

A REVIEW (PART A) – GENERAL APPLICATIONS OF SCHIFF BASE TRANSITION METAL COMPLEXES

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ABSTRACT

Schiff bases are multipurpose ligands which are amalgamated from the condensation of carbonyl compounds with an amino compound. These compounds and their metal complexes are very imperative in an assortment of fields. This review goes over the main points of Schiff bases and their complexes.

Keywords: Schiff base transition metal complexes; Coordination chemistry; Electroluminescent; Electromagnetic fields; Calf thymus DNA; Cellulose polyester.

INTRODUCTION

Coordination chemistry employs Schiff bases which have achieved prime importance in this era. The extensive studies have been conducted on complexation of Schiff bases with metals due to the attractive physicochemical properties of metal complexes and broad range of utilization in various areas of science. Such types of complexes have paved the way for exploration and findings of a variety of metal complexes in recent years. The data available for Schiff bases in literature embraces very wide and diversified subjects, comprising vast areas of organo-metallic compounds and multiple aspects of bioinorganic chemistry. Therefore, a brief discussion of the major applications of Schiff base complexes is as under:

As electroluminescent materials

Tang and Van Styke were reported high performance organic electroluminescent (EL) devices for the first time and since then the organic electroluminescent devices are employed in novel-type flat-panel displays [1]. The multilayer device structure having a receiving layer and an emitting layer was the actual basis for this wonderful discovery. Organic EL devices are generally fabricated by three major organic materials such as organic dyes, chelate metal complexes and polymers. The materials for RGB (red, green and blue) emission are based on high luminescent blue emitting nature of chelate complexes. Schiff bases of calixarene were used for the preparation of complexes of blue luminescent zinc and beryllium [2]. Thin films for these Schiff bases can be easily achieved and are soluble to a good extent in normal solvents. The crystal structure, optoelectronic properties and thermal stability of bis[salicylidene(4-dimethylamino)aniline]zinc (II) [3] were reported by Xie *et. al.* Among organic light emitting diodes (OLEDs), this complex is found to have excellent light emitting and charge transforming properties. The application of Schiff base complexes in full color flat-panel displays are pointed out by these experimental reports as light emitting materials.

In non-linear optical devices

The interactions of various materials with applied electromagnetic fields are dealt by non-linear optics (NLO) for introducing new electromagnetic fields, with different physical properties like frequency and phase. The dynamic image processing, optical communication and optical computing utilizes such type of materials in manipulating photonic signals in an efficient manner which enhances their significance [4-6]. The ability of transition metal complexes to tailor metal-organic interactions and various oxidation states of metals present in such systems makes these complexes as potential building blocks for non-linear optical materials [7-10].

The large variety of structural novelty, diversity of tunable electronic behaviors on account of coordinated metal center and the possibility of enhancing thermal stability of metal complexes as compared to the more common organic molecules, makes a place for them to be used as NLO materials with characteristic electrochemical and magnetic properties. Several research groups are pursuing investigations on NLO properties of metal complexes [11-13]. Di Bella and co-workers reported that good second order NLO properties were exhibited by bis(salicylaldiminato)metal Schiff base complexes [14-20].

In electrochemical sensors

The determinations of cations and anions have been done by employing Schiff bases as potentiometric sensors [21-23]. PVC based chloride membrane sensors were fabricated by using Ru (III) complexes of Schiff bases [24]. Near Nernstian behaviour is displayed by the sensor with a wide range of concentration and composition of 30 % PVC, 62 % benzyl acetate, 3 % hexadecyltrimethyl ammonium bromide and 5 % ruthenium (III) Schiff base complex. The sensor was successfully employed for the determination of chloride ions in serum because it is selective towards chloride ions over a variety of organic and inorganic anions. The potentiometric titration of chloride ions with silver nitrate is carried out by employing such type of sensor as indicator electrodes. The preparation of Mn²⁺ selective sensor employs the use of Schiff base, N,N,N',N''-1,5,8,12-tetraazadodecane-bis(salicylaldiminato) as ionophore. The sensor can be utilized for analyzing Mn²⁺ selectively in various samples by direct potentiometry as it is sufficiently selective for Mn²⁺ over a number of alkali, alkaline and heavy metal ions.

Synthetic action on insecticides

Toxicity against insects has been reported for the Schiff bases derived from sulfane thiazole and thiophene-2-aldehydes or salicylaldehyde and almost similar behaviors is observed for their complexes [25]. The synthesis of photostable pyrrhodin insecticides involves α -amino acid as intermediate [26]. The insectoacracidal activity is enhanced by fluorination on the aldehydic part of Schiff base [27]. The insecticidal activities against bollworm were observed for Schiff bases (thiadiazole derivatives with salicylaldehyde or o-vanillin) and their metal complexes with Mo (II) and cell survival rate for mung bean sprouts is also promoted by them [28].

In medicinal chemistry

Medical importance of Schiff bases is quite clear from the literature and this is the reason that they are used for designing medicinal compounds [29-30]. The chelation of Schiff bases with metals either enhances or minimizes their activity [31-32]. The complexes of

cobalt (II), nickel (II) and copper (II) with Schiff base of 3-substituted-4-amino-5-mercapto-1,2,4-triazole and 8-formyl-7-hydroxy-4-methylcoumarin show the potent antibacterial activity against *Escherichia coli*, *Streptococcus pyogenes*, *Staphylococcus aureus*, *Salmonella typhi* and *Pseudomonas aeruginosa* and antifungal activity against *Aspergillus flavus*, *Aspergillus niger* and *Cladosporium* were found in literature[33]. The considerable antibacterial activity of Ru(II)-PPh₃/AsPh₃ complexes, containing hydrazone oxime ligands, were observed against selected bacterial species. Moreover, they possess binding capability to Herring sperm DNA in mixed modes. The moderate antimicrobial activity is exhibited by the complexes of Cr (III), Fe (III) and Co (III) with tridentate (ONNO) Schiff base ligands such as 1,4-bis[3-(2-hydroxy-1-naphthalidimine)propyl]piperazine and 1,8-bis[3-(2-hydroxy-1-naphthalidimine)-*p*-menthane on comparison with standards. The chelation of tridentate Schiff base, formed by condensation of 2-amino-3-carboxyethyl-4,5-dimethylthiophene with salicylaldehyde and also with transition metals improves their antibacterial activity. The antibacterial activity of vanillin and DL- α -aminobutyric acid derived Schiff base complexes of Co (II), Ni (II), Cu (II) and Zn (II) were much greater than Schiff bases[34]. Similarly the Schiff base derived from phenylaminoacetohydrazide and dibenzoylmethane, have less potential of bactericides and fungicides than their mono and binuclear complexes. The hemozoin aggregation like the antimalarial drug, chloroquine can be targeted by Schiff bases as reported by Sharma and Piwnica-Worms[35-37].

The development of sensitive chemical probes for DNA and interaction of transition metal complexes with DNA guided us to an approach for finding and to lead for ration drug design[38-44]. In this regard, both non-covalent and covalent interactions are involved. The nitrogen base of DNA usually replaces the labile part of complexes in case of covalent binding. The groove binding of cationic metal complexes along periphery of the DNA helix, intercalative and electrostatic interactions are among the non-covalent interactions. The partial insertion of aromatic heterocyclic rings between the DNA base pairs is the basis of intercalation. The binding properties of DNA with a series of transition metal complexes of 2,6-dibenzoyl 4-methylphenol and diamines derived Schiff bases having potential NNO-tridentate donors were reported by Gupta and coworkers[45-51]. The binding studies of Ni (II) complexes of 5-triethyl ammonium methyl salicylidene ortho-phenylendiimine ligand, with DNA reflect that strong interaction occurs between DNA and complexes[52]. The intercalating binding mode or native calf thymus DNA by groove interacts with Zn (II) and Cu (II) complexes of this Schiff base[53].

The interaction of calf-thymus DNA occurs with salicylaldehyde-2-phenylquinoline-4-carboxylhydrazone complexes of Co (II) and Ni (II) through a binding mode involving groove[54]. The literature revealed the interaction of calf thymus DNA (CT-DNA) with salen = N,N'-ethylenebis(salicylideneimine), chromium (III) Schiff base complexes, [Cr(salen)(H₂O)₂]⁺ and [Cr(salprn)(H₂O)₂]⁺, whereas salprn = N,N'-propylenebis(salicylideneimine)[55]. The interaction of CT-DNA with Cr (III) complexes derived from chiral binaphthyl Schiff base ligands (R- and S-2,2'-bis(salicylideneamino)1,10-binaphthyl) also occurs through groove binding[56]. The effective cleavage of plasmid DNA takes place in the presence of hydrogen peroxide at pH 7.2 and 37 °C without the addition of any external agent through binuclear Co (II) complexes having the Schiff base ligand, N,N'-bis(3,5-tert-butylsalicylidene-2-hydroxy)-1,3-propanediamine. The complexes examined here are capable of DNA damage through oxidative pathway as reflected by DNA cleavage mechanism studies[57]. The interaction between native calf thymus deoxyribonucleic acid (DNA) takes place through an electrostatic binding between Fe^{III}-N,N'-ethylene-bis (salicylideneiminato)-chloride, Fe(Salen)Cl and Fe(Salen)⁺ cation as illustrated by Silvestri et al.[58]. The capability of intercalation into the double-stranded salmon sperm DNA for Mn (II) complex, MnL (L = sodium (E)-3-(1-carboxyethylimino)methyl)-4-hydroxybenzenesulfonate), is reported[59]. Schiff bases derived from diethylenetriamine and 2-thiophene-carboxaldehyde/2-furaldehyde/2-pyrrole-2-carboxaldehyde were employed by Chaviara et al. for the preparation of Cu (II) complexes of the Schiff bases. The interaction of these compounds with DNA was determined by DNA

electrophoretic mobility studies which reflected that either a simple coordination mode followed by formation of DNA complex ionic adduct or their performance as nucleases for degradation is involved in such type of interactions.

Plant growth regulator

The growth inhibition activity of seedling of wheat, barley and rye was shown by N-acetylated compounds[60]. The significant activities of Schiff bases were also reported on plant hormones like auxins i.e., a root growth hormone[61]. The plant growth hormones are also affected by Schiff bases of carboxylic acids and esters[62]. The activity of plant growth regulation towards cytokine and auxin were observed for Schiff bases of thiodiazole[63].

Dyes

Leathers, foods packages and wools etc., can be fastly colored with chromium azomethine complexes, cobalt complex Schiff base[64], un-symmetrical complex 1:2 chromium[65]. Cellulose polyester textiles can be dyed by using azo groups containing metal complexes[66]. Polyfibers can be dyed by using metal complexes[67]. The excellent storage and resistance ability of light has been reported for cobalt complex[68] of a Schiff base (salicylaldehyde with diamine) and its use is safe even in acidic atmosphere of CO₂ like gas. Some natural food samples are analyzed for the presence of Ni by using novel tetradentate Schiff base which are utilized as chromogenic reagents[69].

Polymer

The natural rubber gives amine terminated liquid natural rubber (ATNR) upon photochemical degradation in presence of ethylenediamine and conducted in solution[69]. Poly Schiff base is obtained by the reaction of ATNR with glyoxal[69], which is much better for aging resistance. The co-polymerization of dienyl and vinyl monomers and emulsion polymerization are usually initiated by organo-cobalt complexes with tridentate Schiff bases[70].

Chemistry of vision

The chemistry of vision makes use of an imine linkage between the aldehyde derived from vitamin A and the opsin protein situated in the retina of eye. The chemical changes in the cell take place with the help of larder proteins which catalyze the changes and vitamins play their role as coenzymes i.e., they are assisting the functioning of many enzymes. The most important example in this regard is the active form of the vitamin B₆ which is pyridoxal phosphate in actual sense. The most important feature to be considered is that amino acid groups in the enzymes make an imine with the aldehydic groups in vitamin B₆. The transfer of the amino group from one amino acid to another i.e., transamination is actually catalyzed by the coenzymes which are bound to enzymes and possesses significant importance in the biosynthesis of amino acids. The imine to pyridoxal and the modified amino acid linkage is cleaved by the enzyme-catalyzed hydrolysis in the last step.

Corrosion inhibitor

The Schiff bases which are able to form protective layers on the surface can be utilized for the preparation of anticorrosive materials and can therefore, serve as corrosion inhibitors. The commercially employed corrosion inhibitors include many aldehydes or amines. Moreover, the presence of C=N functionality in Schiff bases makes them more efficient for this purpose[71]. As far as, the use of Schiff bases as corrosion inhibitors is concerned, chemisorptions is the major interaction[72]. The capability of the inhibitor molecules to make bonds with the metal surface needs certain electron rich centers available with the inhibitor molecules. The inhibitors are supposed to behave as Lewis bases and metal will act as electrophile. In addition to that, free electrons are available with the oxygen, nitrogen and other atoms of the protecting compounds which will act as nucleophilic centers to make bonds with metal. The multiple absorption sites for the inhibitors assist the inhibitor compounds for making a stable monolayer which is due to involvement of whole benzene ring and its atoms[73].

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