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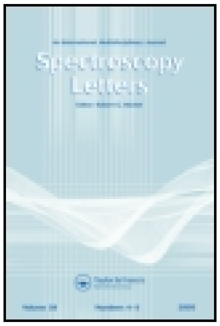

Spectroscopy Letters: An International Journal for Rapid Communication
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lstl20

Synthesis, Spectral Characterization and Antimicrobial Activities of Schiff Base Complexes Derived From 4-Aminoantipyrine

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Accepted author version posted online: 22 Jul 2013.

To cite this article: Spectroscopy Letters (2013): Synthesis, Spectral Characterization and Antimicrobial Activities of Schiff Base Complexes Derived From 4-Aminoantipyrine, Spectroscopy Letters: An International Journal for Rapid Communication, DOI: 10.1080/00387010.2013.820196

To link to this article: http://dx.doi.org/10.1080/00387010.2013.820196

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SYNTHESIS, SPECTRAL CHARACTERIZATION AND ANTIMICROBIAL ACTIVITIES OF SCHIFF BASE COMPLEXES DERIVED FROM 4-AMINOANTIPYRINE

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Abstract

Novel cobalt(II), nickel(II), copper(II) and zinc(II) complexes were synthesized from Schiff base ligand derived from 4-aminoantipyrine, vanillin and o-anisidine. The structural features were derived from their elemental analysis, molar conductance, magnetic measurements, and various spectroscopic techniques such as infrared, ultraviolet visible, nuclear magnetic resonance and electron paramagnetic resonance spectroscopy. Antimicrobial screening tests were performed against bacteria and fungi. The comparative study of the minimum inhibitory concentration values of the Schiff base and its metal complexes indicate that the metal complexes exhibit greater antimicrobial activity than the free ligand.

KEYWORDS: Schiff base, 4-Aminoantipyrine, Vanillin, o-Anisidine, Ultraviolet visible

INTRODUCTION

Schiff bases are widely designed and prepared for its high yield and one-step procedure via condensation of amines and aldehydes.[1] The various classes of Schiff bases that can be prepared by condensation of different types of amines and carbonyl compounds are very popular due to diverse chelating ability.[2] Schiff bases are widely used as analytical reactants since they allow simple and inexpensive determination of several organic and inorganic substances.[3] They also form stable complexes with metals that perform important role in biological systems.[4-7] The booming application of metal complexes in the treatment of numerous human diseases is vigorously expanding area in biomedical and inorganic chemistry.[8,9] In recent years, 4-aminoantipyrine transition metal complexes and their derivatives have been extensively examined due to their wide applications in various fields.[10, 11] Schiff bases of 4-aminoantipyrine and its complexes have a variety of applications in biological, clinical, analytical and pharmacological areas.[12, 13] Studies of a new kind of chemotherapeutic Schiff bases are now attracting the attention of biochemists.[14, 15] The coordinating properties of 4-aminoantipyrine have been modified to give a flexible ligand system, formed by condensation with a variety of reagents like aldehydes, ketones, thiosemicarbazide and carbazide *etc*.[16-27] Here in we report the synthesis, characterization and antimicrobial studies of Schiff base derived from vanillin, 4-aminoantipyrine and o-anisidine.

MATERIALS AND METHODS

All the chemicals, 4-aminoantipyrine, vanillin, o-anisidine and cobalt(II), nickel(II), copper(II) and zinc(II) acetates are Analar grade and were purchased from E-Merck and

Loba Chemie, India. The solvents like ethanol, methanol, *etc* were purified and dried by the standard procedures.[28, 29]

Molar conductance of the complexes was measured using a coronation digital conductivity meter. Magnetic moments were measured by Gouy method and corrected for the diamagnetism of the component using Pascal's constants. Infrared (IR) spectra were recorded on Schimadzu FT IR 8400S spectrometer in 4000-400 cm^{-1} range using KBr pellet. The ultraviolet visible(UV-Vis.) spectra were recorded on a Schimadzu UV spectrometer in the wavelength range 200-800 nm. The electron paramagnetic resonance (EPR) spectrum was recorded by using Bruker EMX EPR instrument at 300 & 77 K. The nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on a Bruker NMR 300 MHz spectrometer using DMSO d_6 as solvent and TMS as internal standard. The antimicrobial activity was determined with disc diffusion method. Stock solutions were prepared by dissolving the compounds in DMSO and serial dilutions of the compounds were prepared in sterile distilled water to determine the minimum inhibitory concentration (MIC).

PREPARATION OFTHE LIGAND

An ethanolic solution of 4-aminoantipyrine (2.03 g, 0.01 mol, 20 mL) was taken in a dropping funnel and added drop wise to the ethanolic solution of vanillin (1.52 g, 0.01 mol, 20 mL) with constant stirring for 3 h. The yellow compound formed was filtered and recrystallised from ethanol. The ethanolic solution of the solid product (3.373 g, 0.01 mol) was added to an ethanolic solution of o-anisidine (1.2 mL, 0.01 mol). The mixture was refluxed for about 30 h. The contents were poured into crushed ice, the dark yellow solid was separated, filtered and recrystallised from ethanol (Scheme 1).

PREPARATION OF THE COMPLEXES

A solution of metal acetate in ethanol (0.01 mol) was refluxed with hot ethanolic solution of Schiff base (0.01 mol) with few drops of glacial acetic acid on a water bath for 5 h. Then the solution was reduced to one third of its volume and cooled. The precipitated complex was filtered, washed with ethanol and dried in vacuum.

ANTIMICROBIAL ACTIVITY

Test Organisms

The bacterial species *Pseudomonas aeruginosa (P. aeruginosa)*, *Proteus mirabilis (P. mirabilis)* and *Escherichia coli* (E. coli) and fungal species *Aspergillus niger (A. niger), Aspergillus fumigatus (A. fumigatus)* and *Candida albicans (C. albicans)* were used as test organisms and they are maintained on Mueller Hinton Agar solid media (MHA) and Sabouraud's dextrose (SDA) media.[30-32]

Assay Of Antimicrobial Activity

Agar diffusion assay was carried out to evaluate the antimicrobial activity of some synthesized compounds. The plates were incubated at 37 °C for 24 h during which activity was evidenced by the presence of a zone of inhibition surrounding the well and antibacterial and antifungal activity was expressed as mean of diameter of inhibition zones (mm) produced by the synthesized compounds when compared to controls. The

MIC(minimum inhibitory concentration) value was recorded as the lowest concentration of drug in the medium that showed no microbial growth by visual observation.

EXPERIMENTAL

MHA and SDA were prepared with lawn culture using desired test organisms. The inoculated plates were kept aside for few minutes. Using well cutter two wells were made in the plates at required distance. In each step of well cutting, the well cutter was thoroughly wiped with alcohol. Using sterilized micropipette, 20 μL of compound extract was added into one well and to another well the same volume of corresponding control was added. After diffusion, the plates were incubated at 37 °C for 24 h. After incubation, the growth of inhibition was analyzed and the results were recorded.

RESULTS AND DISCUSSION

All the metal complexes were coloured solids, stable towards air and moisture. They get decomposed at higher temperature and were insoluble in common organic solvents and soluble in DMSO and DMF. The elemental analysis data (Table 1) of the ligand (L) and its metal complexes are consistent with the calculated results from the empirical formula of each compound. The purity of the Schiff base and its metal complexes was confirmed by TLC. The low conductance values of the complexes (Table 2) support the non-electrolytic nature.[33] The observed magnetic moment value of cobalt(II) complex is 4.71 BM, which is the expected range for tetrahedral cobalt(II) complexes. For tetrahedral nickel(II) complexes, μ expected is in the range 2.9-3.9 B.M. In the present case, the nickel(II) complex has the magnetic moment of 3.1 B.M. in accordance with tetrahedral geometry. The square planar copper(II) complexes exhibit magnetic moments from 1.8-2.1 B.M. The magnetic moment obtained for the present copper(II) complex is 1.95 B.M. The magnetic moments obtained are in accordance with the proposed geometries. zinc(II) complex with d^{10} electronic configuration is diamagnetic[34] and would have tetrahedral geometry. The proposed structure of the complexes is given in Fig. 1.

In order to study the binding mode of the Schiff base to the metal in the complexes, the IR spectrum of the free ligand was compared with the spectra of the complexes. The IR spectra of ligand (2a) and its copper(II) complex (2b) are given in Fig. 2a, b. The IR spectrum of the ligand shows a strong band at 3104 cm^{-1} assigned to OH group. The phenolic OH stretching appear at 3104 cm^{-1} and does not undergo any appreciable change in the spectra of complexes, indicates that phenolic OH group does not participate in the bond formation with the metal. The spectrum of the ligand shows the characteristic –C=N band at 1628 cm^{-1} which is shifted to lower frequencies in the spectra of complexes (1585-1579 cm^{-1}) indicates the coordination of azomethine nitrogen atom with metal ion. The spectra of the metal complexes also show some new bands in the 500-482 cm^{-1} and 474-449 cm^{-1} which are probably due to the formation of M-O and M-N bonds respectively.[35, 36] Two bands were observed at 1625 cm^{-1} and 1397- 1378 cm^{-1} assigned to $\upsilon_{asym}(COO^-)$ and $\upsilon_{sy}(COO^-)$ in complexes.[37] The vibrational frequencies of the free ligand and the metal complexes are given in Table 3.

The electronic spectral measurements were used for assigning the stereochemistry of metal ions in the complexes based on the positions and number of d-d transition peaks.

The electronic absorption spectral data of the Schiff base ligand and its complexes were recorded in DMF in the range of 200-800 nm is presented in Table 4. The absorption spectrum of free ligand consists of an intense band centered at 345 nm attributed to n-π* transitions of the azomethine group. Another intense band in higher energy region of the spectrum of the free ligand was related to π-π* transitions of benzene rings. These transitions are also found in the spectra of the complexes, but they are shifted towards lower frequencies confirming the coordination of the ligand with the metal ion. Further the d-d transition of the complex showed a broad band centered at 535-542 nm for cobalt(II), nickel(II) and copper(II) complexes. The spectra of cobalt(II) complex shows band at 542 nm, which can be attributed to ${}^4A_2(F)\rightarrow{}^4T_1(P)$ transition for the tetrahedral geometry. The electronic spectra of nickel(II) complex shows d-d transition at 540 nm, due to ${}^3T_1(F) \rightarrow {}^3T_1(P)$ transition for tetrahedral nickel(II) complex. The copper(II) complex shows broad band at 535 nm, due to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transition[38, 39] suggesting square planar geometry. The zinc(II) complex does not show any d-d transitions. In general four coordinate zinc(II) complexes would have tetrahedral geometry.

The EPR spectrum of copper(II) complex (Fig. 3a, b) provide information about the extent of the delocalization of unpaired electron. In the present study the EPR spectrum of the copper(II) complex were recorded at liquid nitrogen temperature (77 K) and room temperature (300 K). From the spectra of copper(II) complex $g_{||}$, $g_{\perp}$, g_{ave} and G have been calculated as 2.1418, 2.0057, 2.0497 and > 4 respectively. EPR spectra of the copper(II) complex revealed the trend $g_{||}>g_{\perp}$ shows that the unpaired electron is delocalized in $d_{x^2-y^2}$ orbital in the ground state of metal and spectra are characteristics of axial symmetry. The parameter g_{ave} was obtained by equation [$g_{ave}=1/3(g_{ll}+2g_{\perp})$]. Kivelson and Neiman have reported that $g_{ll}>2.3$ are the characteristics of an ionic environment and $g_{11}<2.3$ indicate a covalent character in metal ligand bonding. Applying this criterion g_{ll} (2.1418) indicate the prevalence of covalent character in metal ligand bond.[40, 41] The exchange coupling interaction has been explained by Hathaway expression $G = g_{ll}-2.0023/g_{\perp} - 2.0023$. According to Hathaway if the value of G is greater than four (G>4) the exchange interaction is negligible whereas when the value of G is less than four (G<4), a considerable exchange interaction is indicated in the complex. It is observed that G value of the complex is greater than four (G>4) indicating the exchange interaction is negligible.[42, 43] When the complex is frozen to liquid nitrogen temperature, four well resolved peaks are obtained. This shows square planar geometry of the copper(II) complex.

The ^{1}H-NMR spectra of the ligand (Fig. 4a) and its zinc(II) complex (Fig. 4b) were recorded in DMSO d_6. The ^{1}H-NMR shows peak at δ 5.9 to the aromatic OH. The presence of this peak noted for the zinc(II) complex confirms the –OH proton free from complexation. The peak for benzene rings appears in the region δ 6.9-7.4. The peaks for O-CH_3, C-CH_3 and N-CH_3 appear in region δ 3.1 (O-CH_3 for vanillin moiety), δ 3.9 (O-CH_3 for o-anisidine moiety), δ 1.61 and δ 2.4 respectively. The azomethine proton signal at δ 9.531 in the spectrum of zinc(II) complex is shifted to downfield compared to the free ligand, suggesting deshielding of azomethine group due to the coordination with metal ion. The rest of the peaks appear in the same region.[44]

The reactivity of the synthesized compounds towards the biological systems is important features of the current research and Schiff bases of transition metal complexes. All the synthesized compounds (Tables 5 & 6) showed a remarkable biological activity against all the bacterial and fungal species under investigation. Among the synthesized compounds nickel(II) complex showed very good antibacterial and antifungal activity. The toxicity of the complexes was found to be better than the ligand owing to the theory of Tweedy.[45-50] This is probably due to the greater lipophilic nature of the complexes. Such increased activity of the metal chelates can be explained on the basis of Overtone's concept of cell permeability. The lipid membrane that surrounds the cell favors the passage of lipid soluble materials due to which liposolubility is an important factor which controls the antimicrobial activity. On chelation, the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of positive charge of the metal ion with donor groups. Further, it increases the delocalization of π electrons over the whole chelate ring and enhances the lipophilicity of the complexes. This increased lipophilicity enhances the penetration of the complexes into lipid membrane and blocks the metal binding sites on enzymes of microorganisms.

CONCLUSION

Cobalt(II), nickel(II), copper(II) and zinc(II) complexes with Schiff base derived from vanillidene-4-aminoantipyrine and o-anisidine have been synthesized and characterized. Elemental analysis and low molar conductance values indicate mono nuclear and non electrolytic nature of the complexes. The Schiff base acts as a bidentate ligand and the possible coordination sites are two azomethine nitrogen atoms. Spectral data and magnetic moment studies suggest that cobalt(II), nickel(II), and zinc(II) complexes have tetrahedral geometry while the copper(II) complex has square planar geometry. Antimicrobial studies show that the complexes are more active than the ligand.

REFERENCES

1. Nunez, C.; Lodeiro, J. F.; Diniz, M.; Galesion, M. Versatile Schiff base hydrazone fluorescent receptors: Synthesis, spectroscopy and complexation studies. *Inorg. Chim. Acta.* **2012**, *380*, 40-49.
2. Manikshete, A. H.; Sarsamkar, S. K.; Deodware, S. A.; Kamble, V. N.; Asabe, M. R. Synthesis, characterization and antimicrobial activity of cobalt(II), nickel(II) and copper(II) complexes with 2-(2-hydroxy-1,2-diphenylethylideneamino)benzoic acid. *Inorg. Chem. Commun.* **2011**, *14*(5), 618-621.
3. Cimernman, Z.; Galic, N.; Bosner, B. The Schiff bases of salicylaldehyde and aminopyridines as highly sensitive analytical reagents. *Anal. Chim. Acta.* **1997**, *343*, 145-153.
4. Raptopoulou, C. P.; Papadopoulos, A. N.; Malamatari, D. A.; Loannidis, E.; Molsidis, G.; Terzis, A.; Kessissoglou, D. P. Nickel(II) and copper(II) Schiff base complexes with an extended H-bond network. *Inorg. Chim. Acta.* **1998**, *272*(1-2), 283-290.
5. Karthikeyan, M. S.; Prasad, D. J.; Bhat, K. B. P. S.; Holla, B. S. Synthesis and biological activity of Schiff and Mannich bases bearing 2,4-dichloro-5-fluorophenyl moiety. *Bioorg. Med. Chem.* **2006**, *14*(22), 7482-7489.

6. Li, Y.; Yang, Z. S.; Zhang, H.; Cao, B. J.; Wang, F. D. Artemisinin derivatives bearing Mannich base group: synthesis and antimalarial activity. *Bioorg. Med. Chem.* **2003**, *11*(20), 4363-4368.

7. Chityala, V. K.; Kumar, K. S.; Subhashini, N. J. P.; Raghavaiah, P.; Shivaraj. Synthesis, crystal structure, spectroscopic, and biological studies on copper(II) complexes of N,O donor dimethyl isoxazole Schiff bases. *J. Coord. Chem.* **2013**, *66*, 274-286.

8. Blower, P. J. Inorganic Pharmaceuticals. *Annual Reports on the Progress of Chem. A*, **2001**, *97*, 587-603.

9. Sessler, J. L.; Doctrow, S. R.; McMurry, T. J.; Lippard, S. J. Mechanistic studies of platinum and ruthenium compounds with antitumour properties. *Med. Inorg. Chem.* **2005**, *903*, 252-262.

10. Raman, N.; Sobha, S. Inspired research on the DNA binding ability of 4-aminoantiprine derived mixed ligand complexes. *Inorg. Chem. Comm.* **2012**, *17*, 120-123.

11. Joseph, J.; Nagashri, K.; Janaki, G, B. Novel metal based anti-tuberculosis agent: Synthesis, characterization, catalytic and pharmacological activities of copper complexes. *Eur. J. Med. Chem.* **2012**, *49*, 151-163.

12. Hitoshi, T.; Tamao, N.; Hideyuki, A.; Manabu, F.; Takayuki, M. Preparation and characterization of novel cyclic tetranuclear manganese(III) complexes: $MnIII_4$ (X-salmphen)$_6$ (X-salmphen,H_2 = N,N′-di-substituted-salicylidene-1,3-diaminobenzene (X = H, 5-Br)). *Polyhedron* **1997**, *16*(21), 3787-3794.

13. Punniyamoorthy, T.; Kalra, S. J. S.; Iqbal, J. Cobalt(II) catalyzed biomimetic oxidation of hydrocarbons in the presence of dioxygen and 2-methylpropanal. *Tetrahedron Lett.* **1995**, *36*(46), 8497-8500.

14. Choli, Y. K.; Chjo, K. H.; Park, S. M.; Doddapanenai, N. Oxygen reduction at cobalt(II)$_2$ disalophen modified carbon electrodes. *J. Electrochem. Soc.* **1995**, *142*(12), 4107-4112.

15. Katia, B.; Simon, L.; Anne, R.; Gerard, C.; Francoise, D.; Bernard, M. Synthesis and characterization of new chiral Schiff base complexes with diiminobinaphthyl or diiminocyclohexyl moieties as potential enantioselective epoxidation catalysts. *Inorg. Chem.* **1996**, *35*(2), 387-396.

16. Radhakrishnan, P. K. Complexes of lanthanide perchlorates with 4-N-(2′-hydroxy-1′-naphthylidene)aminoantipyrine. *Polyhedron* **1986**, *5*(4), 995-998.

17. Maurya, R. C.; Mishra, D. D.; Pandey, M.; Shukla, P.; Rathour, R. Synthesis and spectral studies of octa coordinated dioxouranium(VI) complexes with some Schiff bases derived from 4-acetyl-2,3-dimethyl-l-(4-methylphenyl)-3-pyrazoline-5-one and aromatic amines. *Synth. React. Inorg. Met-Org. Chem.* **1992**, *23*(1), 161-174.

18. Agarwal, R. K.; Garg, P.; Agarwal, H.; Chandra, J. Synthesis, magneto-spectral and thermal studies of cobalt(II) and nickel(II) complexes of 4-[N-(4-dimethylamino benzylidene)amino]antipyrine. *Synth. React. Inorg. Met-Org. Chem.* **1997**, *27*(2), 251-268.

19. Singh, L.; Tyagi, N.; Dhaka, N. P.; Sindhu, S. K.; Synthesis, spectral and thermal studies of some lanthanide(III) complexes of 4-[N-(benzalidene)amino]antipyrinethiosemi- carbazone. *Asian J. Chem.* **1999**, *11*(2), 503-508.

20. Jha, N. K.; Joshi, D. M. Thiorganoantimony(V) Complexes of Schiff bases obtained from substituted salicylaldehydes and o-phenylenediamine or 2-aminopyridine. *Synth. React. Inorg. Met-Org. Chem.* **1986**, *16*(7), 947-961.

21. Singha, H. L.; Singha, J. B.; Sachedvaa, H. Synthesis, spectroscopic and antimicrobial studies of lead(II) complexes of Schiff bases derived from amino acids and isatins. *Spectrosc. Lett.* **2013**, *46*(4), 286-296.

22. Mishra, A. P.; Srinivastava, V.; Srinivastava, S. K. Complexes of cobalt(II), nickel(II) and copper(II) with 2-furfurylidene-P-chloroaniline Schiff bases. *Synth. React. Inorg. Met-Org. Chem.* **1995**, *25*(1), 21-30.

23. Shankar, R.; Kumar, R. P.; Ramalingam, S. K. 4-Aminoantipyrine Schiff base complexes of lanthanide and uranyl ions. *Polyhedron* **1986**, *5*(4), 991-994.

24. Kriza, A.; Reiss, A.; Florea, S.; Caproiu, T. Studies on complexes of cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II) with Schiff base derived from 3-aminodibenzofuran and salicylaldehyde. *J. Indian Chem. Soc.* **2000**, *77*, 207-208.

25. Bu. R.; Xiu, F. L.; Mintz, X. Z.; You, R. X.; Wang, Q.; Yue, Q. J.; Meng, Y. J.; Lu, D. V. Derveer. Synthesis and characterization of vanadyl complexes with unsymmetrical bis-schiff base ligands containing a cis-N_2O_2 coordinate chromophore. *Polyhedron* **1996**, *15*(24), 4585-4591.

26. Dharmaraj, P.; Viswanathamurthi, K.; Natarajan, K. Ruthenium(II) complexes containing bidentate Schiff bases and their antifungal activity. *Transition Met. Chem.* **2001**, *26*(1-2), 105-109.

27. Raman, N.; Kulandaisamy, A.; Jayasubramanian, K. Synthesis, structural characterization, redox and antimicrobial studies of Schiff base cobalt(II), nickel(II),

copper(II), manganese(II), zinc(II) and vanadium(II) complexes derived from benzil and 2-aminobenzyl alcohol. *Polish J. Chem.* **2002**, *76*(8), 1085-1094.

28. Vogel, A. I. *A Text Book of Quantitative Inorganic Chemistry*, Longman Group Limited 1978, 158.

29. Haller, M.; Garland, C. W. *Molecular Vibrations*; McGraw Hill: New York, 1962.

30. Jayabalakrishnan, C.; Natarajan, K. Ruthenium(II) carbonyl complexes with tridentate Schiff bases and their antibacterial activity. *Transition Met. Chem.* **2002**, *27*(1), 75-79.

31. Lakshmi, S. S.; Tajudeen, S.; Geetha, K. Studies on antimicrobial activities of Schiff base complex derived from Dapsone. *J. Pharm. Res.* **2011**, *4*(5), 1531-1532.

32. Tajudeen, S.; Lakshmi, S. S.; Geetha, K. Studies on antimicrobial activity of some hydrazones and its copper complexes. *J. Pharm. Res.* **2010**, *3*(11) 2759-2760.

33. Geary, W. J. The use of conductivity measurements in organic solvents for the characterisation of coordination compounds. *Coord. Chem. Rev.* **1971**, *7*(1), 81-122.

34. Banerjea, D. *Coordination Chemistry*, Tata McGraw-Hill, India, 1993.

35. Mishra, A. P.; Sharma, N.; Jai. Synthesis and structure of some novel Schiff base complexes with copper(II) and nickel(II). *J. Indian Chem. Soc.* **2011**, *88*, 1429-1434.

36. Raman, N.; Raja, S. J.; Joseph, J.; Raja, J. D. Synthesis, spectral characterization and DNA cleavage study of heterocyclic Schiff base metal complexes. *J. Chilean Chem. Soc.* **2007**, *52*(2), 1138-1141.

37. Sebastian, M.; Arun, V.; Robinson, P. P.; Leeju, P.; Varghese, D.; Varsha, G.; Yusuff, K. K. M. Template synthesis and spectral characterization of some Schiff base

complexes derived from quinoxaline-2-carboxaldehyde and L-histidine. *J. Coord. Chem.* **2011**, *64*(3), 525-533.

38. Sharadha, L. N.; Ganorkar, M. C. Synthesis and structural studies of VO(IV), manganese(II), cobalt(II), nickel(II) and copper(II) complexes with new tridentate Schiff base having ONO and ONN donor systems. *Indian J. Chem*. **1988**, *27*, 617-621.

39. Nair, M. S.; David, S. T.; Anbu, M. Schiff base complexes cobalt(II), nickel(II), copper(II), manganese(II), zinc(II) with pyridinecarboxaldehyde and a potentially tridentate amino acid. *Indian J. Chem.* **2001**, *38A*, 823-825.

40. Maki, A. H.; Mcgarvey, B. R. Electron spin resonance in transition metal chelates copper(II) bis-acetylacetonate. *J. Chem. Phy.* **1958**, *29*(1), 31-35.

41. Abragam, A.; Bleaney, B. *EPR of Transition Ions*, Oxford, 1970.

42. Halcrow, M. A.; Chia, L. M. L.; Liu, X.; Mclnner, E. J. L.; Davies, J. E. Spectroscopic characterisation of a copper(II) complex of a thioether-substituted phenoxyl radical: A new model for galactose oxidase. *Chem. Commun.* **1998**, *22*, 2465-2466.

43. Mishra, P.; Khare, M.; Gautam, S. K. Synthesis, physico-chemical characterization and antibacterial studies of some bioactive Schiff bases and their metal chelates. *Synth. React. Inorg. Met-Org. Chem.* **2002**, *32*(8), 1485-1500.

44. Devi, J.; Kumari, S.; Asijaa, S.; Malhotra, R. Synthetic, spectroscopic, and biological aspects of triorganosilicon(IV) complexes of tridentate Schiff bases. *Phosphorus, Sulfur, Silicon Relat. Elem*. **2012**, *187*, 1409-1417.

45. Chohan, Z. H.; Pervez, H.; Rauf, A.; Khan, K. M.; Supuran, C. T. Isatin-derived antibacterial and antifungal compounds and their transition metal complexes. *J. Enz. Inhib. Med. Chem.* **2004**, *39*(5), 417-423.

46. Coombs, R. R.; Westcott, S. A.; Decken, A.; Baerlocher, F. J. Palladium(II) Schiff base complexes derived from sulfanilamides and aminobenzothiazoles. *Transition Met. Chem.* **2005**, *30*(4), 411-418.

47. Mohamed, G.; Omar, M.; Ibrahim, A. Biological activity studies on metal complexes of novel tridentate Schiff base ligand. Spectroscopic and thermal characterization. *Eur. J. Med. Chem.* **2009**, *44*(12), 4801-4812.

48. Suraj, A, B.; Deshpande, M. N.; Kolhatkar, D. G.; Bhagat, S. M. Synthesis, characterization of tridentate Schiff base metal chelates and their antimicrobial activity. *J. Chem. Pharm. Res.* 2012, 4 (1), 105-111.

49. Gupta, A. K. S.; Barhate, V. D. Synthesis, characterization and study of microbiological activity of some transition metal ion complexes with [N-(o-hydroxybenzylidene)pyridine -2-amine]. *Res. J. Pharm. Biol. Chem.* **2012**, *3*(3), 1013-1026.

50. Tweedy, B. G. Plant extracts with metal ions as potential antimicrobial agents. *Phytopathology* **1964**, *55*, 910-914.

TABLE 1. Physical characterization and analytical data of ligand and complexes

Compound	Mol. Formula (Colour)	Mol. Wt (Yield %)	Found (Calcd.) %				
			C	H	N	O	M
L	$C_{26}H_{26}O_3N_4$ (Yellow)	442 (85)	70.31 (70.59)	5.35 (5.88)	12.18 (12.67)	10.67 (10.86)	-
[CoL(OAc)$_2$]	$C_{30}H_{32}O_7N_4Co$ (Pink)	618.9 (53)	57.93 (58.17)	5.38 (5.17)	8.95 (9.05)	18.01 (18.10)	9.13 (9.52)
[NiL(OAc)$_2$]	$C_{30}H_{32}O_7N_4Ni$ (Green)	618.7 (57)	58.01 (58.18)	5.10 (5.17)	9.01 (9.05)	18.10 (18.10)	9.09 (9.49)
[CuL(OAc)$_2$]	$C_{30}H_{32}O_7N_4Cu$ (Brown)	623.5 (54)	57.31 (57.74)	5.03 (5.13)	8.48 (8.98)	17.35 (17.96)	10.05 (10.18)
[ZnL(OAc)$_2$]	$C_{30}H_{32}O_7N_4Zn$ (Brown)	625.3 (68)	57.15 (59.37)	5.0 (5.12)	8.56 (8.96)	17.48 (17.91)	10.06 (10.46)

TABLE 2. Molar conductance data of metal complexes

Compound	Molar conductance ($\Omega^{-1} cm^{2} mol^{-1}$)
[CoL(OAc)$_2$]	5.20
[NiL(OAc)$_2$]	7.50
[CuL(OAc)$_2$]	10.20
[ZnL(OAc)$_2$]	11.25

TABLE 3. IR spectral data of ligand and complexes

Compound	OH(Phenolic)	C = N	M-O	M-N
L	3104	1628	-	-
[$CoL(OAc)_2$]	3104	1579	482	453
[$NiL(OAc)_2$]	3112	1579	495	449
[$CuL(OAc)_2$]	2923	1585	500	474
[$ZnL(OAc)_2$]	3150	1581	490	464

TABLE 4. UV-Vis. spectral and molar conductance data of ligand and complexes

Compound	d-d	π-π*	n→π*	Geometry
L	-	260, 253	345	-
$[CoL(OAc)_2]$	542	245, 279	347	Tetrahedral
$[NiL(OAc)_2]$	540	249, 289	348	Tetrahedral
$[CuL(OAc)_2]$	535	241, 27	349	Square Planar

TABLE 5. Antibacterial activities of ligand and its complexes (Diameter of inhibition zone in mm)

Compound	*P. Aeruginosa*	*P. mirabilis*	*E. coli*
L	-	-	-
[$CoL(OAc)_2$]	-	-	-
[$NiL(OAc)_2$]	18	20	20
[$CuL(OAc)_2$]	7	5	25
[$ZnL(OAc)_2$]	-	-	-
Ciprofloxacin[a]	18	23	17

[a] Standard

TABLE 6. Antifungal activities of ligand and its complexes (Diameter of inhibition zone in mm)

Compound	*A. niger*	*A. fumigatus*	*C. albicans*
L	-	-	-
[CoL(OAc)$_2$]	-	-	-
[NiL(OAc)$_2$]	11	8	21
[CuL(OAc)$_2$]	9	-	27
[ZnL(OAc)$_2$]	-	-	-
Amphoterecin-B[a]	20	21	-

[a] Standard

Scheme 1. Synthetic route of Schiff base ligand

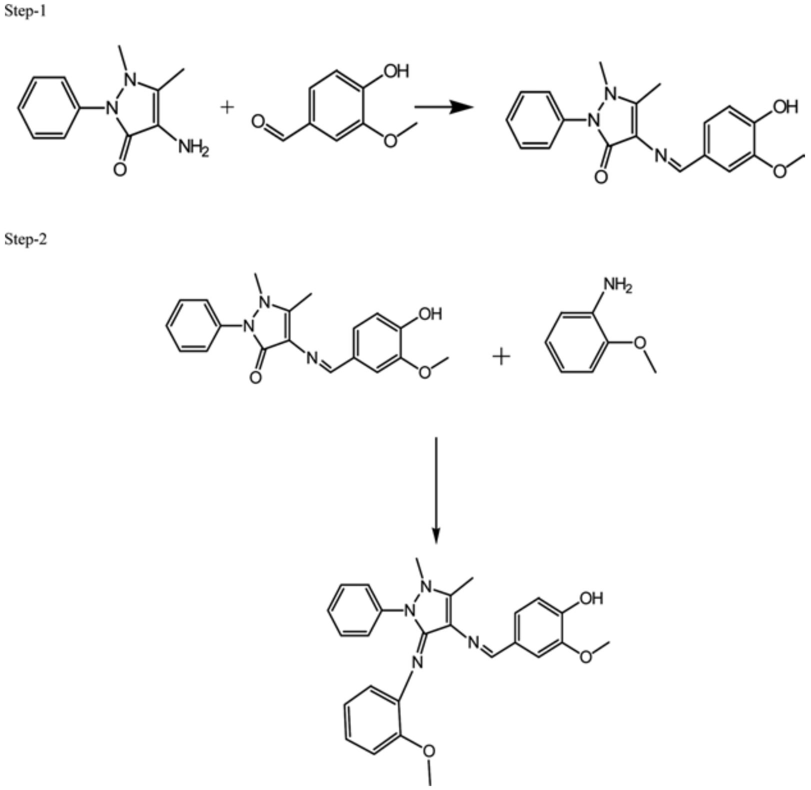
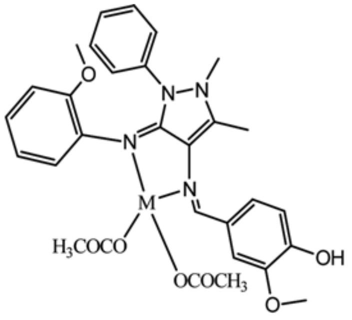
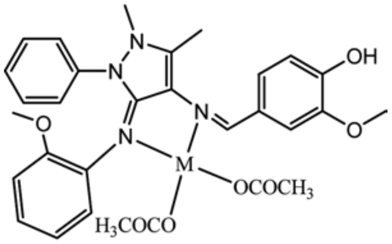


Figure 1. Proposed structure of metal complexes



M=Co(II), Ni(II) and Zn(II)



M=Cu(II)

Figure 2. IR spectra of (a) ligand and its (b) copper(II) complex

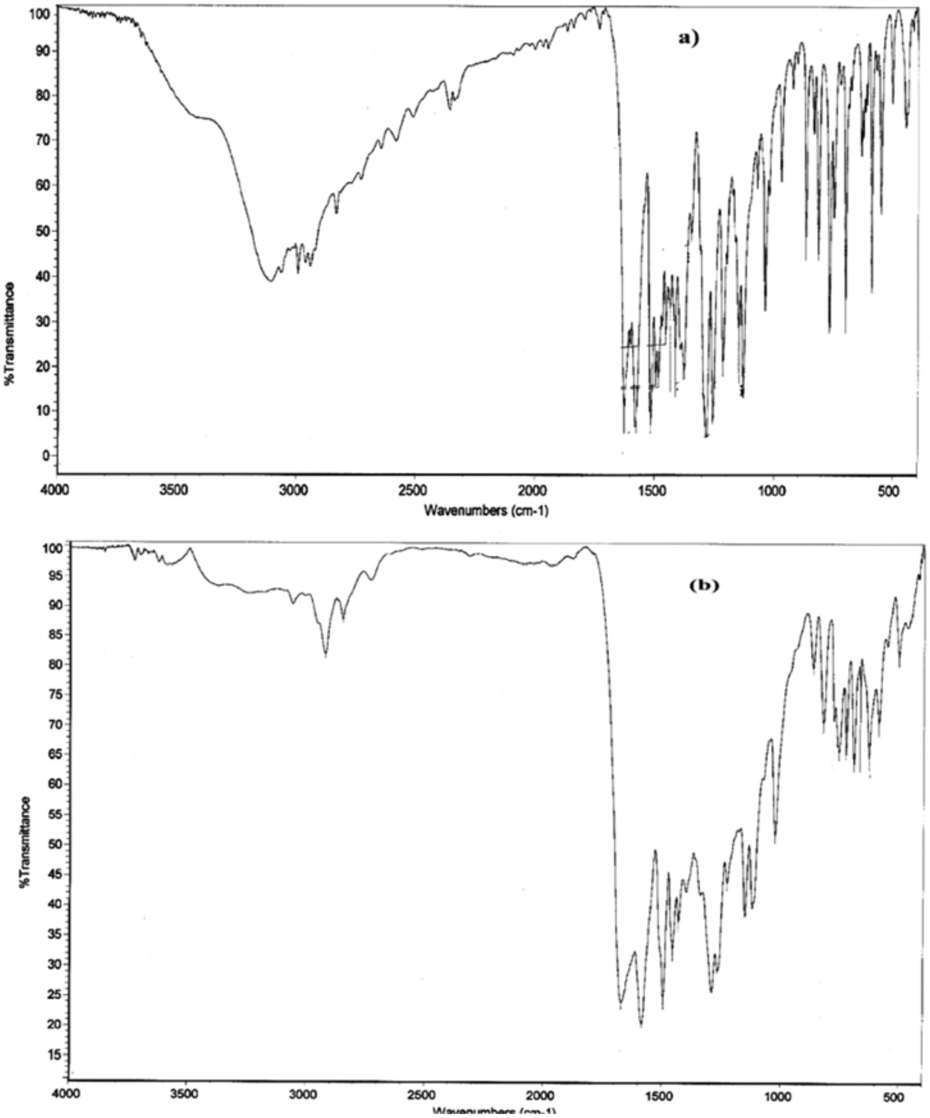
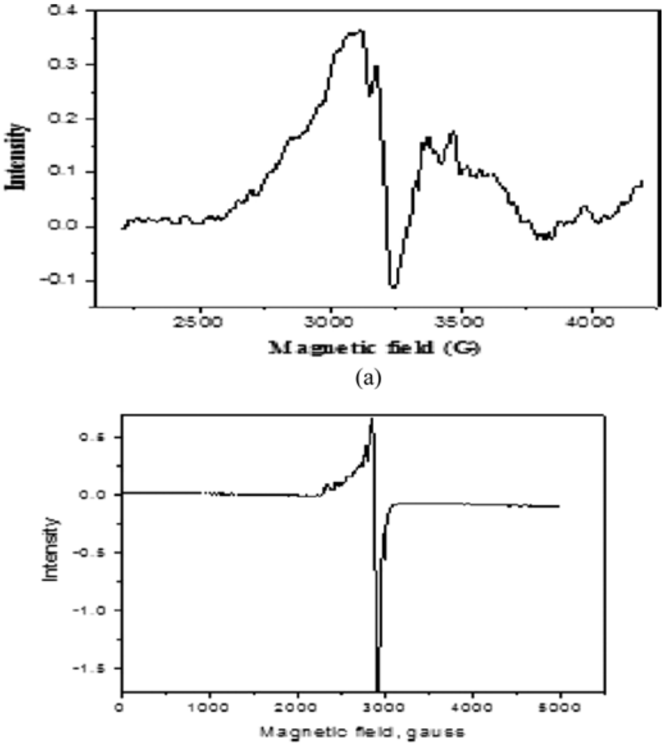


Figure 3. EPR spectra of copper(II) complex at (a) 77 K and (b) 300 K



(a)

(b)

Figure 4. NMR spectra of (a) ligand and its (b) zinc(II) complex