



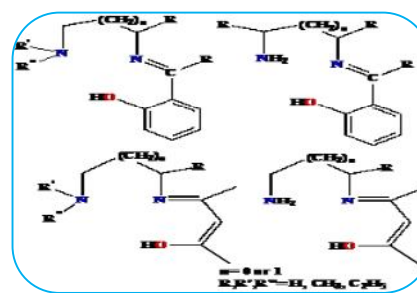
## REVIEW ON SOME COMPLEXES WITH N AND N, O DONOR LIGANDS & CHOICE OF TRANSITION METALS

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### ABSTRACT:

Studies of Cu(II) and Ni(II) complexes of N and N,O donor ligands may bring a great opportunity in the understanding of the structural variations that may bring about substantial changes in their noncovalent interactions, magnetic and catalytic properties. All these have prompted us to synthesize polynuclear Cu(II) and Ni(II) complexes containing N and N,O donor ligands with several bridging coligands (e.g. azide, cyanate, thiocyanate, dicyanamide, benzoate, phenoxido, hydroxido, 4,4-bipyridine etc.) and explore their noncovalent interactions, catalytic properties and magnetostructural correlations. In this review work, synthesis of different kind of N and N,O donor ligands and characterization of their Cu(II) and Ni(II) complexes are done.



**KEYWORDS:** Ligands; Schiff base; Cu(II) & Ni(II); Complexes; Polynuclear.

### INTRODUCTION:

In the past few decades, significant progress has been achieved in understanding the chemistry of transition metal complexes with N and N,O donor ligands [1,2]. The synthesis of polynuclear complexes of N and N,O donor ligands with polyatomic anions has been developed to a considerable extent because of their interesting applications in the field of structural chemistry [3-6], magnetism [3,7], gas storage [8-9], catalysis [10-12], luminescence [5, 13-14], bioinorganic chemistry [15-16], etc. The steric and electronic effects of the N and N,O donor ligands as well as the polyatomic bridging ligands play a vital role in constructing the polymeric structures. In particular, condensation of a carbonyl compound (e.g. *o*-hydroxyacetophenone, *o*-hydroxynaphthaldehyde etc.) and one ended substituted diamine produces tridentate N<sub>2</sub>O donor Schiff base ligands. The tridentate N<sub>2</sub>O donor Schiff base ligands, along with some additional bridging coligands e.g. azide, cyanate, thiocyanate, dicyanamide, benzoate, hydroxido, 4,4'-bipyridine etc, favours the formation of multinuclear transition metal complexes showing interesting magnetic exchange interactions. It has been shown that the competitive as well as the cooperative role among the bridging anions is very important in constructing the polymeric architectures [17-19]. However, the tridentate Schiff base can coordinate to metal ions either in meridional or facial configurations and this difference in configuration might be very important in building a desired polynuclear complex with bridging coligand. Among the several paramagnetic transition metal centers, the exploration of structure and magnetic properties of octahedrally coordinated polynuclear Cu(II) and Ni(II) complexes of 1) monoanionic tridentate N<sub>2</sub>O Schiff base ligands and 2) N donor ligands like diamine and N<sub>3</sub> donor Schiff base along with polyatomic anions still remain very significant area of research. Furthermore, development in the field of

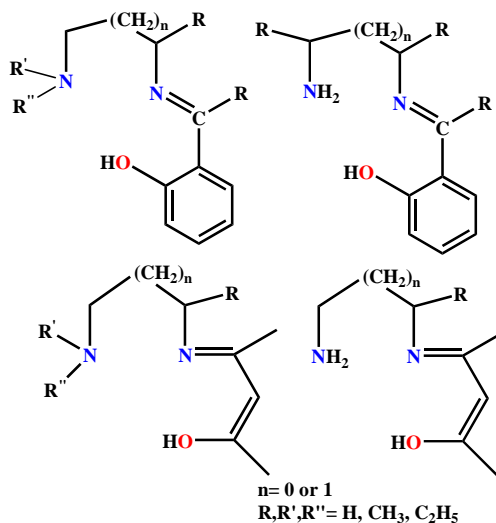
bioinorganic chemistry has also led to an increased interest in Cu(II) and Ni(II) complexes of N,O donor ligands since it has been recognized that many of these complexes may serve as models for biologically important species having N and O as bonding sites [20].

### CHOICE OF LIGANDS

The proposed review work focuses on the systematic study of the polynuclear Cu(II) and Ni(II) complexes containing 1) tridentate N<sub>2</sub>O donor Schiff base ligands as N,O donor and 2) N-methyl-1,3-propanediamine and N<sub>3</sub> donor Schiff base ligand as N donor, in presence of several auxiliary bridging groups.

### Tridentate N<sub>2</sub>O donor Schiff base ligands as N,O donor

The tridentate Schiff bases are usually the condensation products of aliphatic or aromatic carbonyl compounds (e.g. salicylaldehyde, *o*-hydroxyacetophenone, acetylacetone, *o*-hydroxynaphthaldehyde etc.) and several N-substituted diamines e.g. N-methyl-1,3-propanediamine, N,N-dimethyl-1,3-propanediamine, N,N-diethyl-1,2-ethanediamine, N-methyl-1,2-ethanediamine, N,N-dimethyl-1,2-ethanediamine etc. (Scheme I). The Schiff base ligands with N-substituted diamines can easily be synthesized by reacting the carbonyl compounds and diamines in 1:1 molar ratio in a suitable solvent. Synthesis of the single condensed tridentates Schiff bases of unsubstituted diamine are not so simple because the reaction of carbonyl compound with diamines yields the symmetrical tetradentate Schiff bases (2:1 condensation product). To overcome this problem, Costes *et al.* (in 1982) applied very efficiently high dilution technique to condense one of the NH<sub>2</sub> group of ethylenediamine with acetylacetone to synthesize tridentate Schiff base [21]. The single condensation of 1,3-diaminopropane with acetylacetone was first done by Kwiatkowski *et al.* [22].



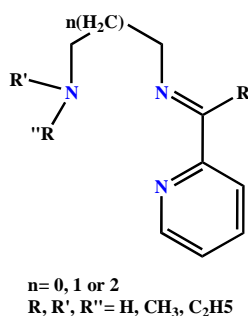
**Scheme I. Tridentate N<sub>2</sub>O donor Schiff base ligands.**

The tridentate Schiff bases can coordinate to metal ions easily to form various types of complexes. Usually, two such ligands coordinate to a metal centre to produce hexacoordinated mononuclear complexes. On the other hand, one tridentate ligand along with various anionic coligands may produce complexes of different nuclearities. It has been shown that the competitive as well as the cooperative role of the bridging anion and pseudohalide is very important in constructing the polymeric architecture [23]. Therefore the tridentate Schiff bases along with the bridging anions is a very good combination to synthesize polynuclear complexes with interesting magnetic properties [24].

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

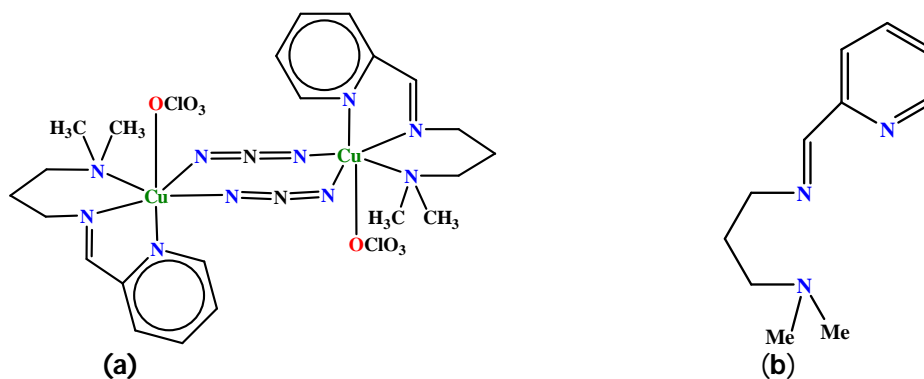
Significant contemporary interests in inorganic-organic hybrid materials [25] reflect their potential applications in areas such as catalysis, molecular electronics, magnetism and photochemistry [26-27]. Schiff bases are useful chelators because of their preoperational accessibility, structural varieties and varied denticities [28-29]. Copper complexes are of considerable interest mainly due to their variety in coordination geometry, exquisite colors, technical application, spectroscopic properties and their biochemical significance [30-31]. Recent years have also seen extensive studies of the magnetic properties of polynuclear metal complexes with exchange coupled magnetic centers [32-33]. 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 [34] and enhancing the anisotropy of single-molecule type systems [35].

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 II) for the synthesis of mono-, di- or polynuclear complexes of transition metal since long [36].



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

One such interesting compound is the binuclear complex  $[\text{Cu}_2(\text{L}^{\text{A}})_2(\mu_{1,3}\text{-N}_3)_2(\text{ClO}_4)_2]$  (Scheme IIIa) where the L<sup>A</sup> is N,N-dimethyl-N'-pyridin-2-ylmethylene-propane-1,3-diamine (Scheme IIIb) [37] 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  $[\text{Cu}(\text{L}^{\text{B}})(\mu_{1,3}\text{-N}_3)(\text{ClO}_4)]_n$  where L<sup>B</sup> = tridentate Schiff base ligand formed by the condensation of pyridine-2-carboxaldehyde and 1-(2-aminoethyl)-pipyridine [38]. Ferrromagnetic interaction is also observed in doubly *end-to-end* azide bridged 1D polymer  $[\text{Cu}\{4\text{-dimethylamino}(\text{pyridine})_2(\text{N}_3)_2\}]_n$  [39].

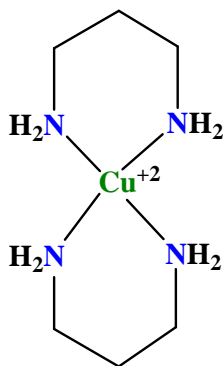


**Scheme III. Schematic representation of (a)  $[\text{Cu}_2(\text{L}^{\text{A}})_2(\mu_{1,3}\text{-N}_3)_2(\text{ClO}_4)_2]$  and (b) L<sup>A</sup> = N,N-dimethyl-N'-pyridin-2-ylmethylene-propane-1,3-diamine.**

### Propane-1,3-diamine as N donor

During the past several decades, diamines and their derivatives have been extensively investigated in both basic research and their application. The result shows that they can form stable complexes with many transition metals. These complexes would be widely applied in various fields such as biotechnology [40], synthesis [41], food processing industry [42], environmental science [43], biochemistry [44], magnetic material [45] *etc.* Among them propane-1,3-diamine is well known and thoroughly studied bidentate ligand due to their wide application in the synthesis of heterocycles [46], biotechnology [47], and preparation of coordination complexes used in drug industries [48].

In propane-1,3-diamine, nitrogen atom is the donor or ligand atom to the central metal atom or ion. The structure of the bidentate ligand based complex,  $\{[Cu^{+2}(pn)_2](SCN)_2\}$  where pn = propane-1,3-diamine, is shown [Scheme IV] as a representative example with Cu(II) as metal center [49]. Due to bidentate nature of ligand pn, a cyclic complex with two 6-membered rings is formed. These complexes have high stability constants due to chelate effect.



**Scheme IV. Schematic representation of  $[Cu^{+2}(pn)_2](SCN)_2$ .**

Since 1970, propane-1,3-diamine and its different substituent were extensively used as N donor bidentate chelating ligand. Use of propane-1,3-diamine as ligand was first done by A. Pajunen et al. [50]. Synthesis of mono- [49], di- [51] or polynuclear [52] complexes of transition metals with propane-1,3-diamine and their derivatives as N donor has a lot of research interest.

### Choice of metals

#### Why transition metals?

The rigidity of transition metal atoms along with their moderate rates of oxidation in air and wide range of oxidation states allow to provide a rich and interesting chemistry. They form a much more extensive range of coordination [53] and organometallic complexes [54]. Their range of oxidation states accounts for interesting electronic properties of many solid compounds, the ability to participate in catalysis [55] and their subtle and interesting role in biochemical processes [56]. Moreover, presence of one or more unpaired electron makes the transition metal atoms paramagnetic. The spin-spin interaction occurs in multinuclear transition metal complexes results a number of interesting magnetic properties *e.g.* ferromagnetism [57], antiferromagnetism [58], ferrimagnetism [59] *etc.* the ferromagnetic materials may also show molecular magnetism and can be used in electronic devices.

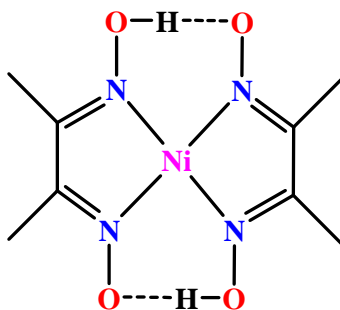
### Nickel

Nickel has an enormous and important organometallic [54] and catalytic chemistry [55a-b]. It shows a range of oxidation states from  $-I$  to  $+IV$  but its chemistry is predominantly of the  $+II$  state.  $Ni^{+1}$  species are being studied increasingly because of the possible involvement of these oxidation states in nickel containing metalloenzymes. Zerovalent nickel compounds occur with  $\pi$ -withdrawing ligands *e.g.* CO. Zerovalent nickel complexes with phosphine ligands are important catalyst precursor.  $Ni(-I)$  is

found in the carbonyl anion  $[\text{Ni}_2(\text{CO})_6]^{2-}$ .  $\text{Ni}^{3+}$  species has been found *e.g.*, in  $\text{NiBr}_3(\text{PR}_3)_2$ ,  $[\text{NiF}_6]^{3-}$ ,  $[\text{Ni}(\text{diars})_2\text{Cl}_2]^+$  *etc.* The chemistry of the Ni(III) complexes has increasing interest due to the suspected contribution of this oxidation state in nickel containing metalloenzymes [56]. The highest oxidation state +IV, attained by nickel is found in  $\text{NiF}_4$ .

Among all the above mentioned oxidation states, +2 states is the most versatile one. Square planar or octahedral complexes are generally formed with  $\text{Ni}^{2+}$  depending upon the ligand field strength and a few tetrahedral, trigonal bipyramidal and square based pyramidal structures are also known. Octahedral  $\text{Ni}^{2+}$  complexes are generally blue or green in colour and are paramagnetic as the  $d^8$  ion has two unpaired electrons, whereas with strong field's ligands, the electrons are forced to pair up resulting diamagnetic square planar complexes.

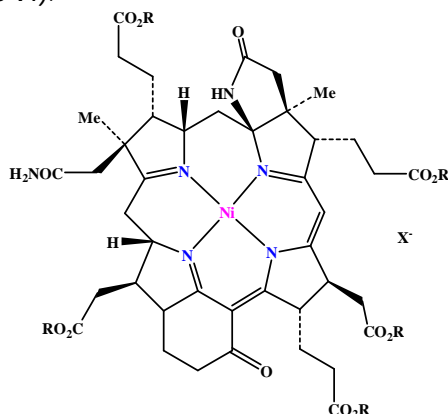
The square planar complexes are generally red, brown or yellow in color owing to the presence of an absorption band in the range of 450-600 nm. An important example of red coloured square planar Ni(II) complex is  $\text{Ni}(\text{HDMG})_2$  (Scheme V) ( $\text{H}_2\text{DMG}$  = Dimethylglyoxime) [53c]. This gives a stacked polymer.



**Scheme V. Schematic representation of the structure of  $\text{Ni}(\text{HDMG})_2$ .**

Several tetrahedral  $\text{Ni}^{2+}$  complexes are known with halide, phosphine, phosphine oxide or arsine ligands *e.g.*  $[(\text{Ph}_3\text{P})_2\text{NiCl}_2]$ ,  $[(\text{Ph}_3\text{AsO})_2\text{NiBr}_2]$  *etc.* [53a]. These complexes are typically intensely blue coloured and can be easily distinguished from square planar complexes both by the colour and because they are paramagnetic.

It is known that nickel is an essential component in at least four types of enzymes: urease, carbon monoxide dehydrogenase (CODH, or acetyl coenzyme A synthase), hydrogenase, and methyl-S-coenzyme M reductase [56]. The last one contains a prosthetic group consisting of a redox active  $\text{NiN}_4$  macrocycle (factor  $\text{F}_{430}$ ) (Scheme VI).



**Scheme VI. Active site structure of methyl-coenzyme M reductase.**

## Copper

Copper species are widely found in nature and are present in many oxidase enzymes [60] as an oxygen carrier in invertebrates and in photosynthesis. Although increasing attention has been paid to the design of copper complexes with polydentate ligands as model copper oxidases [60-61] and some mononuclear compounds have been recognized as catalysts for alkane oxidation [62], the use of multinuclear copper complexes for such reactions still remains a challenging area of research. There is also a great interest in various mixed oxides of copper which act as superconductor.

Copper shows oxidation states of +I, +II and +III. However the only simple hydrated ion found in solution is  $\text{Cu}^{2+}$ . Cu(I), being "soft" (according to Pearsons *Hard-Soft* classification) prefers  $\pi$ -acids like CO, olefins, phosphines, nitriles *etc.* which are *soft*. Cu(I) binds those N-donor ligands which are not "hard" and usually avoids O-donor ligands. However, the oxygen sensitivity of Cu(I) complexes of N-donor ligands has been effectively exposed by several workers to generate interesting Cu(I)-dioxygen chemistry in attempts to mimic the  $\text{O}_2$  binding properties of hemocyanin. Very few aqua complexes of Cu(I) are known. In fact,  $\text{Cu}^+$  disproportionates in water. Most of the simple compounds and complexes of Cu(I) are diamagnetic and colorless because of the  $d^{10}$  electronic configuration. There are a few colored compounds (*e.g.*  $\text{Cu}_2\text{O}$ -yellow or red,  $\text{Cu}_2\text{CO}_3$ -yellow, CuI-brown *etc.*), where color arises from charge transfer bands. Cu(I) complexes are usually four coordinate showing tetrahedral or distorted tetrahedral geometry. The +II state is the most stable and important for copper. Most Cu(II) complexes have a distorted octahedral structure and are blue or green in color. The metal ion has  $d^9$  electronic configuration. This leaves only one 'hole' into which an electron may be promoted, so the spectra should be similar to the  $d^1$  case and have a single broad band in absorption spectra. This is actually observed and these complexes absorb in the region 11,000-16,000  $\text{cm}^{-1}$ . However, octahedral  $\text{Cu}^{2+}$  complexes are appreciably distorted showing more than one peak.

The +III state is uncommon and corresponds to  $d^8$  configuration. The Cu(III) complexes are stable in square planar environment and are diamagnetic. The only exception is  $\text{K}_3\text{CuF}_6$ , in which Cu(III) ion is in high spin state and is paramagnetic. Cu(III) is strongly oxidizing and it can easily be reduced. Hence +3 states only occur when stabilized in complexes or as insoluble compounds.

## CONCLUSION

The review reports the synthesis of the polynuclear Cu(II) complexes containing tridentate  $\text{N}_2\text{O}$  donor Schiff base ligands as N,O donor obtained from the 1:1 condensation of different kind of diamine and aromatic carbonyl moiety in presence of several auxiliary bridging ligands. The proposed area of review also focuses on the study of Cu(II) and Ni(II) complexes of N donor ligands like  $\text{N}_3$  donor Schiff bases and N-methyl-1,3-propanediamine and azide or thiocyanate as anionic coligand.

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