



## METAL COMPLEXES OF SCHIFF BASES

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### Abstract

*Some novel transition metal [Cu (II), Ni (II) and Zn (II)] complexes of substituted pyridine Schiff-bases have been prepared and characterized by physical, spectral and analytical data. The synthesized Schiff-bases act as deprotonated tridentate for the complexation reaction with Cu (II), Ni (II) and Zn(II) ions. In order to evaluate the effect of metal ions upon chelation, the Schiff bases and their complexes have been screened for antibacterial activity against the strains such as Escherichia coli, Staphylococcus aureus, and Pseudomonas aeruginosa. The complexed Schiff bases have shown to be more antibacterial against one more bacterial species as compared to uncomplexed Schiff-bases.*

**Keywords:** Schiff base, Transition metal complexes of Cu (II), Ni (II).



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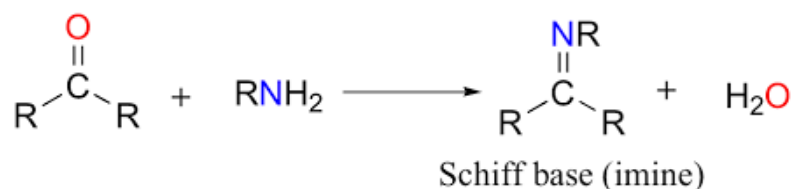
### Introduction

The field of coordination chemistry is one of the most scholarly, attractive and experimentally demanding frontiers in modern chemical sciences. It has grown in a half century from a readily defined and limited area into the most active research field of inorganic chemistry. Coordination compounds brought about a synthetic revolution in inorganic chemistry which leads to new products of equally novel applications in wide range of areas such as fungicides, paints, pigments, polymers, pharmaceuticals, catalysis, and photoconductors. Complexation reactions are used in qualitative as well as quantitative analysis of metals. There are some extremely sensitive and selective organic reagents for the determination of metal ions. Coordination chemistry, by its very nature, deals with metals and ligands. Metal coordination occurs when lone pair electrons from a ligand are donated to an empty orbital in a metal ion. There are many broad classes of ligands such as classical,

organo-metallic, cluster and bioinorganic. A classical ligand, also called a Werner complex after coordination chemistry's founder Alfred Werner, is a ligand that binds through the lone pairs of the main group atom of the ligand. Many metal-ligand interactions seen in nature are classical ligands. Metals are known to have first choice for certain ligands and for certain geometries. Classical cases are the so-called Schiff-base couplings; in other cases rather unique ligands can be formed only when the metal is present.

### **Schiff-base**

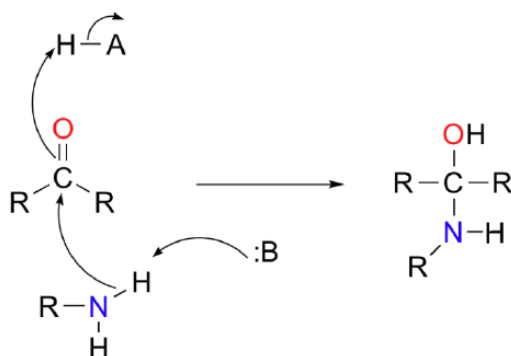
A German chemist Hugo Schiff in 1864 developed a new class of organic compounds. The group of compounds, imines are often referred to as Schiff bases in his honor. The preparations of these compounds are simple and attractive. They are prepared by condensing a carbonyl compound with an amine, generally refluxing in alcohol. The active and well-designed Schiff base ligands are considered as "privileged ligands". In fact, Schiff bases are able to stabilize many different metals in various oxidation states, controlling the performance of metals in a large variety of useful catalytic transformations. Several studies showed that the presence of a lone pair of electrons in a  $Sp^2$  hybrid orbital of nitrogen atom of the azomethine group is of considerable chemical and biological importance. Ligands containing  $Sp^2$  hybridized nitrogen atoms, particularly those in which the N-atom is a part of the aromatic system, show very extensive coordination chemistry. Because of the relative easiness of preparation, synthetic flexibility, and the special property of C=N group, Schiff bases are considered as excellent chelating agents especially when a functional group like -OH or -SH is present close to the azomethine group so as to form a five or six membered chelate ring with the metal ion. A reaction for preparation of Schiff base begins with nucleophilic addition of primary amines of the type  $RNH^2$ ,  $ArNH^2$  to carbonyl compounds (ketones or aldehydes). The following scheme shows a chemical reaction between carbonyl compounds and primary amines.



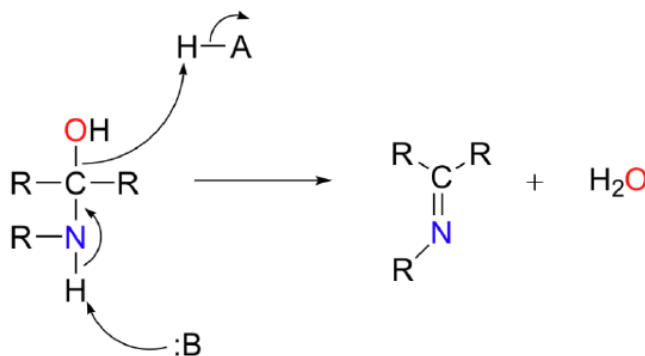
Scheme 1. General preparation method of Schiff base R groups may substituted variously.

Schiff bases that contain aryl substituent's are substantially more stable and more readily synthesized, while those which contain alkyl substituent's are relatively unstable. Schiff bases of aliphatic aldehydes are relatively unstable and readily polymerizable while those of

aromatic aldehydes having effective conjugation are more stable. In general, aldehydes react faster than ketones in condensation reactions, leading to the formation of Schiff bases as the reaction centre of aldehyde are sterically less hindered than that of ketone. Furthermore, the extra carbon of ketone donates electron density to the azomethine carbon and thus makes the ketone less electrophilic compared to aldehyde. Schiff bases are generally bidentate, tridentate, tetradentate or polydentate ligands capable of forming very stable complexes with transition metals. They can only act as coordinating ligands if they bear a functional group, usually the hydroxyl, sufficiently near the site of condensation in such a way that a five or six member ring can be formed when reacting with a metal ion. The electrophilic carbon atoms of aldehydes and ketones can be targets of nucleophilic attack by amines. The end result of this reaction is a compound in which the C=O double bond is replaced by a C=N double bond. This type of compound is known as an imines, or Schiff base. Mechanistically, the formation of an imines involve two steps. First, the amine nitrogen acts as a nucleophile, attacking the carbonyl carbon. This is closely analogous to hemiacetal and hemiketal formation.



What happens next step is that the nitrogen is deprotonated, and the electrons from this N-H bond 'push' the oxygen off of the carbon, leaving as with a C=N double bond (an imine) and a displaced water molecule.

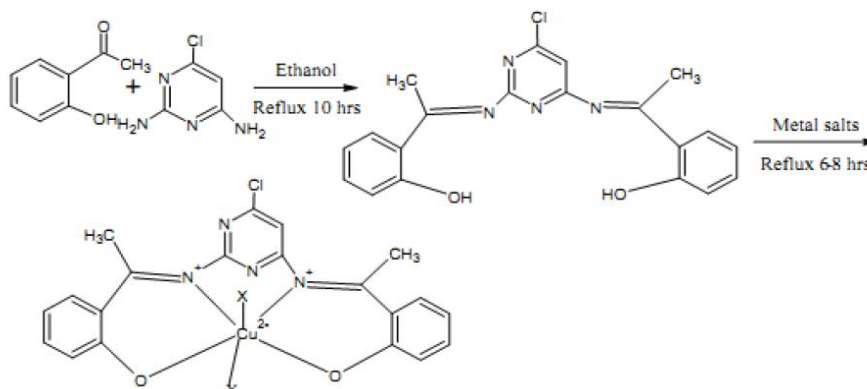


Scheme 2. Mechanistic explanation of the formation of Schiff base

Transition metals are known to form Schiff base complexes and Schiff bases have often been used as chelating ligands in the field of coordination chemistry. Their metal complexes have been of great interest for many years. It is well known that N and S atoms play a key role in the coordination of metals at the active sites of numerous metallo-bio-molecules (Brown and Smith, 1990). Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer, antiviral and herbicidal applications. They serve as models for biologically important species and find applications in biomimetic catalytic reactions. Chelating ligands containing N, S and O donor atoms show broad biological activity and are of special interest because of the variety of ways in which they are bonded to metal ions. It is known that the existence of metal ions bonded to biologically active compounds may enhance their activities.

### **Preparation methods of Schiff base complexes :( Bydirect interaction of the Schiff base with the metal salts)**

The Schiff base can be synthesized without using the metal ion and then followed by addition of the metal ion as salt solution for complex formation. This can be easily described by the following example.



Scheme 3. Preparation of Schiff base complex by direct method

A variety of Schiff bases can be obtained by changing aldehydes or amines. Thus synthesis of large number of Schiff bases with diverse structural features could be possible with ease. They can have additional donor groups like oxygen, sulphur, phosphorus etc. which makes them good candidates for metal ion complexation and for mimicking biological systems. They can be functionalized by the insertion of appropriate groups in the aliphatic or aromatic chains.

### **The Chemistry of Ni (II) Complexes**

Nickel (Ni) is a member of first transition series. It has valence shell configuration of  $3d^8 4s^2$ . It generally exists in zero and +2 oxidation states. Nickel in zero oxidation state forms very

stable complexes with tetrahedral geometry. The electronic configuration of the Ni (II) is  $d^8$ .  $Ni^{2+}$  may have a variety of co-ordination numbers and geometries, the main structural types being octahedral, tetrahedral, and square-planar. Octahedral nickel (II) complexes having  ${}^3A_{2g}$  ground state are expected to have three spin-allowed transitions :  ${}^3A_{2g} \rightarrow {}^3T_{2g}$ ,  ${}^3A_{2g} \rightarrow {}^3T_{1g}$  (P) and  ${}^3A_{2g} \rightarrow {}^3T_{1g}$  (F) in the ranges of 7000-13000, 11000-20000 and 19000-27000  $cm^{-1}$  respectively. Two spin forbidden transitions:  ${}^3A_{2g} \rightarrow {}^1E_g$  and  ${}^3A_{2g} \rightarrow {}^1T_{2g}$  are also observed near the second spin-allowed transition, and between second and third spin-allowed transitions respectively. Octahedral nickel (II) complexes have two unpaired electrons and thus possess magnetic moments ranging from 2.9 to 3.4 B.M. depending on the orbital angular momentum contribution. For regular or nearly regular tetrahedral complexes there are characteristic spectral and magnetic properties. Irregular geometries are less likely to meet these specifications. The tetrahedral nickel (II) complexes with  ${}^3T_1$  (F) ground state generally exhibit four transitions.  ${}^3T_1 \rightarrow {}^3A_2$ ,  ${}^3T_1 \rightarrow {}^1E$ ,  ${}^3T_1 \rightarrow {}^3T_1$  (P) and  ${}^3T_2 \rightarrow {}^1T_1$ . The band  ${}^3T_1 \rightarrow {}^3T_1$  (P) is a strong band of high intensity compared with others. The transition from the ground  ${}^3T_1$  (F) state to the  ${}^3T_1$  (P) state occurs in the visible region ( $\sim 15,000\text{ cm}^{-1}$ ) and is relatively strong ( $\epsilon \approx 102$ ) compared to the corresponding  ${}^3A_{2g} \rightarrow {}^3T_{1g}$  transition in octahedral complexes. Thus tetrahedral complexes are generally strongly colored and tend to be blue or green unless the ligands also have absorption bands in the visible region. Because the ground state  ${}^3T_1$  (F) has much inherent orbital angular momentum, the magnetic moments of truly tetrahedral Ni (II) should be about 4.2 B.M. at room temperature. However, even slight distortions reduce this value markedly (by splitting the orbital degeneracy). Thus fairly regular tetrahedral complexes have moments of 3.5 to 4.0 B.M.; for the more distorted ones the moments are 3.0 to 3.5 B.M. (i.e., in the same range as six coordinated complexes).

For the vast majority of four coordinated nickel (II) complexes, square planar geometry is preferred. This is a natural consequence of the  $d^8$  configuration, since the square planar ligand set causes one of the d orbital's ( $dx^2-y^2$ ) to be uniquely high in energy and the eight electrons can occupy the other four d orbital's but leave this strongly anti bonding one vacant. In tetrahedral coordination, on the other hand, occupation of anti bonding orbital's is unavoidable. Square Planar complexes of nickel (II) are thus invariably diamagnetic. They are frequently red, yellow or brown owing to the presence of the absorption band of medium intensity ( $\epsilon \approx 60$ ) in the range 450-600 nm, but other colors do occur when additional absorption bands are present. In square planar nickel (II) complexes, three spin allowed d-d bands corresponding to  ${}^1A_{1g} \rightarrow {}^1A_{2g}$ ,  ${}^1A_{1g} \rightarrow {}^1B_{1g}$ , and  ${}^1A_{1g} \rightarrow {}^1E_g$  transitions are expected.

Majority of the square planar nickel (II) complexes exhibit strong absorptions in 15000-25000 and 23000-30000 cm<sup>-1</sup> region.

Square planar nickel (II) complexes do not have any absorption band below 10000 cm<sup>-1</sup>, due to large crystal field splitting. Hence they can be clearly distinguished from octahedral and tetrahedral complexes.

### **The Chemistry of Cu(II) Complexes**

The familiar oxidation state of copper is +2 in which the copper ion has nine d-electrons, and most of the divalent compounds are four-coordinate. There are a number of quite stable, five-coordinate complexes of Cu<sup>2+</sup>, all involving ligands that are considered to be  $\pi$  acceptors. Copper(II) complexes are generally blue or green. The origin of the color is due to the maximum of four electronic transitions; d-d transitions; charge transfer transitions (both metal to ligand and ligand to metal), and internal ligand transitions. Such transitions occur between the ground state and the excited states of the crystal field levels. The d<sup>9</sup> ion is associated with large distortions; thus, electronic spectroscopy cannot be used on its own as a tool for identification of structure. There is a large number of copper(II) electronic spectra in the literature where the structure is known but the assignment is not certain. An example of this uncertainty can be found in the  ${}^2T_{2g} \rightarrow {}^2E_g$  transition for octahedral copper(II) complexes in which the  $t_{2g} \rightarrow e_g$  separations are from approximately 769 nm for CuO<sub>2</sub> to about 556 nm for CuN<sub>6</sub>. Several absorption bands may be expected in this region for a tetragonally distorted octahedral copper(II) complex. These bands correspond to transitions from sublevels (dxz, dyz and dxy) of  ${}^2T_{2g}$  to  $dx^2 - dy^2$  and  $dz^2$  of the  $E_g$ ; this is due to splitting of the  ${}^2E_g$  and  ${}^2T_{2g}$  ground terms of an octahedron as the result of Jahn-Teller distortion and in turn results in overlapping of bands and a more complex spectrum, with the appearance of a low energy shoulder. For a tetra coordinated copper(II) complex square planar geometry is more favored. The distortion of this system commonly leads to four transitions, namely from the ground state  ${}^2B_2$  to  ${}^2A_2$ , to  ${}^2A_2$ , to  ${}^2B_1$  and to  ${}^2A_1$ . Absorptions above 500 nm have been observed for distorted tetrahedral square planar [CuBr<sub>4</sub>]<sup>2-</sup> and [CuCl<sub>4</sub>]<sup>2-</sup> while the tetra-coordinated copper(II) ion with stronger field ligands such as imines will appear blue shifted. Copper(II) ion complexes are susceptible to ligand-solvent exchange or the possibility of more than one species in equilibrium, depending on coordination number involved established that copper(II) complexes with N-alkylsalicyladimines can occur in square planar or tetrahedral configuration, depending on the bulkiness of the alkyl group and the ring constituents. However, only a few examples of tetragonal distortion from square planar are known. In the case of tetra or penta-dentate Schiff base copper(II) complexes like 1,3-

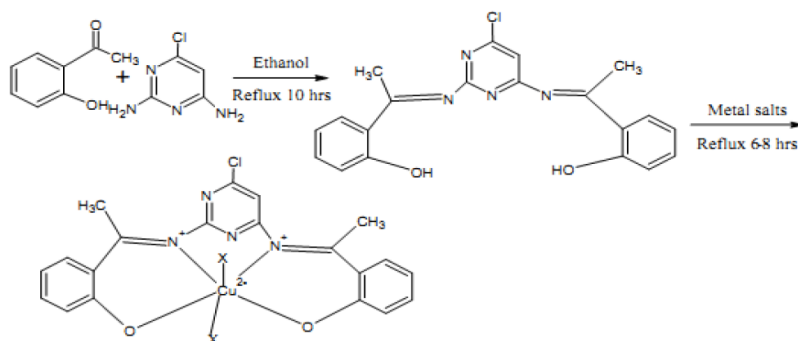
bis(salicylaldehyde)propan-2-olcopper(II), the co-ordination geometry of the copper is regular square planar significantly distorted toward tetrahedral with two oxygens and two nitrogens from salicylaldehyde moieties. The Cu(II) complex in DMF (dark green) gave an electronic spectrum with two absorption bands at 370 and 611 nm. The former band being as a result of  $\pi \rightarrow \pi^*$  (imine) and the latter band due to internal charge transfer or d-d transitions. To understand the preferential formation of square planar Cu(II) complexes of this kind, it is necessary to consider the crystal field splitting of the various geometries. The essence of this crystal field theory (CFT) is that the five d-orbitals, which are degenerate and equal in energy in the gaseous metal ion, become differentiated in the presence of the electrostatic field due to the ligands. Those orbitals lying in the direction of the ligands are raised in energy with respect to those lying away from the ligands. By preferentially filling the low-lying levels, the d-electrons can stabilize the system as compared to the case of random filling of the d-orbitals. The gain in bonding energy achieved in this way may be called the crystal field stabilization energy (CFSE). With the above mentioned in mind, the fact that  $\text{Cu}^{2+}$  has nine d-electrons, it is easy to see why square planar geometry would be favored, since it is possible to leave the  $dx^2-y^2$  orbital half-empty. For strong tetragonal (or square planar) geometry, ligand orbitals along the z-axis are absent; therefore, the energy of the d-orbitals along the z-axis drops to below  $d_{xy}$ , and  $dxz$  and  $dyz$  becomes doubly degenerate. In the case of weak tetragonal (or square pyramidal) geometry, imagine the ligand orbitals being pulled away along the z-axis such that those lying on the z-axis become lower in energy than those on the  $(x^2-y^2)$ -axis, and  $dxz$  and  $dyz$  are at lower energy than  $d_{xy}$ .

### **Schiff Base Transition Metal Complexes**

Schiff base complexes have attracted wide attention due to their important role in analytical chemistry, organic synthesis, metallurgy, refining of metals, electroplating and photography. Pfeiffer et al., (1931) have made a systematic study on Schiff base complexes. The nature of metal ion in addition to ligands determine the properties of the complexes. There is a continuing interest in the synthesis of Schiff base complexes of metal ions due to their preparative convenience and wide applications. The followings are some of the Schiff base transition metal complexes.

### **Tetra dentate Schiff base and its complexes of Cu(II) and Ni(II)**





Where Cu(II) can be substituted by Ni(II) and X = H<sub>2</sub>O

Scheme 4. Synthesis of tetra dentate ligand and Schiff base metal complexes

### A tri-dentate Schiff base and its complexes of Ni(II) and Zn(II)

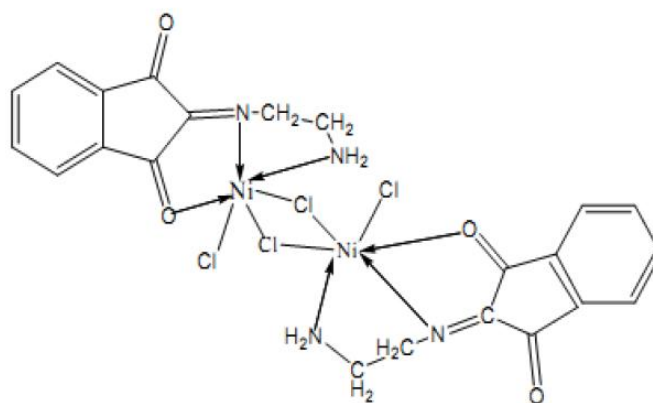


Figure 1. Proposed structure of the Ni complex

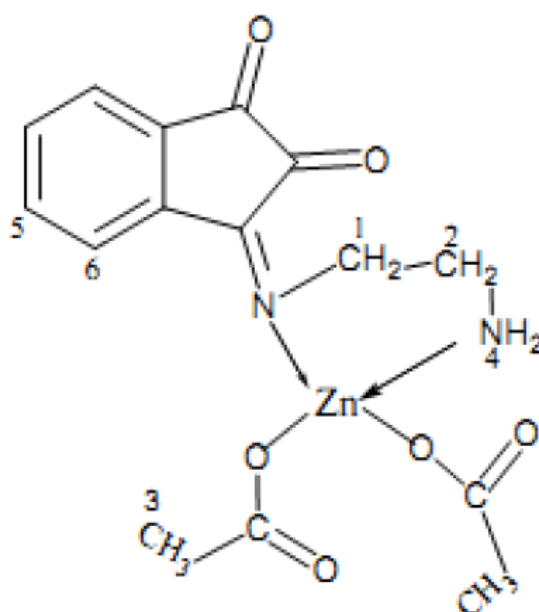


Figure 2. Proposed structure of Zn complex

### Application of metal complexes of Schiff bases



Metal complexes of schiff bases have large numbers of application some of important application are ase below:

- 1) Catalyst
- 2) Biological Activity as;
  - i) AntimicrobialActivity
  - ii) Antifungal Activity
  - iii) Antiviral Activity
  - iv) Synergistic Action on Insecticides
  - v) Plants Growth Regulators and much more,
- 3) In Dyes
- 4) Polymers

### **Conclusions**

The complexes of Cu(II) and Ni(II) were synthesized by direct reaction of the synthesized ligand with the respective metal salts both in 1:1 ratio. The synthesized ligand was characterized by IR, UV-Vis spectroscopic techniques and conductivity test and its complexes were characterized by AAS, IR UV-Vis techniques as well as from the results of their respective conductivity and magnetic susceptibility measurements. On the basis of the combined analytical results, distorted octahedral and square planar structures were proposed for the Cu(II) and Ni(II) complexes respectively

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