



Date of Publication
June 2022

vidyavarta™

International Multilingual Research Journal



Vidyavarta is peer reviewed research journal. The review committee & editorial board formed/appointed by Harshwardhan Publication scrutinizes the received research papers and articles. Then the recommended papers and articles are published. The editor or publisher doesn't claim that this is UGC CARE approved journal or recommended by any university. We publish this journal for creating awareness and aptitude regarding educational research and literary criticism.

The Views expressed in the published articles, Research Papers etc. are their writers own. This Journal dose not take any libility regarding appoval/disapproval by any university, institute, academic body and others. The agreement of the Editor, Editorial Board or Publicaton is not necessary. Editors and publishers have the right to convert all texts published in Vidyavarta (e.g. CD / DVD / Video / Audio / Edited book / Abstract Etc. and other formats).

If any judicial matter occurs, the jurisdiction is limited up to Beed (Maharashtra) court only.



<http://www.printingarea.blogspot.com>

विद्यवार्ता: Interdisciplinary Multilingual Refereed Journal Impact Factor 8.14 (IJIF)



8. Patil A. A. and Ahire D. V., J. Chem. Bio. Phy. Sci. Sec. C, 3(1), 840(2013).
9. Ganorkar R. P. and Khan N.H., International Journal of Chemical and Pharmaceutical Analysis, 1(4), 190(2014).
10. Ganorkar R. P. and Chinchmalatpure P. G., Int. J. Chemical, Env. And Pharmaceutical Research, 4(2&3), 46(2013).
11. Gurdeep, Chatwal, R., and Harish Sharma, (2005). A text book of environmental studies I edition, Himalaya publishing house, pg-281.
12. Atulkumar H. Patel (2015). International Journal of Science and Research, Vol 4 (7) pg-1994-1997.
13. Dr. Syes Ummul Khair Saema Et.al (2015) IJIRD, Vol.4(13) Pg.84-8



PRINCIPAL

Late Ramesh Warpukar (ACS)
College, Sonpeth Dist. Parbhani

06

Synthesis and Biological Activity of Metal Complexes Derived from Schiff's Bases.

Sandipkumar M. Devraye
Department of Chemistry, Late Ramesh
Warpukar ACS College Sonpeth Dist. Parbhani.
Maharashtra. INDIA

ABSTRACT :

Synthesis of the Schiff base derived from p-dimethylamino benzaldehyde and m-aminobenzoic acid. Co(II), Ni(II), Cu(II) complexes were prepared from Schiff base. The synthesized TRANSITION metal complexes were characterized by elemental analysis, IR, UV-Vis. The IR results reveals the bidentate binding mode of the ligand involving azomethine nitrogen and carboxylate oxygen atoms. The antimicrobial activity of the synthesized ligand and its metal complexes were screened by disc diffusion method. The results show that the metal complexes were found to be more active than the ligand.

Key words: Schiff's base, ligands, transition metal complexes, anti-microbial activity.

1. INTRODUCTION

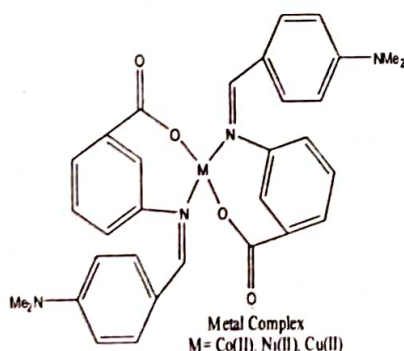
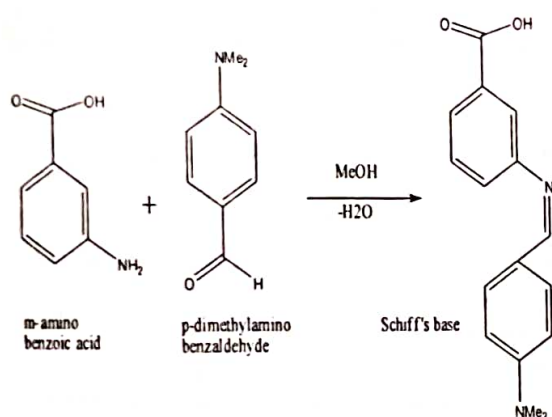
There is wide range of applications of Schiff bases ligands and transition metal complexes in biological, clinical, analytical and industrial area [1]. The heterocyclic Schiff base ligands and their metal complexes are more important due to their pharmacological properties [2]. nowadays, they are extensively being used for their promising applications in the treatment of several diseases and also been used as synthetic and analytical reagents [3]. Currently researchers take towards the study of Schiff bases and their transition metal complexes due to the synthetic flexibilities and approach of ligands towards transition metal ions [4]. Due to keto-enol tautomerism ligand show unusual

coordination numbers. [5–9].

2. EXPERIMENTAL

2.1. Materials:

The chemicals, metal chloride i.e. Co(II)/Ni(II)/Cu(II) chlorides and solvent was purchased from Thomas Baker, and the solvents were purified by standard methods. Solvents were purified and distilled before use. The metal content present in the complexes was determined by EDTA titration [10-13]



2.2. Preparation of Schiff base ligand:

2 mmol solution of m-aminobenzoic acid in methanol, 2 mmol solution of Substituted benzaldehyde in methanol was added dropwise. The above mixture was magnetically stirred and refluxed for about 8 hrs. Then the reaction mixture solvent was evaporated and cooled at room temperature. The crystals were separated out. It was washed with alcohol, ether and recrystallized from ethanol and finally dried under vacuum (yield: 75%). [10-13]

2.3. Preparation of metal Schiff base complexes:

2 mmol solution of Schiff base ligand dissolved in methanol and 1mmol solution of Co(II), Ni(II), Cu(II) chloride dissolved in methanol was added dropwise. The above mixture was magnetically stirred and refluxed for 1 hr. The obtained complexes were filtered, washed with ethanol and finally dried under vacuum (yield: 73–82%). [10-13]

2.4. Physical measurements:

The IR spectra was measured by Nicolet 380 FT-IR spectrometer using KBr pellet having range 4000–400 cm^{-1} .

Electronic spectra also recorded by Perkin Elmer Lambda-25 UV/ VIS spectrometer having range 200–900 nm. Magnetic measurements carried out using Guoy balance at room temperature. [12-16]

2.5. Anti-bacterial Study:

The antibacterial activity of synthesized Schiff base and their transition metal complexes was studied by well diffusion method. By dissolving the compounds in DMSO to form 0.001 mol stock solution, and the solutions were serially diluted and check minimum inhibitory concentration (MIC) values ($\mu\text{g mL}^{-1}$). The bacterial stains (Staphylococcus aureus and Escherichia coli) were incubated for 24 h at 37°C. Streptomycin was used for comparison under similar conditions. Antimicrobial activity studies were performed in triplicate, and the average was taken as the final reading. [12-17]

3. RESULTS AND DISCUSSION

The analytical data and physical properties of the ligand and transition metal complexes are listed in Table 1. The Schiff base ligand (L) is soluble in common organic solvents. The resultant Schiff base complexes are soluble in DMF and DMSO and insoluble in other common organic solvents. The analytical data (Table 1) indicate that the metal to ligand ratio is 1:2 for all the complex systems. The molar conductance of all the complexes was measured in DMSO using 10⁻³ M solutions at room temperature. The low molar conductivity values of the metal complexes (Table 1) suggest the non-electrolytic nature [12-15, 18]



Table 1: Analytical data and physical properties of the ligand and metal complexes.

Complex	Elemental analysis and calcd.	Found	Elemental analysis (Found)			M.P. (°C)	Yield (%)
			C	H	N		
L	C ₁₂ H ₁₀ N ₂ O ₂	64.41	64.41	4.44	16.15	140-145	85
[Co(L)2]	C ₂₄ H ₂₀ N ₄ O ₄	64.41	64.75	4.44	16.15	140-145	85
[Ni(L)2]	C ₂₄ H ₂₀ N ₄ O ₄	64.41	64.78	4.44	16.15	140-145	85
[Cu(L)2]	C ₂₄ H ₂₀ N ₄ O ₄	64.41	64.75	4.44	16.15	140-145	85

3.1. Infrared spectra:

The IR spectral data of the ligand and its complexes were given in Table 2. The free ligand exhibits IR bands at 3420 cm⁻¹ν (N-H), 1680 cm⁻¹ν (C=O), and 1620 cm⁻¹ν (C=N). The bands at 3450 and 2940 cm⁻¹ in the free ligand are attributed to the free OH stretching of phenolic moiety [19]. The IR spectrum of the free ligand exhibits a sharp band at 1675 cm⁻¹ν, due to the azomethine group vibration. On complexation this band was shifted to lower frequency in the 1660–1630 cm⁻¹ν range indicating the coordination of the azomethine nitrogen atom to the metal ion. [12,13,15] For the free ligand, the observed bands at 1545 and 1360 cm⁻¹ν can be respectively ascribed to asymmetric carboxylates (COO⁻) and symmetric carboxylates (COO⁻) groups [20]. During complexation these bands were shifted to higher frequency by 5–16 cm⁻¹ν range indicating the linkage between the metal ion and carboxylate oxygen atom. [12-13, 15] The large difference between the ν_{as}(COO⁻) and ν_s(COO⁻) value of 200 cm⁻¹ν indicates the monodentate binding nature of the carboxylate group [20] in the complexes. In the lower frequency region the weak bands observed at 580–554 and 460–420 cm⁻¹ν have been assigned respectively to the ν(M-O) and ν(M-N) vibrations [20-24], one can deduce that the ligand binds the metal ion as bidentate fashion (NO). The bonding sites are the azomethine nitrogen and the carboxylate oxygen atoms. In the complexes, the band due to phenolic OH vibrations remained unaltered, suggesting the non involvement of the phenolic proton in the complex formation. [12-13, 25-26]

Table 2: Infrared spectral data of ligand and its complexes (cm⁻¹ν).

Complex	ν(C-N)	ν _{as} (COO ⁻)	ν _s (COO ⁻)	ν(N-H)	ν(O-H)
L	1620	1545	1360	3420	3450
[Co(L)2]	1640	1560	1370	3430	3460
[Ni(L)2]	1630	1550	1375	3430	3460
[Cu(L)2]	1630	1550	1375	3430	3460

3.2. Electronic Spectra and Magnetic Moment: (in Table 1)

The electronic spectrum of free Schiff base ligand shows broad band at 348 nm, which is assigned to π → π* transition of the C=N chromophore. On complexation this band was shifted to lower wavelength region suggesting the coordination of azomethine nitrogen to the central metal ion [18, 27]. The Co(II) complex has the magnetic moment value shows Co(II) complex has tetrahedral (4.63 BM) which is in agreement with the reported value for tetrahedral Ni(II) complexes is tetrahedral its range 3.2–4.1 BM. And Cu (II) complex is monomeric and paramagnetic (1.79 BM) [12-13, 15, 28-30]

3.3. Anti bacterial activities:

The Synthesized transition metal complexes were screening for their antibacterial activity and this is done with the help of disc diffusion method. Microorganism like gram positive bacteria and Gram negative bacteria respectively as Staphylococcus aureus and Escherichia coli. The results reveal that as compare to Ni(II) complex the Cu(II) and Co(II) complex have better activity against bacterial strains, the activity of metal complexes as Cu(II) > Co(II) > Ni(II) > L. High activity owing the metal ions on the normal cell membrane [31]. Due to the combination of polar and non-polar properties permeable into cells and tissues. Also chelation enhance or lower the biopotency of them. The properties like lipophilicity influence the antimicrobial. The mixed-ligand complexes are more beneficial than free ligands. [12-13, 15-17, 28]



Table 3: Minimum inhibitory concentration of the synthesized compounds against the growth of bacteria (µg/ml.)

Compounds	E. coli	S. aureus
1	100	180
[CoL2]	30	27
[NiL2]	42	69
[CuL2]	51	35

4. CONCLUSION

The coordination capabilities of the synthesized Schiff base has been confirmed by complexation reaction with Co(II), Ni(II) ions Cu(II) ions. The newly synthesized schiff's base and their metal complexes are characterized using electronic and infrared spectral data which shows bidentate ligands which co-ordinate through azomethine nitrogen and carboxylate oxygen atoms. Geometry also determined with the help of conductometric, electronic and magnetic studies as Co (II) and Ni(II) complexes have tetrahedral geometry while Cu(II) complex is square planar geometry. The metal complexes show high antimicrobial activity free ligand and the order as Cu(II) > Co(II) > Ni(II) > L.

5. REFERENCES

[1] Gupta, K.C., Sutar, A.K., "Catalytic activities of Schiff base transition metal complexes". *Coord. Chem. Rev.* 252 (12-14), 1420-1450. 2008.
 [2] Budhani, P., Iqbal, S.A., Bhattacharya, S.M.M. "Synthesis, characterization and spectroscopic studies of pyrazinamide metal complexes." *J. Saudi Chem. Soc.* 14, 281-285. 2010.
 [3] P. V. Bernhardt, P. Chin, P. C. Sharpe, J. Y. C. Wang, and D. R. Richardson, "Novel diaroylhydrazine ligands as iron chelators: coordination chemistry and biological activity," *Journal of Biological Inorganic Chemistry*, vol. 10, no. 7, pp. 761-777. 2005.
 [4] C. Imrie, P. Engelbrecht, C. Loubser, and C. W. McClelland, "Monosubstituted thermotropic ferrocenomesogens: an overview 1976-1999," *Applied Organometallic Chemistry*, vol. 15, no. 1, pp. 1-15, 2001.)

[5] M. Bakir, I. Hassan, I. Johnson et al., "X-ray crystallographic, electrochemical and spectroscopic properties of 2-pyridinio 2- pyridyl ketone phenyl hydrazone chloride hydrate," *Journal of Molecular Structure*, vol. 688, no. 1-3, pp. 213-222, 2004.
 [6] S. M. Esmat, E. A. El-Sakel, S. A. About El-Enain, and H. A. El-Shater, "Cobalt(II), nickel(II), copper(II), zinc(II) and hafnium(IV) complexes of N - (F u r a n - 3 - y l m e t h y l e n e) - 2 - (4 - methoxyphenylmimo)acetohydrazone," *Spectrochimica Acta Part A*, vol. 72, no. 2, pp. 291-297, 2009.
 [7] K. Andjelkovic, G. Jakovljevic, and M. Zlatovic, "Acid-base equilibria of the Zn(II) and Fe(II) complexes with condensation products of 2-acetylpyridine and the dihydrazide of oxalic and malonic acid," *Journal of the Serbian Chemical Society*, vol. 69, pp. 651-660, 2004.
 [8] P. V. Bernhardt, P. Chin, P. C. Sharpe, J. Y. C. Wang, and D. R. Richardson, "Novel diaroylhydrazine ligands as iron chelators: coordination chemistry and biological activity," *Journal of Biological Inorganic Chemistry*, vol. 10, no. 7, pp. 761-777, 2005.
 [9] N. Terzioğlu and A. Gürsoy, "Synthesis and anticancer evaluation of some new hydrazone derivatives of 2,6-dimethylimidazo[2,1-b][1,3,4]thiadiazole-5-carbohydrazone," *European Journal of Medicinal Chemistry*, vol. 38, no. 7-8, pp. 781-786, 2003.
 [10] Vogel, A.I., 1978. "A Textbook of Quantitative Inorganic Analysis Including Elementary Instrumental Analysis" fourth ed. Longman, London.
 [11] B. S. Furniss, A. J. Hannaford, and V. Rogers, "Vogel's Textbook of Practical Organic Chemistry", Longman, Inc., New York, NY, USA, 4th edition, 1981.
 [12] M.S. Nair et al., "Synthesis, characterization, antifungal, antibacterial and DNA cleavage studies of some heterocyclic Schiff base metal complexes.", King Saud University, Production and hosting by Elsevier B.V. 2010
 [13] C. Anitha, S. Sumathi, P. et al., "Synthesis, Characterization, and Biological Activity of Some Transition Metal Complexes Derived from Novel Hydrazone Azo Schiff Base Ligand." Hindawi Publishing Corporation



- International Journal of Inorganic Chemistry, Article ID 493942, 8 pages. Volume 2011
- [14] Bauer, A.W., Kirby, W.M.M., Sherris, J.C., Turck, M., "Antibiotic susceptibility testing by a standardized single disc method". Amer. J. Clin. Pathol. 45, 493–496. 1966
- [15] Nayaz Ahmed et.al. "Synthesis, Characterisation, and Biological Evaluation of Zn(II) Complex with Tridentate (NNO Donor) Schiff Base Ligand." Hindawi Publishing Corporation International Journal of Inorganic Chemistry, Article ID 607178, 5 pages. Volume 2015
- [16] Jitendra N. Borase et.al., "Design, synthesis and biological evaluation of heterocyclic methyl substituted pyridine Schiff base transition metal complexes.", SN Applied Sciences 3:197. (2021)
- [17] Thierry Y Fonkuiet.al., "Microbial activity of some heterocyclic Schiff bases and metal complexes: A review.", Tropical Journal of Pharmaceutical Research; 17 (12): 2507-2518. December 2018
- [18] W. Walke and Niren E. Kathale., "Synthesis and Characterization of some Metal Complexes prepared from Schiff Base Ligand having Heterocyclic unit"., Journal of Scientific Research, Volume 65, Issue 6, 2021
- [19] R. Gup and B. Kirkan, "Synthesis and spectroscopic studies of copper(II) and nickel(II) complexes containing hydrazone ligands and heterocyclic coligand," Spectrochimica Acta Part A, vol. 62, no. 4-5, pp. 1188–1195, 2005.
- [20] Deacon, G.B., Phillips, R.J., "Relationships between the carbon–oxygen stretching frequencies of carboxylato complexes and the type of carboxylate coordination". Coord. Chem. Rev. 33 (3), 227–250. 1980.
- [21] Nakamoto, K., "Infrared and Raman Spectra of Inorganic and Coordination Compounds", third ed. John Wiley and Sons. 1978.
- [22] Shebl, M., "Synthesis, spectral studies, and antimicrobial activity of binary and ternary Cu(II), Ni(II), and Fe(III) complexes of new hexadentate Schiff bases derived from 4,6-diacetylresorcinol and amino acids." J. Coord. Chem. 62 (19), 3217–3231. 2009.
- [23] V. D. Bhatt and A. Ray, "Synthesis, characterization and electrical conductivity of polyesters, polyamides and doped polymers." Synthetic Metals, vol. 92, no. 2, pp. 115–120. 1998.
- [24] D. Prakash, C. Kumar, S. Prakash, A. K. Gupta, and K. R. R. P. Singh, "Synthesis, spectral characterization and antimicrobial studies of some new binuclear complexes of Cu(I) and Ni(II) Schiff base." Journal of the Indian Chemical Society, vol. 86, no. 12, pp. 1257–1261. 2009.
- [25] M. L. Hari Kumaran Nair and L. Shamlal, "Synthesis, spectral and thermal studies of copper(II) complexes of azodyes derived from 2,3-dimethyl-1-phenyl-4-amino-5-pyrazolone." Journal of the Indian Chemical Society, vol. 86, no. 2, pp. 133–138. 2009.
- [26] V. Reddy, N. Patil, and B. R. Patel, "Synthesis and characterization of Co(II), Ni(II), and (II) complexes with O,N and S donor ligands." Journal of Indian Council of Chemists, vol. 23, no. 2, pp. 1–3, 2006.
- [27] P. Tharmaraj, D. Kodimunthiri, C. D. Sheela, and C. S. Shanmuga Priya, "Synthesis, spectral characterization, and antimicrobial activity of copper(II), cobalt(II), and nickel(II) complexes of 3-formylchromoniminopropylsilatrane." Journal of Coordination Chemistry, vol. 62, no. 13, pp. 2220–2228, 2009.
- [28] Kettle, S.F.A., Coordination Compounds. ELBS, Essex, UK. 1969
- [29] Cotton, F.A., Wilkinson, G., Advanced Inorganic Chemistry. Wiley-Interscience, New York. 1998
- [30] Parjanya Kumar Shukla et.al., "Significance of Nitrogen Heterocyclic Nuclei in the Search of Pharmacological Active Compounds.", New Perspective in Agriculture and Human health., Researchgate March 2017
- [31] A. K. Sadana, Y. Mirza, K. R. Aneja, and O. Prakash, "Hypervalent iodine mediated synthesis of 1-aryl/heteryl-1,2,4-triazolo[4,3-a] pyridines and 1-aryl/heteryl 5-methyl-1,2,4-triazolo[4,3-a]quinolines as antibacterial agents." European Journal of Medicinal Chemistry, vol. 38, no. 5, pp. 533–536, 2003.

