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A Review of Schiff-base ligands and metal complexes

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Abstract : Schiff-base ligands and corresponding metal complexes have received much attention in recent years due to their wide use as dyes and pigments, catalysts, intermediates in organic synthesis, polymer stabilizers and due to their broad range of biological activities, including anti-fungal, anti-bacterial, anti-malarial, anti-proliferative, anti-inflammatory, anti-viral, and anti-pyretic properties.

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Key Words : Schiff-base ligands, metal complexes

Introduction : Schiff bases are aldehyde or ketone like compounds in which the carbonyl group is replaced by an imine or azomethine group. It contains a carbon-nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group but not hydrogen.

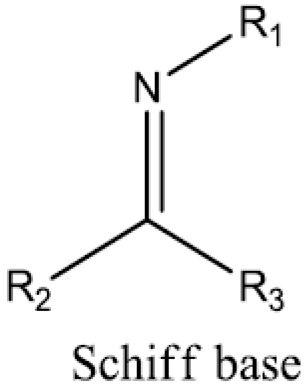


Figure 1.1: The structure of a Schiff base.

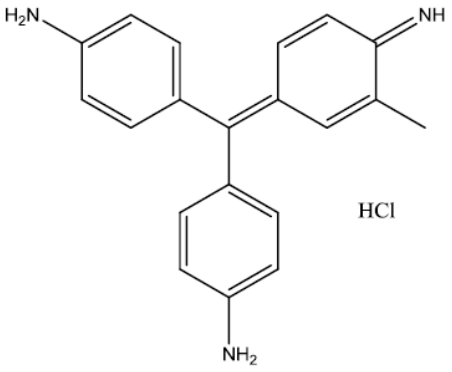
Schiff bases are of general formula R1N=CR2R3, where R1 is a phenyl or alkyl group which gives the Schiff base its stability.5 Although the formation of Schiff bases is reversible, due to the hydrolysis of the imine under certain conditions, it is still straight forward for the reaction to succeed. It is still unknown what type of Schiff base is stable in the presence of water even with acidic solution, while others are very sensitive to water and easily hydrolyse back to aldehyde. To overcome this potential hydrolysis, the reaction of Schiff bases should be undertaken under dry solvent conditions or using some additional procedure to remove the side product, water, in the imine formation.

The lone pair on the nitrogen atom of the imine part can supply electrons which enable the formation of a proper donor bond to a metal ion for complexation to occur. Many Schiff bases have a second functional group, normally OH and SH groups or another N atom, which are near to imine group. These functional groups can allow the formation of five or six member chelate rings when coordinated with different metal ions. The work described in this thesis concentrates on synthesising some novel Schiff-base ligands with several functional groups, such as phenol OH and

N from pyridine ring ligands and to generate their corresponding Zn(II), Hg(II), Cu(II), Ni(II) and Co(II) metal complexes.

History of Schiff-bases

Schiff bases are named after Hugo (Ugo) Schiff (1834-1915), a German chemist. He discovered Schiff bases in 18646 and other imines, and was responsible for research into aldehydes and had the Schiff test named after him. Fuchsine was studied by Schiff as a Schiff reagent in 1866, which was apparently widely used during the last decades of the 19th century for industrial dyes.



Fuchsine

Figure : Structure of Fuchsine.

A well-known Schiff base ligand is a salen-type7 (shown in Figure 1.3) with a bi-functional and tetradentate(ONNO) ligand. Several asymmetric salen type Schiff bases were reported by R.

Atkins8 in 1985, who suggested a more general term salen-type of tetradentate (ONNO) ligands. The 2-hydroxybenzaldehyde is a suitable building block due to the substitution pattern hydroxyl group of the ring. Once the imine bond is formed from primary amine and aldehyde, this orientation of salen-type Schiff bases will form a more stable six member ring when binding to metal ion.

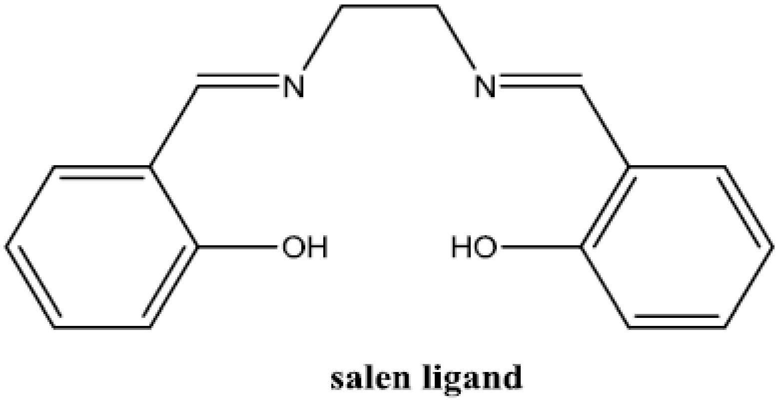


Figure : Typical structure of salen-type ligand.

Synthesis of Schiff-base ligands

A Schiff base reaction is a reversible, acid-catalysed condensation between a primary amine (not ammonia) and either an aldehyde or ketone. A Schiff base is the nitrogen analogue of an aldehyde or ketone, where the carbonyl group is replaced by an imine group (C=N-R), which is shown in Figure 1.4 where R may be an alkyl or an aryl group.

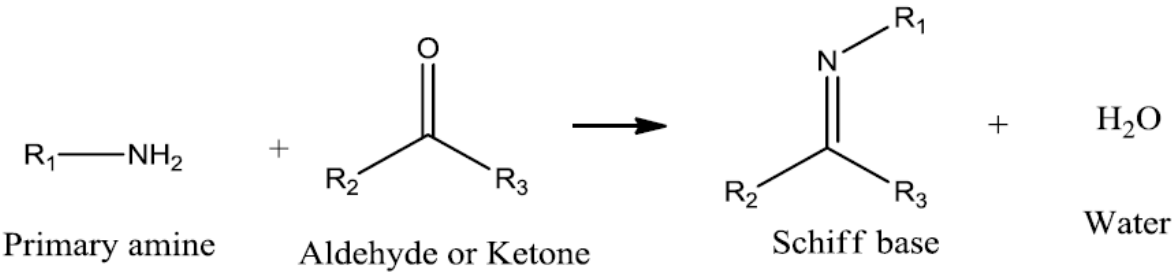


Figure 1.4: Preparation of Schiff Base.

Schiff bases which contain aryl substituents are more stable and more easily synthesized than those that contain alkyl substituents. This means that Schiff bases of aliphatic aldehydes are relatively unstable and they readily undergo polymerisation in comparison to products from conjugation of aromatic aldehydes.

Typically, the formation of Schiff bases from aldehydes or ketones requires a protic solvent which is sufficiently dry in order to prevent potential hydrolysis of the newly formed imine bond. The formation is generally undertaken under acid or base catalysis, or upon heating. The completion of imine formation is controlled by the separation of the product or removal of water, or both.

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