal complexes exhibit broad bands in the range of 3354 to 3423 cm<sup>-1</sup> indicating the presence of coordinated water molecules [12].
- A band at 1618 cm<sup>-1</sup> in free Schiff base is due to  $\nu$ C = N stretching vibration [13].
- But in complexes, the azomethine (C=N) frequency shows a down field or up field indicating coordination through N-atom [14].
- IR spectra of the free ligand show a broadband around 3,350 cm<sup>-1</sup> which can be attributed to NH stretching vibration of benzimidazole moiety.
- The appearance of broadband around 3,400 cm<sup>-1</sup> region was observed in the spectra of metal complexes indicating the presence of coordinated water molecules. Water molecules are coordinated, confirmed by the occurrence of additional band at 800- 880 cm<sup>-1</sup> arising due to OH rocking vibrations [15] and  $\nu$ M-N bands at 450-485 cm<sup>-1</sup>. In addition Vanadyl complex shows a band at 951 cm<sup>-1</sup> corresponding to V=O frequency. [16-19].

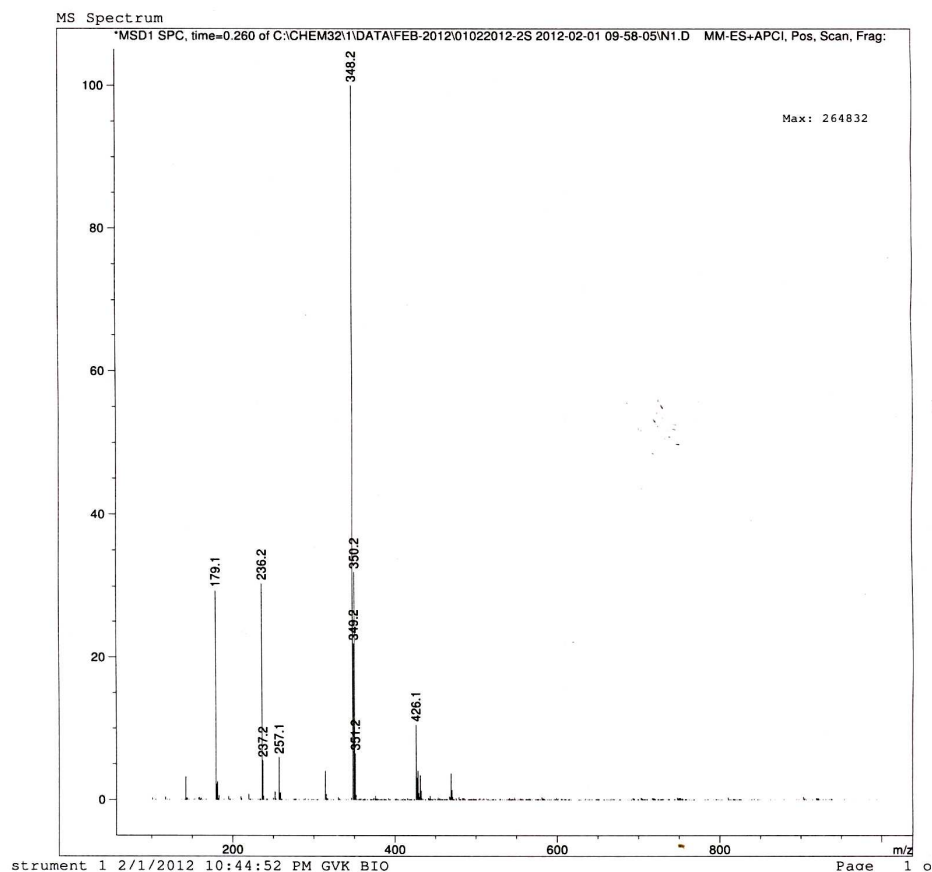


Figure 2 - Mass Spectra of the Ligand

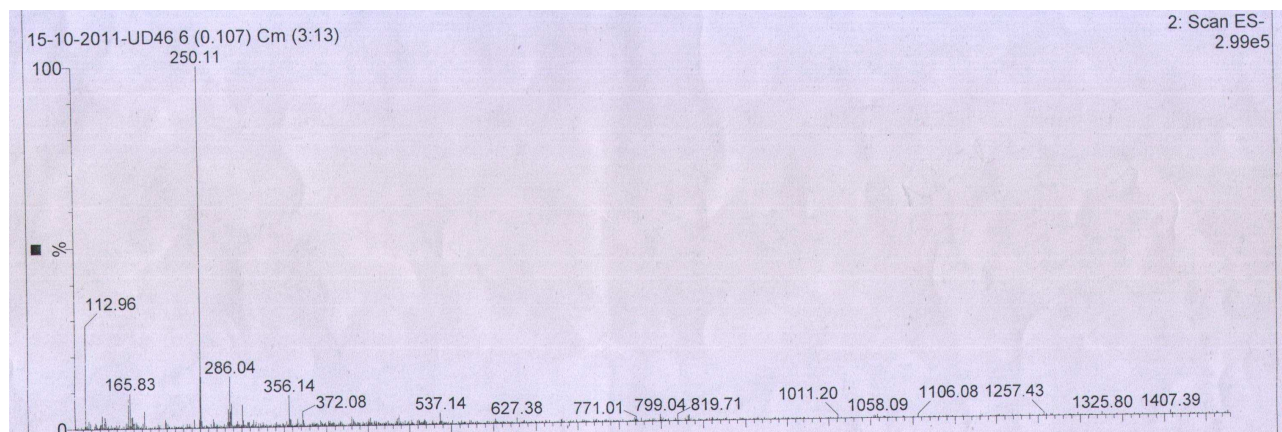


Figure 3 - Mass Spectra of Ni (II)Complex

Table 3: Characteristics IR bands ( $\text{cm}^{-1}$ ) of the compounds studied

| Compound     | $\nu\text{CH}=\text{N}$ | $\nu\text{M}-\text{N}$ | $\nu\text{M}-\text{OH}$ | $\nu\text{V}=\text{O}$ |
|--------------|-------------------------|------------------------|-------------------------|------------------------|
| Ligand(BMCP) | 1618                    | -                      | -                       | -                      |
| Cu- BMCP     | 1610                    | 461                    | 3370                    | -                      |
| Co- BMCP     | 1629                    | 471                    | 3372,826                | -                      |
| Ni -BMCP     | 1631                    | 446                    | 3335,828                | -                      |
| OV -BMCP     | 1589                    | 471                    | 3383,820                | 951                    |

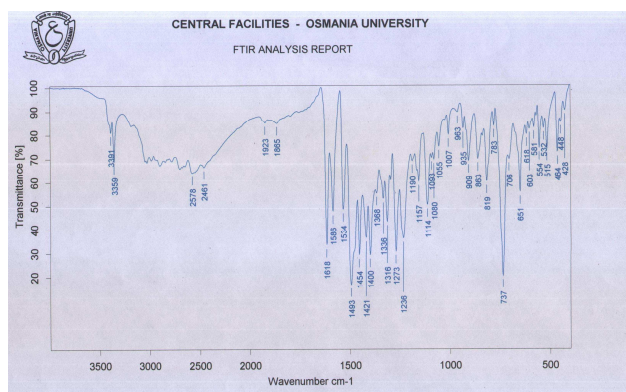


Figure 4 – IR Spectra of the Ligand (BMCP)

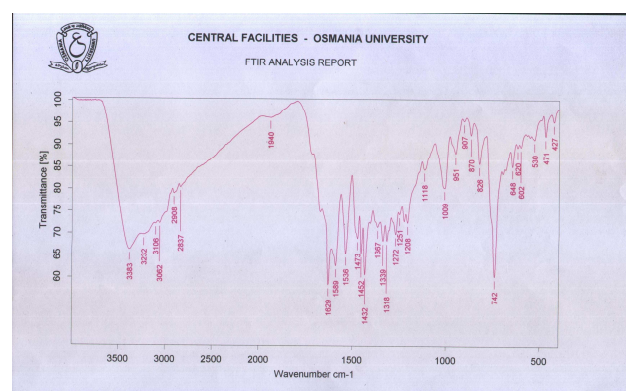


Figure 5 – IR Spectra of OV (IV) Complex

**Magnetic moments & Electronic Spectral Data:**

The electronic spectral data was used to study the geometry the synthesized complexes based on the UV visible spectrum and the complexes were shown to have an Octahedral geometry except the Cu (II) complex which has the square planar geometry. The electronic spectral studies of the metal complexes of Ni (II), Co (II), Cu (II) and VO(IV) with Schiff bases were carried out in DMSO solution. The absorption spectrum of the Co (II) complex shows bands at 18,018, 18,867, 21,367  $\text{cm}^{-1}$  which are attributed to  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$  ( $\nu_1$ ),  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$  ( $\nu_1$ ) and  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$  ( $\nu_3$ ) transitions respectively, that are characteristic of octahedral Configuration [20]. The Co (II) has magnetic moment 4.3 B.M also suggest an Octahedral geometry.

**Table 4: Magnetic moments & Electronic Spectral Data for the complexes:**

| Complex | $\mu_{\text{eff}}$ B.M | Frequency ( $\text{cm}^{-1}$ ) | Assignments   |
|---------|------------------------|--------------------------------|---|
| Cu-BMEP | 1.78                   | 29,585                         | INCT  |
|         |                        | 24,937                         | INCT  |
|         |                        | 21,231                         | ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$                     |
| Co-BMEP | 4.3                    | 18,018                         | ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ |
|         |                        | 18,867                         | ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ |
|         |                        | 21,367                         | ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ |
| Ni-BMEP | 2.8                    | 22,222                         | ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\text{F})$           |
|         |                        | 25,000                         | ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$           |
|         |                        | 27,397                         | ${}^3\text{T}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$           |
| VO-BMEP | 1.6                    | 23,980                         | ${}^2\text{E} \rightarrow {}^2\text{B}_2$                             |
|         |                        | 24,937                         | ${}^2\text{B}_1 \rightarrow {}^2\text{B}_2$                           |
|         |                        | 29,940                         | ${}^2\text{A}_1 \rightarrow {}^2\text{B}_2$                           |

Ni (II) complex exhibits 3 electronic spectral bands at 22,222, 25,000, 27,397  $\text{cm}^{-1}$  can be assigned to  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\text{F})$  ( $\nu_1$ ),  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$  ( $\nu_2$ ) and  ${}^3\text{T}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$  ( $\nu_3$ ) in an Octahedral field. The Ni (II) complex has magnetic moment 2.8 BM also suggest an Octahedral geometry. The electronic spectrum of Cu(II) complex shows bands at 29,585, 24,937, and 21,231  $\text{cm}^{-1}$  respectively, the first band at 29,585  $\text{cm}^{-1}$  and second band at 24,937  $\text{cm}^{-1}$  are assigned for the inter-nuclear charge transfer bands. The third band at 21,231  $\text{cm}^{-1}$  is assigned for  ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$  transition, characteristic for square-planar geometry. The absence of band below 10000  $\text{cm}^{-1}$  excludes the possibility



of tetrahedral geometry. The observed magnetic moment value for Cu (II) complex is 1.78 BM suggestive of square planar nature for the Complex.

The VO(IV) complex exhibited 3 transitions 23,980, 24,937, 29,940  $\text{cm}^{-1}$  which are assignable to  ${}^2\text{E} \rightarrow {}^2\text{B}_2$ ,  ${}^2\text{B}_1 \rightarrow {}^2\text{B}_2$  and  ${}^2\text{A}_1 \rightarrow {}^2\text{B}_2$  respectively, that are characteristic of octahedral geometry.[20]

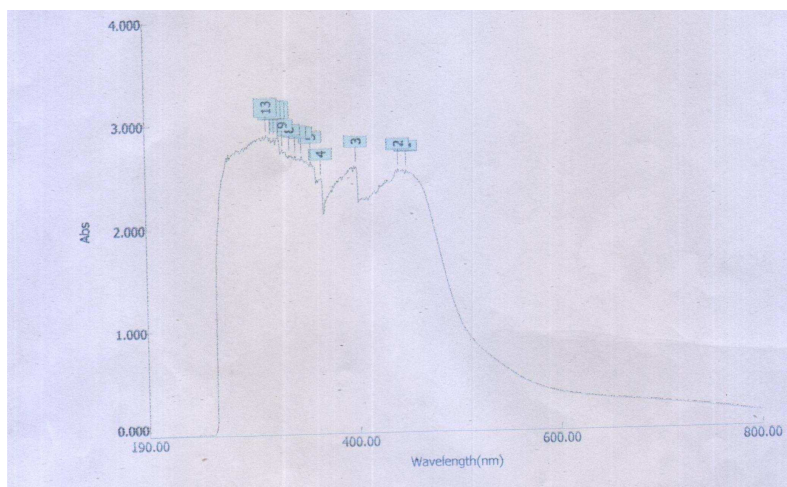


Figure 6– UV Spectra of Ni (II) Complex

#### ${}^1\text{H}$ NMR Spectra:

The  ${}^1\text{H}$  NMR spectrum of the ligand in  $\text{CDCl}_3$  shows the following signals given in Table 4. The sharp singlet at 7.4 attributed to azomethine proton ( $-\text{CH}=\text{N}-$ ) confirms the formation of the ligand as proposed.

Table 5:  ${}^1\text{H}$  NMR data of Schiff base

| Chemical Shift ( $\delta$ , ppm) | Functional Group assigned |
|----------------------------------|---------------------------|
| 7.4 (1H, s)                      | $-\text{CH}=\text{N}-$    |
| 10.5 (1H, s)                     | $-\text{NH}-$             |
| 6.8 – 7.3                        | Phenyl ring               |
| 8.0                              | Benzimidazole             |

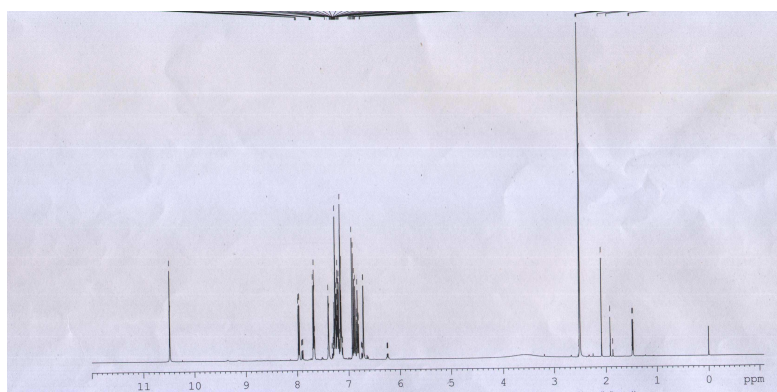


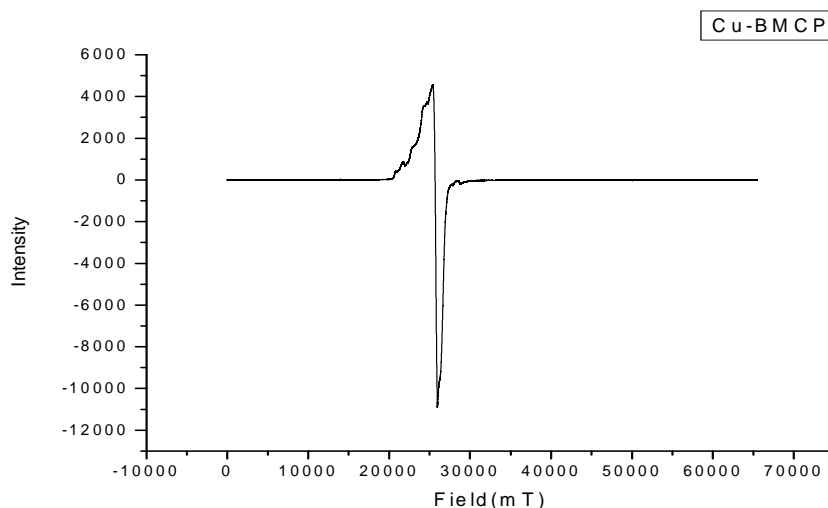
Figure 7– NMR Spectra of the Ligand BMCP

#### ESR Spectra of Cu(II) complex:

The ESR spectral studies of Cu(II) complex provide information of the metal ion environment. The ESR spectrum of Cu(II) was recorded in DMSO at Liquid Nitrogen temperature (LNT). This complex in frozen state at 77K shows four slightly resolved peaks low intensities in the low field region and one intense peak in the high field region. In square planar complexes, the unpaired electron lies in the  $\text{dx}^2\text{-y}^2$  orbital giving  ${}^2\text{B}_{1g}$  as the ground state with the  $g_{\parallel} > g_{\perp}$ , from the observed  $g$  values, it is clear that  $g_{\parallel}$  (2.450)  $>$   $g_{\perp}$  (2.084)  $>$  2.0023, which suggests that the complex is square planar[21-23]. Also it is supported by the fact that the unpaired electron lies predominantly in the  $\text{dx}^2\text{-y}^2$  orbital for the copper complex. The value of exchange interaction term  $G$ , estimated from the following expression is 5.6

$$G = g_{\parallel} - 2.0023 / g_{\perp} - 2.0023$$

According to Hathway, If  $G > 4.0$ , the local tetragonal axes are aligned parallel or only slightly misaligned. If  $G < 4.0$ , significant exchange coupling is present and misalignment is appreciable. The observed value for the exchange interaction term  $G$  suggests that the local tetragonal axes are aligned parallel or slightly misaligned and consistent with  $d_{x^2-y^2}$  ground state. complex has distorted octahedral geometry, and the Schiff base ligand forming Cu(II) complex is considered as strong field ligand.

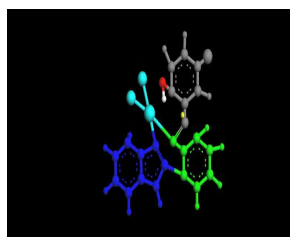


**Figure 8 – ESR Spectra of Copper (II) Complex**

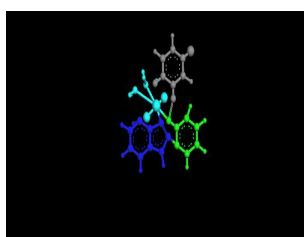
#### Molecular Modeling studies:

The possible geometries of metal complexes were evaluated using the molecular calculation with Argus lab 4.0.1 version software. The metal complexes were built and geometry optimization was done using molecular mechanics uniform force field (UFF) method. The molecular modeling pictures and the energies of metal complexes are shown in figure 9:

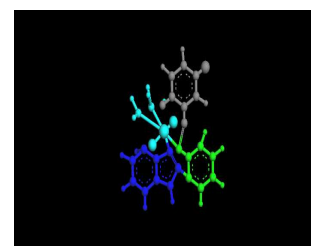
**Figure 9: Molecular modeling structures for metal complexes:**



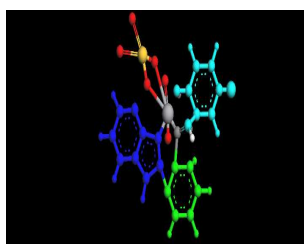
Cu(BMCP)  
( 151K.cal/mol)



[Co(BMCP)(H<sub>2</sub>O)<sub>2</sub>Cl<sub>2</sub>]  
(136 K.cal/mol)



[Ni(BMCP)(H<sub>2</sub>O)<sub>2</sub>Cl<sub>2</sub>]  
(116 K.cal/mol)



[VO (BMCP) (H<sub>2</sub>O) SO<sub>4</sub>]  
(149K.cal/mol)

**Antibacterial studies**

The synthesized Schiff bases and their corresponding metal complexes were screened against *Escherichia.Coli*, *Staphylococcus aureus*, *Bacillus subtilis* and *Pseudomonas. Fluorescence* to assess their potential as antimicrobial agent by diffusion method [24]. Compounds containing  $>C=N$  group have enhanced antimicrobial activity than  $>C=C<$  group. The growth of certain microorganisms take place even in the absence of  $O_2$ . A comparative study of growth inhibition zones values of Schiff base and its complexes indicate that metal complexes exhibit higher antibacterial activity than the free ligands and the same is indicated from the results given in the table 6. This is probably due the greater lipophilic nature of the complexes. Such increased activity of the complexes can be explained on the basis of Overtone's concept[25]. and Tweedy's Chelation theory[26,27]. According to Overtone's concept of cell permeability, the lipid membrane that surrounds the cell favors the passage of only lipid soluble materials due to which liposolubility is an important factor which controls the anti-microbial activity. On chelation, the polarity of the metal ion will be reduced to a greater extent due to overlap of the ligand orbital and partial sharing of positive charge of metal ion with donor groups [28,29] Further, it increases the delocalization of the  $\pi$  electrons over the whole chelate ring and enhances the lipophilicity of the complex. This increased lipophilicity enhances the penetration of the complexes into lipid membrane and the blocks the metal binding sites on enzymes of microorganisms. [30] These metal complexes also disturb the respiration process of the cell and thus block the synthesis of proteins, which restricts further growth of the organism [31].

The diffusion method requires filter paper disk, the medium used is Muller-Hinton agar with 2% of glucose and diameter of inhibition zone is visually read at 24 hours after incubation at 37°C. The compounds are added on to the filter paper containing this medium. The antimicrobial activity was estimated on the seeded agar plates. Streptomycin was used as standard. DMSO was used as solvent control. The zones of inhibition based upon zone size around the discs were measured. The measured zone of inhibition against the growth of various microorganisms is listed in table 5. It is found that metal complexes have higher anti-bacterial activity than the free ligand. Hence the complexation increases the microbial activity [32]. Such increased activity of metal complexes was explained on the bases of Chelation [33].

**Table6: Growth Inhibition Zone of Microbes in mm**

| Compound       | <i>E.coli</i> | <i>P.fluorescence</i> | <i>B.subtilis</i> | <i>S.aureus</i> |
|----------------|---------------|-----------------------|-------------------|-----------------|
| Schiff base    | 10            | 9                     | 11                | 9               |
| Cu(II) Complex | 16            | 11                    | 12                | 13              |
| Co(II) Complex | 14            | 11                    | 14                | 15              |
| Ni(II) Complex | 13            | 12                    | 10                | 17              |
| VO(IV) Complex | 15            | 14                    | 17                | 11              |

**F****Figure 10 – Anti Microbial Activity of Metal Complexes****CONCLUSION**

The bidentate Schiff base ligand and its metal complexes of Ni(II), Co(II) Cu(II), and VO(IV) have been structurally characterized by analytical and spectral techniques. From the electronic absorption spectra, Mass spectra, octahedral



geometry was assigned for all the synthesized complexes, except for the Cu(II) complex which is assigned with square planar geometry. The analytical data show that the metal Ligand stoichiometry in all these complexes is 1:1. All the complexes are non-electrolytes in DMSO. The spectral data show that the ligand is bidentate which coordinates through the tertiary Nitrogen of the imidazole ring, the exocyclic imine nitrogen of 2-(2-Amino phenyl) 1-H-Benzimidazole [34]. From their magnetic susceptibility and ESR spectral data the monomeric nature of the complex was confirmed. Biological studies of these complexes reveal that these complexes show better activity compared to the ligand.

## REFERENCES

- [1] S.Patai, The chemistry of the Carbon-nitrogen double bond, John Wiley & Sons Ltd, London, **1970**
- [2] Yamada S, *Coord chem. Rev.* **1999**, 537, 190-192
- [3] Singh S, Das S and Dhakarey R, *E-J chem.*, **2009**, 6(1), 99-105
- [4] Raman N, syed Ali Fathima S and Dhaweethu Raja *J Serbian chem. Soc.*, **2008**, 73(11), 1063-1071
- [5] Tlimer et.al. *Transition Met.chem.*, 24, 414-420 (**1999**) several adducts of non-transition, early transition
- [6] Goker.H, Alp.M, Yildiz.S. *Molecules* **2005**, 10 1377
- [7] Patzold.F, Zener.F, Heyer.JH and Nichlas. *HJ, Synthetic Commun.* **1992**, 22, 281.
- [8] Vanden Eynde JJ, Delfosse F, Lor P and Van Haverbeke Y, *Tetrahedron*, **1995**, 51, 5813-5818.
- [9] Lee K J and Janda KD, *Can J Chem.*, **2001**, 79 1556-1561.
- [10] Chikashita H, Nishida S, Miyazaki M, Morita Y and Itoh K, *Bull Chem soc JPN.*, **1987**, 60, 737.
- [11] Suresh M S and Prakash V, *Int J Current Res.*, **2011**, 3(2),
- [12] Jezowska B., Lisowski J and chmielewski P. *Polyhedron*, 68-75
- [13] Seema Varghese, *RJPBCS*. **2010**, 2, 347
- [14] Prashanthi, Y and shivraj, *J.Sci.Res.* **2010**, 2(1), 114.
- [15] Poonam. Deshmukh, AMIT.R.Yaul, Jayashree, Bhajane.N and Aanad J Aswan. *World. J.CHEM* **2010**, 5(1), 57.
- [16] Mozaffar asadia, Mohammad hadi ghateea, Susan torabia, khosro mohammadib and fatemeh moosavia. *J. chem.Sci* **2010**, 122, 539
- [17] Hamdi Temel, Umit Cakir and Ibrahim Ugras.I. *Synthesis and reactivity in inorganic and metal organic chemistry*, **2004**, 34, 819
- [18] Nakamoto, K., *Infrared and Raman spectra of inorganic and coordination compounds*, part A & part B, Newyork, NY USA; John Wiley & sons, **1998**
- [19] Silverstein, RM.; Bassler, GC.; Morrill, TC. *Spectroscopic identification of organic compds*, 5<sup>th</sup> edition, Newyork, NY, USA, John wiley & sons; **1991**.
- [20] Lever, A.B.P. *Inorganic electro spectra*, Elsevier, Newyork, **1984**.
- [21] Paulmony Tharmaraj, Deivasigamani Kodimunthiri, Clarence D, Sheela and chappani S shanmuga priya S, *J Serbian Chem Soc.*, **2009**, 74 (8-9), 927-938.
- [22] B.J. Hathaway and A.A.G. Tomlinson, *Coord. Chem. Rev*, 5, 1 (**1970**).
- [23] Procter I M, Hathaway RJ, Billing DE and Nicholls P, *J Chem Soc A* **1968**, 1678.
- [24] Zotta, V. (Ed.) *Chimie farmaceutica, Medical.*; Bucuresti. **1985**, 67.
- [25] N. Dharmaraj, P. Viswanathamurthi and K. Natarajan, *Transition Met. Chem.*, 26, 105 (**2001**).
- [26] R. Malhotra, S. Kumar and K.S. Dhindsa, *Indian J. Chem.* 32A, 457, (**1993**).
- [27] Tweedy B G, *Phyto Pathology.*, **55**, 910 (1964)
- [28] Kralova K, Kissova K, Svajlenova O and Vanco J, *Chem. Pap.*, 58(5), 361 (**2000**)
- [29] Parekh J, Inamdhar P, Nair R, Baluja S and Chanda S, *J. Serb.Chem.Soc.*, **70**, 1161 (**2005**)
- [30] Vaghasia Y, Nair R, Soni M, Baluja S Chanda S, *J. Serb.Chem., Soc.*, **69**, 991 (**2004**)
- [31] Raman N, *Res. J. Chem. Environ.*, **4**, 9. (**2005**)
- [32] Anjaneyula Y and Roa PP, *Synth React Inorg met. Org chem.*, **1986**, 26, 257.
- [33] Thimmaiah K N, Lloyd W D and chandrappa GT, *Inorg chim Acta*, **1985**, 81, 106.
- [34] Pilar Souza, Jose A. Garcia- Vazquez and J.R. Masagner, *Transition met.chem*, 10, 410-412 (**1985**)