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A Study of Application, Structure and Properties of some Schiff Base Metal Complexes

Syed Misbahuddin Quadri[1]*, Prof. (Dr) Menka Surana[2]

[1] Research Scholar, Department of Chemistry, Mewar University, Chittorgarh Rajasthan, India

[2] Department of Chemistry, Mewar University, Chittorgarh Rajasthan, India

Abstract - A variety of amino acids and aldehydes or ketones are employed in a condensation process to produce schiff bases, which are useful chemical molecules. These ligands are regarded as favored since they may be easily produced via condensation. As an O2 detector, they have a variety of applications in the fields of medicine and pharmacology; coordination chemistry; biological activities; food packaging; dyes; and polymer. Imine derivative semicarbazone is formed via the condensation of semicarbazide and a suitable ketone or aldehyde with the imine group. Transition metal complexes including copper, zinc, and cadmium are good precursors for the production of metal or metal chalcogenide nanoparticles because they contain Imine ligands. Due to multiple applications in pharmacology such as antiviral, antifungal, antibacterial, antimalarial, antituberculosis, cancer-fighting, anti-HIV, catalytic oxidation of organic molecules and nanotechnology, researchers have focused a great deal of their attention on Schiff bases in recent years. In this paper review the application, structure and properties of some schiff base metal complexes.

Keywords - schiff base, metal complexes, structure, application

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1. INTRODUCTION

An aldehyde or ketone may be used to create Schiff bases under particular circumstances. The carbonyl group in imine or azomethine is a nitrogen equivalent of an aldehyde or ketone (CO) has been substituted by an imine or azomethine group in the Schiff base's structure.[1]

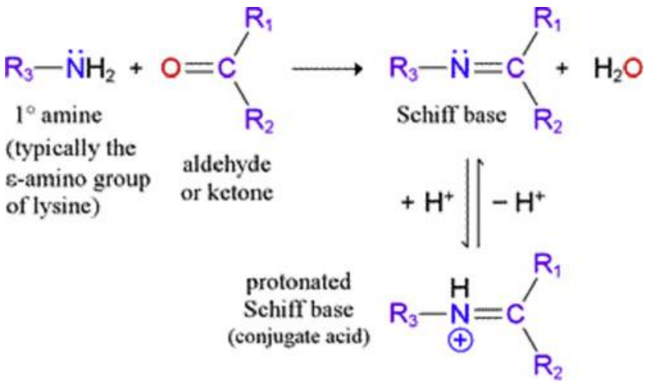

Figure 1: General scheme for formation of Schiff bases.

A variety of metal ions form complexes with the Schiff base ligands, which may be readily produced. As a catalyst in numerous reactions, including polymerization and the reduction of thionyl chloride, thionyl chloride reduction has been widely reported in the past few years. Among these reactions are polymerization, the reduction of thionyl chloride, the oxidation of organic compounds and the reduction reaction of ketones, aldol, Henry and hydrosilylation of ketones.

Biological importance of Schiff base complexes

Recently, there has been an upsurge of interest in Schiff base complexes because to the growing recognition among bioinorganic scientists that many of these complexes might serve as models for physiologically significant species.[2] As a result, we provide them as follows:

- Anti-bacterial activity of Schiff base complexes
- Anti-fungal activity of Schiff base complexes
- Anti-cancer activity of Schiff base complexes
- Antioxidant activity of Schiff bases
- Anti-inflammatory activity of Schiff bases
- Antiviral activity of Schiff bases

2. APPLICATION OF SOME SCHIFF BASE METAL COMPLEXES

Catalysts for a wide range of organic and inorganic reactions might be found in schiff bases. As an example, Li et al. reported asymmetrically synthesized (S)-2-amino-1,1-di(3,5-dit-butylphenyl)propane by employing Cu (II) complexes with Schiff base Schiff base of chiral amino alcohols such (S)-1,1-di(3,5-t-butylphenyl)propanol and substituted salicylaldehyde as catalysts. These chiral amino alcohol Cu (II) complexes have been shown to be efficient in the asymmetric cyclopropanation of styrene, according to the research. Catalytic activity for the amination of Iodobenzene has been reported for several of the Cu (I) complexes with mixed ligands, including the Schiff base [2-methoxy ((5-trifluoromethylphenyl)-pyridine-2yl-methylene-amine) and PPh3/dppe].[3]

A series of Cu (I) complexes containing N-(2-pyridylmethylene)-1,5-dimethyl-2-pyrazole-3-(2H)-one and triphenylphosphine have been developed and tested as an effective catalyst for the Sonogashira cross-coupling process of aryl-halide synthesis using phenylacetylene (Scheme 29). The DNA-binding and DNA-cleaving capabilities of these Cu (II) Schiff base complexes, as well as their mimicry of galactose oxidase, have all been studied extensively.

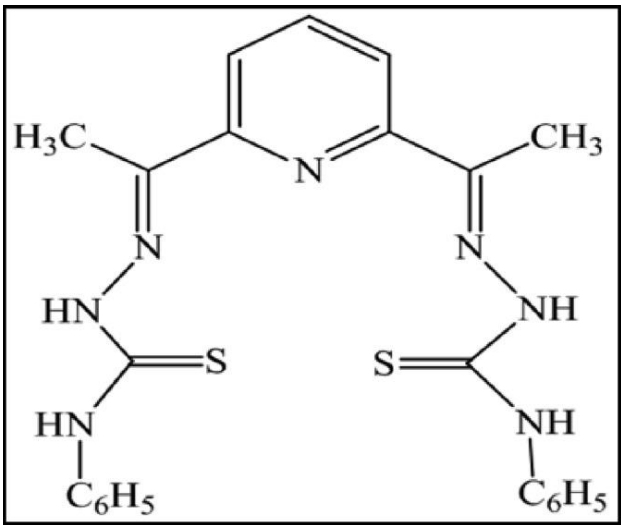

Figure 2: Structure of 2,6-diacetylpyridine bis-4-phenyl-3-thiosemicarbazone

Conductive polymers may be synthesized using imide derivatives. Tridentate Schiff bases and their organo-cobalt complexes are used as initiators and co-polymerizers for the polymerization of dienyl and vinyl monomers in emulsions. ethylenediamine is used in the photochemical decomposition of natural rubber in order to produce the amine-terminated liquid natural rubber (ATNR). A metal deactivator produced from the interaction of ATNR with glyoxal, poly Schiff base, enhances age resistance. The petroleum refining industry uses transition metal complexes containing 1, 10-phenanthroline and 2, 2-bipyridine. It was found that pyridoxal, which has a similar effect on sperm head separation, demonstrates that the sperm head and tail are linked by a Schiff base that is produced between proteins in the nuclear membrane of the sperm. Pregnancy problems, nephritis hepatitis, leprosy, hepatitis in children, anemia and copper levels in blood and urine have been linked to copper's beneficial effects on liver function. Using Schiff base, N-salicylaldehyde amino glucose as a catalyst, Cu (II) and Zn (II) complexes significantly reduce O2 biosynthesis.[4]

The oxygen transport in human and other respiratory systems, as well as photosynthesis, rely on macrocyclic Schiff bases of dithiocarbazic acid. In combination with amido Schiff bases, copper and iron produce chelates that function as thrombin inhibitors. Amylase production is affected by a variety of effects on the membrane caused by transition metal complexes with tetradentate Schiff base ligands. Zinc and Mn compounds increased amylase transport across the membrane, but Ni and Cu complexes decreased it.

3. STRUCTURE SOME SCHIFF BASE METAL COMPLEXES

Iminol tautomeric hydrazides are an example of Schiff bases. Hydrazides are monosubstituted hydrazine derivatives with a carbonyl or sulfonyl group attached directly to one of the nitrogen atoms that preserve their characteristic -NH-NH- nitrogen bridge. The hydrazide moiety that is unique to the terminal hydrazide is as follows: R-NH-NH2.[5]

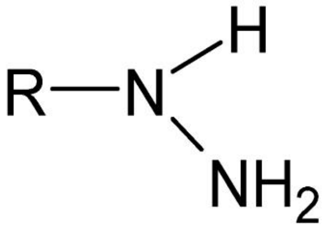

Figure 3: A moiety characteristic of hydrazides, where R is -C(=O)- or -(O=)S(=O)-.

Because of their similarity to (O=)C-NH-, one may conceive of hydrozides as possible peptidomimetics because of the hydrazide moiety's (O=)C-NH- structure. Additionally, due to their close proximity to oxygen and nitrogen atoms that are each endowed with one lone electron pair, the carbonyl and hydrogen atoms that are connected to nitrogen can form torsion angles with each other, allowing for double bond migration, which results in formation of the hydroxyl group by the carbonyl oxygen atoms themselves.[6]

Peptides and hydrazides have the same amide bond tautomerism as peptides.

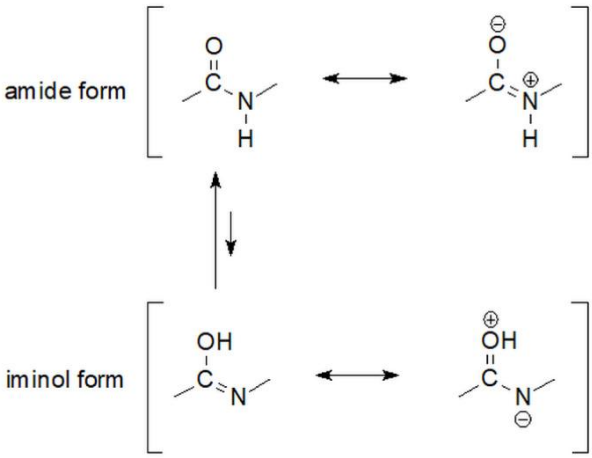

Figure 5: Amino acid-imino acid equilibrium of carbonyl hydrazides is studied

There are iminol forms of hydrazides that occur in the form of E or Z isomers due to the strong rotation barrier around the C=N link. This is comparable to the presence of amide isomers. In addition to the previously noted existence of a directly bonded, following N atom, the distinguishing characteristic of hydrazides sets them apart from amides. Hydrazides' thermodynamic stability is influenced by various variables, including the quantity and steric expansion of the n-atoms in their nucleus, which precludes a universal isomer of the hydrazide from being readily identified Hyper-couplings in hydrazide molecules are more frequent because the N atom supplies an additional electron pair to the existing electron density. On a basic infrared spectrum, at least monosubstituted hydrazides are clearly recognizable from their amide analogs with a CH - group in lieu of the N atom a shift of around 100–150 cm1 toward shorter waves compared to their N-atom amide analogs. [7]

A significant signal in the 2800–2700 cm1 range is produced by the Bohlmann bands, which are named after their discoverer, when a ring member (sp2) or an sp3 carbon atom is present. As a first application, the quinolizidine system, found in the Egyptian waterlily, known as the tiger lotus, as well as the Scotch broom (Fabaceae: Cytisus) and Andean lupin (such as lupinine or sparteine and their oxo-derived derivatives) was used to comprehend the stereochemistry of alkaloid. The core of the Bohlmann effect may be shown using the well-known anomeric phenomenon. Because of this, the electronegative substituent attached to the heteroatom (most often oxygen) is preferred to have an axial orientation, even though this orientation would be less of an issue in terms of spatial considerations had only steric considerations been taken into account, as is the case when using the classic approach. [8]

In the generalized Bohlmann effect, lone electron pairs of an oxygen atom or a nitrogen atom can be transferred to an anti-bonding CH * or CC * orbital, oriented antiperiplanarly towards the orbital on which the lone electron pair is located. The Bohlmann effect is the name given to this electron density transfer. While the Bohlmann effect may be seen in ethers and alcohols, it is more apparent in amines because nitrogen has a lower electronegativity than oxygen (E = 3.04 vs 3.44). There are more electron pairs in oxygen than there are in nitrogen, hence it is simpler to relocate the lone electron pairs of oxygen than to move the lone electron pairs of nitrogen. This shifts the infrared spectrum to a greater extent. The ability of atoms in a given element to attract electrons is known as electronegativity. Absorption in ethers and alcohols is obscured because oxygen (E = 3.98) and fluorine (E = 3.98) have stronger electronegativity. This one is more potent and has a greater influence than nitrogen, unlike the Bohlmann effect. Alcohols have antiperiplanarity toward their acceptor orbitals because of an O-H bond instead of a single oxygen pair.

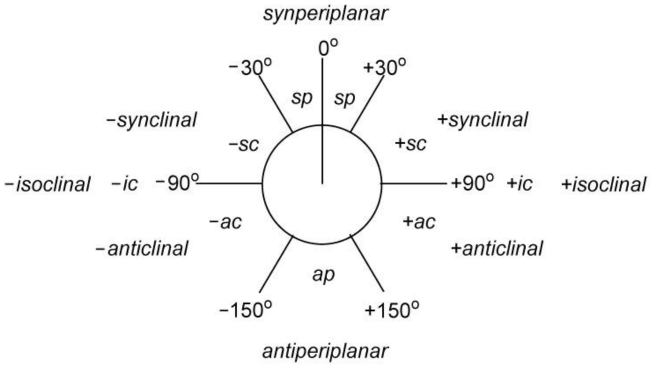

Figure 4: Nomenclature in Newman's projection depending on the value of the torsion angle.

The least energy conformation in at least a monosubstituted amino group indicates the axial arrangement of both the lone electron pair of the nitrogen atom and at least one C-H or C-C bond if we consider the most energetically stable conformers: antiperiplanar and gauche. For example, a disubstituted amino group that has two C-H or C-C bonds arranged axially boosts the strength of Bohlmann bands, and occasionally causes an extra signal to develop and push the original signal toward lower frequency waves. An extra substituent or the production of an ammonium salt in the IR spectrum results in the elimination of Bohlmann bands, demonstrating the role of the nitrogen atom's lone electron pair in the Bohlmann effect. No C-H stretching vibrations (not attenuated as in the axial position of substituent bonds) can be detected in the Bohlmann bands area for gauche conformation.

E/Z descriptors of the CN/C=N bond must be included to the discussion of hydrazide isomerism. This equilibrium between the two isomeric forms is usually maintained by three overarching factors: substituent size, lone pair electrostatic repulsion on oxygen and nitrogen, and macromolecular hydrogen bonding. Hydrazides often live in an equilibrium between these two isomeric forms. For Z isomers, the chemical shift of the carbonyl signal is not more than 170 ppm, but for E isomers, it rises to roughly 175 ppm on the 13C NMR spectrum. This makes it easy to distinguish between the two isomers. There are several ways to compute the proportion of isomers in a 1H NMR spectrum, but a simple one is to use the signal integrity of NHZ and NHE groups.

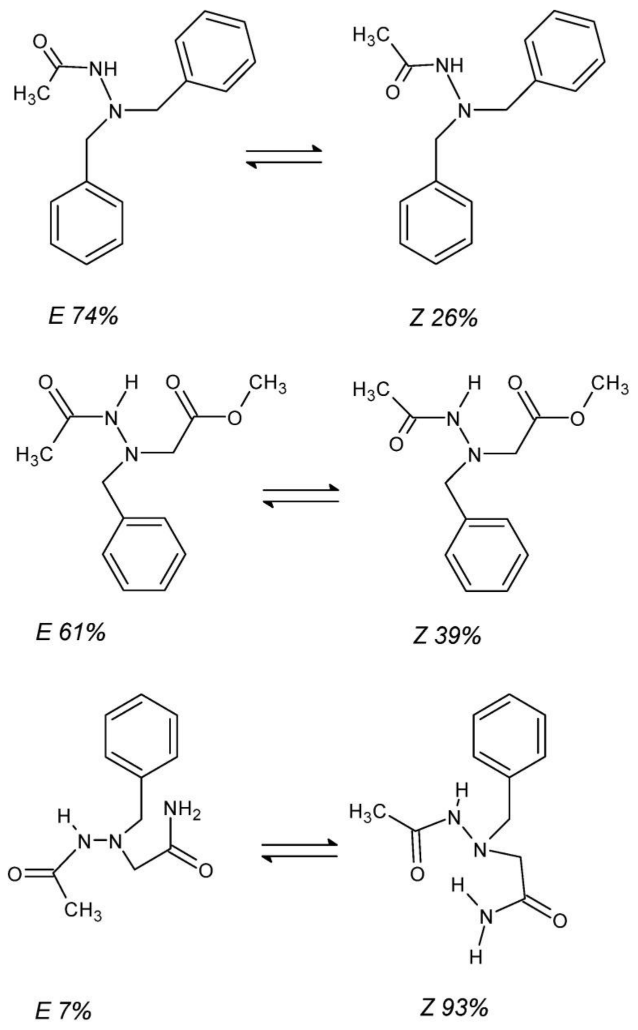

Figure 7: Examples of the isomeric equilibrium of the hydrazides Z and E, respectively. When the folding of the molecule permits the creation of several hydrogen bonds, the Z isomer predominates.

This nitrogen atom's lone electron pair confers Lewis base character to the primary amine group, allowing for intramolecular or intermolecular hydrogen bond formation, as well as hydrogen bond formation with competing solvent molecules. Additionally, the iminol form promotes intramolecular hydrogen bond generation, especially in the presence of appropriately nonpolar solvents.

4. PROPERTIES OF SCHIFF BASE COMPLEXES

Schiff base complexes may be created in a variety of ways:

i) Primary amine reactions with bis- or tris-(carbonyl) compounds in ethanol or chloroform are examples of this. After Schiff's discussion of this strategy, many others have followed suit.
ii) Alkaline acetate is added to alcoholic or aqueous alcoholic media to make the metal complexes of N-aryl-salicylaldimines and, 8-ketoiniines, which are formed by the interaction of the metal ions and Schiff base ligands.
iii) It is possible to synthesize complexes of fl-ketoimines with cobalt, nickel, copper, and zinc by reacting Schiff base ligand with metal hydroxide solution in acetone medium.

Polymers

Natural rubber undergoes photochemical breakdown, producing amine-terminated liquid natural rubber when it is in solution with ethylenediammine (ATNR). ploy Schiff base, an anti-aging chemical, is made when glyoxal and ATNR react together in the presence of ATNR. An initiator for the copolymerization of dienyl and vinyl monomers in emulsions is an organocobalt complex containing a tridentate Schiff base. [9]

Antifertility and Enzymatic Activity

Pregnancy may be affected by Schiff bases of hydrazine carboxamide, hydrazine and hydrazine and metal complexes of dioxo Mo (IV), and Mn (II). In proteins, lysine to alanine or histidine Schiff base linkage with pyridoxal 5'phosphate abolishes enzyme activity.

Dyes

Schiff bases of cobalt complexes, chromium azomethine complexes, and unsymmetrical complex 2:1 Chromium dyes offer fast colors to leather, food packaging, wool, and other materials.. etc. Textiles made of cellulose ployester may be dyed using azo groups containing metal complexes. To mass dye polyfibers, certain metal complexes are used. It has good light and storage resistance and does not deteriorate even in acidic gases, such as sulfuric acid (CO2). For the measurement of Ni in certain natural food samples, researchers used a novel chromogenic reagent, the tetra dentate Schiff base.

Synergistic Action on Insecticides

Isothiophene-2-aldehydes, thiophene-2-aldehydes, and related compounds have been shown to be poisonous to insects. Pheromone insecticides may be synthesized using aminoacids as an intermediary step. An increase in insectoacracicidal action is obtained by flourinating Schiff base's aldehyde portion. Metal complexes of thiadiazoles with salicylaldehyde or o-vanillin have insecticidal properties against bollworms and increase the survival rate of mung bean sprouts in the presence of Mo (IV).[10]

5. CONCLUSION

As far as Schiff bases go, they've been around for quite some time, but their primary use has been in medicinal chemistry and catalysis. Synthetic methods that rely on both conventional chemical reactions as well as solid-state reactions have emerged in recent years, expanding the spectrum of these molecules. In addition, there are instances of the utilization of additional sources of energy during the synthesis. The contemporary day use of materials chemistry and nanotechnology has also been highlighted in recent publications. The overwhelming majority of transition metals can be coordinated by Schiff bases and semicarbazones, making them excellent precursors for next generation nanomaterials based on the metal or its compound semiconductor. Thus, the use of ligands such as Schiff base, semicarbazones and their derivatives for catalytic, pharmaceutical, industrial and other applications has been thoroughly investigated. Since they're so simple to make and may be tailored in so many ways, Schiff base ligands are a particularly intriguing class of compound. Schiff bases and their metal complexes are becoming a popular study area, and the discoveries they're yielding concerning newly created chemicals keep coming in thick and fast. An overview of the biological and catalytic activity of imine ligands and metal complexes has been provided in this paper, with an emphasis on materials chemistry in certain cases.

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Corresponding Author

Syed Misbahuddin Quadri*

Research Scholar, Department of Chemistry, Mewar University, Chittorgarh Rajasthan, India