International Journal of Basic and Applied Chemical Sciences ISSN: 2277-2073 (Online)
An Online International Journal Available at http://www.cibtech.org/jcs.htm
2012 Vol. 2 (1) January-March, pp.84-107/ Singh and Adhikari

Research Article

COMPLEXATION BEHAVIOUR OF SCHIFF BASE LIGANDS WITH TRANSITION METAL IONS

***Bibhesh K Singh and Devjani Adhikari**
Department of Chemistry, Govt. Postgraduate College, Ranikhet-263645(Uttarakhand) India
**Author for Correspondence*

ABSTRACT

This review article deals the complexation behavior of Schiff base ligands with first series of transition metal ions. The coordination behavior of various ligands and their structure formed after complexation with first series transition metal ions and its applications in various fields have been studied. The review mainly discusses the literature of last ten years. This review article is especially useful for inorganic as well as bio-inorganic chemists.

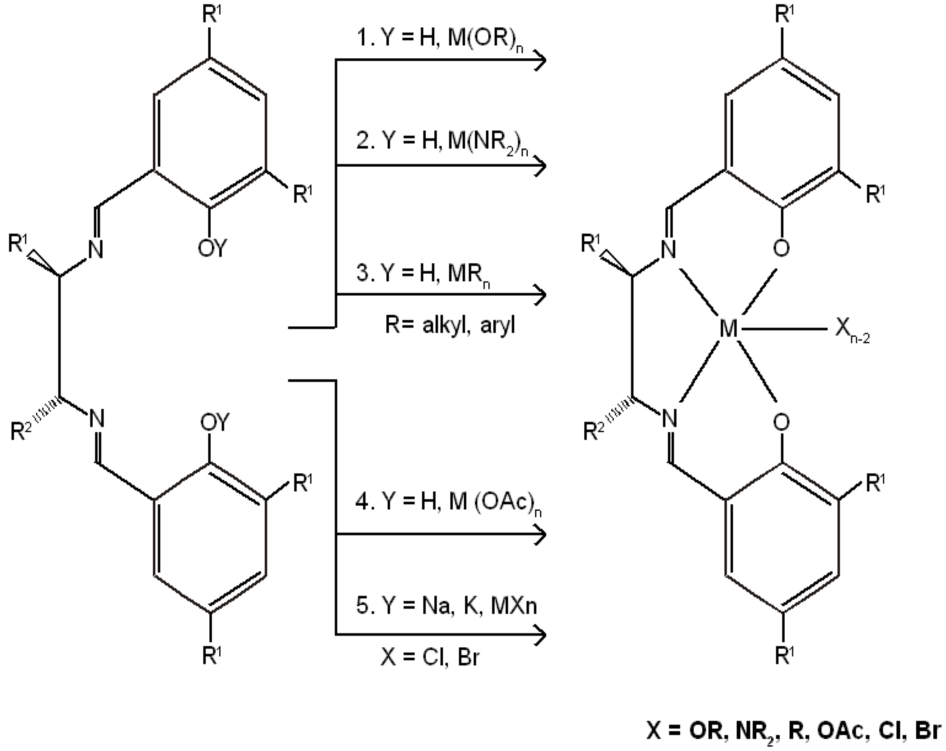
***Key Words**: Complexation, Coordination, Schiff Base, Structure, Transition metal ions,*

INTRODUCTION

Schiff bases named after Hugo Schiff described the condensation between an aldehyde and an amine. Schiff base ligands are able to coordinate metals through imine nitrogen and another group usually linked to aldehyde. Schiff base are straightforward to prepare, monodentate electron donors with easily-tunable electronic and steric effect thus being versatile (Schiff H, 1864; Shibuya et. al , 2008). Modern chemists still prepare Schiff bases, and now days active and well-designed Schiff base ligands are considered privileged ligands (Yoon T P, Jacobsen E N, 2003). In fact, Schiff bases are able to stabilize many different metals in various oxidation states, controlling the performance of metals in a large variety of useful applications in biological, clinical, analytical and industrial in addition to their important roles in catalysis and organic synthesis (Bhendkar et.al, 2004; Mohamed G G, 2006). Not only have they played a seminal role in the development of modern coordination chemistry, but they can also be found at key points in the development of inorganic biochemistry (Kilic A, 2007). A considerable number of Schiff-base complexes have potential biological interest, being used as more or less successful models of biological compounds (Prakash et.al, 2010; Mourya R C, 2006). Schiff base complexes incorporating phenolic group as chelating moieties in the ligand are considered as models for executing important biological reactions and mimic the catalytic activities of metalloenzymes (Khandar et.al, 2005). Furthermore, macrocyclic derivatives of these Schiff bases have many fundamental biological functions, such as photosynthesis and transport of oxygen in mammalian and other respiratory system (Coughlin P K, Lippard S J, 1984; Cai et. al, 2001). Schiff base ligands containing various donor atoms (like N, O, S etc.) show broad biological activity and are of special interest because of the variety of ways in which they are bonded to metal ions. It is known that the existence of metal ions bonded to biologically active compounds may enhance their activities (Mohamed G G, 2006; Shi et. al, 2009; Phaniband M A, Dhumwad S D, 2007). In recent years, because of new interesting applications found in the field of pesticides and medicine, the metal complexes with tridentate O, N, N types of alternative structures have attracted the attention of chemist. Various metal complexes with bi- and tridentate Schiff bases containing nitrogen and oxygen donor atoms play important role in biological system and represent interesting models for metalloenzymes, which efficiently catalyze the reduction of dinitrogen and dioxygen (Kasumov et.al, 2005; Frausto da Silva J, Williams R, 1991, Kaim W, Schwederski B, 1996). This review deals with the complexation behaviour of Schiff bases with various first series transition metal ions.

General methods of preparation of Schiff Base Metal Complexes

Generally Schiff base metal complexes are prepared by producing a reaction between the Schiff base and available metal salt in ethanolic medium. This approach is clearly simple and suitable. Essentially, five different synthetic routes can be identified for the preparation of Schiff base metal complexes (Scheme 1).



Scheme 1: General methods of preparation of Schiff base complexes

Schiff base complexes involves the use of metal alkoxides [$M(OR)_n$]. For early transition metals(M = Ti, Zr), alkoxide derivatives are commercially available and easy to handle, while the use of other alkoxide derivatives is more problematic, particularly in the case of highly moisture-sensitive derivatives of lanthanides. The reaction of a Schiff base with a metal alkoxide is an equilibrium reaction and the identity of the species generated is sometimes difficult to predict. Different complexes can be present in different concentrations, as a function of the equilibrium constant. However, the introduction of a bulky group in the Schiff bases can control the identity and homogeneity of the complex, by shifting the equilibrium towards the formation of a single species. The stability of the complexes is regulated by the equilibrium constant, and a disproportionation between Schiff base metal complexes and the metal alkoxide can occur.

Metal amides [$M(NMe_2)_4$] (M = Ti, Zr) are also highly suitable precursors for the preparation of Schiff base metal complexes of early transition metals. The reaction occurs via the elimination of the acidic phenolic proton of the Schiff bases, occurring at the same time as the formation of volatile $NHMe_2$.

Schiff base metal complexes can be prepared in a clean and effective way using metal alkyl complexes as precursors. Various metal alkyls in the main group of metals ($AlMe_3$, $GaMe_3$, $InMe_3$) are commercially available and can be used in the preparation of Schiff bases by a direct exchange reaction. This method is suitable for the synthesis of iron, manganese, vanadium and copper Schiff bases complexes.

Many Schiff base metal complexes can be obtained through the treatment of the Schiff base with the corresponding metal acetate, normally by heating the Schiff base in the presence of the metal salt under reflux conditions. Copper, cobalt and nickel Schiff bases are prepared using the corresponding acetate salts. Instead of using acetate, a direct exchange with metal halides is also possible.

Another method is quite effective in obtaining Salen metal complexes. It consists of a two-step reaction involving the deprotonation of the Schiff bases and a successive reaction with metal halides.

Deprotonation of the acidic phenolic hydrogen can be realized using lithium bases (MeLi, BuLi). The deprotonation step is normally rapid at room temperature, but heating the reaction mixture to reflux does not cause decomposition. THF is the solvent generally used for this type of preparation, and the sodium or potassium hydride used in excess can be eliminated by filtration, when the formation of the Na_2 (Salen) or K_2(Salen) is complete. However, this synthetic strategy can create problems in the purification steps, during the isolation of the Schiff base metal complex.

Transition Metal Complexes of Schiff Bases

Vanadium Complexes

Schiff base derived from 1-phenylbutane-1, 3-dione mono 5-methylisothiosemicarbazone and 5-phenylazo-o-hydroxybenzaldehyde coordinates to the vanadium ion is realised by means of two nitrogen atom of the isothiosemicarbazide fragment and two oxygen atoms of the benzoylacetonic and salicylidine fragment giving square pyramidal geometry for the complex (Gradinaru et.al, 2007). Salen-type Schiff base complexes having generally a planar structure, the vanadium atom is strategically placed at the centre of the charge-transfer system, allowing the d electrons of the metal to take part in conjugation scheme of the organic ligand (Lacroix P G, 2001) results, enhanced optical nonlinearities are observed after metal complexation, compared to those of the free ligand. The Schiff base derived from salicylaldehyde and o- phenylenediamine coordinates vanadium(IV) (Figure 1), takes place through two azomethine N and two phenolato O atoms after deprotonation giving square pyramidal geometry of the complex (Maurya et.al, 2006). Complexes catalyze the oxidation by H_2O_2 of sulfides (thio ethers) to sulfoxides and further to sulfones. The oxidation of methyl phenyl sulfide gave a mixture of methyl phenyl sulfoxide and methyl phenyl sulfone with a maximum conversion of 98%. Complex is suitable for the catalytic oxidation of styrene to styrene oxide, benzaldehyde, benzoic acid, phenylethane - 1, 2 - diol (Smith T S, Pecorara V L, 2002).

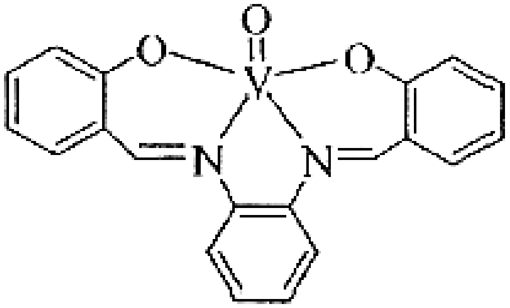


Figure 1: Square pyramidal geometry of VO(II) complex (Maurya et.al, 2006)

Antimicrobial activities of the Schiff base i.e. N, N'-(o-phenylene)-bis-(2-aminobenzamide) and its vanadium (II) complex have been extensively studied on some microorganism like S. aureus, B. subtilis, K. pneumoniae etc (Swamy et.al, 2001). The complex has higher bio-activity than the free ligand. The ligand coordinates through two azomethine nitrogen atoms and two amide nitrogen atoms are giving square pyramidal geometry (Figure 2).

The structure of new dioxovanadium(V) complexes incorporating Schiff bases derived from (S)-(+)-2-(aminomethyl) pyrrolidine and aromatic o-hydroxycarbonyl compounds were studied. The x-ray studies on N-(methylesalcylidene)-(S)-(2-pyrrolidinylmethyl) amine dioxovanadium(V) monohydrate shows that the crystal of that compound is a solid solution of two diastereomers, which differ in conformation of five-membered rings and in absolute configuration of the chiral centre containing the asymmetric carbon atom. The weak predominance in content of S-diastereomer over T-diastereomer in the crystal increases strongly in DMSO solution as evidenced by NMR studies, indicating that the crystallization induces the

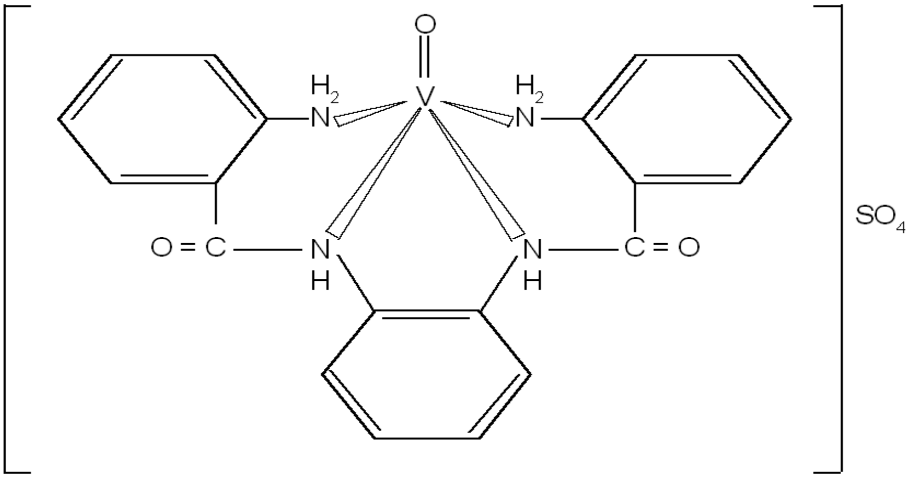


Figure 2: Square pyramidal geometry of complex (Swamy et.al,2001)

asymmetric transformation of S-diastereomer. The free energy of transformation of S –diastereomer into its R analog in DMSO solution is particularly low for complexes containing ethylidene substituent attached to the aromatic ring (Kwiatkowski et.al., 2006).

Chromium Complexes

A new polydentate Schiff base derived from the condensation of 2, 6-diformyl-4-methylphenol and S-methyl hydrazine carbodithionate and its Cr(III) complex has been synthesized and characterized. During metalation, a loss of the OH proton was occured (Al-Shihri A S, 2004). Another polydentate Schiff base has coordination occurs through phenolic oxygen, azomethine N atom and S atom giving octahedral geometry (Ali et.al, 2002). The ligand acts as a pentadentate and the coordination is completed by one water molecule. The complex has been used as catalyst for carbonylation, hydrogenation, and hydroformylation and epoxidation reaction. The complex has many fundamental biological functions such as photosynthesis and transport of oxygen in mammalian and other respiratory system. Cr(III) complex with N, N'-ethylene bis-salicylamide was prepared and reported octahedral geometry (Dash et.al, 2006). Ligand is behaving as dibasic and tetradentate in nature. The coordination occurs through phenolic OH after deprotonation and through N of amide group has been reported. The presence of coordinated water molecule and nitrate is present in outersphere of the complex. Cr(III) complexes incorporating phenolic and amide functions as chelating moieties are considered as models for executing important biological reactions and mimic the catalytic activities of metalloenzymes and may also be useful as starting material in synthesis of precursors for bi-metallic catalyst, molecule based magnet (Bernhardt et.al, 2003). Cr (III) Complexes with N, N'-bis (Salicylidene) ethylenediamine and N, N'- bis (5-bromosalicylidene) ethylenediamine have been synthesized and characterized by spectral studies (Figure 3). During complexation deprotonation of phenol OH group occurred and coordination takes place through azomethine nitrogen, phenolic oxygen and water molecules give octahedral geometry for these complexes (Aranha et.al, 2007).

Chromium (III) is an essential nutrient that is involved in the glucose tolerance factor [GTF] in maintenance of normal carbohydrate and lipid metabolism. In sufficient dietary intake of chromium is linked to increase risk factors associated with type II diabetes and cardiovascular diseases. These complexes are used as a new model of GTF, were also shown to reduce the symptoms of diabetes like, hyperglycemia and cholesterol in diabetic rats (Malinowska et.al, 2004). Chromium-salen complexes are well-known catalysts, both in heterogeneous and homogeneous systems. Other applications of chromium complexes are reported such as the stereo-selective alkene epoxidations, alcohol, oxidation (Li et.al,

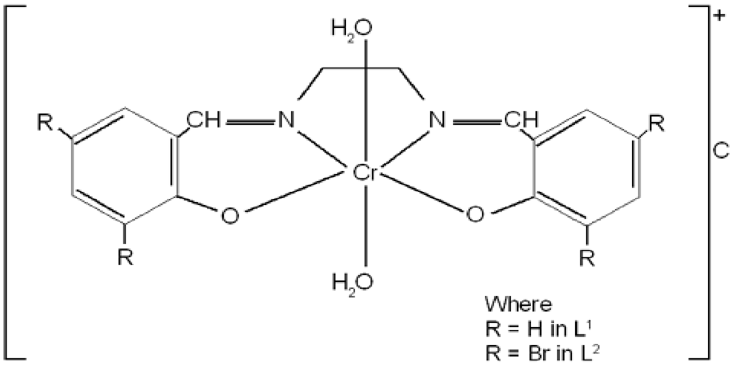


Figure 3: Octahedral geometry of Cr(III) complex (Aranha et.al, 2007)

2005), the asymmetric addition of organometallic reagent to aldehydes and asymmetric hetero Diels-alder reactions (Bandini et.al, 2000). Recently, the interaction of DNA with these complexes was reported. These complexes have been shown to bring apoptosis in lymphocyte cell cultures. The (Salen) Chromium (III)/DMAP catalyst system is used in the fixation of CO_2 with epoxides to form carbonates (Malinowska et.al, 2004).

Sunlight irradiation of the reactions of $[Cr(CO)_6]$ with either N-salicylidene-2-hydroxyaniline(shaH_2) or bis-(salicylaldehyde) phenylene diimine (salphenH_2) in THF gave the complexes$[Cr(shaH_2)_3]$ and $[CrO(salphenH_2)]$ (El-Medani et.al,2005). Interaction of $[Cr(CO)_6]$ and isonicotinic acid hydrazide(inh) in dioxane under sunlight resulted in formation of complex$[CrO_2(ininh)]$, ininh = isonicotinoylisonicotino hydrazide (Ali et.al, 2006). Sunlight irradiation of the reaction of $[Cr(CO)_{6]}$ with salicylaldehyde isonicotinic acid hydrazone (H_2- Salnah) in THF was investigated (Ali S A, 2007) (Figure 4). Interaction of $[Cr(CO)_6]$ with H_2 -Salnah resulted in formation of binuclear complex $[Cr_2O_2(H_2\text{-Salnah})_2]$. Electronic spectra of the complex in DMF displayed visible bands due to ligand to metal charge transfer. Magnetic measurements of the complex at 298K gave a magnetic susceptibility value of 1.09×10^{-6} emu g^{-1} with effective magnetic moments (μ_{eff}) 1.27 BM. Therefore, the paramagnetic oxo complex may contain Cr(II), d^4, in a high – spin configuration. Lowering in μ_{eff} could be due to strong antiferromagnetic coupling between the two Cr(II) centers through the two (μ-O) groups. The IR spectra displayed two bands at 697 and 637 cm^{-1} were assigned to Cr-O-Cr stretching vibrations. From spectroscopic data, the complex may have the structure as

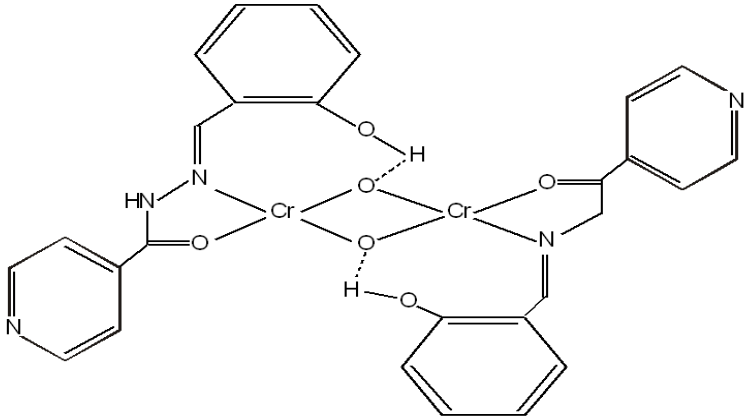


Figure 4: Proposed structure of the complex (Ali S A, 2007)

Manganese Complexes

Manganese and its compounds find very historical importance in medicine and also have some biological importance. Manganese plays a significant role in enzyme activation (Sigel H, 2002). A number of reviews are available on the physiology and biochemistry of manganese in mammals. DNA and RNA polymerases catalyze the replication and transcription of DNA have a specific requirement for manganese(II). The most important role of manganese is the oxidation of water in green plant photosynthesis where its presence in photosystem II is essential (Sigel H, 2002). Mn(II) complex with Schiff base derived from Pyridine-2-carbaldehyde N-oxide and 2-amino phenol was synthesized and characterized (Herchel et.al, 2007). The coordination occurs through azomethine N atom, phenolic oxygen and pyridine oxygen has been suggested. The complex was trinuclear and terminals Mn (II) were pentacoordinated (Dobac C, Astier-Perret V, 2006; Gembicky et.al, 2000).

It was confirmed that linear trinuclear complex exhibits an antiferromagnetic exchange between adjacent centres and a ferromagnetic intermolecular interaction, which is responsible for a high effective magnetic moment. The pyridine N-oxide analogues of the Schiff base complexes have been widely studied in the past decade. 2-Pyridine carbaldehyde N-oxide serves as a precursor for several Schiff base type condensations with aliphatic and aromatic amines (Dobac C, Astier-Perret V, 2006; Gembicky et.al, 2000). The Schiff base was obtained by the condensation of benzaldehyde, aniline and diphenyl chlorophosphate and its Mn(II) complexes have been prepared and characterized (Abd El-Waheb Z H, El-Sarang M R, 2004). Mn atom coordinated through phosphate oxygen and azomethine nitrogen atom giving tetrahedral / octahedral geometry for the complexes. To assess the biological potential of the phosphate Schiff base ligand and their Mn(II) complexes, were found to be remarkable bactericidal and fungicidal properties. It is however, interesting that the biological activity gets enhanced on undergoing complexation.

Tetradentate complex of Mn(II) with Schiff base derived from 1-phenyl-2, 3-dimethyl-4(4-iminopentan - 2-one) pyrazol -5- one and 2-aminophenol has been prepared and spectral studies suggested octahedral geometry of the complex (Zhang C Sun J et.al, 2000). Thermal studies show the presence of two water molecules coordinated to the Mn (II) ion. The remaining four positions of the octahedron coordinated by two phenolic group and two enolic group of pentane -2, 4-dione moiety of the Schiff base on chelation. Antimicrobial activity of the base and complex was studied on some microorganism like Aspergillus niger, Trichoderma viridi and Shigella flexneri. Manganese (II) macrocyclic complexes were prepared with different macrocyclic ligands, containing cyclic skeleton bearing organic component which have different chromospheres like nitrogen, oxygen and sulphur donor atoms and spectrochemistry (Kumar R, Chandra S, 2007). Thus six macrocyclic ligands, were prepared and the capacity to retain the manganese (II) ion in solid as well as in aqueous solution was determined and characterized by different studies. Significant distortion of the manganese (II) ion in observed geometry is evident from the angle subtended by the different membered chelate ions and the angles spanned by trans donor atoms giving octahedral geometry (Figure 5). Cyclic voltammetric studies indicate that complexes with all ligands undergoes one electron oxidation from manganese (II) to manganese (III) followed by a further oxidation to manganese (IV) at a significantly more positive potential.

The Schiff base ligands N,N'-bis(2-hydroxyacetophenone)-1,2-diaminoethane and N,N'-bis(2-hydroxyacetophenone)-1,3-diaminpropane, prepared *in situ* were used to synthesize two new Mn (II) complexes which were characterized by crystallography and variable temperature magnetic measurements (Bhargavi et.al, 2009). $[Mn(acphen)NCS]_2$ is a phenoxo-bridged dimeric compound with the thiocyanato coordinating in the usual bent mode (Mn-N-C angle,152^0) and is weakly antiferromagnetic. Since there are no significant inter-dimer constants in the crystal, the low temperature magnetic behavior is influenced by single ion zero field splitting. $Mn(acphpn)(H_2O)NCS$ is monomeric with an unusual linearly coordinated thiocyanato (Mn-N-C angle,178^0). Two lattice water molecules link the Mn(III) complex molecules through hydrogen bonds to form one-dimensional chairs in the crystal. Magnetic

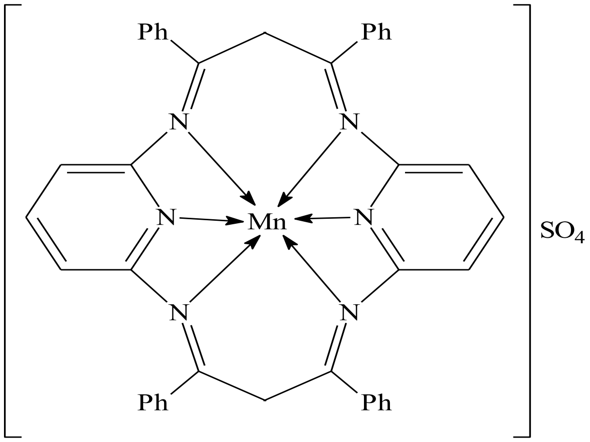


Figure 5: Structure of the manganese complex (Kumar R, Chandra S, 2007)

exchange along the chain makes this compound also weakly antiferrmagnetic with J~2 cm^{-1}. Two pyrimidine based NNS tridentate Schiff base ligands S-methyl-3-[(2-S-methyl-6-methyl-4-pyrimidyl)methyl] dithiocarbazate and S-benzyl-3-[(2-S-methyl-6-methyl-4-methyl-4-pyrimidyl) methyl]dithiocarbazate and their Mn(II) complexes have been synthesized (Roy et.al, 2008). All the bis-chelate complexes have a distorted octahedral arrangement with an N_4S_2 chromophore around the central metal ion. In the free ligand moieties, the pyrimidine nitrogen atoms, azomethine nitrogen atoms and thione sulphur atoms are in EEE orientation to each other. During chelation, all the donor sites of the ligands are reoriented to ZEZ configuration in order to facilitate the chelation process. All complexes were analyzed by single crystal x-ray diffraction and significant differences concerning the distortion from octahedral geometry of the coordination environment were observed. The deprotonation accompanied with tautomerization produces a delocalized ring system with overall intermediate interatomic bond distances on the ligand network. Cyclic voltametry studies show an irreversible anodic process and a quasi-reversible reduction.

Mn(II) complexes with a quindentate Schiff base 2,6-diacetylpyridine bis (thiocarbohydrazone), have been synthesized and characterized by various physiochemical techniques (Chandra S, Sharma A K, 2009). The complexes were [M(L)X]X, where M=Mn(II), L = 2,6-diacetylpyridine bis (thiocarbohydrazone) and X=NO_3^- and OAc^-. The ligands with five coordination sites forms six coordinated complexes with octahedral geometry (figure 6). The A_{iso} values, nephelauxetic parameter (β) and orbital reduction factor (k) indicate the covalent nature of the metal-ligand bond. The electronic spectra of complexes display absorption bands in the range 17,094-18,691 cm^{-1}; 23,848-24,630 cm^{-1}; 26,975-28,868 cm^{-1} and 33,333-37,313cm^{-1} which may be assigned to the ${}^6A_{1g}\rightarrow{}^4T_{1g}({}^4G)$, ${}^6A_{1g}\rightarrow{}^4E_g$, ${}^4A_{1g}({}^4G)$, ${}^6A_{1g}\rightarrow{}^4E_g({}^4D)$ and ${}^6A_{1g}\rightarrow{}^4T_{1g}(P)$ transitions, respectively and supported to octahedral geometry of complexes.

New Mn(II) and Mn(III) complexes with N,N□-bis(salicylidene)-1,2-diimino-2-methylethane (Figure 7) has been prepared and characterized (Maneiro et.al,2003). The tetradentate Schiff bases, H_2L used in this study readily react with Mn(II) perchlorate, in the presence of sodium hydroxide and air to give two types of compounds owing to the different nature of the Schiff bases. Thus inspite of the oxidant conditions, ligands with electron withdrawing substituent in their phenyl rings stabilize compounds formulated as $[MnL(H_2O)_2]$ with manganese in oxidation state II. The structural study of the complex $[Mn(II)L(H_2O)_2]$ suggest an octahedral geometry around the manganese with the tetradentate Schiff base occupying the equatorial plane with coordinated water molecules filling the axial positions. An unequivocal structure in solution for the $[Mn(III)L(H_2O)_n(ClO_4)]$ complexes cannot be established. All the data limit the geometries of the likely candidates to a five-coordinate site with square pyramidal geometry (III) or a six-coordinate site with octahedral geometry.

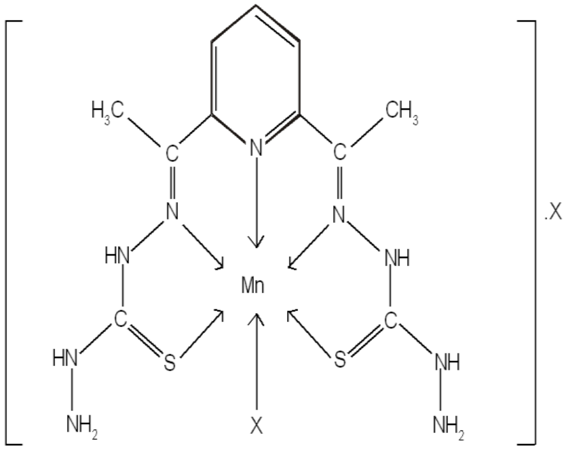


Figure 6: Octahedral geometry of Mn(II) –Schiff base complex (Chandra S, Sharma A K, 2009)

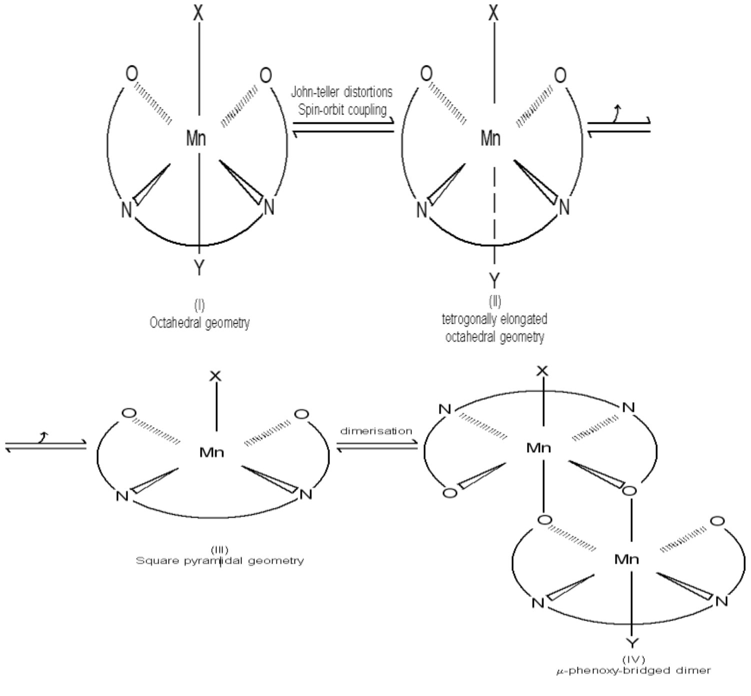


Figure 7: Proposed structure of Schiff base complex (Maneiro et.al,2003).

Iron Complexes

The Fe (II) complex with Schiff base derived from S-methyldithiocarbazate and 5-methyl-2-furfuraldehyde and 2-furyl-methylketone have been studied. The coordination takes place through the thio sulphur after deprotonation with the azomethine nitrogen (Chew et.al, 2004; Tarafdar et.al, 2002). In this way the ligand behaves as uninegatively charged and in bidentate manner. The oxygen of furan ring will not taken part in the coordination. The biological activities of complexes were tested against Candida lypolytica and Aspergillus ochraceous and found more active than standard drug nystatin (Chew et.al, 2004; Tarafdar et.al, 2002). Mixed ligand complexes of iron (II) complexes with Schiff base (derived from pyridine carbaldehyde and trialkoxy aniline) and thiocyanate were synthesized and characterized by various studies. It has been reported that the iron atom was surrounded by six nitrogen atoms belonging to the two NCS group and two bidentate ligands (Figure 8). The complexes posses octahedral geometry and were non-electrolytic in nature (Hayami et.al,2007).

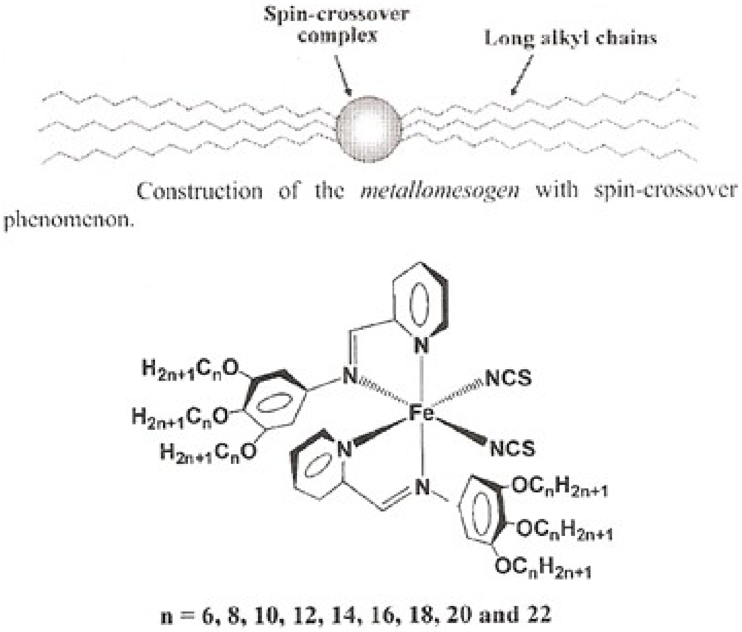


Figure 8: Octahedral complex of Fe(III)- Schiff base (Hayami et.al,2007)

The spin cross over (SCO) phenomenon occurs when transforming between high spin and low spin states reversibly, stimulated by external perturbations (e.g., temperature, pressure, magnetic field or light), when the ligand field strength is comparable to the mean spin-pairing energy. At low temperature, the thermodynamically low spin state, of lowest enthalpy (Kahn O., 1993). While, when the temperature is higher than SCO temperature, the high spin state becomes the thermodynamically stable state. It has been reported that a SCO iron (III) compound ($S = ½ \leftrightarrow S = 5/2$) with liquid crystal properties (Galyametdinov et.al, 2001). This compound consists of an iron (III) ion coordinated to the Schiff base ligands with long alkyl chains are exhibits a rod like geometry. For iron (II) SCO compounds ($S = O \leftrightarrow S = 2$), light induced LS → HS conversion can be observed by illumination. A mechanism for this phenomenon denoted as "light induced excited spin state trapping" (LIESST) has been proposed (Decurtins et.al, 1984; Gutlich et.al, 1994). Iron (II) complex with Schiff base derived from 5, 6-diamino 2-(4,5- bis propylthio-1, 3-dithio-2-ylidene)- benzo-1, 3 - dithiole and salicylaldehyde was synthesized and characterized by various studies (Wu et.al, 2008). Infrared spectrum of the complex showed that there is decrease in the frequencies of azomethine group and phenol group indicating that the nitrogen atom of azomethine group and oxygen of phenolate group are coordinated to the metal ion. The IR spectrum also shows the presence of Fe-O-Fe bond (Oyaizu et.al, 2001). The ligand acts as tetradentate and dibasic in nature. The electronic spectrum of the complex shows square pyramidal geometry. Mossbauer spectroscopy of the complex also indicated high spin Fe (III) ($S = 5/2$) complex (Renz et.al, 2007). The complex has been studied as homogeneous catalyst for a variety of organic transformations and as mimics of natural carriers in recognizing and transporting specific anions or neutral molecules (Takao K, Ikeda Y, 2007). Particular features of interest involve a transition metal's ability to effect catalytic reactions or the binding capacity for small molecules (CO, O_2, NO etc.). Thereby, such studies might generate simple models for biologically occurring metalloproteins and metalloenzymes and help in a deeper understanding of biological system (Cort et.al, 2007).

Binuclear complexes of Fe(II) with Schiff bases derived from 2, 6 – di- isopropyl aniline was synthesized and characterized by various studies (Champouret et.al, 2006). The infrared spectrum of the complex showed that the involvement of azomethine N atom in coordination. The complex is paramagnetic and the value being consistent with two non interacting high spin Fe(II) - Fe(II), S = 2 and 2, respectively. In complex the phenolate oxygen atom bridges the metals and two separate pyridylimine units acting as chelates. Each metal center is further bound by one terminal chloride and one bridging chloride to complete two independent five coordinate geometries (Champouret et.al, 2006). The use of dinucleating ligands as a means to impose close special confinement on two metal centers has been widely documented because of the relevance of the resulting bimetallic complexes to the active sites of a variety of naturally occurring metalloenzymes (Sakiyama et.al, 2001). The complexes were screened as precatalysts for oligomerisation or polymerization of ethylene. Indeed, good catalytic performances have been observed and cooperative effects by the neighboring polymerization - active metal centers have been suggested (Bellc C, Pierrc J L, 2003).

Synthesis and characterization of a Schiff base derived from 2-hydroxy-5-methylacetophenone and glycine and its coordination with compound Fe(II) are described. The ligand is a dibasic tridentate (ONO) donor (Badwal et.al, 2009). The solid state electrical conductivity of ligand and complex have been measured over 313-398 K and the complex was semi conducting. Antibacterial activities of ligand and its complex have been determined by screening the compounds against various gram (+) and gram (-) bacterial strains.

Two new iron(III) complexes [Fe(pythsal I)]Cl_2 and [Fe(pythsalBr)]Cl_2 with the NSNO- donor tetradentate Schiff base ligands pythsalHX[(5-X-N-(2-pyridylethylsulfanylethyl)salicylideneimine](X=I,Br) has been synthesized from the inserted condensation of 1-(2-pyridyl)-3-thia-5-aminopentane with the respective derivative salicylaldehyde (Shabani et.al,2010). Infrared spectral data agreed with the coordination to the central metal ion through deprotonated phenolic oxygen, imine and pyridine type nitrogens and the thioether sulfur atoms. From ligand field spectral data an octahedral geometry was assigned to the iron(III) ion in all these complexes (Figure 9). These new compounds have showed anti tumor activity against two kinds of cancer cells that was K562 (human chronic myeloid leukemia) and Jurkat (human T lymphocyte carcinoma).

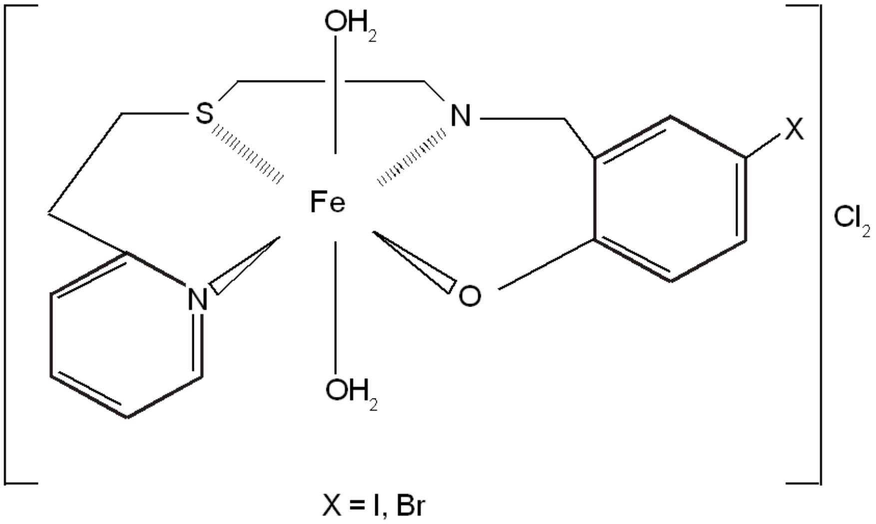


Figure 9: Octahedral geometry of Fe(III) –Schiff base complex (Shabani et.al,2010).

Research Article

Cobalt Complexes

Cobalt is an essential trace element for all animals, as the active center of coenzymes called cobalamins. These include vitamin B_{12} which is essential for mammals. Cobalt is also an active nutrient for bacteria, algae and fungi.

The bioactive Co(II) complex with Schiff base derived from the condensation of furan-2-carbaldehyde and 2-aminobenzoic acid has been synthesized and characterized (Omar et.al, 2006). Coordination takes place through amine N atom, furan ring oxygen and oxygen of carboxyl group forming octahedral geometry (Zayed et.al, 2004). The complex could be applied fairly in the treatment of some common diseases caused by E.coli eg. Septiaemia, Gastroenteritis, urinary tract infections and hospital acquired infections. The pink coloured complex of Co(II) with Schiff base derived from 3-formyl salicylic acid and 1, 2- diamino cyclohexane was prepared and characterized (Lalehzari et.al, 2008). The ligand behaves as tridentate and uninegatively charged with the carboxylic acid group remaining uncoordinated and forms octahedral geometry of the complex (Telfer et.al, 2004). ABC-type ligands can coordinate to a metal center in either a facial (i) or meridional (ii) fashion. The facial mode has 11 possible stereoisomers, whereas the meridional mode has two (Figure 10). Thus, stereo chemical control is more easily achieved for meridional complexes. In this contribution, the coordination of a new chiral Schiff base ligand (iii) does not provide a carboxylate donor when coordinated to a single metal. The complex containing helical species is of great interest because of the similarities to bioinorganic molecules as well as their uses in asymmetric catalysis and supramolecular chemistry (Seitz et.al, 2004).

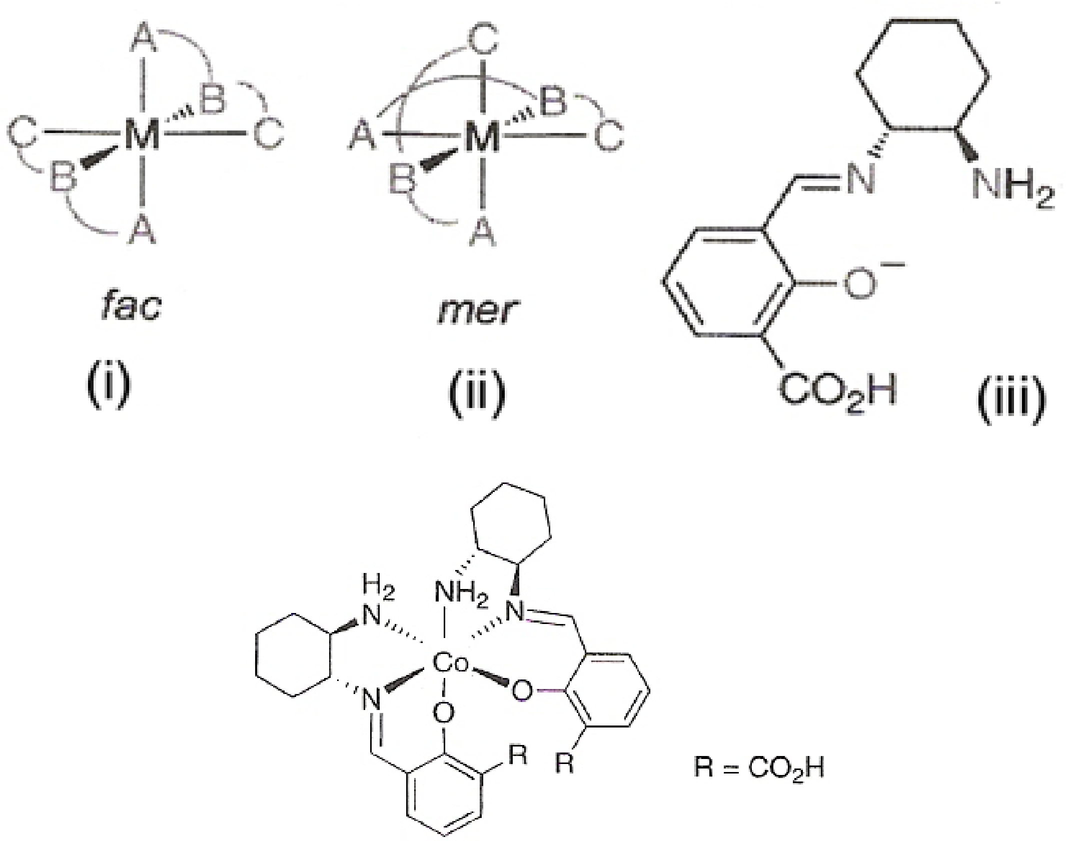


Figure 10: Octahedral Co(II)- Schiff base complexes (Lalehzari et.al, 2008)

The mixed ligand complexes of Co(II) with Schiff base 2, 6- pyridine di-carbaldehyde bis (p-hydroxyphenylamine) and 2-aminopyridine has been studied (Mohamed G G, Abd El-Wahab Z H, 2005). The Schiff base coordinated to the metal ion in a tridentate manner with Pyridine N, two azomethine N, while 2- amino pyridine coordinated to the metal ion via its pyridine N giving octahedral geometry. A large number of mixed-ligands complexes involving heterocyclic bases have been reported due to their bioinorganic applications and thermal stability. The complex had a variety of applications including biological, clinical, analytical and industrial in addition to their important role in catalysis and organic synthesis (Ouyang et.al, 2002 ; Sharghi H, Nasseri M A, 2003). The complex was found to be very active against T-lymphoblastic leukemic cells (CEM-SS). The complex of Co (II) with Schiff base derived from o-hydroxy benzaldehyde, o-hydroxy acetophenone and ethylenediamine has been discussed (Rabie et.al, 2008). Coordination takes place through two phenolic oxygen, two azomethine N atom and two water molecules gives octahedral geometry of the complex. The complex is very useful in bioinorganic chemistry especially in the elucidation of the composition and geometry of the metal ion that binding in the metallo-proteins and enzymes, as catalyst for many reactions and relation to synthetic and natural carriers (Daneshwar et.al, 2003).

The Co(II) complex with Schiff base i.e., disodium [{bis (4-hydroxy-5-sulfo salicylaldehyde)-4, 5-dimethyl-o-phenylenediiminato}cobalt] is being regarded as important material for the use as organic superconductor and photo catalyst (Boghaei D M, Gharagozlou M, 2005). Recent application of the electron donor-acceptor (EDA) complex includes non linear activity, surface chemistry and molecular recognition. The retinal chromophore is bound covalently to the protein via a protonated Schiff base. ATP, CTP, GTP and other nucleoside triphosphates are the principal biological energy store and of great importance in the life science. The nucleotide ATP is one of the four main components of DNA and about one-sixth of all enzyme systems need ATP or a related adenine cofactor. Their biological importance rests on the fact that they function as major carriers of chemical energy in the cells. With this fact properties of nucleotides are receiving much attention. This water soluble cobalt (II) Schiff base complex is very important to determine the properties of nucleotides (Ali et.al, 2004).

A novel Schiff base, N-(4-n-butyl) phenyl pyridoxaldimine, was prepared and formed a complex $[Co(bppyr)_2(H_2O)_2].nH_2O$ with coordination through the azomethine nitrogen and phenolate oxygen (Prasad et.al,2009). Schiff base and metal complex were characterized by various physiochemical techniques. The room temperature magnetic moment of the Co(II) complex (4.35 BM) in conjunction with the color (reddish brown) and electronic spectral data implied a high spin octahedral geometry (Figure 11). The calculated ligand field parameters suggested the covalent nature of M-L bond in the complex. In the complex, the additional bonding sites were provided by two water molecules. The pyridine nitrogen was found to be non-coordinating on the basis of electrochemical and IR spectral data. The proposed structure of the complex is

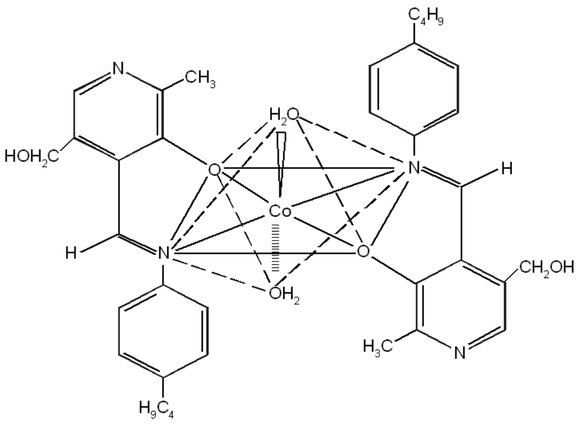


Figure 11: Octahedral geometry of Co(II)-Schiff base complex (Prasad et.al,2009)

Nickel Complexes

Nickel is one of the most toxic among transition metals**.** It shows the toxicity even in low doses to both plants and animals. Excess nasal and lung cancers are known to be associated with the refining of nickel. Epidemiological data and animal study confirm that crystalline nickel compounds are carcinogenic, while amorphous nickel compounds are weak or non-carcinogenic (Swearingen J K, West D X, 2001). The coordination behavior of Ni(II) complex with hexadentate Schiff base (2-hydroxy-benzaldehyde-triethylenetetramine) has been studied (Chantarasiri et.al, 2000). The coordination takes place through phenolic oxygen, azomethine N atom and amino N atom. Electronic and magnetic studies suggested octahedral geometry of the complex. Cross linking of the diglycidyl ether of bisphenol A (DGEBA) with this Ni complex to yield Ni containing epoxy polymer was studied (Chantarasiri et.al, 2000). Since the metal complex is hexadentate the chelation between NH and Ni should be broken to give a free NH which is available for the cross linking reaction. This NH group than opens the epoxide group of DGEBA to give a secondary alcohol. Another NH of the Ni complex or an oxygen of the newly formed secondary alcohol can then attack the epoxy group of another DGEBA molecule. It is found that thermal stability of epoxy polymer can be improved by using this cross linking agent; other good properties of resulting epoxy polymer are high mechanical strength and high deflection temperature (Chantarasiri et.al, 2000). The bioactive orange colored Ni (II) complex with tridentate Schiff base derived from salicylaldehyde and S-benzyldithiocarbazate has been studied (Tarafder et.al, 2000). The Schiff base behaves as a dinegatively charged ligand coordinating through the thiolo sulphur, the azomethine N and hydroxyl oxygen. The fourth site coordinated by water giving square planar structure for the complex. The complex was most effective against Pseudomonas aeruginosa (gram negative bacteria) and Bacillus cereus (gram positive bacteria) (Tarafder et.al, 2000).

Ni(II) complex with tetradentate Schiff base derived from thiosemicarbazide and glyoxal has been studied (Singh N K, Srivastava A, 2000). The infrared spectrum of the complex suggested that the absence of any thiol tautomer, the coordination takes place through four azomethine nitrogen atom and the sulphur atom does not involve in the coordination. The coordination through nitrato group has also been suggesting octahedral geometry. The complex has many applications in pharmacology as it has anticancer, antibacterial antifungal and other biological properties (Singh N K, Srivastava A, 2000). Ni (II) complex with Schiff base derived from 3, 5-di-tert- butylsalicylaldehyde with 1, 3-diaminopropane has been studied. The complexation of ligand through azomethine N atom and phenolic oxygen after deprotonation forms square planar complex (Kasumov et.al, 2005). The complex has achieved a special status in the last decades because of very interesting O_2-binding reactivity, redox chemistry unusual magnetic and structural properties (Kasumov et.al, 2005). The complex has been used recently as catalytically active material to develop surface-modified electrodes for sensoring applications and as source of planar supramolecular building blocks. Ni (II) complex with N, N'-disalicylidene-3, 4-diamino toluene has been studied (Klein et.al, 2000). The complex is diamagnetic in nature and gives square planar geometry. The ^{1}H NMR spectra of the Schiff base indicated the presence of two azomethine groups, as two signals are recorded for the azomethine protons. The ^{1}H NMR spectra of complex showed a down -field shift in the frequency of azomethine protons suggested coordination of the metal ion to both groups. In complex no signals is recorded for phenolic hydrogen in the 12-13.5 ppm region, as in the case of the Schiff base indicating deprotonation of the orthohydroxyl groups (Garg B S, Kumar D N, 2003). The complex has potential biological interest, being used as successful models of biological compounds. Complex has also been used in catalytic reactions (Alexiou et.al, 2005). Nickel(II) complexes, having the general composition $Ni(L)_2X_2$, have been synthesized [where L: isopropyl methyl ketone semicabazone(LLA), isopropyl methyl ketone thiosemicarbozone (LLB), 4-aminoacetophenone semicarazone(LLC) and 4-aminoacetophenone thiosemicarbozone(LLD) and X = Cl , 1/2SO_4]. All the nickel complexes have been characterized by elemental analysis, magnetic moments and spectral studies. All the complexes were found to have magnetic moments corresponding to two unpaired electrons. The possible geometry (Figure 12) of the chloro complexes of semi carbazone was assigned on the basis of spectral studies.

Newly synthesized ligands and its nickel (II) complexes have been screened against different bacterial and fungal growth (Chandra S, Gupta K L, 2005).

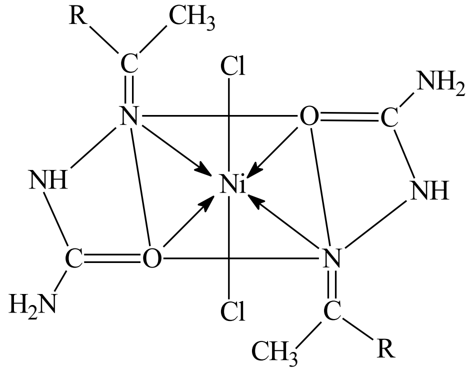


Figure 12: Octahedral geometry of Ni(II)-Schiff base complex (Chandra S, Gupta K L, 2005)

Copper Complexes

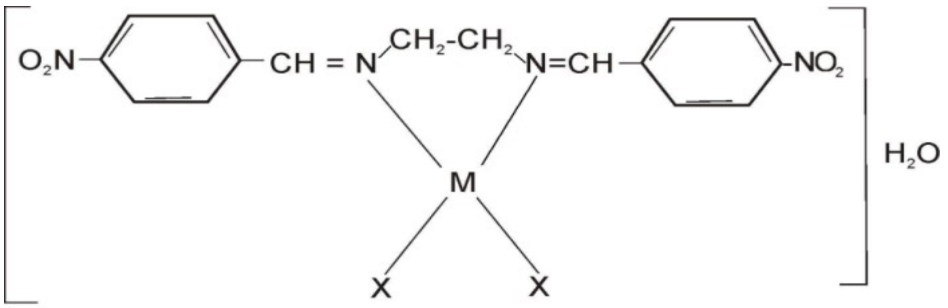
Copper is an important trace element for plants and animals and is involved in mixed ligand complex formation in a number of biological processes. Copper complexes containing Schiff base ligands are of great interest since they exhibit numerous biological activities such as anti tumor, anticandida (Saha et.al,2004), antimicrobial activities, etc. It has been reported that some copper complexes inhibit cellular proteasome and cause inhibition of cancer cell growth (Chen et.al, 2006).

The Cu(II) complex of Schiff base is important in catalysis and acts as model in bioinorganic system because of charge symmetry and the possible fine-tuning of the electronic properties, originating from the different substitutions, can create active sites with potential regioselective molecular recognition, as suggested by the head-to-tail arrangements of the molecules found in the crystal structures (Rigamanti et.al, 2006; Huber et.al, 2005). Cu (II) complex with Schiff base derived from 5-nitro-salicylaldehyde and ethylene diamine suggests coordination through azomethine N atom and phenolic oxygen after deprotonation (Rigamanti et.al, 2006; Huber et.al, 2005). The Copper complex offered a large variety of molecular structures and electronic properties as well as the possibility of enhancing, or 'switching on' the NLO (nonlinear optical) properties of the organic ligands through complexation to a metal center (Costes et.al, 2005). Cu (II) complex with Schiff base (salicylaldehyde-amino ethanol) and phenanthroline base has suggested square pyramidal geometry (Dhar et.al, 2006). The Schiff base coordinates in tridentate manner through ONO system, while heterocyclic base in bidentate manner through N- N system (Dhar et.al, 2006). The complex exhibits visible light-induced cleavage of double standard DNA and thus is of current importance for therapeutic applications (Chifotides H T, Durbar K R, 2005; Karidi et.al, 2005). The photo excited electronic state of complex initiates a series of chemical reactions that lead to the oxidative cleavage of the nucleic acid. The compound exhibits red-light-induced photo cleavage of DNA and has found clinical applications in the emerging field of Photodynamic therapy [PDT] of various cancers (Clarke M J, 2003; Henderson B W, 2000) and hepatotoxicity.

The brown colored Cu(II) complex with Schiff base derived from 4-aminoantipyrine and 2-hydroxy-1-naphthaldehyde has been characterized (Raafat et.al, 2005). The ligand is monobasic and tridentate in nature forms complex through azomethine nitrogen, antipyrine ring oxygen, phenolic oxygen after deprotonation and acetate ion forming square planar geometry. The complex exhibits wide applications in biological system and industrial uses, especially in catalysis and dying. Cu (II) complexes with two flexible Schiff bases, bis-[(N, N' -3, 5-di-tert-butylsalicylidene)-4, 4'-diaminodiphenyl] ether and bis-[(N,N'-3-tert-butyl-5-methylsalicylidene) 4, 4'-diaminodiphenyl] ether were prepared in high yields and their structures were determined by x-ray single-crystal diffraction (Chu Z, Huang W, 2007). Infrared spectrum of the complexes shows coordination through azomethine nitrogen atom and deprotonated phenolic oxygen atom. The x-ray structure shows clearly that complex is a double helical structure. The neutral helix contains two Cu(II) ions and two deprotonated ligands with the Cu....Cu separation, that is shorter than other analogous Schiff base dinuclear Cu (II) complexes (Kruger et.al, 2001). Each copper center is bonded to two salicyladimine units to attain pseudo-tetrahedral coordination geometry. The complexes have attracted much attention because of the fundamental role of helicity in biology and the potential applications in the fields of asymmetric catalysis and non-linear optical materials (Hamacek et.al, 2006). A new macrocyclic ligand was synthesized by reaction of 2, 6-diaminopyridine and 1,7-bis(2-formylphenyl)-1,4,7-trioxaheptane. Its Cu(II) complex was synthesized by template effect is binuclear. The comparative electrochemical study shows that the complex exhibited a quasi-irreversible reduction process in DMSO solution (Iihan et.al, 2007).

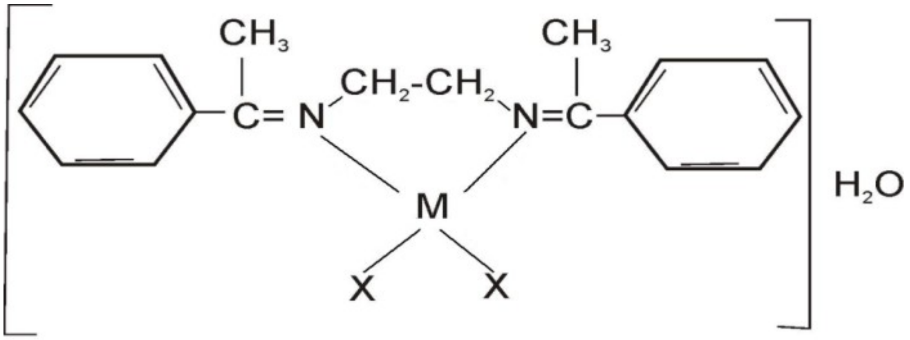
Zinc Complexes

In recent years metal compounds, which have a stable d^{10} electronic configuration, have received a lot of attention in the fields of inorganic chemistry, biochemistry and environmental chemistry. About twenty zinc enzymes are known in which zinc is generally tetrahedrally four coordinate and bonded to hard donor atoms such as nitrogen (Marchettic et.al, 1999). Zinc complexes have been shown to be active as antitumor, anti-HIV and antimicrobial agents (Sheng et.al, 2008; Kaczmareka et.al, 2009; Cowley et.al, 2005; Koike et.al, 1996). Zn(II) complexes with Schiff bases derived from 4-nitrobezaldehyde/acetophenone and ethylenediamine were prepared and characterized by different physicochemical studies (Prakash et.al, 2010). Metal complexes are found to be monomer and tetrahedrally coordinated (Figure 13-14). The antimicrobial data reveal that the Zn(II) complexes are more bioactive than the free ligands against E. coli and S. aureus. The enhanced activity of the complexes may be ascribed to the increased lipophilic nature of the complexes arising due to chelation.



Here M = Zn(II) , X = $CH_3CO_2^-$

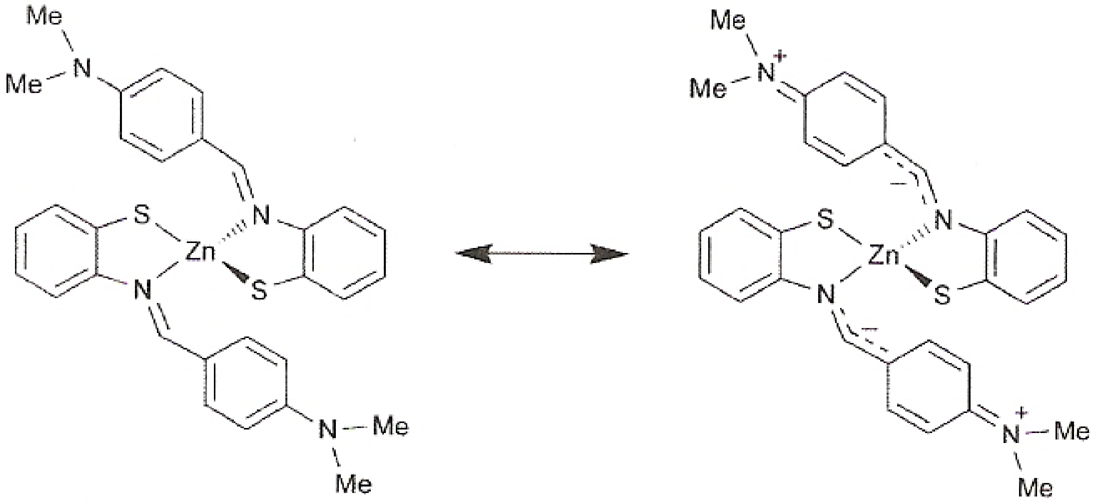
Figure 13: Tetrahedral structure of Zn(II)- Schiff base complexes (Prakash et.al, 2010)



Here M = Zn(II) , X = $CH_3CO_2^-$

Figure 14: Tetrahedral structure of Zn(II)- Schiff base complexes (Prakash et.al, 2010)

The distorted tetrahedral geometry complex has been suggested for Zn (II) with the benzothiazoline derived from 2-aminobenzenethiol and N, N□-dimethyl-4-amino benzaldehyde (Kawamoto et.al, 2008). The ligand reacts in dibasic and bidentate manner. The coordination takes place through two thiolato sulphur and two imino nitrogen atoms from two Schiff base ligands (Scheme 2).



Scheme 1.2: Resonance in Zn(II) – Schiff base complex (Kawamoto et.al, 2008)

The azomethine C = N bond distanc

) between the nitrogen atom of the dimethylamino group and the aromatic carbon atom are relatively short as a C-N single bond, and the sum of the angles around each nitrogen atom is close to 360°. Therefore, the resonance contribution is considered to the ligand structure of the complex. Zn (II) complex with benzothiazole is luminescent and has been used as an effective emitting layer. Bowl-shaped complex of Zn(II) with Schiff base diformyldihydroxybenzene - diethoxyphenylenediamine has been studied (Ma et.al, 2004). On metalation, coordination takes place through phenolic oxygen atom and azomethine nitrogen atom. In this way ligand is behaved in tetradentate and dibasic in nature. Electrospray ionization mass spectrometry of the complex indicated the formation of trimetalated macrocycle ring and bowl shaped structure (Gullant et.al, 2006). The molecule has a bowl shape with nearly C_{3v} symmetry. The side of the bowl is formed by a trimetalated macrocycle with three Zn(II) ions in square-pyramidal geometry (Yu et.al, 2006).

The molecule possess a bowl-shaped interior that contains Zn(II) ions with accessible coordination sites inside the bowl, as indicated by single-crystal x-ray diffraction structure of the complex (Alexious et.al, 2005). The presence of vacant coordination sites within the bowl makes these attractive as site constrained crystals, and as mimics of Zn-containing enzymes, such as carbonic anhydrase.

A new Schiff base 2-aminophenol-pyrrole-2-carbaldehyde and its Zn(II) complex has been synthesized and characterized (Singh et.al, 2010). The ligand behaving in monobasic tridentate manner and deprotonation of phenolic hydroxyl group takes place during complexation (Figure 15). The Zn complex showed better activity against E. coli and S. aureus. The presence of N and O donor groups in the ligand and complex inhibited enzyme production because enzymes that require free hydroxyl group for their activity appear to be especially susceptible to deactivation by the metal ion of complexes.

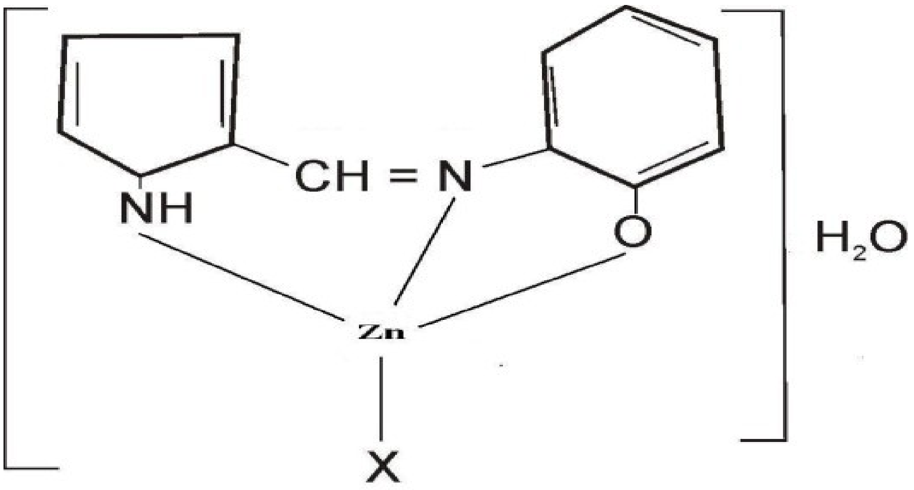


Figure 15: Structure of Zn(II) – Schiff base complex (Singh et.al, 2010)

Mixed ligand complexes have been extensively studied in solution as well as in the solid state. Ternary complexes are found to be more stable than binary complexes. Mixed ligand complex of Zn(II) with [N-(salicylidine) sulphabenzamide] (LH) and 1, 10 phenanthroline (phen) has been studied (Mourya et.al, 2007). Thermal analysis indicates the presence of coordinated water molecule in the complex. The presence of CH_3COO^- in the coordination sphere (Mourya et.al, 2003) and the coordination of azomethine nitrogen and phenolic oxygen after deprotonation have been confirmed. Steric effect and back donation have also been involved to account for the preferred formation of mixed ligand complexes. The metal complexes of Schiff bases derived from sulfa drugs have gained considerable importance due to their pronounced biological activity (Raman et.al, 2002). They have been found to posses effective fungicidal activity.

ACKNOWLEDGEMENT

B K Singh is thankful of Council of Scientific and Industrial Research (CSIR) New Delhi, and University Grants Commission, New Delhi India for financial assistance.

REFERENCES

Abd EI-Wahab Z H, EI-Sarrag M R (2004) Derivatives of phosphate Schiff base transition metal complexes: synthesis, studies and biological activity, *Spectrochim. Acta Part A* **60** : 271.

Alexiou M, Katsoulakou E, Dendrinou C, Raptopoulou C P (2005) Di-2-pyridyl Ketone Oxime in Zinc Chemistry: Inverse 12-Metallacrown-4 Complexes and Cationic Pentanuclear Clusters(10) *European Journal of Inorganic Chemistry.*1964.

Ali S A (2007) Reactions of group 6 metal carbonyls with salicylaldehyde isonicotinic acid hydrazone, *Journal of Coordination Chemistry.* **60**(24) : 2739.

Ali S A, Soliman A A, Aboaly M M, Ramadan R M (2002) Chromium, Molybdenum and Ruthenium Complexes of 2-Hydroxyacetophenone Schiff Bases, *Journal of Coordination Chemistry.* **55**(1): 1161.

Ali S R, Kamaluddin J A (2004) Interaction of ribose nucleotides with metal ferrocyanides and its relevance in chemical evolution, *Colloid Surf. A : Physico –Chem, Eng. Aspects* **236** : 165.

Ali S.A., Mohamed H.A., Ramadan R.M. (2006) Novel chromium and molybdenum complexes of a dimerized isonicotinic acid hydrazide, *Journal of Coordination Chemistry*. **59**(5) : 467.

Al-Shihri A S (2004) Synthesis, characterization and thermal analysis of some new transition metal complexes of a polydentate Schiff base, *Spectrochim. Acta A* **60**(5) : 1189.

Aranha P E, Santos M P dos, Romer's, Docker (2007) Synthesis, characterization, and spectroscopic studies of tetradentate Schiff base chromium(III) complexes, *Polyhedron* **26**(7) : 1373.

Badwaik V B, Deshmukh R D, Aswar A S(2009) Transition metal complexes of a Schiff base: synthesis, characterization, and antibacterial studies, *Journal of Coordination Chemistry* .**62**(12) : 2037.

Bandini M, Cozzi P G, Umani-Ronchi A (2000) Salen as a Chiral Activator: *anti* versus *syn* Switchable Diastereoselection in the Enantioselective Addition of Crotyl Bromide to Aromatic Aldehydes *Angewandte Chemie International Edition* **39**(13): 2327.

Belle C, Pierrc J L (2003) Asymmetry in Bridged Binuclear Metalloenzymes: Lessons for the Chemist *European Journal of Inorganic Chemistry* 4137.

Bernhardt P V, Bozoglian F, Macpherson B P, Martinz M (2005) Structural and Spectroscopic Models of the [iron-iron]-hydrogenase Enzyme Coordination Chemistry Reviews **249**: 1902.

Bhargavi G, Rajasekharan M V, Tuchagues J P (2009) Antiferromagnetic interactions through phenoxo bridges and lattice water: Synthesis, structure, and magnetic properties of new Mn(III) Schiff base complexes in combination with thiocyanate ligand, *Inorganica Chimica Acta* **362**(9): 3247.

Bhendkar A K, Vijay K, Raut A W (2004) Synthesis of some novel Schiff bases of 2- aminopyrimidine and their antimicrobial activity. *Acta ciencia indica* (*chemistry*) **30**: 29.

Boghaei D M, Gharagozlou M (2005) Spectrophotometric studies of molecular complex formation between water-soluble cobalt(II) Schiff base complex and nucleotides in mixed solvent systems, *Spectrochim. Acta A* **61**(13-14): 3061.

Cai Y P, Su C Y, Xu A W, Kang B S, Tong Y X, Liu H Q, Jie S (2001) Syntheses and characterization of copper(II) complexes of bis(acetylacetone)trimethylenediimine , *Polyhedron* **20(7-8)** : 657.

Champouret Y D M, Fawcett J, Nodes W J, Singh K, Solan G A (2006) Spacially Confined M2 Centers (M = Fe, Co, Ni, Zn) on a Sterically Bulky Binucleating Support: Synthesis, Structures and Ethylene Oligomerization Studies, *Inorg. Chem.* **45(24)** : 9890.

Champouret Y D M, Marcchal J D, Dadhiwala T, Faweett J, Palmer D, Singh K, Solan G A (2006) Mono- vs. bi-metallic assembly on a bulky bis(imino)terpyridine framework: a combined experimental and theoretical study,*Dalton Trans.* **19:** 2350.

Chandra S, Gupta L K (2005)_Spectroscopic and biological studies on newly synthesized nickel(II) complexes of semicarbazones and thiosemicarbazones, *Spectrochim. Acta A Mol Biomol Spectrosc,* **62(4-5)**: 1089.

Chandra S, Sharma A K (2009) Biological and spectral studies of transition metal complexes with a quinquedentate Schiff base, 2,6-diacetylpyridine bis(thiocarbohydrazone), *J Coord. Chem.* **62(22)** : 3688**.**

Chantarasiri N, Tuntulani T, Chanma N (2000) Application of hexadentate Schiff base metal complexes as crosslinking agents for diglycidyl ether of bisphenol A, *Eur. Polymer J* **36(5)** : 889.

Chantarasiri N, Tuntulani T, Tongraung R, Magee R S, Wannarong W (2000) New metal-containing epoxy polymers from diglycidyl ether of bisphenol A and tetradentate Schiff base metal complexes, *Eur. Polym. J* **36(4)** : 695.

Chen D, Cui C Q Z, Yang H J, Dou Q P (2006) A Clinically Used Anti-Alcoholism Drug and Copper-Binding Agent, Induces Apoptotic Cell Death in Breast Cancer Cultures and Xenografts via Inhibition of the Proteasome Activity, *Cancer Res.* **66** : 10425.

Chew K B, Tarafder M T H, Crouse K A, Ali A M, Yamin B M, Fun H K (2004) Synthesis, characterization and bio-activity of metal complexes of bidentate N-S isomeric Schiff bases derived from S-methyldithiocarbazate (SMDTC) and the X-ray structure of the bis[S-methyl-b-N-(2-furyl-methylketone)dihitocarbazato]cadmium(II) complex, *Polyhedron* **23** : 1385.

Chifotides H T, Durbar K R (2005) Interactions of metal-metal-bonded antitumor active complexes with DNA fragments and DNA, *Acc. Chem. Res.* **38(2)** : 146.

Chu Z, Huang W (2007) Syntheses and structures of two new bis-N,O-bidentate Schiff base ligands and their respective copper(II) complexes with dinuclear double-helical configuration, *J Mol. Struct.* **837(1-3)** : 15.

Clarke M J (2003) Ruthenium metallopharmaceuticals, *Coord. Chem. Rev.* **236(1-2)** : 209.

Cort A D, Mandolini L, Pasquini C, Rissanen K, Russo L, Schiaffino L (2007) Zinc–salophen complexes as selective receptors for tertiary amines, *New J Chem.* **31(9)** : 1633.

Costes J P, Lamere J F, Lepetit C, Lacroix P G, Dahan F, Nakatani K (2005) Synthesis, crystal structures, and nonlinear optical (NLO) properties of new Schiff-base nickel(II) complexes. Toward a new type of molecular switch?, *Inorg. Chem.* **44** : 1973.

Coughlin P K, Lippard S J (1984) Copper(II) chemistry in hexaaza binucleating macrocycles: hydroxide and acetate derivatives, *J Am. Chem. Soc.* **106(8)** : 2328.

Cowley A. R., Davis J., Dilworth J. R., Donnelly P. S., Dobson R., Nightingale A., Peach J. M., Shore B, Kerr D, Seymour L (2005) Fluorescence studies of the intra-cellular distribution of zinc bis(thiosemicarbazone) complexes in human cancer cells, *Chem. Comm.* 845.

Daneshwar N, Entezami A A, Khandar A A, Saghatforoush L A (2003) Synthesis and characterization Of Copper(II) complexes with dissymmetric tetradentate Schiff base ligands derived from aminothioether pyridine. crystal structures of [Cu(PYTISAL)]ClO_4·0.5CH_3OH AND [Cu(PYTAZOSAL)]ClO_4, *Polyhedron* **22(11)** : 1437.

Dash S C, Brahma C S, Das R, Das N N, Mohanty P (2006) Synthesis, characterisation and substitution reaction of trans-(diaqua) (N,N '-ethylene-bis-salicylamide)chromium(III) ion, *Ind. J Chem.* **45 A** : 2406.

Decurtins S, Gutlich P, Kohler C P, Spiering H, Hauser A (1984) Light-induced excited spin state trapping in a transition-metal complex: The hexa-1-propyltetrazole-iron (II) tetrafluoroborate spin-crossover system, *Chem. Phys. Lett.* **105(1)**:1-4.

Dhar S, Nethaji M, Chakravarty R (2006) DNA Cleavage on Photoexposure at the d-d Band in Ternary Copper(II) Complexes Using Red-Light Laser, *Inorg. Chem.* **45** : 11043.

Duboc C, Astier-Perret V,Chen H,Pecuat J,Crebtree R H, Brudvig G W,Collomb M N (2006) A multifrequency high-field EPR (9–285 GHz) investigation of a series of dichloride mononuclear penta-coordinated Mn(II) complexes *Inorg. Chim. Acta* 359(5) : 1541.

El-Medani S M, Ali O A M, Ramadan R M (2005) Photochemical reactions of group 6 metal carbonyls with N-salicylidene-2-hydroxyaniline and bis-(salicylaldehyde)phenylenediimine, *J Mol. Struc.* **738** : 173.

Frausto da Silva J, Williams R (1991) The Biological Chemistry of the Elements, *Clarendon Press, Oxford*.

Galyametdinov Y, Kscnofontov V, Prosvirin A, Ovchinnikov I, Ivanova G, Gitlich P, Haase W (2001) First Example of Coexistence of Thermal Spin Transition and Liquid-Crystal Properties *Angew. Chem. Int. Ed.* **40(22)** : 4269.

Garg B S, Kumar D N (2003) Spectral studies of complexes of nickel(II) with tetradentate schiff bases having N2O2 donor groups, *Spectrochim. Acta A* **59** : 229.

Gembicky M, Baran P, Boca R, Fucess H, Svoboda I, Valko M (2000) An unexpected dinuclear Mn(II,III) complex of an asymmetric macrocyclic ligand with a mono-arm *Inorg. Chim. Acta* **303:**175

Gradinaru J, Forni A, Druta V, Tessore F, Zecchin S, Quici S, Garbalau N (2007) Structural, spectral, electric-field-induced second harmonic, and theoretical study of Ni(II), Cu(II), Zn(II), and VO(II) complexes with [N2O2] unsymmetrical schiff bases of S-methylisothiosemicarbazide derivatives, *Inorg. Chem.* **46(3)** : 884.

Gallant A J, Chong J H, Mark J, Lachlan M (2006) Heptametallic Bowl-Shaped Complexes Derived From Conjugated Schiff-base Macrocycles: Synthesis, Characterization, and X-ray Crystal Structures, *Inorg. Chem.* **45** : 5248.

Gutlich P, Hauser A, Spiering H (1994) Thermal and Optical Switching of Iron(II) Complexes, *Angew. Chem. Int. Ed.* **33(20)** : 2024.

Hamacek J, Borkovec M, Piguet C (2006) Simple Thermodynamics for Unravelling Sophisticated Self-assembly Processes, *Dalton Trans,***12**: 1473.

Hayami S, Motokawa N, Shuto A, Masuhara N, Someya T, Ogawa Y, Inoue K, Maeda Y (2007) Photoinduced spin transition for Iron(II) compounds with liquid-crystal properties**,** *Inorg. Chem.* **46**(5): 1789.

Henderson B W (2000) Photofrin photodynamic therapy can significantly deplete or preserve oxygenation in human basal cell carcinomas during treatment, depending on fluence rate, *Cancer Res.* **60** : 525.

Herchel R, Boca R, Gembicky M, Falk K (2007) Magnetic properties of a manganese(II) trinuclear complex involving a tridentate Schiff-Base ligand, *Inorg.Chem.* **46(5)** : 1544.

Huber A, Muller L, Elias H, Klement R, Valko M (2005) Cobalt(II) Complexes with Substituted Salen-Type Ligands and Their Dioxygen Affinity in N,N-Dimethylformamide at Various Temperatures, *Eur. J Inorg. Chem.***8:** 1459.

Ilhan S, Temel H, Yilmaz I, Sekerci M (2007) Synthesis and characterization of new macrocyclic Schiff base derived from 2,6-diaminopyridine and 1,7-bis(2-formylphenyl)-1,4,7-trioxaheptane and its Cu(II), Ni(II), Pb(II), Co(III) and La(III) complexes, *Polyhedron* **26(12)** : 2795.

Kaczmareka M T, Jastrzaba R, Holderna- Kedziab E, Radecka- Paryzek W (2009) *Inorg Chim. Acta* DOI:10.1016/j.ica.2009.02.012.

Kahn O (1993) Chemistry and physics of supramolecular magnetic material,*Molecular Magnetism, VCH, New York.*

Kaim W, Schwederski B (1996) “Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life”, *Wiley, NewYork.*

Karidi K, Garoufis A, Tsipis A, Reedijk J (2005) Synthesis, characterization, in vitro antitumor activity, DNA-binding properties and electronic structure (DFT) of the new complex cis-(Cl,Cl)[RuIICl2(NO+)(terpy)]Cl,*Dalton Trans.*7: 1176.

Kasumov V T, Ozalp-Yaman S, Tas E (2005) Synthesis, spectroscopy and electrochemical behaviors of nickel(II) complexes with tetradentate shiff bases derived from 3,5-Bu(2)(t)-salicylaldehyde, *Spectrochim. Acta A* **62(1-3)** : 716.

Kawamoto T, Nishiwaki M, Tsunekawa Y, Nozaki K, Konno T (2008) Synthesis and Characterization of Luminescent Zinc(II) and Cadmium(II) Complexes with N,S-Chelating Schiff Base Ligands, *Inorg. Chem.* **47**: 3095.

Khandar A A, Hosseini-Yazdi S A, Zarei S A, Rabie U M (2005) Synthesis, characterization and X-ray crystal structures of copper(II) and nickel(II) complexes with potentially hexadentate Schiff base ligands, *Inorg. Chim. Acta* **358**(11): 3211.

Kilic A, Tas E, Deverec B, Yilmaz I (2007) Synthesis, electrochemical and *in situ* spectroelectrochemical studies of new transition metal complexes with two new Schiff-bases containing N_2O_2/N_2O_4 donor groups
Polyhedron **26** : 4009.

Klein L J, Alleman K S, Peters D G, Karty J A, Reilly J P (2000) Catalytic reduction of ethyl chloroacetate by cobalt(I) salen electrogenerated at vitreous carbon cathodes, *J Electroanal. Chem.***481**(1): 24.

Koike T, Takashige M, Kimura E, Fujioka H, Shiro M (1996) Bis(ZnII–cyclen) Complex as a Novel Receptor of Barbiturates in Aqueous Solution, *Chem. Eur. J* **2**(6) : 617.

Kruger P E, Martin N, Nieuwenhuyzen M (2001) Dinuclear double helicates with a twist: synthesis, structure and supramolecular entanglement in $[M_2L_2]$ metallo-helices {M = Co(II), Cu(II), H_2L = bis(*N*-salicylidene-4,4′-diaminodiphenyl)methane}*,J,Chem. Soc.,Dalton Trans***. 13***:*1966.

Kumar R, Chandra S (2007) Spectroscopic techniques and cyclic voltammetry with synthesis: Manganese(II) coordination stability and its ligand field parameters effect on macrocyclic ligands**,** *Spectrochim. Acta A* **67**(1) : 188.

Kwiatkowski E, Romanowski G, Nowicki W, Kwiatkowski M (2006) Dioxovanadium(V) complexes of Schiff bases derived from *S*-(+)-2-(aminomethyl)pyrrolidine and aromatic *o*-hydroxycarbonyl compounds: Synthesis, characterization and structure, *Polyhedron* **25**(15) : 2809.

Lacroix P G (2001) Second-Order Optical Nonlinearities in Coordination Chemistry: The Case of Bis(salicylaldiminato)metal Schiff Base Complexes, *Eur. J Inorg. Chem,***2001**(2): 339.

Lalehzari A, Desper J, Christopher J, Levy J (2008) Double-Stranded Monohelical Complexes from an Unsymmetrical Chiral Schiff-Base Ligand, *Inorg. Chem.* **47**: 1120.

Li Z K, Liang L, Yang L, Chem H, Zhou X G (2005) Asymmetric epoxidation catalyzed by Cr(III)-binaphthyl Schiff base complexes**,** *J Mol. Catal. A* **235(1-2)** : 108.

Ma C, Lo A, Abdolmalcki A, Lachlan M M (2004) Synthesis and Metalation of Novel Fluorescent Conjugated Macrocycles *J Org. Lett.* 6: 3841.

Malinowska M, Kwiatkowski P, Jurczak J (2004) The enantioselective high-pressure Diels–Alder reaction of 1-methoxybuta-1,3-diene with tert-butyldimethylsilyloxyacetaldehyde catalyzed by (salen)Co(II) and (salen)Cr(III)Cl complexes, *Tetrahed. Lett.* **45**(41): 7693.

Maneiro M, Bermejo M R, Fernandez M I, Forneas E G, Noya A N M G, Tyryshkin A M (2003) A new type of manganese-Schiff base complex, catalysts for the disproportionation of hydrogen peroxide as peroxidase mimics*, New J Chem.* **27**(4) : 727.

Marchettic F, Pettinari C, Pettinari R, Cingolani A, Leanesi D, Lorenotti A (1999) Group 12 metal complexes of tetradentate N_2O_2–Schiff-base ligands incorporating pyrazole: Synthesis, characterisation and reactivity toward S-donors, N-donors, copper and tin acceptors *Polyhedron* **18**(23): 3041.

Maurya M R, Kumar A, Ebel M, Rehder D (2006) Synthesis, Characterization, Reactivity, and Catalytic Potential of Model Vanadium(IV, V) Complexes with Benzimidazole-Derived ONN Donor Ligands *Inorg. Chem.* **45**: 5924.

Mohamed G G (2006) Synthesis, characterization and biological activity of bis(phenylimine) Schiff base ligands and their metal complexes, *Spectrochim. Acta A* **64**(1): 188.

Mohamed G G, Abd El-Wahab Z H (2005) Mixed ligand complexes of bis(phenylimine) Schiff base ligands incorporating pyridinium moiety Synthesis, characterization and antibacterial activity, *Spectrochim. Acta A* **61**(6) : 1059.

Mourya R C, Rajput S (2006) Oxovanadium(IV) complexes of bioinorganic and medicinal relevance: Synthesis, characterization and 3D molecular modeling and analysis of some oxovanadium(IV) complexes involving the O, N-donor environment of pyrazolone-based sulfa drug Schiff bases, *J Mol. Struct.* **794**(1-3): 24.

Mourya R C, Chourasia J, Sharma P (2007) Synthesis, characterization and 3D molecular modeling of some ternary complexes of Cu(II), Ni(II), Co(II), Zn(II), Sm(III), Th(IV) and UO_2(VI) with Schiff base derived from the sulfa drug sulfabenzamide and 1,10-phenanthroline*, Ind. J Chem.* **46A**(10) : 1594.

Omar M M, Mohamed G G, Hindy A M M (2006) Transition metal complexes of heterocyclic Schiff base, *J Therm. Anal. Cal.* **86**(2) : 315.

Ouyang X M, Fei B L, Okamuro T A, Sun W Y, Tang W X, Veyama N (2002) Synthesis, crystal structure and superoxide dismutase (SOD) activity of novel seven-coordinated manganese(II) complex with multidentate di-schiff base ligands, *Chem. Lett.***3:** 362.

Oyaizu K, Dewi E L, Tsuchida E (2001) A μ-oxo diiron(III) complex with a short Fe–Fe distance: crystal structure of (μ-oxo)bis[*N*,*N*′-*o*-phenylenebis(salicylideneiminato)iron(III)], *Inorg. Chima. Acta* **321**(1-2): 205.

Phaniband M A, Dhumwad S D (2007) Synthesis, characterization and biological studies of Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} complexes of Schiff bases derived from 4-substituted carbostyrils[quinolin2(1H)-ones], *Trans. Met. Chem.* **32**(8): 1117.

Prakash A, Singh B K (2010) Complexation Behaviour of Transition Metal
Ions with Schiff bases, *Int. J Pure Applied Chem.* **5**(4): 291.

Prakash A, Singh B K, Bhojak N, Adhikari D (2010) Synthesis and characterization of bioactive zinc(II) and cadmium(II) complexes with new Schiff bases derived from 4-nitrobenzaldehyde and acetophenone with ethylenediamine, *Spectrochim. Acta A* **76**(3-4): 356.

Prakash A, Singh B K, Rajour H K, Bhojak N (2010) Synthesis, Characterization and bioactivities of new Schiff bases with Main group metal ions *Main Group Met. Chem*. **33**(4-5): 183.

Prasad A, Rao C P, Mohan S, Singh A K, Prakash R, Rao T R (2009) *Synthesis and Reactivity in Inorganic, Metal-Organic,and Nano-Metal Chemistry* **39**: 129.

Raafat M I, Abdulla M K, Rizk H F (2005) UV–vis, IR and ^{1}H NMR spectroscopic studies of some Schiff bases derivatives of 4-aminoantipyrine, *Spectrochim. Acta A* **62**(1-3): 621.

Rabie U M, Assran A S A, Abou-El- Wafa M H M (2008) Unsymmetrical Schiff bases functionalize as bibasic tetradentate (ONNO) and monobasic tridentate (NNO) ligands on complexation with some transition metal ions, *J Mol. Struct.* **872**(2-3): 113.

Raman N, Kulandaisamy A, Jeyasubramanian K (2002) Synthesis, spectral, redox and biological studies of some Schiff base copper(II), nickel(II), cobalt(II), manganese(II), zinc(II) and oxovanadium(II) complexes derived from 1-phenyl-2,3-dimethyl-4(4-iminopentan-2-one) pyrazol-5-one and 2-aminophenol/2-amino- thiophenol, *Ind. J Chem.* **41A**(5): 942.

Renz F, Hill D, Klein M, Hefner J (2007) Unprecedented multistability in dodecanuclear complex compound obsereved by Mössbauer spectroscopy, *Polyhedron* **26**: 2325.

Rigamanti L, Demartin F, Forni A, Righetto S, Pasini A (2006) Copper(II) Complexes of salen Analogues with Two Differently Substituted (Push−Pull) Salicylaldehyde Moieties. A Study on the Modulation of Electronic Asymmetry and Nonlinear Optical Properties**,** *Inorg. Chem.* **45**(26): 10976.

Roy S, Mandal T N, Barik A K, Gupta S, Butcher R J, Nethaji M, Kar S K (2008) Syntheses, characterization and X-ray crystal structures of Co(III) and Mn(II) complexes of pyrimidine derived Schiff base ligands, *Polyhedron* **27**(2): 593.

Saha D K, Sandbhor U, Shirisha K, Paddye S, Deobagkar D, Ansond C E, Powell A K (2004) A novel mixed-ligand antimycobacterial dimeric copper complex of ciprofloxacin and phenanthroline, *Bioorg. Med. Chem. Lett.* **14**(12): 3027.

Sakiyama H O, Ito R, Kumagai H, Inoue K, Sakamoto M, Nishida Y, Yamasaki M (2001) Dinuclear Cobalt(II) Complexes of an Acyclic Phenol-Based Dinucleating Ligand with Four Methoxyethyl Chelating Arms − First Magnetic Analyses in an Axially Distorted Octahedral Field, *Eur. J Inorg. Chem.,* **8:** 2027.

Schiff H (1864) Synthesis of Sciiff Bases. *Ann. Suppl*. **3**: 343.

Seitz M., Kaiser A., Stempfhuber S., Zabel M., Reiser O. (2004) Helical, nonracemic inorganic-organic hybrid polymers of cadmium halides with pentadentate bis(oxazoline) ligands, *J. Am. Chem. Soc*. **126**(37): 11426.

Shabani F, Saghatforoush L A, Ghammamy S (2010) Synthesis, characterization and anti-tumour activity of iron(III) Schiff base complexes with unsymmetric tetradentate ligands, *Bull Chem. Soc.* **24**(2): 193.

Sharghi H, Nasseri M A (2003) Schiff-Base Metal(II) Complexes as New Catalysts in the Efficient, Mild and Regioselective Conversion of 1,2-Epoxyethanes to 2-Hydroxyethyl Thiocyanates with Ammonium Thiocyanate, *Bull Chem. Soc. (JPN)* **76**(1): 137.

Sheng X, Guo X, Lu X M, Lu G Y, Shao Y, Liu F, Xu Q (2008) DNA binding, cleavage, and cytotoxic activity of the preorganized dinuclear zinc(II) complex of triazacyclononane derivatives, *Bioconjugate Chem.***19**(2): 490.

Shi L, Mao W J, Yang Y, Zhu H L (2009) *J Coord. Chem.* **62** (21): 3471.

Shibuya Y, Nabari K, Kondo M, Yasue S, Maeda K, Uchida F, Kawaguchi H (2008) The copper(II) complex with two didentate Schiff base ligands. The unique rearrangment that proceeds under alcohol vapor in the solid state to construct noninclusion structure, *Chem. Lett.* **37**(1): 78.

Sigel (Ed.) H (2002) Metal Ions in Biological System, *Marcel Dekker, New York* **13**: 981.

Singh B K, Prakash A, Rajour H K, Bhojak N, Adhikari D (2010) Spectroscopic characterization and biological activity of Zn(II), Cd(II), Sn(II) and Pb(II) complexes with Schiff base derived from pyrrole-2-carboxaldehyde and 2-amino phenol, *Spectrochim Acta A* **76**(3-4): 376.

Singh N K, Srivastava A (2000) In vitro and in vivo antitumour studies of a new thiosemicarbazide derivative and its complexes with 3d –metal ions, *Trans. Met. Chem.* **25**: 133.

Smith T S, Pecorara V L (2002) Oxidation of Organic Sulfides By Vanadium Haloperoxidase Model Complexes, *Inorg. Chem.* **41**: 6754.

Swamy S J, Reddy A D, Bhaskar K (2001) Synthesis and spectral studies of some oxavanadium(IV) and vanadium(IV) complexes, *Ind. J Chem.* **40A**: 1166.

Swearingen J K, West D X (2001) Structural and spectral studies of di-2-pyridyl ketone 3-piperidyl- and 3-hexamethyleneiminylthiosemicarbazone and their cobalt(II), nickel(II) and copper(II) complexes, *Trans. Met. Chem.* **26**(3): 252.

Takao K, Ikeda Y (2007) Structural characterization and reactivity of UO2(salophen)L and [UO2(salophen)]2: dimerization of UO2(salophen) fragments in noncoordinating solvents (salophen = N,N'-disalicylidene-o-phenylenediaminate, L = N,N-dimethylformamide, dimethyl sulfoxide), *Inorg. Chem.* **46**(5): 1550.

Tarafdar M T H, Khoo Teng-Jin, Crouse K A, Ali A M, Yamin B M, Fun H K (2002) Coordination chemistry and bioactivity of some metal complexes containing two isomeric bidentate NS Schiff bases derived from S-benzyldithiocarbazate and the X-ray crystal structures of S-benzyl-b-N-(5-methyl-2-furylmethylene)dithiocarbazate and bis[S-benzyl-b-N-(2 furylmethylketone)dithiocarbazato]cadmium(II), *Polyhedron* **21**: 2691.

Tarafder M T H, Ali M A, Wee D J, Azahari K, Silong S, Crouse K A (2000) Complexes of a tridentate ONS Schiff base. Synthesis and biological properties, *Trans. Met. Chem.* **25**(4): 456.

Telfer S G, Sato T, Harada T, Kuroda R, Lefebure J, Leznoff D B (2004) Mono- and dinuclear complexes of chiral tri- and tetradentate schiff-base ligands derived from 1,1'-binaphthyl-2,2'-diamine, *Inorg. Chem.* **43** : 6168.

Wu Jin-Cal, Liu Shi-Xia, Keene T D, Neels A, Mereacre V, Powell A K, Decurtins S (2008) Coordination Chemistry of a π-Extended, Rigid and Redox-Active Tetrathiafulvalene-Fused Schiff-Base Ligand, *Inorg. Chem.* **47**(8): 3452.

Yoon T P, Jacobsen E N (2003) Privileged Chiral Catalysts, *Science* **299**: 1691.

Yu S Y, Kaukawa T, Biradha K, Fujita M (2000) Hydrophobic Assembling of a Coordination Nanobowl into a Dimeric Capsule Which Can Accommodate up to Six Large Organic Molecules . *J Am. Chem. Soc.* **122**(11): 2665.

Zayed M A, Nour F A, Mohamed G G, El- Gamel A (2004) Structure investigation, spectral, thermal, X-ray and mass characterization of piroxicam and its metal complexes, *Spectrochim. Acta A* **60**(12): 2843.

Zhang C, Sun J, Kong X, Zhao C (2000) Synthesis and characterization of Manganese(Iii) Hydroxyl-containing Schiff-base complexes: [Mn(III)(Hvanpa)$_2$(NCS)] AND [Mn(III)(Hvanpa)$_2$]Cl · H_2O (h$_2$vanpa 1-(3-METHOXYSALICYLALDENEAMINO)-3-HYDROXYPROPANE) J Coord.Chem**. 50:** 353.