



Synthesis, Characterization and Antimicrobial Activities of Transition Metal Complexes of Co(II), Ni(II) and Cu(II) with Tridentate Schiff Base Ligand

Kamlesh Kumar Singh^{1*}, Kalyan Chandra Singh² and Manan Sharma³

^{1*}Department of chemistry, DAV Post Graduate College, Siwan-841226, India

²Department of chemistry, Sanjay Gandhi Inter College, Nagra, Saran, India

³Department of chemistry, Manjhi Inter College, Manjhi, Saran, India

ABSTRACT

The coordination complexes of Co (II), Ni (II) and Cu (II) were prepared from tridentate Schiff base. The Schiff base ligand was synthesized by the condensation of 3-ethoxy- 4-hydroxy benzaldehyde with 2-amino butanoic acid. The ligand and its metal complexes were characterized by elemental analysis, molar conductance, electronic spectra, IR spectra, NMR spectra, electrical conductivity and magnetic susceptibility. The transition metal complexes are colored and stable in air. In the metal complexes the metal -ligand found to be 1:1. A sharp band at 1625 cm^{-1} is characteristics of the azomethine group present in the Schiff base ligand. This band was shifted to lower frequency ($1585 - 1605\text{ cm}^{-1}$) in all the metal complexes, which indicates the coordination of the azomethine nitrogen to metal ion in complexes. The IR spectra of the free ligand having phenolic (-OH) group showed a broad band at 3450 cm^{-1} , the disappearance of this band in metal complexes indicates the deprotonation of the hydroxyl group and coordinated through oxygen atom. A band at 1690 cm^{-1} is assigned to $\nu(\text{C}=\text{O})$ stretching frequency of ligand, which is shifted to lower regions ($1612\text{-}1640\text{ cm}^{-1}$) in metal complexes indicating the coordination of oxygen atom with metal ion after deprotonation of -COOH group. The molar conductivity data of the complexes in DMSO solution indicates they are non-electrolytic nature. On the basis of magnetic susceptibility and electronic spectral data Co (II) and Ni (II) complexes have tetrahedral geometry, while Cu (II) complex square planar geometry has been suggested. The synthesized Schiff base complexes exhibit higher antimicrobial activity than the free Schiff base ligand.

Keywords: Schiff base, metal complexes, 3-ethoxy-4-hydroxybenzaldehyde, antimicrobial activity.

1. INTRODUCTION

Metal complexes have been receiving considerable attention for many years, due to their interesting characteristics in the field of biological systems and material science. A large number of Schiff base and their metal complexes may exhibit the properties like to reversibly bind oxygen, transfer of an amino group as nano precursors and varied complexing ability. Schiff bases are formed when condensation of primary amines with active carbonyl compounds under specific conditions and were first synthesized by Hugo Schiff in 1864. Schiff bases are represented as $R - CH = N - R^1$ where R and R^1 may be alkyl, aryl or heterocyclic. Azomethine functional group present in Schiff bases. Due to effective conjugation Schiff bases of aromatic aldehydes are more stable than aliphatic aldehydes. Ketones react slower than aldehydes in condensation reaction due to steric hinderance. Schiff bases are generally unidentate, bidentate, tridentate, tetradentate and polydentate ligands to form stable complexes with transition metals. Schiff bases are effective ligands due to presence of azomethine group. Schiff bases derived from aromatic carbonyl compounds and primary amines have more applications in the fields of biological, analytical, inorganic chemistry, catalysis and optical materials. Schiff base ligands have donor atoms may be nitrogen, oxygen or Sulphur which provided binding sites through non- bonding electrons. The presence of $-CH=N$ group in the transition metal complexes which contains donor nitrogen atom is responsible for stability, reactivity and biological activity of complexes. 2-Amino butanoic acid is a non-proteinogenic α -amino acid, which is a derivative of alanine with a side chain that is one carbon longer than the alanine side chain. It is synthesized through the transamination of oxo butyrate and is non-ribosomal peptides. Transition metal Schiff base complexes are wide applications in medicinal chemistry, catalysis, polymerization reactions, dyes, corrosion, plant growth regulators and analytical chemistry. Due to chelation transition metal Schiff base complexes are more stable and have wide applications in antibacterial, antifungal, antiviral, anticancer, and anti-inflammatory. Schiff base ligands acts as chelating ligands and their biological activity enhanced on coordination. The present aim of the work is to synthesize a Schiff base derived from 3-ethoxy-4-hydroxy benzaldehyde and α -amino butanoic acid and to prepare its transition metal complexes, characterize them and study their antibacterial and antifungal activities.

2. MATERIALS AND METHODS

All the chemicals and solvents used for present work of Anal-R grade and used without further purification. Metal salts were purchased from Loba Chemie. 3-Ethoxy-4-hydroxybenzaldehyde and 2-amino butanoic acid were obtained from Sigma-Aldrich. The percentage (%) of Co, Ni and Cu were determined by EDTA complexometric titration. The elemental analysis (C, H and N) data was obtained using 2400 CHN Perkin-Elmer elemental analyzer. The molar conductivity of the complexes in DMSO solution ($10^{-3}M$) were measured by using DI-909 digital conductivity meter. The IR spectra of the ligand and metal complexes were recorded on Shimadzu FTIR spectrophotometer using KBr disc. The magnetic susceptibility data were measured by Gouy method using $Hg [Co (SCN)_4]$ as a calibrant. The electronic spectra of the complexes were recorded by using Shimadzu model UV-1601 spectrophotometer in DMSO solution.

Synthesis of Schiff base ligand

The Schiff base ligand was prepared by the condensation of 3-ethoxy-4-hydroxybenzaldehyde (1.66g, 0.01 mol) with 2-amino butanoic acid (1.03g, 0.01 mol) in ethanol (25 ml) and the mixture was refluxed for 2 h. After cooling, the yellow coloured solid was obtained. Which was filtered and washed with ether and recrystallized from ethanol and dried in a vacuum desiccator.

Synthesis of metal complexes

The metal complexes were prepared by mixing (50 ml) ethanolic solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ / $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ / $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with the (50 ml) ethanolic solution of Schiff base in a metal-ligand ratio 1:1. The resulting mixture was refluxed on water bath for 2-3 h. The complex obtained in each time was cooled, filtered and washed with ether and recrystallized with ethanol and dried under reduced pressure over anhydrous CaCl_2 in a desiccator.

3. RESULTS AND DISCUSSION

The physical properties and analytical data of ligand and its metal complexes are listed in Table 1. All the metal complexes are colored, solid and stable at room temperature. They decompose on heating at high temperature. The metal ligand ratio in all the metal complexes have 1:1. Schiff base acts as tridentate ligand. The molar conductivities in DMSO solution show that all metal complexes are non-electrolytic nature.

FTIR Spectra

The important infrared spectral bands of the Schiff base and its metal complexes are listed in Table 2. The coordination sites in chelate compounds are determined by the IR spectra of free ligand compared with that of complexes. The IR spectrum of the synthesized Schiff base ligand showed absorption band at 1625 cm^{-1} is characteristic of azomethine ($>\text{C}=\text{N}$) group present in the Schiff base ligand. This band was shifted to lower regions ($1583\text{-}1605 \text{ cm}^{-1}$) in the metal complexes, which indicates the bonding of the metal to the azomethine nitrogen. The spectra of metal complexes exhibit broad bands in the range of $3412 - 3442 \text{ cm}^{-1}$ indicating the presence of coordinated water molecule. The IR spectra of the ligand having phenolic $-\text{OH}$ group showed a broad band at 3450 cm^{-1} . The disappearance of this band in metal complexes suggests deprotonation of the phenolic $-\text{OH}$ group after its chelation with the metal ion. A medium intensity ligand band at 1290 cm^{-1} (phenolic $\nu(\text{C}-\text{O})$) which gets shifted to a lower frequency ($1270 - 1236 \text{ cm}^{-1}$) in the complexes, which suggests the participation of phenolic oxygen in coordination with metal ion. Two new bands appearing in the low frequency range $425\text{-}435 \text{ cm}^{-1}$ and $518\text{-}565 \text{ cm}^{-1}$ are indicate the formation of M-O and M-N bond in the complexes. A band at 1690 cm^{-1} is assigned to $\nu(\text{C}=\text{O})$ stretching frequency of ligand, which is shifted to lower regions ($1612\text{-}1640 \text{ cm}^{-1}$) in metal complexes indicating the coordination of oxygen atom with metal ion after deprotonation of $-\text{COOH}$ group. Thus, the IR spectrum indicates that the ligand in all the metal complexes behaves as tridentate and the binding sites are azomethine nitrogen, phenolic oxygen and carboxylate oxygen atom in the metal complexes.

Electronic absorption spectra

The electronic absorption spectra of metal complexes were recorded in DMSO as solvent. The electronic spectrum of the $[\text{CoL}(\text{H}_2\text{O})]$ complex showed three absorption bands around 14200 cm^{-1} , 17300 cm^{-1} and 22000 cm^{-1} , which assigned to the transition ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$. The value of the magnetic moment of Co-complex was 4.61 B.M, tetrahedral geometry is suggested. The electronic spectrum of the $[\text{NiL}(\text{H}_2\text{O})]$ complex showed three absorption bands around 15250 cm^{-1} , 21200 cm^{-1} and 26300 cm^{-1} , which assigned to the transition ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1(\text{P})$ and LMCT respectively. The value of the magnetic moment of Ni-complex was 3.61 B.M, tetrahedral geometry is suggested. The electronic spectrum of the $[\text{CuL}(\text{H}_2\text{O})]$ complex showed two absorption bands around 17850 cm^{-1} and 31300 cm^{-1} , which assigned to the transition ${}^2\text{B}_1(\text{g}) \rightarrow {}^2\text{A}_1(\text{g})$ and LMCT respectively. The value of the magnetic moment of Cu-complex was 1.81 B.M, square planar geometry is suggested.

Antimicrobial activity

The synthesized ligand and its complexes were screened for their in vitro antibacterial activity against *Escherichia coli* and *Staphylococcus aureus* and antifungal activity against *Aspergillus niger* and *Candida albicans* by minimum inhibitory concentration method. The minimum inhibitory concentration profiles of all the compounds against bacteria and fungi are presented in Table 3. The MIC values indicated that all the complexes show more activity compared to the free ligand against microorganisms, and this activity is found to be enhanced on coordination with the metal ions. This also can be explained on the basis of Tweedy's chelation theory and the effect of the metal ion on the normal cell processes. It was further noted that the delocalization of electrons over the whole chelate ring enhanced the lipophilicity of the complexes. This increased lipophilicity enhanced the penetration of the complexes into lipid membrane and blocking the metal sites on enzymes of microorganisms. The antimicrobial activities show that Cu- complex is more active than the other metal complexes.

Table 1. Physical properties and analytical data of ligand and metal complexes

| Compounds | Colour | Elemental analysis, Found (Calcd.) % | | | | Molar conductance $\Omega^{-1}\text{cm}^2 \text{mol}^{-1}$ |
|--|-------------|--------------------------------------|------------|------------|--------------|--|
| | | C | H | N | M | |
| Ligand $\text{C}_{13}\text{H}_{17}\text{NO}_4$ | Yellow | 62.15(62.03) | 6.77(6.54) | 5.57(5.46) | - | - |
| $[\text{Co } \text{C}_{13}\text{H}_{17}\text{NO}_5]$ | Brown | 47.86(47.76) | 5.21(5.12) | 4.29(4.16) | 18.08(17.96) | 12.5 |
| $[\text{Ni } \text{C}_{13}\text{H}_{17}\text{NO}_5]$ | Light green | 47.89(47.78) | 5.22(5.14) | 4.29(4.16) | 18.02(17.87) | 9.6 |
| $[\text{Cu } \text{C}_{13}\text{H}_{17}\text{NO}_5]$ | Green | 47.20(47.12) | 5.14(5.06) | 4.23(4.17) | 19.21(19.06) | 7.8 |

Table 2. IR spectral data of ligand and its metal complexes

| Compounds | $\nu (\text{O-H})/\text{H}_2\text{O}$ cm^{-1} | $\nu (\text{C-O})$ cm^{-1} | $\nu (\text{C=N})$ cm^{-1} | $\nu (\text{C=O})$ cm^{-1} | $\nu (\text{M-N})$ cm^{-1} | $\nu (\text{M-O})$ cm^{-1} |
|--|--|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|
| $\text{L} = \text{C}_{13}\text{H}_{17}\text{NO}_4$ | 3450 | 1290 | 1625 | 1690 | - | - |
| $[\text{Co}(\text{L}) (\text{H}_2\text{O})]$ | 3412 | 1262 | 1605 | 1638 | 518 | 425 |
| $[\text{Ni}(\text{L}) (\text{H}_2\text{O})]$ | 3438 | 1270 | 1592 | 1640 | 525 | 431 |
| $[\text{Cu}(\text{L}) (\text{H}_2\text{O})]$ | 3442 | 1236 | 1585 | 1612 | 565 | 435 |

Table 3. Antimicrobial data of ligand and metal complexes

| S.No | CompoundS | Minimum inhibition concentration (mg /ml) | | | |
|------|----------------------------|---|-----------|----------|-------------|
| | | E. coli | S. aureus | A. niger | C. albicans |
| 1. | Schiff base | 6 | 7 | 9 | 12 |
| 2. | [Co(L) (H ₂ O)] | 12 | 10 | 11 | 14 |
| 3. | [Ni(L) (H ₂ O)] | 10 | 12 | 14 | 16 |
| 4. | [Cu(L) (H ₂ O)] | 14 | 16 | 18 | 20 |

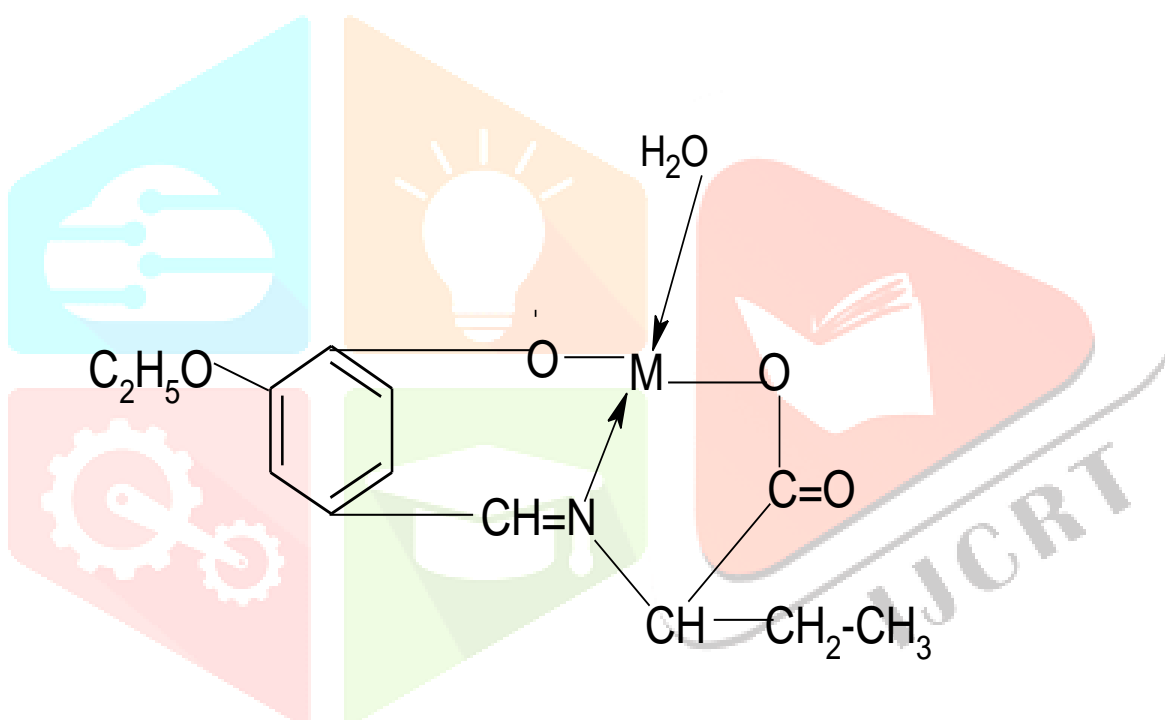


Fig 1. Proposed structure of metal complexes . M= Co(II), Ni(II) and Cu(II)

4. CONCLUSION

The Schiff base derived from 3-ethoxy-4-hydroxybenzaldehyde and 2-amino butanoic acid and its metal complexes of Co(II), Ni(II) and Cu(II) were synthesized and characterized by analytical and spectroscopic techniques. The Schiff base ligand acts as tridentate and coordinated with the metal ion through azomethine nitrogen and oxygen atoms of phenolic and carboxylic group. The analytical data show the composition of the metal complexes to be [M(L)(H₂O)], where L= Schiff base ligand and M = Co(II), Ni(II) and Cu(II). The molar conductivity data of the complexes in DMSO solution indicates they are non-electrolytic nature. On the basis of magnetic susceptibility and electronic spectral data Co (II) and Ni (II) complexes have tetrahedral geometry, while Cu (II) complex square planar geometry has been suggested. The synthesized Schiff base complexes exhibit higher antimicrobial activity than the free Schiff base ligand.

REFERENCES

1. Duta. S, Biswas.P. Structural spectroscopic and magnetic properties of a diphenolate-bridged Fe (III) and Ni(II) complex showing excellent phosphodiester cleavage activity. *Polyhedron*, 2012; 31(1): 110-117.
2. Tiwari Vivek and Singhai Rashmi. Ligational behaviour of Vanillin derived Schiff bases towards Nickel(II) and Cu(II). *Asian.J.Chem.* 2003; 15(1) : 435-438.
3. Zhao Guoliang. Synthesis, characterization and thermal behaviour of Mn(II),Co(II),Ni(II),Cu(II) and Zn(II) complexes of vanillin. *Asian. J.Chem.* 2008; 20(4):2769-2773.
4. Kumar Raman. Synthesis and spectral studies of macrocyclic Ni(II) complexes with multidentate ligands. *Res. J. Chem. and Env.*2019; 23(9): 68-70.
5. Rai B.K and Sharma K.K. Synthesis, physico-chemical and antimicrobial structure of bidentate Schiff base complexes of Co(II),Ni(II) and Cu(II). *Oriental. J.Chem.*2011;27(1):143-146.
6. Joseph J.N, K. Ayisha Bini Rani. Synthesis, characterization and antimicrobial activities of copper complexes derived from 4-Aminoantipyrine derivatives. *Journal of studies chemical society.*2013; 17(3) :285-294.
7. Doiezel P, Kuban V. Mass spectrometric study of platinum complexes based on cisplatin. *Chemical Papers.* 2002; 56(4): 236-240.
8. Singh KK. Synthesis, characterization and antimicrobial activity of Schiff base complexes derived from vanillin and 2-amino-4-chlorobenzoic acid. *J. Emer. Tec. And Inn. Res.* 2019; 6: 1733-1739.
9. Albarki NS, Maihub AA, Ei-ajjaily MM. Synthesis and physiochemical studies of some mixed Schiff base complexes. *Acad. J. Chem.* 2016; 1(3): 66-75
10. Ahmadi RA, Amani S. Synthesis, spectroscopy, thermal analysis, magnetic properties and biological activity of Cu(II) and Co (II) complexes with Schiff base ligands. *Molecules.* 2012; 17(6): 6434-6448.
11. Karabasannavar S, Allolli P, Kalshetty BM. Synthesis, characterization and antimicrobial activity of metal complexes derived from nitro aniline and 3-aldehydosalicylic acid. *Drug. Inv. Today.* 2017;9(1): 1-8.
12. Mishra AP, Mishra RK and Shrivastava SP. Structural and antimicrobial studies of coordination compounds of VO(II),Co(II) and Cu(II) with some Schiff bases involving 2-amino-4-chlorophenol. *Journal of the Serbian Chemical Society.* 2009; 74(5): 523-535.
13. Maher KA, Mohammed SR. Metal complexes of Schiff base derived from salicylaldehyde- a review. *Int. J. Cur. Res. Rev.* 2015; 7(2): 6-16.
14. Rathore K, Singh RK and Singh HB. Structural, spectroscopic and biological aspects of O,N- donor Schiff base ligand and its Cr(III), Co(II), Ni(II) and Cu(II) complexes synthesized through green chemical approach. 2010; 7(S1): S556-S572.
15. M. Usharani, E. Akila and R. Rajavel. Mixed ligand Schiff base complexes: synthesis, spectral characterization and antimicrobial activity. *J.Chem. and Pharm. Res.* 2012; 4(1): 726-731.

16. Ashokarajan R, Pazhani R and Paulpandiyam R. Antimicrobial studies on Knoevenagel condensate β -diketone complexes: synthesis and characterization. *J. Adv. Sci. Res.* 2019;10(4):235-239.
17. Siddapa K and Sultana MN. Synthesis, physico-chemical investigations and biological screening of metal(II) complexes with hydrazone Schiff base derived from 5-fluoro-3-hydrazonoindolin-2-one and isophthalaldehyde. *Int. J. Pharm. Sci. Res.* 2016; 7(1): 236-243.
18. Xavier A and Srividhya N. Synthesis and study of Schiff base. *Journal of Applied Chemistry.* 2014;7(11):6-15.
19. Singh KK. Synthesis and characterization of mixed ligand complexes of Co(II) Ni(II) and Cu(II) with bidentate Schiff base and various anions. *J. Emerg. Tec. Innov. Res.* 2018;5(11)382-390.
20. Zeinab H. Mononuclear metal complexes of organic carboxylic acid derivatives: Synthesis, spectroscopic characterization and antimicrobial activity. *Spectrochimica Acta Part – A.* 2007;67: 25-38.
21. Singh KK, Singh KC and Sharma M. Synthesis, characterization and antimicrobial studies of Co(II) Ni(II) and Cu(II) complexes derived from α -Amino acetohydroxamic acid. *Int. J. Curr. Res. Chem. Pharm. Sci.* 2020;7(10):1-7.

