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1.1. Introduction

Schiff base ligands are considered ‘‘privileged ligands’’[1] because they are easily prepared by the condensation between aldehydes and amines. Stereogenic centres or other elements of chirality (planes, axes) can be introduced in the synthetic design. Schiff base ligands are able to coordinate many different metals, and to stabilize them in various oxidation states, enabling the use of Schiff base metal complexes for a large variety of useful catalytic transformations.

Since the seminal works by Ettling, Schiff and Pfeiffer [2], metal Schiff base complexes have continued to play the role of one of the most important stereochemical models in main group and transition metal coordination chemistry due to their preparative, accessiblility, diversity, and structural variability.

1.2. Definition of 'Schiff base'

This is one of the most prevalent and important of the mixed donor systems in coordination chemistry. Schiff bases are condensation products of primary amines with carbonyl compounds and they were first reported by Schiff [3] in 1864. The common structural feature of these compounds is the azomethine group with a general formula RHC=N-R′, where R and R′ are alkyl, aryl, cyclo alkyl or heterocyclic groups which may be variously substituted. These compounds are also knows as anils, imines or azomethines. Several studies showed that the presence of a lone pair of electrons in an sp^2 hybridised orbital of nitrogen atom of the azomethine group is of considerable chemical and biological importance. Because of the relative easiness of preparation, synthetic flexibility, and the special property of C=N group, Schiff bases are generally 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 ring with the metal ion. Versatility of Schiff base ligands and biological, analytical and industrial applications of their complexes make further investigations in this area highly desirable [4].

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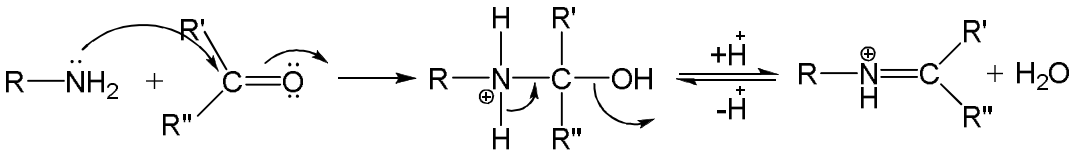
1.3. Formation of Schiff base compounds

Actually another name for an imine functional group, in biochemistry a Schiff base is formed from the condensation of an amine group with the carbonyl group of an aldehyde or ketone, as shown in the Scheme 1-1.



A

Scheme 1-1

Where R may be an alkyl or an aryl group. Schiff bases that contain aryl substituents are substantially more stable and more readily synthesized, while those which contain alkyl substituents are relatively unstable. Schiff base aliphatic aldehydes are relatively unstable and readily polymerizable, while those of aromatic aldehydes having effective conjugation are more stable [5].

The reaction is acid-catalyzed and is generally carried out by refluxing the carbonyl compound and amine, with an azeotroping agent if necessary, and separating the water as formed. In the reaction, initially, a carbinolamine (A), an unstable intermediate, was formed which rapidly eliminates water to give the Schiff base compound.

Aliphatic ketones react with amines more slowly than aldehydes to form Schiff base. This requires higher reaction temperatures and longer reaction times than required for the aldehydes. Acidic catalysts are helpful and water should be removed definitely from the reaction mixture. Fairly high yields of imines can be obtained in this way.

Although a number of Schiff bases have primarily nitrogen donor atoms, many can display bi-, tri-, tetra-, or polydentate mixed donor capabilities. In general, the donor nature of the ligands depends on both the type of aldehyde or ketone used and the nature of primary amine or diamine. Figs. 1-1 and 1-2 demonstrate Schiff bases having different donor sets.

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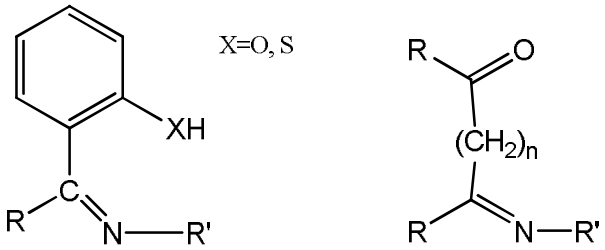

Fig. 1-1: Two bidentate Schiff bases with [NO] and [NS] donor sets

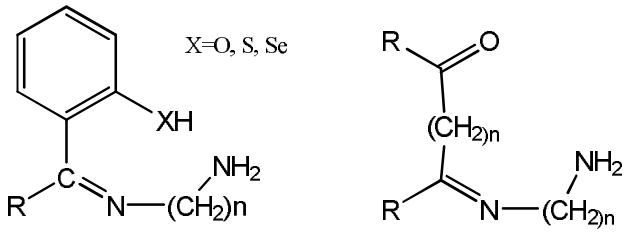

Fig. 1-2: Two tridentate Schiff bases with [N_2O], [N_2S]and [N_2Se] donor sets

The reaction between two moles carbonyl containing compounds and one mole of diamine lead to more complicated Schiff bases with higher denticity, as show in Fig. 1-3.

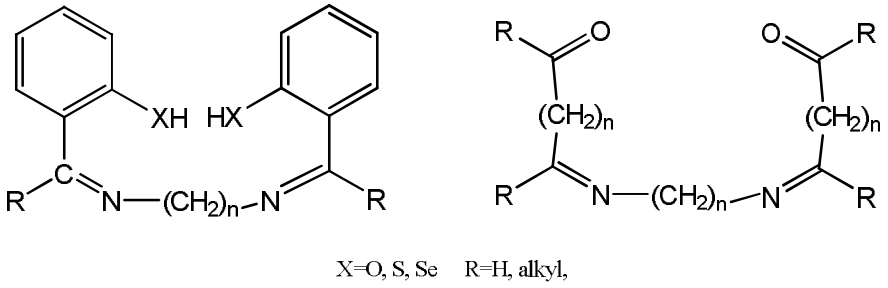

Fig. 1-3: Two tetradentate Schiff bases with [N_2O_2] and [N_2X_2] donor sets

Pentadentate ligands also give coordination compounds with different geometric isomers, depending on the flexibility of the overall ligand geometry. Pentadentate ligands are probably the least studied of the higher multidentate chelating agents.

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The known structural types, include (1) linear open chain, (2) branched chain where the bifurcation occurs at the donor atom, (3) a tetradentate macrocyclic ligand which is attached to a side chain containing a fifth donor atom, (4) a macrocyclic [5] ligand in which all five potential donors are in the ring, and (5) a "basket-like" macrocyclic ligand [6] Fig. 1-4 demonstrate pentadentate Schiff bases.

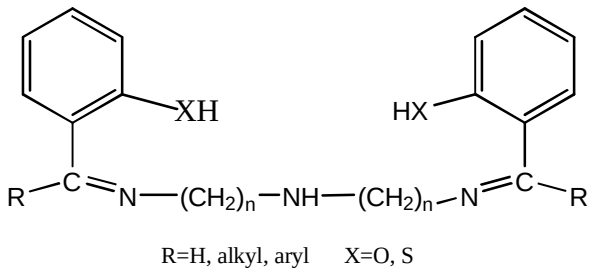

Fig. 1-4: pentdentate Schiff base with $[N_3O_2]$donor sets

1.4. Macrocyclic Schiff bases

Macracyclic ligands are defined as cyclic molecules generally consisting of organic frames into which heteroatoms, capable of binding to substrates (as opposed to the naturally occurring species such as porphyrins, corrins, and chlorins) appeared as early as 1936, when the first synthesis of 1,4,8,11-tetraazacyclotetradecane was reported [7].

The Schiff bases condensation of 2,6-diacetylpyridine with 1,2-diaminobenzene was first studied by Stotz and Stoufer [8], who reported the formation of macrocyclic ligands shown in Fig. 1-5**.**

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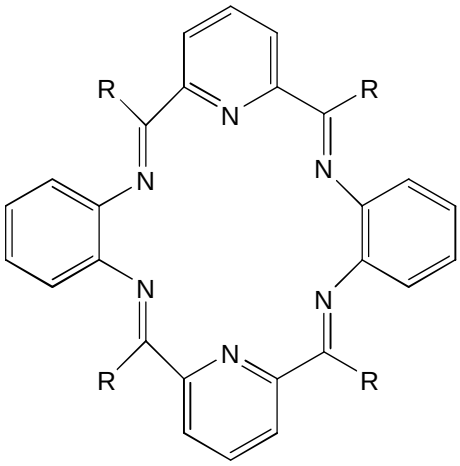

R=H
R=CH3

Fig. 1-5

Temel has been reported the synthesis of Schiff base macrocycles Fig. 1-6 and their complexes with Cu (II), Ni (II), Pb(II), Co(II) and La (III) ions [8].

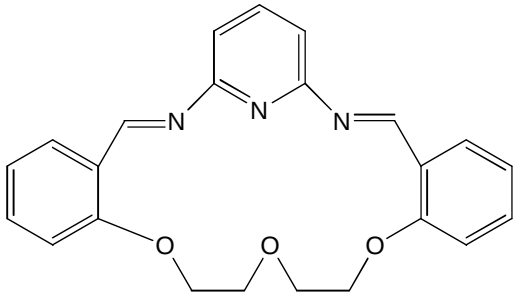

Fig. 1-6

1. 5. Synthesis of Schiff base complexes

The usual methods for preparation of metal chelate complexes include:

(a) direct interaction of the Schiff base with the metal salts.

(b) template condensation of aldehydes (ketones), primary amines and metal salts.

(c) reaction of aldehydato metal complexes with amines.

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1. 6. Schiff base complexes of transition metals

Metal Schiff base complexes, Fig. 1-7 have been known since the mid-nineteeth century, and even before the general preparation of Schiff base ligands themselves [9]. Metal complexes of Sciff bases have occupied a central place in the development of coordination chemistry.

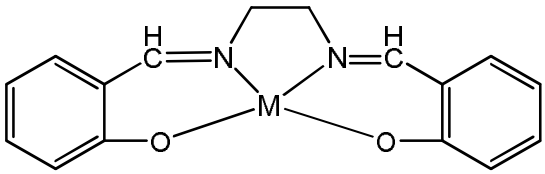

Fig. 1-7

However, there was no comprehensive, systematic study until the preparative work of Pfeiffer and associates [10]. Pfeiffer and his workers [10] reported a series of complexes derived from Schiff bases of salicylaldehyde and its substitution. Of all the Schiff base complexes, those derived from salicylaldimines have been thoroughly studied so far. A variety of physicochemical investigations on these complexes provide a clear understanding of their stereochemical and electronic properties. The advantage of the salicylaldimines ligand systems is the considerable flexibility of the synthetic procedures, which have resulted in the preparations of a wide variety of complexes with a given metal whose properties are often dependent on the ligand structure. A considerable number of compounds containing salicylaldiminato ligands have been examined. Ever these investigations are mostly devoted to first row transition metal complexes [11].

This work still serves as a source of chemical and preparative detail for the contemporary chemist and its importance may be gauged by the relatively large

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number of citations of these reports in the modern literature. Since Pfeiffers initial contributions, the interest in Schiff base complexes has increased significantly [12].

The electronic absorption spectra of salicylaldimine transition metal complexes have been the subject of a number of investigations which have been mainly concerned with the assignment of the d-d absorption bands [13].

Single crystal spectral techniques have found wide use in recent times to help elucidate problems relating to the electronic structure of transition metal ions. As a rule, however, these techniques have been confined to compounds in which the coordination around the central ion is four or six.

The chemistry of Schiff base complexes has developed rapidly in the 40 years solving problems related to stereochemistry and fertilizing related fields in coordination chemistry. Stereochemistry and electronic factors largely govern the reactivity and stability of chelate compounds. The stereochemistry and electronic structure of chelates determined many properties, such as their redox properties and reactivity ability to form adducts. These properties are important for understanding many catalytic processes and phenomena occurring in living organisms.

During the last decade, intensive studies have been carried out on the biochemical, pharmacological and physicochemical functions of the molybdenum. In particular, many kinds of dioxomolybdenum (VI) compounds have been synthesized as models of molybdoenzymes in order to study and elucidate catalytic oxygen atom transfer reactions [14].

Schiff bases have been widely used as ligands in the dioxomolybdenum chemistry. Tridentate Schiff base ligands, such as H_2sal-OHYBA (*o*-$HOC_6H_4CH=NC_6H_4OH$), N-2-hydroxy-1-naphthyliden-(2-mercaptoaniline)or
$ClC_6H_3(OH)CH=NC(Me)(CH_2OH)_2$, react with $MoO_2(acac)_2$, yielding $MoO_2L(solv)$ type complexes [15].

Ligands containing the Schiff base semi-carbazide (-C=N-N=C-) group have been prepared and used in the molybdenum dioxide coordination chemistry. Bidentate ligands such as $dpcH_2$ ($dpcH_2$ = $C_6H_5(H)NNC(O)(H)NNC_6H_5$) or $dptcH_2$ ($dptcH_2$ =

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$C_6H_5(H)NNC(S)(H)NNC_6H_5$), reacted with $MoO_2(acac)_2$ affording MoO_2LL' complexes (L=dpc(-1), dptc(-2); L´ = dpcH (-1), dptcH (-1)) [16].

Recently Ghosh et al. [17] reported a five-coordinate complex $[MoO_2L]$, where H_2L is the ONO donor ligand 2-hydroxyacetophenone hydrazone of 2-aminobenzoyl hydrazine which is quite interesting with respect to coordination chemistry. Fig. 1-8 Because penta-coordinated Mo(VI) complexes, in general, are rare and those with an ONO donor environment are rarer still. The vacant position is found to act as a substrate-binding site, and six-coordinate adducts, like $[MoO_2L(Py)]$ and $[MoO_2L(Im)]$, are easily formed by the attachment of pyridine or imidazole to this position. MoO_2L is found to mimic the active center of oxo transfer molybdoenzymes and hence is of interest in bioinorganic chemistry.

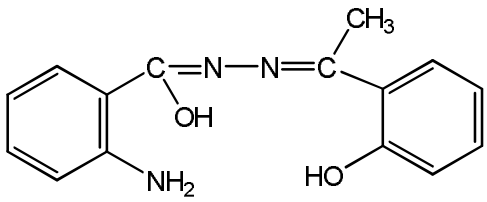

Fig: 1-8

Schiff bases derived from salicylaldehyde and aminoalcohols bearing both alcoholic and phenolic hydroxyl groups and also one neutral nitrogen donor (CH=N imino group) can be used as multidentate ligands in dioxomolybdenum chemistry [18].

1. 7. The importance and application of Schiff base complexes

A large number of Schiff base compounds are often used as ligands in coordination chemistry for their metal binding ability. Schiff base-metal complexes are characterized by interesting and important properties, such as their ability to reversibly binding oxygen in epoxidation reaction, biological activity, complexing ability towards some toxic metals, catalytic activites in hydroxylation, hydrogenation of olefins, polymerization reaction, ring opening reaction [19-25].

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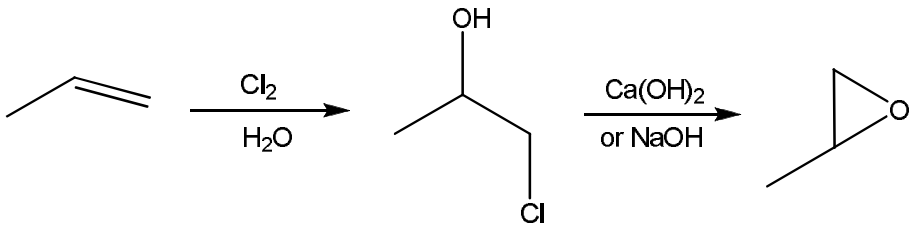
1. 7. 1. Catalytic oxidation

The Schiff base complexes of transition metal ions shown high catalytic activities in various chemical reactions such as oxidation of olefins, alcohols and sulfides [25].

1.7. 1. 1. Catalytic epoxidation of olefins

Epoxides, particularly ethylene and propene oxides, are key raw material for a wide variety of chemicals (such as glycols, glycol ethers and alkanolamines) and they can also be used as building blocks for polymers (polyesters and polyurethanes).

The simplest epoxide, ethylene epoxides, is produced commercially by vapor-phase oxidation of ethylene with air or oxygen over a silver catalyst, promoted by alkali metals and supported on a non-porous form of α-alumina. This process was introduced by Union Carbide in 1937 and by Shell in 1958 to replace the practice of ethylene oxide production via the chlorohydrin process. However, this silver catalyzed process can only be applied to olefins which do not possess C-H allylic bonds, such as ethylene, 1,3-butadiene and styrene. For all the other olefins, such as propene, low yields of the desired product are obtained, due to the competing oxidation of allylic C-H bonds, which leads to numerous by-products. Propene oxide producers have traditionally employed the chlorohydrin route which comprises reacting propylene with hypochlorous acid to form propylene chlorohydrin and the dehydrochlorination of the propylene chlorohydrin to form propylenen oxide (Scheme 1-2) [26]. But these processes are currently being subjected to increasing environmental pressure, due to the use of expensive, toxic and corrosive chlorine as reagent and highly toxic by-products.



Scheme 1-2: The chlorohydrin route formation

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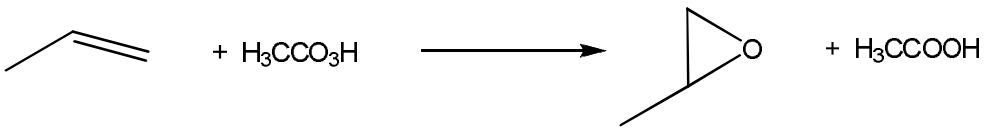
In light of the complexity and cost of the chlorohydrin route, the peracid route was developed [26]. This route involves the formation of a peracid, such as peracetic acid, through the reaction of hydrogen peroxide with the organic acid and the epoxidation of an olefin with the peracid (Scheme 1-3). The disadvantages of the peracid route, however, are sufficient to preclude significant commercialization. The reagents are expensive, corrosive and nonregenerable, and the overall efficiency of the process is low.



Scheme 1-3: The peracid route formation

Subsequent attempts to develop olefin epoxidation systems included the use of hydrogen peroxide alone or in the presence of osmium tetraoxide, manganese dioxide, tungsten and molybdenum oxides. However, none of the systems was considered commercially feasible. Hawkins was the first to report a metal-catalysed epoxidation with an alkyl hydroperoxide in the synthesis of cyclohexene oxide in 30 % yield using cumene hydroperoxide in combination with V_2O_5. Subsequently, Brill described the use of *tert*-butyl hydroperoxide (TBHP) in the precence of catalytic amounts of hydrocarbon soluble acetyl acetonates of molybdenum, vanadium and chromium [27].

The most important industrial epoxidation processes, based on high valent transition metal catalysts in combination with alkyl hydroperoxides as the oxygen source, are the SHELL and the ARCO/HALCON processes for propene oxide synthesis [28]. HALCON [29] and Atlantic Richfield (ARCO) [30] independently developed processes for the production of epoxides using an alkyl hydroperoxide in the presence of homogeneous catalysts based on molybdenum, tungsten, titanium, columbium, tantalum, rhenium, selenium, chromium, zirconium, tellurium, uranium and vanadium. From the all the referred metals, molybdenum, tungsten and titanium are considered better options. The inventors suggested utilization of the molybdenum

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