Biochem. Cell. Arch. Vol. 15, No. 2, pp. 535-537, 2015 | *ISSN 0972-5075*

SYNTHESIS AND CHARACTERIZATION OF Ni (II), Cu (II), Zn(II) SCHIFF BASE COMPLEXES WITH LIGAND CARRY AZOMETHINE GROUP

Munesh Sharma

Department of Chemistry, J. V. College, Baraut, Baghpat - 250 611, India.
e-mail: munesh004@gmail.com

(Accepted 31 August 2015)

ABSTRACT : Different Schiff bases derived by nucleophilic addition of (i) 4-amino-3-ethyl-5-mercapto-s-triazole and 4-amino-5-mercapto-3-n-propyl-s-triazole to p-chlorobenzaldehyde, 2-acetyl pyridine, 4-methyl acetophenone, 2,5-dinitroacetophenone (ii) 4-amino-5-mercapto-3-trifluoromethyl-s-triazole to p-chlorobenzaldehyde and 4-methylacetophenone and their metal complexes of Ni(ii), Cu(ii), have been synthesized and characterized by elemental analysis, IR, PMR, Electronic magnetic and conductance measurement.

Key words : Schiff bases, Azomethine group, IR, NMR etc.

INTRODUCTION

Schiff bases and their metal complexes find extensive use in organic synthesis. The azomethine group of the Schiff base gets polarized (>C=N-) and undergoes addition reactions (Patai, 1970). Schiff bases are used as anticorrosives (Costain and Terry, 1976), 3-amino-1, 2, 4-triazole is used as herbecides for control of perennial weeds. Schiff bases (Sabms and Kulkaram, 1963) have antitumour activity against lymphoid leukemia, dunning leukemia and carcinosaroma in rats. Schiff bases are found to have fungicidal and bactericidial activities against micro organism (Negrevergne and Offen, 1973). For biological activity of azomethine derivatives, the C=N linkage is essential. Schiff bases have wide applications in agrochemical, fungicidal, catalysis, analytical chemistry, dye industry, food industry and biological activities. They also played a remarkable role in the development of inorganic biochemistry. Due to their preparative accessibility and structural variety, Schiff bases complexes are most important in transition metal coordination chemistry.

MATERIALS AND METHODS

All chemicals (Clak, 1994 and Vogel, 1989) used at different stages of synthesis of ligands and their metal complexes were of A.R. Grade.

Synthesis of ligands

Ligands prepared in several steps. Thiocarbohydrazide (Andrieth *et al*, 1954) as an starting metarial, was used to prepare traizoles.

4-amino-3-ethyl-5-mercapto-s-triazole (AMET)

(10gm.) Thiocarbohydrazide in (60ml.) of propionic acid was refluxed for 4 h on a heating plate. Light yellow solids started separating within 1 h of refluxing. The reaction mixture was cooled and the product so obtained, was filtered, dried well and recrystallized form water.

4-amino-5-mercapto-3-n-propyl-s-triazole (AMPT)

(10gm.) Thiocarbohydrazied in (30 ml.) of n-butyric acid were taken in round bottom flask and refluxed for 4 h using a heating mantle. The excess of butyricacid was distilled off under reduced pressure. The reaction mixture was then allowed to stand for 24 h at room temperature. The colourless solid so obtained was filtered dried well and recystallized from dioxane-water giving shining creamy flakes.

4-amino-5-mercapto-3-trifluromethyl-s-triazole (AMTT)

(20gm.) Thiocarbohydrazide in 60ml. of trifluoroacetic acid was refluxed for 4 h and excess of TFA was removed under vacuo. The residue was triturated with ether-n-hexane (1:1) solution. Colourless crystals of AMTT were obtained.

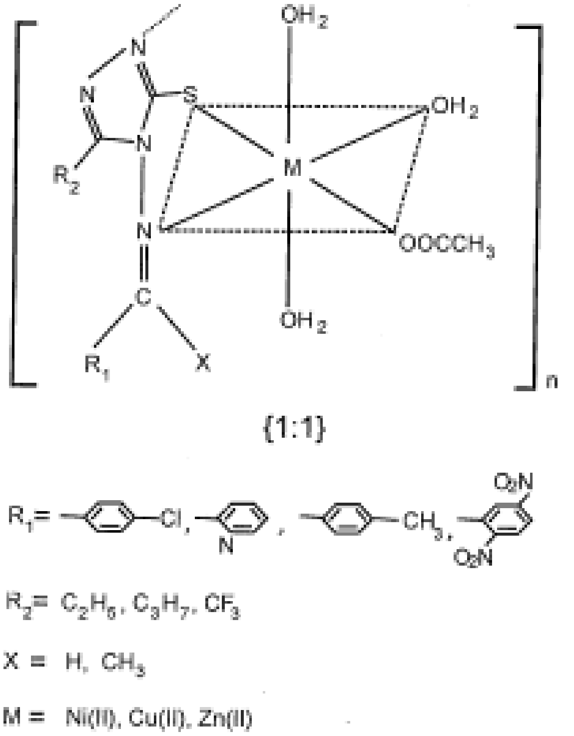
Preparation of Schiff bases ligand is carried out in hot ethanolic solution by the condensation of 4-amino-3-ethyl-5-mercapto-s-triazole (AEMT), 4-amino-5-mercapto-3-n-propyl-s-triazole (AMPT), with p-chlorobenazldehyde, 2-acetyl pyridine, 4-methyl acetophenone, 2,5-dinitro acetophenone and 4-amino-5-mercapto-3-trifluoro-methyl-s-triazole with p-chlorobenzaldehyde, 4-methyl acetophenone.

Synthesis of Complexes

Schiff bases complexes of Ni(II), Cu(II), Zn(II) prepared by the reaction of Schiff bases ligand with metal acetate were carried out in 1:1, 1:2 and 1: excess (metal-ligand) stoichiometric molar ratio.

Magnetic moment measurement of complexes were carried out at room temperature using Gouy balance. Estimation of Nickel as Nickel dimethyl glyoximate, copper as copper thiocyanate and zinc as zinc ammonium phosphate by gravimetric method. Using fusion method sulfur was estimated as barium sulphate. Infrared spectra of ligands and their metal derivatives were recorded in nujal mulls and KBr pellets using Perkin-Elmer 842-spectrophotometer in 4000-350 cm^{-1} region.

The electronic spectra of compounds were recorded on Hitachi U-200 spectrophotometer in the range 1100-200 nm. PMR spectra of the ligands and their metal complexes were recorded on Bruker Ac-300MH_ZFT NMR Using TMS as internal standard. The millimolar (1.0×10^{-3}M) solution of the complexes were prepared in N, N-dimethyl formamide and acetic acid for conductivity measurements.



Structure of Schiff Bases Metal (II) Complexes

RESULTS AND DISCUSSION

The conductivity measurements of 10^{-3}M solution in DMF revealed the non ionic character (Geary, 1971) of complexes with values 4.2-7.5 mhos cm^2 mol^{-1}. Complexes are also found insoluble in water and common organic solvents. They possess very high melting points and are infusible at higher temperature which suggest the polymeric in nature (Trost *et al,* 2004; Keisham *et al,* 2004; Rogan *et al,* 2000; Siddiqui *et al,* 2010; Haribabu *et al,* 2011; Gwaram *et al,* 2012; Manjula *et al,* 2013 and Kumar *et al,* 2012).

The strong band in the region 1600-1625 cm^{-1} in the spectra of free ligands due to ν (N=CH) Shift towards lower frequency by 15-25 cm^{-1} in the spectra of metal complexes indicating coordination of azomethine nitrogen (Sharma *et al,* 2013; Haribabu *et al,* 2013 and Shayma *et al,* 2012). Another band in the region 440-400 cm^{-1} suggests for formation of M-N bond in the metal complexes. The strong bands at ~1340 cm^{-1} and 1530 cm^{-1} due to nitro group remained unchanged in the spectra of complexes. A strong band around 1720 cm^{-1} and two other bands at ~1280cm^{-1} and ~1120cm^{-1} were observed in the spectra of (1:1) complexes due to the coordinated acetate group [ν (CH_3COO)]. A broad band is observed in the region 3440-3380 cm^{-1} due to ν (O-H) of coordinated water molecules.

All the Nickel (II) complexes showed three absorption bands in the region 7000-13000 cm^{-1} (ν_1), 13000-20000 cm^{-1} (ν_2) and 19000-27000 cm^{-1} (ν_3) suggesting octahedral complexes. Magnetic moment in the range 2.8-3.5 BM for d^8 configuration.

Copper (II) complexes exhibited only one broad band around 1700 cm^{-1} which assigned to $2Eg \rightarrow 2T_{2g}$ transition, characteristics of square planer geometry. Magnetic moment found to be within 1.7-2.0 BM expected for d^9 system.

Zn(II) complexes are diamagnetic as expected d^{10} configuration. Data suggested six coordinated octahedral complexes.

The expected spin allowed transition of Ni(II) octahedral complexes are $3A_{2g}(F) \rightarrow$

$3T_{2g}(F)(\nu_1)$ (7000-13000cm^{-1})

$3T_{2g}(F) \rightarrow 3T_{1g}(F)$ (ν_2) (11000-20000 cm^{-1}) and

$3A_{2g}(F) \rightarrow 3T_{1g}$ (F) (ν_3) (20000-30000cm^{-1})

The signals at δ10.4, 8.8, 10.2 and 11.0 for he azomethine proton in the PMR spectra of the free ligands shifted towards lower field to δ10.8, 9.2, 10.5 and 11.4 in the spectra of their (1:1) and (1:2) zinc complexes. Further signals obtained at δ13.8, 10.6, 12.38 and 11.4 due to SH portion in free ligand, disappeared in the spectra of their metal complexes.This agains proves the coordination through sulphur (Sandhya *et al,* 2012, 2014 and Bayoumi *et al,* 2013).

REFERENCES

Patai S (1970) The Chemistry of Carbon Nitrogen Double bond. Interscience Pub. Inc., New York.

Costain W and Terry B W H (1976) *Brit.* 1,434, 354.

Chem Abstract (1976) **85**, 147255a.

Sabms S S and Kulkaram K D (1963) *Indian Chem.* 447.

Negrevergne G and Ger Offen (1973) **2**, 303, 521.

Chem Abstr. (1974) **80**, 3232q .

Clak J H (1994) Supported reagents in organic reaction, VCH, Weinheim.

Vogel A I (1989) *Text Book of Practical Organic Chemistry.* 5th Edn., Longmans, London.

Andrieth L F, Cott E S and Kipper P S (1954) *J. Org. Chem.* **19**, 733.

Geary W J (1971) *Coord. Chem. Rev*. 781

Trost V H, Charles A and Mebi C A (2004) *Organometallics* **23**, 5127

Keisham S S, Mozharivskyi Y A, Carrals P J and Rao K M (2004) *J. Organomet. Chem.* 648-1249.

Rogan J, Poleti D, Karanovi L, Bogdanovic G and Bired A S (2000) *Polyhedron* **196**, 1415.

Siddiqui N, Ali R, Shamsher Alam M and Ahsan W (2010) *J. Chem. Pharm. Res*. **2**, 309.

Haribabu V, Anantha Lakshmi P V and Jayatyaga Raju V (2011) *Der Pharma Chem*. **3**, 413.

Gwaram N S, Ali H M, Khaledi H, Abdulla M A, Hadi A H A, Lin T K, Ching C L and Ooi C L (2012) *Molecules* **17**, 5952.

Manjula B and Arul S (2013) *Asian J. Biochem. Pharm. Res*. **1**, 168.

Kumar K R, Guru Prasad A R, Srilalitha V, Swami G N and Ravindranath L K (2012) *Chem. Bull. Politehnica Univ.* (Timisoara) **57**, 7.

Sharma A, Mehta T and Shah M K (2013) *Der Chem. Sin.* **4**, 141.

Haribabu V, Anantha Lakshmi P V and Jayatyaga Raju V(2013) *Int. J. Chem.Tech. Res.* **5**, 1512.

Shayma A S, Yang F, Abbas A S, Alhadi A A, Shaker S A, Suleiman N, Wagee G, Yehye A and Ali H M (2012) *J. Chil. Chem. Soc.* **57**, 1283.

Sandhya Rani D, Anantha Lakshmi P V, Kamala Prasad V and Jayatyaga Raju V (2012) *Chin. J. Inorg. Chem.* **28**, 1245.

Sandhya Rani D, Anantha Lakshmi P V and Jayatyaga Raju V(2014) *Res. J. Pharm. Biol. Chem. Sci.* **5**, 1304.

Bayoumi H A, Abdel-Nasser, Alaghaz M A and Mutlak sh. Aljahdali (2013) *Int. J. Electrochem. Sci*. **8**, 9399