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# Physicochemical Studies of Some Metal Complexes with O N S Donor Ligands

**Vivekaenandan[1]* T. Adinaveen[2]**

[1] Assistant Professor, Dhanalakshmi Srinivasan College of Arts and Science for Women, Perambalur, Tamil Nadu, India

[2] Assistant Professor, Dhanalakshmi Srinivasan College of Arts and Science for Women, Perambalur, Tamil Nadu, India

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## *ABSTRACT*

*The present work is presented in five chapters entitled "Physicochemical Studies of Some Metal Complexes with O, N/S donor legends." Below, a chapter wise summary is given. It deals with the introduction of the chemistry of coordination and briefly with theories. In this section, an account of Schiff bases, their metal complexes and their significance was discussed. A brief review of the literature on previous studies on thiosemicarbazone metal complexes and their stereochemistry, coordination mode study. Related schemes have been incorporated for the substituted thiosemicarbazones related to the present work. The aim of the present investigation has been outlined at the end of this topic.*

***Keywords** – Physicochemical, Complexes, Donor Ligands*

## INTRODUCTION

One of the most active areas of research in inorganic chemistry is coordination chemistry, the chemistry of metal complexes. In today's context, the study of coordination chemistry began with two notable scientists, Alfred Werner and Sorphus Mads Jorgenson. Werner's pioneering contribution to the study of coordination chemistry earned him the Nobel Prize in chemistry in 1913. Despite all the advanced technical developments that have taken place since his days, Werner's basic ideas on the stereochemistry of metal complexes, mechanism of isomerism etc. remain unchallenged even today. However, our understanding of the nature of the metal-ligand bond, the structure and stereochemistry of metal complexes, their stability and other properties has been significantly enriched by the advent of sophisticated physicochemical techniques of high precision and capacity. In terms of the growth that coordination chemistry has experienced over the last few decades, research has come a long way from the era of Werner and Jorgenson. Their work was a step for the growth of modern inorganic chemistry, which in today's context is truly a multidisciplinary one.

Chemistry coordination encompasses fields as diverse as dyes, colour photography, mineral extraction, nuclear fuels, toxicology, bioinorganic chemistry, medicine, catalysis, material science, ceramics, microelectronics, photonics, etc. The organic chemicals, pharmaceuticals, petrochemicals and plastics industries owe a great deal to the results in the field of coordination chemistry. Nature uses coordination compounds extensively and their study is becoming increasingly important in both biology and chemistry. Many of the biologically active compounds are complexes, and in investigating body processes, even the simpler kinds of complexes have served as model compounds. Coordination compounds partially support the living system. Oxygen is carried to animal cells by haemoglobin, an iron complex. Some of the other significant complex compounds in living systems are myoglobin, chlorophyll, and cytochromes. Inorganic compounds are essential cofactors in a variety of enzymes and proteins that are partially metallic ions and complexes. Coordination chemistry is rapidly developing in the pharmaceutical sector, and novel therapeutic and diagnostic metal complexes are currently having an impact in the medical field. Alfred Werner begins with modern studies of coordination compounds. The classical idea of coordination bond by Alfred Werner in 1893 gave much to the development of coordination chemistry.[1] The theory postulated that the metal exhibits two types of valencies, i.e. primary and secondary, in coordination compounds. The primary valency is non-directional and ionisable, while the secondary valency is non-ionisable and directional.

The bonds between the ligand and the metal ion are attributable to secondary metal ion valencies. The creation of Kossel, Sidgewick, Lewis, Langmuir, Fajan and others of electronic valency theory[2] cleared the concepts of primary (oxidation state) and secondary (coordination number) valencies in complexes. In 1931, Pauling introduced the theory of valence bond (VBT) based on the electronic structure of the central metal ion in its ground state, type of bonding, geometry (i.e. shape) and complex magnetic properties. [3] According to this theory, a number of empty atomic orbitals s, p and d are made available by the central metal atom or ion equal to its coordination number. These empty orbitals combine to form hybrid orbitals that are the same in number as the atomic orbitals that hybridise together. These are empty and have comparable power and definite geometry. At least one σ-orbital containing a lone pair of electrons is in the ligands. The empty hybrid orbitals of the metal atom or ion overlap with the filled σ-orbitals of the ligands to form the ligand-metal σ-bond (containing a lone pair of electrons). In particular, this theory describes the electronic structure of the central metal ion, complex shapes, magnetic moments and stereochemistry. However, the maximum pairing, spectrum of complexes and quantitative interpretation of magnetic properties are not properly explained.

Bethe[4Crystal ]'s Field Theory (CFT) was originally applied primarily to ionic crystals in 1929 and is therefore referred to as crystal field theory (CFT). As a combination of central ions surrounded by other ions or molecules with electric dipoles, CFT sees a complex (i.e ligands). CFT does not consider covalent bonding in complexes in its simplest treatment, but the bonding between the metal cation and ligands arises from the electrostatic attraction between the metal cation nucleus and the partial negative charge invariably present on the ligands. The connection between the cation electrons and those of the ligands is completely repulsive. These repulsive forces are responsible for causing the division of the metal cation's d-orbitals into two energy sublevels, t2g-triplet and eg-doublet. The energies of these sublevels rely on the geometry type. The energy differences between t2g and eg levels are known as the energy of stabilisation of the crystal field and are denoted by x or 10 Dq. The 10 Dq magnitude depends on the nature of the ligand and the central metal ion charge. CFT interprets, quantitatively, the magnetic and spectral properties of transition metal complexes.

The molecular orbital theory, developed although more complicated than the theories of VBT and CFT, explains the nature of bonding involved in coordination complexes more satisfactorily. The formation of a covalent bond with a metal ion and a donor group takes place with or without the replacement of an organic functional group of hydrogen atoms. A complex, as defined by as a species, consists of the association of two or more simple species, each capable of being independent. If one of the species is a metal ion, the metal complex is known as the resulting entity. The term legend is applied to the specific molecule or ion attached to the central metal ion. Some legends are connected by more than one atom to the central metal ion to form a ring in such a way. This is known as chelation, and metal chelates are the resulting complex. [8] Chelate stability is dependent on the size of the ring. In general, coordinated compounds consisting of a saturated five-member ring are more stable than those consisting of five-membered rings that are unsaturated. However, with the formation of six member rings, the great stability of metal chelate is achieved.

The study of coordination compounds present in the living system is the focus of rapid development in the field of bio-inorganic chemistry.[10] Therefore, it is not surprising that the use of coordination compounds such as metal-based drugs has recently become a very active research area. The use of inorganic chemistry in medicine is a rapidly developing field and new complexes of therapeutic and diagnostic metals that are currently used clinically. [11-14] The synthesis and study of metal complexes with drugs[15] or biomolecules[16] as ligands is an area of considerable interest for research, especially with regard to complexes which exhibit synergistic effects between ligands and metals. Subjects of considerable interest are metal ions with biologically active ligands. In a vast number of biological processes, metal ions thus play an important role. Via chelation, some of the biologically active compounds act. But for most of them, little is known about how their capacity is affected by metal binding. [17] Vanadium, for instance, is a trace but essential component with relevant biological properties and has a spectral status among biometals, whereas iron present in food and drink as a trace component is of critical importance for the normal growth and development of infants. The metabolism of other nutrients is affected by the nutritional status of iron. [18] In approximately one third of enzymes, metal ions play an essential role. [19] In a substrate or enzyme, these ions can alter the flow of electrons. Catalyzed enzyme reactions are thus effectively controlled. In relation to functional groups in the active sites, they can serve to bind and orient substrates and can provide a redox activity site if the metal has multiple valence states. A biochemical reaction catalysed by a particular metal enzyme would proceed very slowly, if at all, without the appropriate metal ions.

## MPORTANCE OF COORDINATION COMPLEXES AS DRUGS:

Importance of transition metal complexes as potential therapeutic agents-Transition metals exhibit different oxidation states and can interact with a number of negatively charged molecules. This benefit of transition metals has started the development of metal-based drugs with promising pharmacological application and may offer unique therapeutic opportunities. Now a day, transition metals have an important place within medicinal biochemistry. Significant progress has been done in utilization of transition metal complexes as drug to treat several human diseases like cancer, anti-inflammatory, diabetes and neurological disorders.

### Transition metals as anti diabetic agent-

Glucose level in the blood plasma can be controlled by administration of vanadium and zinc in the form of inorganic salts. The complexes of vanadium with organic ligands have proved to be less toxic, with improved lipophilicity. A number of vanadium complexes have been developed, all of which have insulin-mimetic properties. Chromium supplementation significantly improved glycemia among patients with diabetes.

### Transition metal complexes are anticancer agents-

Titanium complexes such as Titanocene dichloride had been recognized as active anticancer drug against breast and gastrointestinal carcinomas. Gold complexes also show anticancer activity. Certain gold complexes with aromatic bipyridyl ligands have shown cytotoxicity against cancer cells.

### Transition metals as anti-HIV-

Recent studies showed that ox vanadium complexes of theorem and vanadium substituted polyoxotungstates exhibit potent anti-HIV properties towards infected immortalized T-cells.

### Transition metal complexes as anti-infective agents-

Many magnesium complexes have been screened against a number of pathogenic fungi and bacteria to evaluate growth and potential.  Nitrogen containing macro cyclic complexes of Mg (II) have shown antimicrobial activity. An octahedral geometry for these complexes has been confirmed by spectroscopic analysis. Transition metals like silver have been used for years as antimicrobial agent's silver has low toxicity as compared to other transition metals. One of most commonly used compound is silver (I) sulfazine, it is used to treat severe burns to prevent them from bacterial infections.

### Transition metals as neurological drugs-

Transition metal complexes are also used in the treatment of neurological disorders. [25] Other transition metals like zinc are involved as a transmitter in the neuronal signaling pathways. Neuronal Zn (II) serves as an important, highly regulated signaling component responsible for the initiation of a neuroprotective pathway.

### Historical Background: Schiff Base Ligands or O, N/S Donor Ligands

Schiff bases, named after Hugo Schiff (1834-1915), and their transition metal complexes continue to be of interest even after over hundred years of study. The condensation product of primary amines with carbonyl compounds were first reported by Schiff in 1864 and the products are often referred to as Schiff's bases. Schiff's bases are compounds containing azomethine group (C=N) and have the general structure R-N=C-R ' where R and R ' are aryl, alkyl, cycloalkyl or heterocyclic groups which may be variously substituted. Often they are referred to as anils, imines or azomethines. The synthesis and properties of Schiff bases have been widely reviewed. The viability of different types of amines and carbonyl compounds enabled the synthesis of Schiff bases with diverse structural features. Nevertheless, most of the studies are on metal complexes derived from salicylaldehyde.

The presence of phenolic –OH group sufficiently near to the azomethine group of salicyldimines makes them versatile multidentate ligands completing with almost all metal ions. In order to understand the chemistry of metal chelates, awareness about the formation and stability of complexes is of great help. The bonding ability of the ligands depends on the nature of the atoms that act as coordination site, their electro negativity and satiric factors. By virtue of the presence of a lone pair of electrons on the nitrogen atom, electron donating character of the double bond and low electro negativity of nitrogen, N of the azomethine group (C=N) act as a good donor site and Schiff base as active ligands. The formation of chelates gives extra stability to the complexes especially when the ring is five or six membered. Hence the presence of a functional group with replaceable hydrogen atom near to C=N will be additional factor of stability. First of all Ettling in 1840 has isolated Schiff base complexes of copper. But the systematic synthetic study of Schiff base complexes started with the work of Pfeiffer and coworkers in 1931. [40] Jencks [41] has shown the formation of carbinolamine as an intermediate product which loses a water molecule to yield a schiff base.

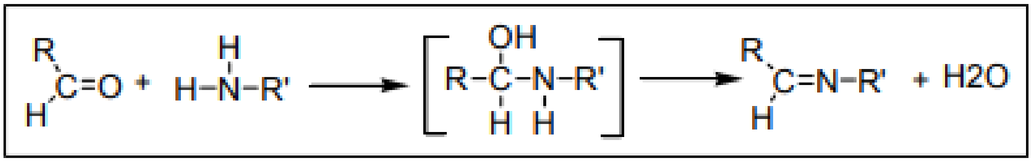
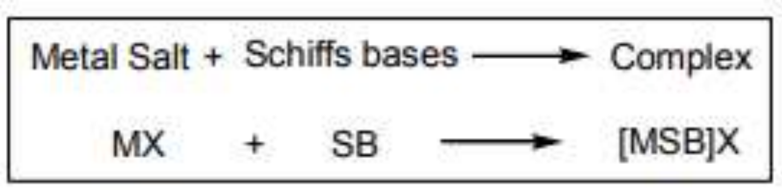


**Fig.1.1 Systematic route for the synthesis of Schiff base**

**Metal Complexes of Schiff Base-**

Metal complexes of Schiff bases have occupied a central role in the development of coordination chemistry. The situation is manifested by the huge number of publications. [42-47] In general, metal complexes of Schiff bases were prepared by one of the following general method.



Metal Salt + Schiffs bases ⟶ Complex

MX + SB ⟶ [MSB]X

**Where X= NO3 - , Cl- , CH3COOand ½ SO4 2- etc**

**Fig.1.2 General Reaction of synthesis of metal complex**

Schiff base-metal complexes were formed by nearly all the metals of the periodic table. Although the number of known complexing agents is very large, the donor atoms, which undergo combination with the metal, were restricted to the strongly non-metallic elements of group 15 and 16.

## THIOSEMICARBAZONES- Important Schiff

base In organic chemistry, a thiosemicarbazone is a derivative of an aldehyde or ketone formed by a condensation reaction between a ketone or aldehyde and thiosemicarbazide.

$$H_2NNHC(=X)\ NH_2 + RC(=O)R \rightarrow R_2C{=}NNH(C{=}O)NH_2$$

For thiosemicarbazide X=S then product is aldehyde / ketone thiosemicarbazone. Thiosemicarbazones are a group of highly reactive compounds that form chelate complexes with transition metal ions. They have the general formula.

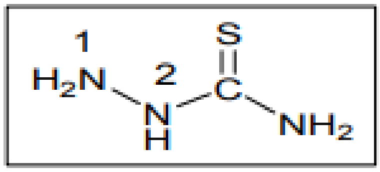


**Fig. 1.3 Structure of thiosemicarbazide**

When their 4N nitrogen is substituted, they can be represented by the following formula:

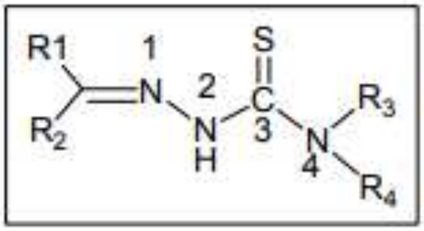


**Fig. 1.4 4N, 4N-Disubstituted thiosemicarbazone**

Where, R1 is generally an alkyl or aryl group and R2 is hydrogen, methyl, higher aliphatic or aromatic groups. R3 and R4 can be the same aliphatic or aromatic group or both can be a part of cyclic system. Thiosemicarbazones generally exist in the enonic or thionic form in the solid state respectively, but in solution they probably exist as an equilibrium mixture of enone and enol or thione and thiol. They usually act as a chelating agents with agents with metal ions by bonding through X and hydrazine nitrogen atoms. [49] Thiosemicarbazones are versatile ligands in both neutral (HL) and anionic (L-) forms.

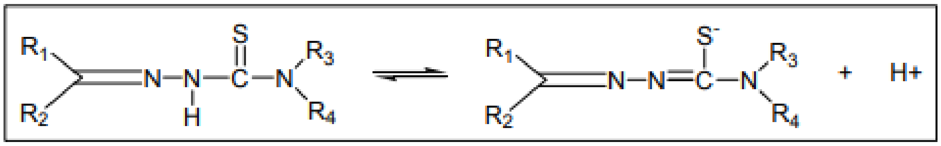


**Fig. 1.5 Neutral and anionic form of thiosemicarbazone**

The R1 and R2 groups may provide additional donor atoms and R3 and R4 are the N-(4)-substituents. Although the proton lost by the anions formally belongs to the hydrazinic NH-group, the anion is usually presented in the canonical form I, II and III and usually in the Z-configuration.

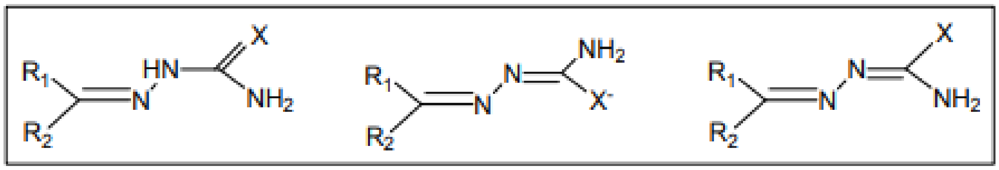


**Fig. 1.6 Different canonical forms of thiosemicarbazone**

The IUPAC numbering scheme of the ligand is shown in Figure 1.7

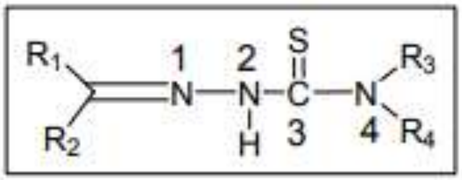


**Fig. 1.7 IUPAC Number scheme of the ligand**

Depending on the nature of coordination, by bonding through deprotonation of thiol or alcohol, they may act as neutral bidentate or sometimes as anionic bidentate. These molecules are planar and, with respect to the C-N bond,-NH2 is Trans. By condensing the aldehyde with functional groups such as-OH,-NH2 etc., additional bonding sites are made available and this will offer more options when it comes to complexity. Because of their chemistry and pharmacological properties, thiosemicarbazones are molecules of great interest. In the early years of the twentieth century, they attracted attention as prospective drugs and were found to be effective against a range of diseases. Potential antitumor, antiviral, ant malarial, antibacterial and antifungal agents are scores reporting the biological activity of this class of compounds.

## CONCLUSION

By condensation of substituted thiosemicarbazide and salicylaldehyde, the Schiff bases used in the present study were synthesized. These legends are all color-different and soluble in chloroform, THF, DMF, and DMSO. In the range of 160-250 °C, the melting points indicate thermal stability at room temperature. In nature, all of them are diamagnetic. Depending on the functional group present in it, the UV/VIS and FTIR spectra of these legends showed absorption bands in different regions. Using proper logic, these absorption bands are assigned. They were used to synthesize Cr (III), Fe (III), Co (II), Cu (II), and Zn (II) metal complexes after characterizing legends with regard to all the above parameters. With respect to various analytical, spectral and biological investigations, each of these complexes was diagnosed.

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