



## CU(II)/NI(II) COMPLEXES WITH TRIDENTATE N<sub>3</sub> DONOR SCHIFF BASE LIGANDS DERIVED FROM ACETYL PYRIDINE AND DERIVATIVES ETHYLENEDIAMINE/PROPANEDIAMINE: A LITERATURE SURVEY

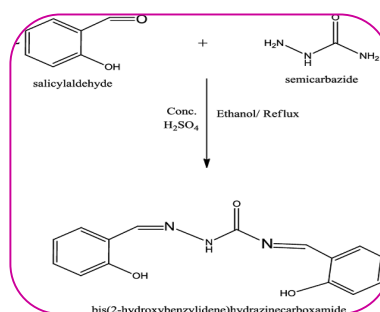
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### ABSTRACT

This paper contains a comprehensive review on Cu(II)/Ni(II) complexes of tridentate N<sub>3</sub> donor Schiff base obtained from acetyl pyridine and derivatives of ethylenediamine/propanediamine. Synthesis, nuclearity, structure and magnetic properties of complexes are elaborately explained. Role of coligands like; azido, thiocyanato, halide, etc. on nuclearity and magnetic behavior of complexes are also depicted here.

**KEYWORDS:** Crystal structure; Copper(II); Nickel(II); Schiff base; Acetyl pyridine; Dinuclear, Polynuclear, Square pyramidal; Octohedral; Antiferromagnetic.

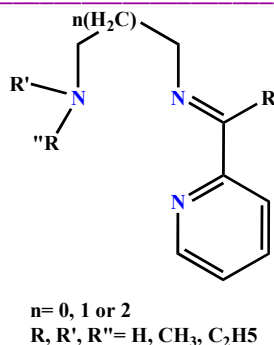


### INTRODUCTION:

Significant contemporary interests in inorganic-organic hybrid materials [1] reflect their potential applications in areas such as catalysis, molecular electronics, magnetism and photochemistry [2-3]. N<sub>3</sub> donor Schiff bases are useful chelators because of their preoperational accessibility, structural varieties and varied denticities [4-5]. Cu(II)/Ni(II) complexes are of considerable interest mainly due to their variety in coordination geometry, exquisite colors, technical application, spectroscopic properties and their biochemical significance [6-7]. Recent years have also seen extensive studies of the magnetic properties of polynuclear metal complexes with exchange coupled magnetic centers [8-9]. One of the major incentives is to obtain nanoscale molecular magnets, and current activities focus on increasing the nuclearity of single-molecule clusters that have ground electronic states with a large spin [10] and enhancing the anisotropy of single-molecule type systems [11].

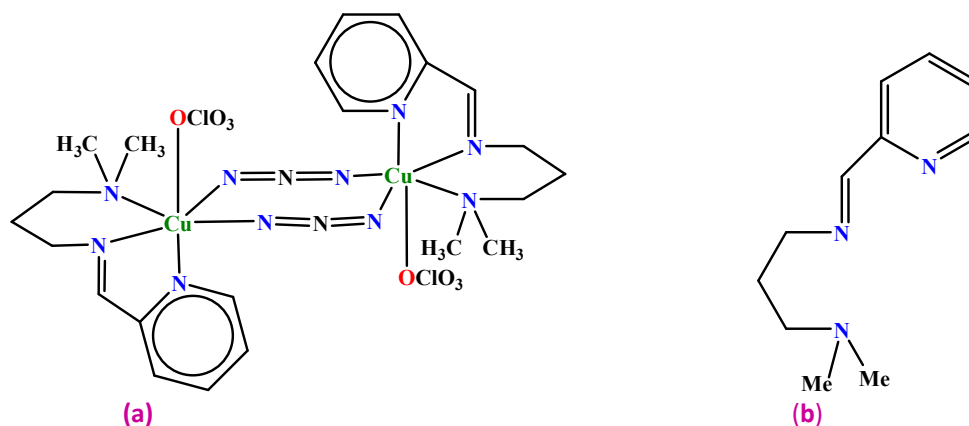
### Tridentate N<sub>3</sub> donor Schiff base ligands

The condensation products of the N-substituted diamines with 2-pyridyl acetone have been used as N<sub>3</sub> donor tridentate Schiff base ligands (Scheme 1) for the synthesis of mono-, di- or polynuclear complexes of transition metal since long [12].



**Scheme 1. Tridentate N<sub>3</sub> donor Schiff base ligands.**

One such interesting compound is the binuclear complex  $[Cu_2(L^A)_2(\mu_{1,3}-N_3)_2(ClO_4)_2]$  (Scheme 2a) where the  $L^A$  is N,N-dimethyl-N'-pyridin-2-ylmethylene-propane-1,3-diamine (Scheme 2b) [13] which shows unusual intradimer ferromagnetic interactions through the *end-to-end* azido pathway. Another example is a ferromagnetic, *end-to-end* single azido bridged 1D polymeric copper complex  $[Cu(L^B)(\mu_{1,3}-N_3)(ClO_4)]_n$  where  $L^B$  = tridentate Schiff base ligand formed by the condensation of pyridine-2-carboxaldehyde and 1-(2-aminoethyl)-piperidine [14]. Ferromagnetic interaction is also observed in doubly *end-to-end* azide bridged 1D polymer  $[Cu\{4\text{-dimethylamino}pyridine\}_2(N_3)_2]_n$  [15].



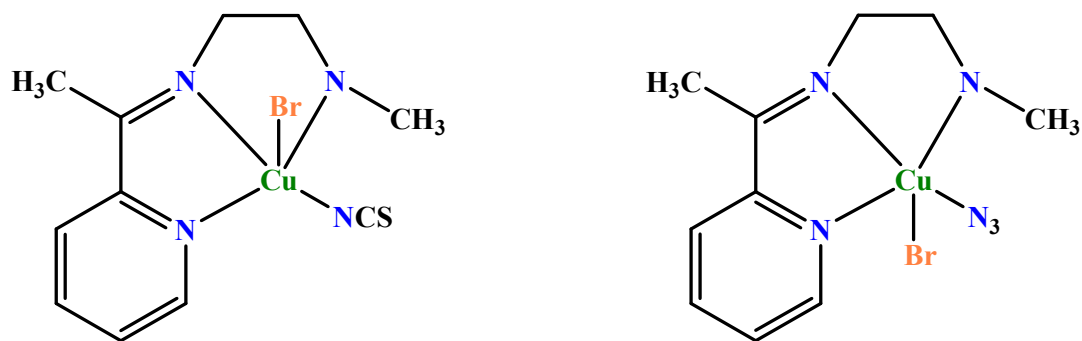
**Scheme 2.** Schematic representation of (a)  $[Cu_2(L^A)_2(\mu_{1,3}-N_3)_2(ClO_4)_2]$  and (b)  $L^A$  = N,N-dimethyl-N'-pyridin-2-ylmethylene-propane-1,3-diamine.

**Cu(II)/Ni(II) complexes with tridentate N<sub>3</sub> donor Schiff base ligands derived from acetyl pyridine and derivatives ethylenediamine/propanediamine**

Under this section we have discussed about the synthesis, single crystal X-ray structure and magnetic properties of the Cu(II)/Ni(II) complexes of tridentate N<sub>3</sub> donor Schiff base ligands derived from the 1:1 condensation of acetyl pyridine and N-substituted ethylenediamine/propanediamine.

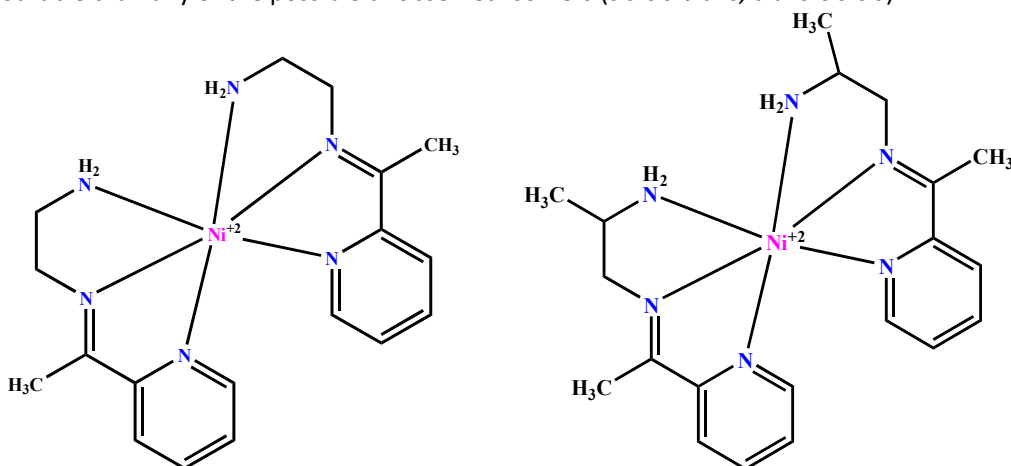
**MONONUCLEAR COMPLEXES**

The crystal structures of limited no of mononuclear Cu(II)/Ni(II) complexes of these type of Schiff base ligands have been reported in the literature. Most of the mononuclear Cu(II) complexes have (4+1) square pyramidal geometry, in which the three donor atoms of the Schiff base coordinate at basal plane and various anionic coligands (e.g. thiocyanate, azide, halide, etc.) being coordinated to the remaining site (Scheme 3) [16].



**Scheme 3.** Schematic view of two (4+1) square pyramidal mononuclear Cu(II) complexes of N<sub>3</sub> donor Schiff Base.

Whereas, mononuclear Ni(II) complexes are of octahedral geometry [Scheme 4] [17], two N<sub>3</sub> donor Schiff base ligands simultaneously bind the metal through six nitrogen atoms (two pyridyl N, two imine N and two amino N). Several isomers are theoretically possible considering the relative arrangement of three types of coordinated nitrogen atoms around the metal centre, although *cis-trans-cis* geometry is sterically more favourable than any of the possible unobserved isomers (*cis-cis-trans*, *trans-cis-cis*).

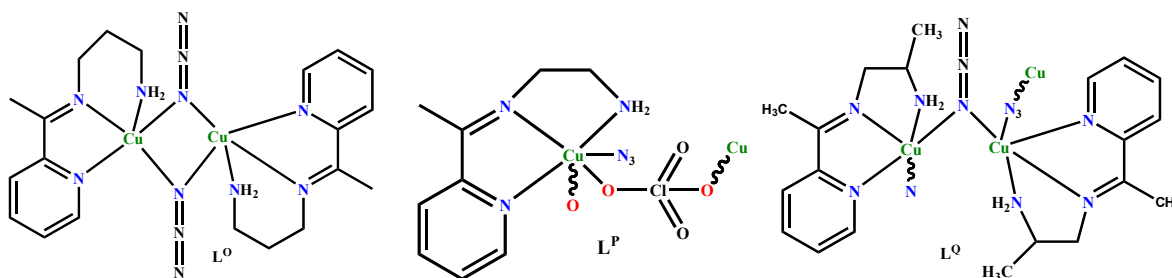


**Scheme 4.** Schematic view of two octahedral mononuclear Ni(II) complexes of N<sub>3</sub> donor Schiff Base.

#### DINUCLEAR AND POLYNUCLEAR COMPLEXES

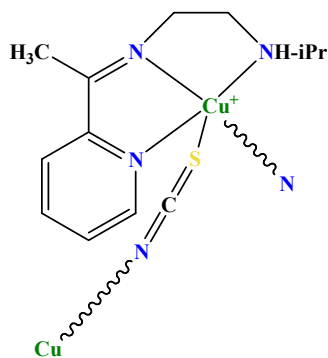
Chattopadhyay *et al.* report the synthesis, structural characterization, and variable temperature magnetic behavior of three new Cu(II) complexes:  $[(\text{CuL}^{\text{O}}\text{N}_3)_2](\text{ClO}_4)_2$ ,  $[\text{CuL}^{\text{P}}(\text{N}_3)(\text{ClO}_4)]_n$  and  $[\text{CuL}^{\text{Q}}(\mu_{1,1}\text{-N}_3)(\mu_{1,3}\text{-N}_3)(\text{ClO}_4)]_n$  where  $\text{L}^{\text{O}} = \text{N} \cdot \text{-(1-pyridin-2-yl-ethylidene)propane-1,3-diamine}$ ,  $\text{L}^{\text{P}} = \text{N} \cdot \text{-(1-pyridin-2-yl-ethylidene)ethane-1,2-diamine}$  and  $\text{L}^{\text{Q}} = \text{N} \cdot \text{-(1-pyridin-2-yl-ethylidene)propane-1,2-diamine}$  are three N<sub>3</sub> donor Schiff base ligands [18]. First complex is a double basal-apical *end-on* (EO) azido bridged dinuclear with square pyramidal geometry. In second complex the square planar mononuclear  $[\text{CuL}^{\text{P}}(\text{N}_3)]$  units are joined by weakly coordinated perchlorate ions in the axial positions of Cu(II) to form a one-dimensional chain. Third one consists of 1D chains in which the Cu(II) ions with a square pyramidal geometry are alternately bridged by single *end-on* (EO) and *end-to-end* (EE) azido ligands, both adopting a basal-apical disposition [Scheme 5]. Variable temperature (300–2K) magnetic susceptibility measurements and magnetization measurements at 2 K were performed by the authors. Results show that, dinuclear azido bridged complex is antiferromagnetic and double azido bridged polynuclear complex is ferromagnetic.

Perchlorate bridged polynuclear complex shows both antiferromagnetic and ferromagnetic coupling interactions through two different kinds of hydrogen bond.



**Scheme 5.** Schematic view of one dinuclear azido bridge Cu(II) complex (left) and two polynuclear complexes bridged by perchlorate and double azido simultaneously (middle & right) of N<sub>3</sub> donor Schiff Bases.

X.-M. Hu *et al.* reported a complex {catena-[(μ<sub>2</sub>-thiocyanato)-(N-isopropyl-N-(1-(pyridin-2-yl)ethylidene)ethane-1,2-diamine)-di-copper tetrafluoroborate]} using a N<sub>3</sub> donor Schiff base derived from 1:1 condensation between acetyl pyridine and N-isopropylethane-1,2-diamine [19]. The complex is a μ<sub>1-3</sub>-thiocyanate bridged 1D polymeric chain [Scheme 6], the basal plane is formed by four nitrogen atoms (three nitrogen atom from N<sub>3</sub> donor Schiff base and one from thiocyanate) and sulphur atom from thiocyanate binds at axial position. The geometry around all Cu(II) atoms in the chain is distorted (4+1) square pyramid.



**Scheme 6.** Schematic view of μ<sub>1-3</sub>-thiocyanate bridged 1D polymeric chain of Cu(II) complex formed by N<sub>3</sub> donor Schiff Base.

## CONCLUSION

The structural, magnetic and catalytic properties of polynuclear Cu(II)/Ni(II) complexes of N<sub>3</sub> donor Schiff base ligands with polyatomic anions have been developed to a considerable extent because of their interesting applications in the different fields of chemistry. Recent interest in the magnetic study and weak forces of polynuclear Cu(II)/Ni(II) complexes with various bridging groups emerges from their potential use as functional materials. The selection of both N<sub>3</sub> donor and bridging ligands is crucial for the formation of the desired polynuclear complexes with specific bridging modes of the ligands. Among the several transition metal centers, the exploration of structure, catalytic activity, non-covalent interactions and magnetic properties of polynuclear Cu(II)/Ni(II) complexes N<sub>3</sub> donor ligands and polyatomic anions still remain relatively limited. Therefore the synthesis of the new polynuclear Cu(II)/Ni(II) complexes with various bridging groups are expected to help in better understanding of the factors that govern the catalytic

properties and coupling between the metal centers, which in turn would help to design and produce functional materials.

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