



# INTERNATIONAL JOURNAL OF ADVANCE RESEARCH AND DEVELOPMENT

(Volume2, Issue3)

Available online at: [www.ijarnd.com](http://www.ijarnd.com)

## Synthesis, Characterization and Biological Importance of Acid Hydrazone Complexes

Fernandes Anil Juje<sup>1</sup>, Dr. H.V Jayaprakash<sup>2</sup>

<sup>1</sup>Research Scholar, Sri Siddhartha Institute of Technology, Sri Siddhartha Academy of Higher Education, Karnataka, India

<sup>2</sup>Associate professor, Sri Siddhartha Institute of Technology, Sri Siddhartha Academy of Higher Education, Karnataka, India

[anilfernandes39@gmail.com](mailto:anilfernandes39@gmail.com), [jpvpsb@gmail.com](mailto:jpvpsb@gmail.com)

### ABSTRACT

The new azomethine compound derived from Valerophenone and *m*-Anicichydrazide has been prepared. Further it is synthesized with Ni(II) and Zn(II) salts to form stable complexes. The ligand and metal complexes have been characterized by Elemental analysis, IR, NMR, UV/Vis Spectrometry, conductivity, biological activities and Gouy Balance method. The nature of bonding and the stereochemistry of the complexes have been deduced from infrared spectra, electronic spectra, magnetic susceptibility, an octahedral geometry has been suggested for Nickel (II) and tetrahedral geometry for Zinc (II) complex. The complexes are non-hygroscopic, and photo stable crystalline powders with different melting points. The coordination process takes place through the carbonyl oxygen and the azomethine nitrogen atom.

**Key words:** Complexes, Hydrazones, Valerophenone, *m*-Anicichydrazide Synthesis, Characterization.

### 1. INTRODUCTION

Schiff bases and their complexes have a variety of applications in biological clinical and analytical fields. Recently there has been a considerable interest in the chemistry of hydrazine and hydrazone compounds because of their potential pharmacological applications. The remarkable biological activity of acid hydrazides  $R-CO-NH-NH_2$ , their corresponding arylhydrazones  $R-CO-NH-N=CHR$ , and also their mode of chelation with transition metal ions has aroused interest in the past due to possible biomimetic applications. The coordination compounds of arylhydrazones have been reported to act as enzyme inhibitors and are useful due to their pharmacological applications. In the present paper, we describe the synthesis, characterization, and biological activity of some Nickel (II) and Zinc (II) complexes of Schiff bases.

### 2. EXPERIMENTAL

#### 2.1. Characterization of the complexes

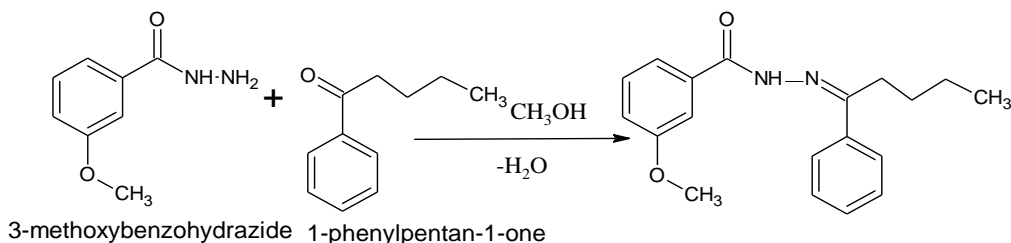
##### Materials

All the chemicals used were of AR-grade and were procured from Sigma-Aldrich. The microanalyses % C, N, and H are estimated (on Heraeus elemental analyzer), IR spectra were recorded (on Perkin Elmer 881 Spectrometer). Room temperature molar conductance (on Elico-CM82 Conductivity Bridge) electronic absorption measurements (on Shimadzu UV-Vis spectrophotometer) have been done. Magnetic susceptibilities were measured by using a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temperature using  $Hg[Co(SCN)_4]$  as a calibrant. <sup>1</sup>H NMR spectra were taken from a Bruker GmbH Dpx-400 MHz High Performance Digital FT-NMR spectrometer. Newly synthesized compounds have been tested for their

antibacterial activity against gram positive and gram negative bacteria. The discs which are used in this method have 5 mm diameters. 0.01 M of DMF (as a solvent).

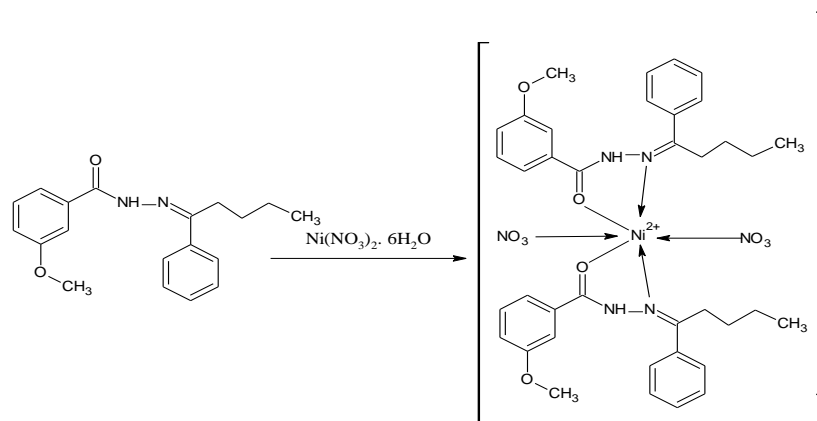
## 2.2. Synthesis of Schiff bases (ligands) and complexes

Schiff bases (has been synthesized by condensing the methanolic solution of m-AnicicHydrazide (0.06mol) to the methanol solution of Valerophenone(0.06mol)

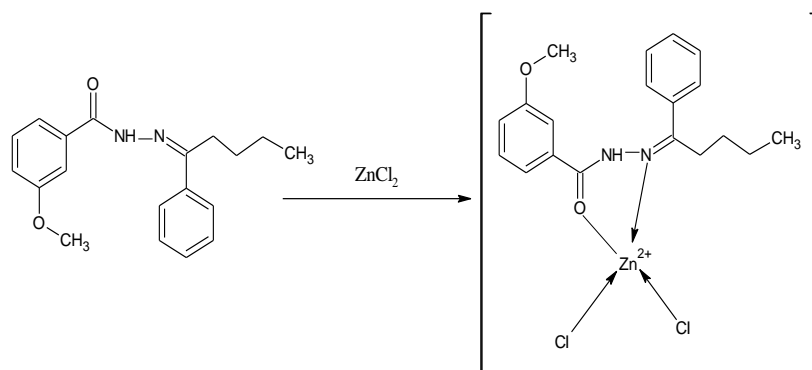


The condensation product was filtered, washed with methanol and ether, recrystallized with methanol, and dried under reduced pressure over anhydrous  $\text{CaCl}_2$ . The Ni(II) and Zn(II) complexes have been prepared by mixing the methanolic solution of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{ZnCl}_2$  (0.06mmol) to the methanolic solution of Schiff base ( $\text{L}_1$ ) (0.012mmol) in 1 : 2 and 1:1 molar ratio. The resulting mixture was then heated on a magnetic hot plate for 5–6 hours. The precipitated complexes were recrystallized twice with methanol, finally washed with petroleum ether (60–80°C), and dried under reduced pressure over anhydrous  $\text{CaCl}_2$  in a desiccator.

## 2.3. Scheme of synthesis of Nickel complex



## 2.4. Scheme of synthesis of Zinc complex:



## 3. RESULTS AND DISCUSSION

The analytical and physical data of the metal complexes are presented in Table 1. Elemental analysis of the complexes indicates the stoichiometry to be 1:2 metal: ligand (Schiff base)

Table; 1; Analytical And Physical Data Of Ligand And Metal Complexes.

Ligands/ Complexes	yield	Mol. Formula	Analysis% calc.) (found)	Mol Wt	Color	Mag. Mome nt [ $\mu_{\text{eff}}$ ]	Condu ohm <sup>1</sup> cm <sup>2</sup> mol <sup>-1</sup>	Melting Pt.
Valerophenone-m-Anicic hydrazone.	52%	C <sub>19</sub> O <sub>2</sub> H <sub>22</sub> N <sub>2</sub>	C(73.54)(73.4) H(7.09)(7.01) N(9.03)(9.01) O(10.32)(10.2)	310	Yellowish-White	-----	-----	167 °C
Ni(NO <sub>3</sub> ) <sub>2</sub> Valerophenone m-anicic hydrazone	32%	NiC <sub>38</sub> O <sub>10</sub> H <sub>44</sub> N <sub>6</sub>	C(56.78)(56.6) H(5.47)(5.40) N(10.46)(10.4) O(19.92)(19.8)	803	Greenish Brown	2.83	20	< 250°C
ZnCl <sub>2</sub> .Valerophenone m-Anicic hydrazone.	27%	ZnCl <sub>2</sub> C <sub>19</sub> O <sub>2</sub> H <sub>22</sub> N <sub>2</sub>	C(51.07)(51.1) H(4.92)(4.85) N(6.27)(6.23) O(7.16)(7.08) Zn((14.6)(14.)	446	White	0.00	18	< 250°C

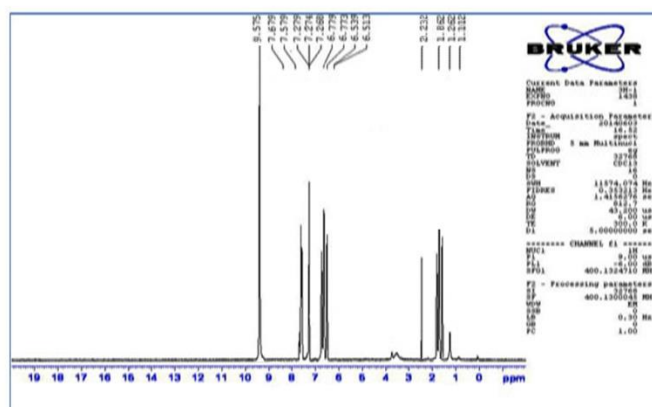
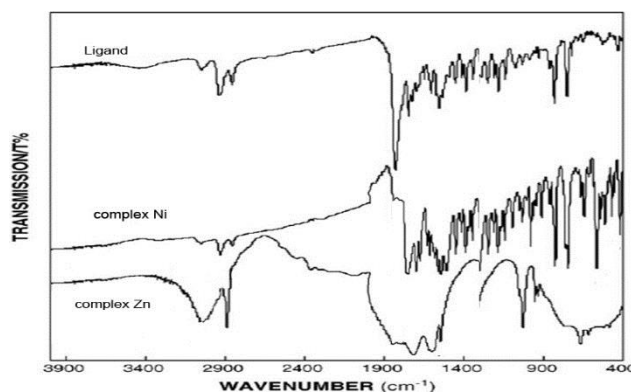


Fig:NMR Spectrum of the Ligand

<sup>1</sup>H NMR Studies The Schiff base shows <sup>1</sup>H NMR signal at  $\delta$  8.576 due to N-H – group . The observed signal at  $\delta$  6.513-7.679 (H-9 proton) are assigned for the aromatic group..The appearance of <sup>1</sup>H NMR spectra as a new multiplet peak at 1.112-1.252 ppm is assigned due to the presence of CH<sub>2</sub> and CH<sub>3</sub> group.The medium singlet peak at  $\delta$  2.232 ppm corresponds to OCH<sub>3</sub>

### 3.1 INFRARED SPECTRA of Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O with Valerophenone m-Anicichydrazone. and ZnCl<sub>2</sub> with Valerophenone m-Anicic acid hydrazone.

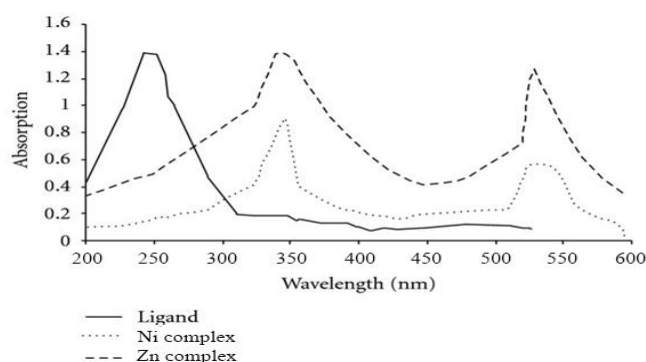
IR spectrum shows band at 1800 cm<sup>-1</sup>  $\nu$ (C=O); this has shifted to lower frequency region 1790 in the Nickel complex and 1780 cm<sup>-1</sup> in Zinc complex indicating the participation of amide (C=O) group in chelation. The ligand band at 1750 cm<sup>-1</sup> due to  $\nu$ (C=N) azomethine group has shifted to lower frequency 1740 cm<sup>-1</sup> in the Nickel complex and 1600 cm<sup>-1</sup> indicating coordination through azomethine nitrogen. The appearance of bands at 2850 and 3100 cm<sup>-1</sup> in the spectra of ligands and complexes has been assigned to associate CH<sub>3</sub>,NH, and OCH<sub>3</sub> groups A medium intensity band at 550 cm<sup>-1</sup> Nickel(II) complex and 655 cm<sup>-1</sup> in Zn(II) complex is assignable due to M-O bonding. Some new bands of weaker intensity at 520 cm<sup>-1</sup> and 470 cm<sup>-1</sup>, in both the complexes, give inferences about  $\nu$ (M-N) bonding.



IR spectra of Ligand and complexes.

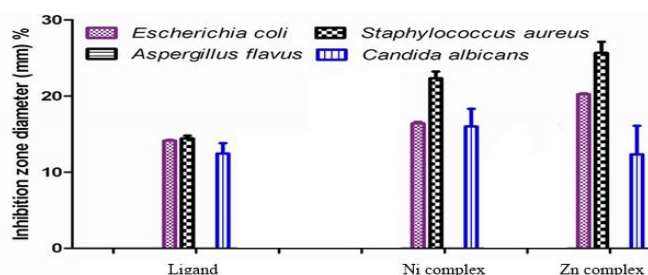
### 3.2 ELECTRONIC SPECTRA OF LIGAND AND COMPLEXES

The electronic spectrum of Ni(II) complex presents two d→d absorption bands at 10720 and 16340 cm<sup>-1</sup> in an octahedral environment corresponding to  ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)(\nu_1)$  and  ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)(\nu_2)$  transitions. For d<sup>8</sup> ions in an octahedral environment. The magnetic moment value of Ni(II) complex is 3.12 BM indicating the presence of two unpaired electrons on Ni(II) ion and suggesting that this complex has an octahedral geometry. The electronic spectrum of Zn(II) complex is due to charge transfer transition.



### 4. BIOLOGICAL ACTIVITY

These observations show that the compounds are more active than their respective Schiff base. The higher activity of the metal complexes may be owing to the effect of metal ions on the normal cell membrane. Metal chelates bear polar and nonpolar properties together; this makes them suitable for permeation to the cells and tissues. The nickel (II) complex was found to have 15mm inhibition against *Pseudomonas aerogens*, 14mm against *Escherichia coli*, 8mm against *Klebsiella pneumonia*, and 8mm against *Staphylococcus aureus*. It is known that chelating tends to make the ligand act as more powerful and potent bactericidal agents, thus killing more of the bacteria than the ligand.



### 5. CONCLUSION

The analytical results show 1:2 and 1:1 metal: ligand stoichiometry. The molar conductance value reveals the presence of non-electrolytic compound with no inorganic anion outside the coordination sphere. The molar conductance values in methanol (10<sup>-3</sup> M) are 20 and 18 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>, respectively, for Ni (II) and Zn (II) complexes. The magnetic moment and electronic spectra studies suggest an octahedral and tetrahedral structure. The spectral data shows that the complexation takes place through oxygen and nitrogen atom. The antibacterial

activity of the Schiff base complex became more pronounced when coordinated with the metal ions. In view of the above facts, an octahedral structure is proposed for nickel (II) Schiff base complex and tetrahedral structure for Zinc (II). ).

## 6. REFERENCES

- [1] Osman, A.H. Synthesis and Characterization of Cobalt(II) and Nickel(II) Complexes of Some Schiff Bases Derived from 3-hydrazino-6-methyl[1,2,4] triazin-5(4H)one, *Trans. Met. Chem.* 2006, 31, 35-41.
- [2] Chen, D.; Martel, A.E. Dioxygen affinities of synthetic cobalt Schiff base complexes. *Inorg. Chem.* 1987, 26, 1026-1030.
- [3] Costamagna, J.; Vargas, J.; Latorre, R.; Alvarado, A.; Mena, G. Coordination compounds of copper, nickel and iron with Schiff bases derived from hydroxynaphthaldehydes and salicylaldehydes, *Coord. Chem. Rev.* 1992, 119, 67-88.
- [4] Enamullah, M.; Vasylyeva, V.; Janiak, C. Chirality and diastereoselection of  $\Delta/\Lambda$ -configured tetrahedral zinc (II) complexes with enantiopure or racemic Schiff base ligands, *Inorg. Chim. Acta* 2013, 408, 109-119.
- [5] Raman N, Muthuraj V, Ravichandran S, Kulandaisamy A. Synthesis, characterisation and electrochemical behaviour of Cu(II), Co(II), Ni(II) and Zn(II) complexes derived from acetylacetone and *p*-anisidine and their antimicrobial activity. *Journal of Chemical Sciences.* 2003;115(3):161-167.
- [6] Chohan ZH, Sherazi SKA. Synthesis, characterization and role of anions (nitrate, sulphate, oxalate and acetate) in the biological activity of hydrazine derived compounds and their metal chelates. *Metal-Based Drugs.* 1997;4(6):327-332.
- [7] Agarwal RK, Singh L, Sharma DK, Singh R. Synthesis, spectral and thermal investigations of some oxovanadium(IV) complexes of hydrazones of isonicotinic acid hydrazide. *Turkish Journal of Chemistry.* 2005;29(3):309-316.
- [8] Lever ABP. *Inorganic Electronic Spectroscopy*. 2nd edition. Amsterdam, The Netherlands: Elsevier; 1984.
- [9] Figgis BN. *Introduction to Ligand Field Theory*. 2nd edition. New Delhi, India: Wiley East; 1976.
- [10] Sreeja PB, Kurup MRP. Synthesis and spectral characterization of ternary complexes of oxovanadium(IV) containing some acid hydrazones and 2,2'-bipyridine. *Spectrochimica Acta Part A.* 2005;61(1-2):331-336.
- [11] P. Mishra and Monika Soni, Hindawi Publishing Corporation, vol.10, p.7, 2008.
- [12] M. Rudden and Wilson; *Elements of Solid State Physics*; New York, (1980).
- [13] J. S. Hadi, Ph. D. Thesis, University of Basrah (2001).
- [14] T.M.Ebrahim, Ph.D. Thesis. Basrah of University, Iraq (2007).
- [15] K. Nakanishi and P. Solomon. "Infrared Absorption Spectroscopy". HOLDEN-DAY, Inc., London, Sydney. (1977).
- [16] Nakamoto K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part A and Part B*. New York, NY, USA: John Wiley & Sons; 1998.
- [17] Silverstein RM, Bassler GC, Morrill TC. *Spectroscopic Identification of Organic Compounds*. 5th edition. New York, NY, USA: John Wiley & Sons; 1991.
- [18] Dey K, Bandyopadhyay D. *Indian Journal of Chemistry A.* 1992;31:34 pages.
- [19] Panda AK, Dash DC, Mishra P, Mohanty H. Synthesis and characterization of copper(II), nickel(II) and cobalt(II) complexes with a new Schiff base derivative of isonicotinic acid hydrazide. *Indian Journal of Chemistry A.* 1996;35(4):324-327.
- [20] Mishra AP, Pandey LR. Synthesis, characterization and solid state structural studies of oxovanadium (IV)—O, N donor Schiff base chelates. *Indian Journal of Chemistry A.* 2005;44(1):94-97.