

CHAPTER I

1. Introduction

Of the ninety two naturally occurring elements nature has preferred to engage only twenty seven elements in order to sustain life. These chosen elements are important for development of body and hence are termed as essential elements. Of the 27 essential elements 15 are metals. Among these metals the transition metals like Cu, Zn, Fe, Ni, Mn, Mo, V, Cr are very important for plants. Since they are required in very trace amount, they are called micronutrients. The micronutrient deficiency and micronutrient toxicity in plants are of major concern for both the chemists and biologists. Micronutrients play pivotal role in cellular metabolism.¹⁻³ Some biological processes such as protein and carbohydrate metabolism, anti-oxidative defense and various enzyme activities are largely dependent upon micronutrients.⁴ They serve as structural and catalytic components of several proteins and enzymes which are required for growth and development. In 1972, Emanuel Epstein defined micronutrients as:⁵

“It is an element, absolutely required for the maintenance of life, its absence results several malfunction of body and ultimately resulting death.”

Several additional criteria regarding micronutrients are as follows:

- a) A physiological deficiency must appear when the element is removed from the diet.
- b) The deficiency can be relieved by the addition of specific element.
- c) A specific biochemical function is associated with a particular element.
- d) The effect of essential element cannot be fully replaced by any other element.
- e) The element should have direct influence on the organism and be involved in the metabolism.

2. The Dose-Response Curve of essential micronutrients:

The ‘Dose-Response’ curve shows a correlation between the ‘Dose’, *i.e.*, the concentration of essential element and its effects on living system termed as the ‘Response’ of that particular living system. Every micronutrient has an optimal concentration for a particular living system. Above that optimal concentration the system will become toxic even death can happen and below that optimal range there will be some deficiency symptoms. For example, Fluorine is an essential element and its daily intake of 0.5 mg will enable human body to survive normally. But an intake

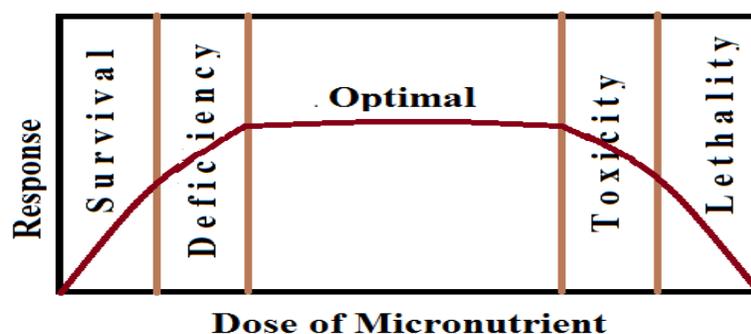


Fig 1.1. Dose-Response curve for a particular micronutrient.

of 2 mg/day of Fluorine will show some deficiency symptoms. However, if the intake is raised up to 10 mg/day, then it will be optimum for performing normal biochemical functions. Further increase of its concentration will make the body toxic and if the dose is raised to 100 mg/day death may occur.⁶

2.1. Role of Selected Micronutrients

In this dissertation three essential transition metals, *viz.*, Zn, Cu and V are selected for the study. These three metals are chosen due to their wide and diverse role in plant's body. All the three metals serve as structural and catalytic component of several proteins and enzymes required for the growth and development.

2.1.1. Role of Zinc

Zinc being one of the most important micronutrient in plants, acts as cofactors of enzymes like dehydrogenases, anhydrases, peroxidases and oxidases.⁷⁻⁹ Several biochemical pathways such as anti-oxidative defense and various enzyme activities are largely dependent upon Zn. Zinc has a major role to play in carbohydrate and protein metabolism process.^{10,11} It is found that zinc can increase the biosynthesis of chlorophyll and carotenoid-these two are associated in photosynthetic pathways.¹² But in reality it is found that 51% of world's soil is deficient of Zinc.¹³ So Zn deficiency is rather a global threat in agricultural field, since this deficiency can reduce the crop yields and crop quality. Some of the symptoms of zinc deficiency in plants are listed below:

- a) Stunting and reduced height of plants
- b) Intervenal chlorosis
- c) Brown spot on upper leaves
- d) Distorted leaves.



Fig 1.2. Zinc deficiency in maize plants (foreground) with healthier maize plants with no zinc deficiency (background). This figure has been adapted from Ref. No 14.

2.1.2. Role of Copper

Copper is one of the important redox active transition metal for plants. It mainly acts as a structural component of electron transfer proteins and enzymes like plastocyanin, cytochrome oxidase, *etc.*¹⁵ It plays important role in photosynthetic pathways, respiration and protein metabolism.¹⁶ In plants, copper is necessary for performing the normal role of cytosol, endoplasmic reticulum, chloroplast stroma, thylakoid lumen, *etc.* Although it is required in very trace amount, its deficiency can reduce the nitrogen fixation, thereby lowering the protein levels. Some of the symptoms of copper deficiency in plants are as follows:

- a) Dieback of stems and twigs
- b) Yellowing of leaves
- c) Stunted growth of plants
- d) Pale green leaves that can be wither easily.

2.1.3. Role of Vanadium

Vanadium is one of the important trace elements for plants. Although it is toxic to terrestrial plants but it is very influential for plant growth and development if applied in trace level.¹⁸ Vanadium can initiate the rate of photosynthesis. It has large effect on the synthesis of chlorophyll, carotene and it participates in nitrogen metabolism.¹⁹ It also triggers the germination stages.



Fig 1.3. Copper deficient rose leaves in right (smaller size, chlorosis) compared to normal leaves. This figure has been adapted from Ref. No 17.

Some of the symptoms of vanadium deficiency in plants are as follows:

- a) Growth reduction in plants.
- b) Changed color of the leaves, particularly from the leaf margin towards the midrib.
- c) Intervential chlorosis.



Fig1.4. Intervential chlorosis in tomato leaf due to vanadium and magnesium deficiency. This figure has been adapted from Ref. No 20.

2.2. Micronutrient deficiency: a global problem

Deficiency of micronutrients in soil is a global problem. A study in India, with 14683 soil samples collected from all over the country, reveals 49% of the soil samples are deficient of Zn, 12% in Fe and 3% in Cu.²¹ No doubt that the green revolution helped the production of the crops in last few decades but this also depletes the micronutrients pool in drastic level. Farmers have a tendency to apply micronutrients only when the deficiency symptoms are observed but not preparing the soils first. Moreover some common farming practice is also responsible for the degradation of micronutrient pool. To solve the micronutrient deficiency the most conventional and straight forward way is to apply metal salts to the soil. Most of the metal contained fertilizers are inorganic in origin. Although these metal contained fertilizers work well to solve the problem but they lead to certain changes in soil that ultimately make the soil infertile after few decades.²² The repeated use of inorganic fertilizers may lead to following problems:

2.2.1. Increase of salt concentration in soil

Excessive use of metal salts of inorganic origin may increase the salt concentration in soil and such a situation is very harmful for the crops. This compels plants to spend more energy to drag water from soil and as a result their growth becomes ceased and their morphology gets changed. This effect is significant for plants which are sensitive in high salinity soils.

2.2.2. Chance of contamination

Inorganic salts being ionic in nature are generally water soluble. So after rainfall the salts can be washed away from soils and can be mixed with the rivers and ponds, *etc.*, and thus the situation will make the water toxic and can be harmful for aquatic systems.

2.2.3. Toxicity for plants

Micronutrients are required by plants in very trace level. Since inorganic fertilizers are ionic they are highly reactive. So if they are slightly overdosed then plants will undergo stress and the body will become very toxic. This happens frequently for the inorganic supplements and thus some common symptoms like defoliation, wilting or decreased growth are observed in plants.

2.2.4. Leaching

Leaching is observed for the inorganic fertilizers when used in sandy soils. The inorganic metal salts can be leached away from the plant's root. If this happens then the applied salt will no longer be available for plants.

2.2.5. Change of soil pH and free electron activity

Most of the metal fertilizers contain oxide or sulphate or nitrate as counter anions. For these types of fertilizers the metal ion is incorporated in plants body but the counter anions remain in soil and ultimately converts to corresponding acid, which will alter the pH of the medium. Moreover they can hamper the free electron activity of the soil.²³

2.3. Solving micronutrient deficiency: A modern approach

To solve the micronutrient deficiency an alternative is the use of metal chelates instead of inorganic fertilizers. Metal chelates have the benefit that unlike the inorganic fertilizers they are less reactive and thereby less toxic.²⁴ At the early stages the most common chelators that were used extensively were ethylenediamine tetraacetic acid (EDTA) and diethylenetriamine pentaacetic acid (DTPA).²⁵ EDTA type of chelates due to their multiple binding sites (Hexadentate) can bind with almost all the transition metals and their metal complexes are very stable. That's why EDTA is used in the complexometric titrations in analytical chemistry. It is found that most of the EDTA containing metal chelates are soluble in water. These water soluble metal chelates can be absorbed in root pours and can be transmitted to cells.²⁶ They have the advantage that they are not responsible for drastic pH change of the medium. But recent study reveals that although they are useful to minimize the micronutrient deficiency but chelators like EDTA, DTPA have certain disadvantages which cannot be overlooked. The disadvantages are as follows:

- a) Since EDTA type of ligands can bind with almost all the transition metals, so after the incorporation of the desired metal to plants body, the free ligand can bind with the other metals present in system. This will lower the availability of the other metals in plants.²⁷
- b) Another disadvantage of these metal chelates is that they undergo photo degradation in the medium in presence of UV radiation. The photo degradation leads to some undesirable products like glyoxylic acid, formaldehyde, *etc.*, that are harmful for plant growth and development.²⁸

Besides the EDTA type of ligands literature study reveals the use of amino acids as a ligand. Ghasemi *et al.*²⁹ in their work made Fe- amino acid complexes and found their positive effect over Fe-EDTA when applied to the tomato seedlings. Same types of observations were found for Zn-amino acid complexes when they were treated in lettuce plant. But the problem of using amino acid type of ligands is that since they are water soluble they can be leached from the soil if remain unused and can contaminate other systems.

2.4. Tusk specific polydentate ligands: an alternative

From the above discussions it is clear that in order to act as a potential plant micronutrient supplier, the chelates must be selective as well specific. Otherwise they will solve one specific micronutrient deficiency but can lead deficiencies for other micronutrients. Another important factor is the solubility of the metal chelates. Solubility will be such that the leaching should be minimal. In view of these special type of tailor made polydentate ligands like Schiff bases have drawn the attentions of researchers recently. Schiff base is the condensation product of an amine and aldehyde. It acts as an important class of ligands since it can bind the metal ion through the azomethine (-C=N) group.^{30,31} Due to easy preparative way and vast applications in different fields they are often be called as 'privileged ligands'. Schiff base metal complexes show catalytic properties in different homogeneous and heterogeneous reactions.³² Just altering the functional groups, Schiff base and their derivatives may become at the same time 'specific and selective' to perform number of task specific applications.

2.4.1. Schiff base chemistry

Schiff bases containing azomethine group (-HC=N-) have now been proved to be privileged compounds and such compounds were first prepared by Hugo Schiff in 1864. The general synthetic route of formation of Schiff base is as follows:

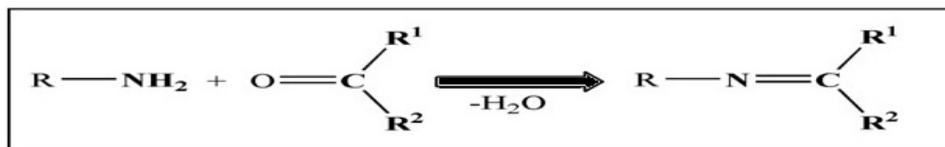


Fig 1.5. Condensation of amine and aldehyde to form Schiff base. Here R¹ and R² are different substituents like alkyl, aryl, cycloalkyl and heterocyclic groups, *etc.*

Chapter I

Investigation suggests that not only aldehydes but also ketones can form Schiff bases, although the rate of formation is somewhat lower than those with the aldehydes. Literature suggests that Schiff base derived from aromatic aldehydes are supposed to be more stable than aliphatic aldehydes.³³ If one or more donor atom is present near to the azomethine group the chelating power of such ligands increases very much. Depending on the donor sites Schiff bases may act as bi-, tri-, tetra- or polydentate ligands. Schiff base derived from salicylaldehyde and 1, 2-diamines such as ethylene diamine, phenylene diamine results tetradentate ligand system, commonly known as “Salen” or “Salophen” are highly potential ligand systems in coordination chemistry.

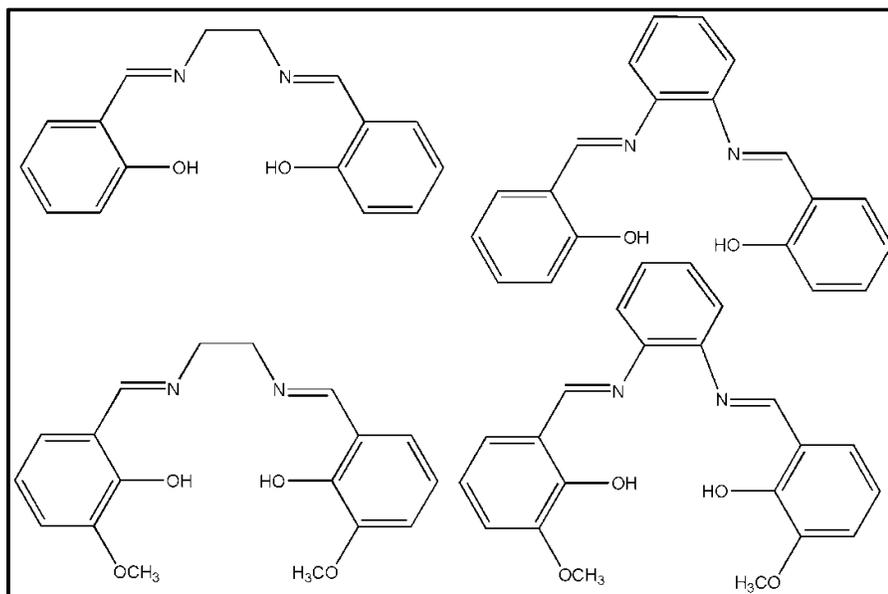


Fig 1.6. Examples of some Schiff bases derived from the condensation of different aromatic aldehydes and diamines.

These types of N_2O_2 ligands (Fig 1.6) show excellent chelating effects. This is due to the fact that the phenolate oxygen is a hard donor which can stabilize the higher oxidation state of the metal, whereas nitrogen being the borderline donor can stabilize the lower oxidation state of the metal.³⁴ Another key factor of these types of complexes is that they can undergo keto-enol tautomerism. Not only that by taking suitable formyl- or keto- and primary amines a large number of Schiff base macrocycles can be synthesized. These macrocycles have vast applications in supramolecular chemistry.^{35,36}

2.4.2. Schiff base transition metal complexes

Due to the versatility in the donor sites Schiff bases can form complexes with almost all the transition metal ions. Although they were very well known but their application in various fields of chemistry made them interesting till now.^{37,38} Organometallic compounds of Schiff bases have played a vital role in chemistry, mainly due to their ease of preparation, structural variability and widespread applications such as catalyst, functional materials and antibacterial reagents, *etc.*³⁹⁻⁴¹ The first synthesized Schiff base complex was dark green bis(salicyldiamino)Cu(II). This was prepared by the condensation of cupric acetate, salicylaldehyde and aqueous ammonia.⁴²

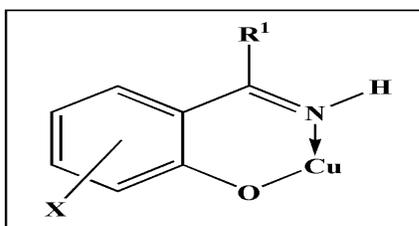


Fig 1.7. Structure of bis(salicyldiamino)Cu(II)

Although synthesized very long ago, the Schiff base metal complexes have not lost their significance because of the following factors:

- They can stabilize various oxidation states of metal ions by altering the hardness and softness of the binding sites.
- They can enhance the stability and solubility of the homogeneous and heterogeneous catalysts by altering the substituents.⁴³
- They can act as synthetic models of metal containing sites for various metalloproteins and metalloenzymes.⁴⁴⁻⁴⁵
- Complexes of transition metal ions with Schiff bases provide a large and growing class of compounds with both stereochemical and magnetochemical interest.
- Unsymmetrical Schiff base ligands have exhibited many advantages over their symmetrical counterparts in the elucidation of the composition and the geometry of the metal binding sites in the metalloprotein and the metalloenzymes and the selectivity of the natural systems with synthetic materials.⁴⁶

Chapter I

Although Schiff base metal complexes were discovered since the mid nineteenth century, after the work of Jorgensen and Werner these types of complexes have gained interest of many chemists in the field of coordination chemistry.⁴⁷ One of the crucial discovery of Schiff base complex is the formation of “Jacobsens’s catalyst” where the Schiff base was used obtained by the condensation of trans-1,2-diaminocyclohexane and 3,5-di-tert-butyl-2-hydroxybenzaldehyde followed by the treatment of ligand with Mn(III) acetate in open air.

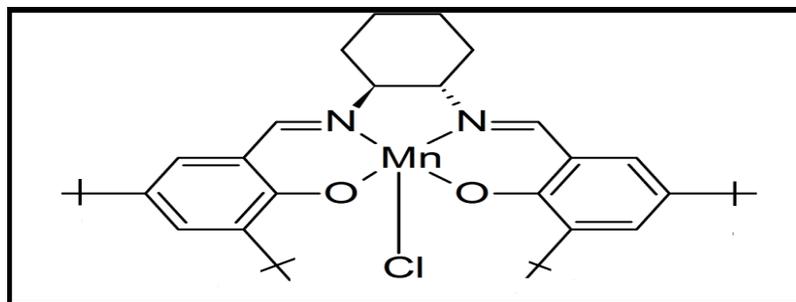


Fig 1.8. Jacobsen's catalyst

Not only with Mn(III), different Schiff complexes of transition metals like Co(II), Ni(II), Fe(III), Cr(III), Zn(II) were prepared with the aid of different techniques.⁴⁸

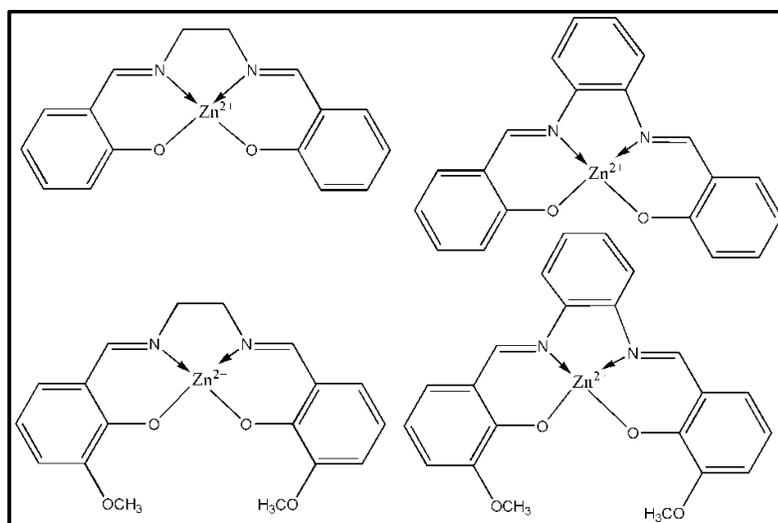


Fig.1.9. Various Schiff base-Zn²⁺ complexes.

Actually Schiff base metal complexes can be prepared without any difficulty and they offer diverse applications and most importantly they act as artificial models of various biologically active compounds.

2.4.3. Applications of Schiff base transition metal complexes

Schiff bases and their metal complexes not only have played an important role in the development of modern coordination chemistry, but they can also be found at key points in the development of inorganic biochemistry, catalysis, optical materials, *etc.*^{49,50} Some important applications of Schiff base metal complexes are as follows:

2.4.3.1. As Catalysts

A large number of homogenous and heterogeneous reactions are affected by Schiff base metal complexes. Such complexes play major roles and their effects can be varied by altering metal ions, coordination sites and the ligand types. A literature survey revealed that chiral Schiff base complexes are more selective in various reactions like hydroxylation, oxidation, epoxidation and aldol condensation, *etc.*^{51,52} Schiff base complexes of Cr(III), Mn(III), Fe(II), Co(II), Ni(II) and Zn(II) are used for the oxidation of cyclohexane.⁵³ Several substituted salen type Mn(III) can be encapsulated in Zeolites-Y for aerobic oxidation of styrene to benzaldehyde, styrene oxide and phenyl acetaldehyde.⁵⁴ Silyl ketone undergoes asymmetric oxidation with high enantioselectivity in presence of Mn(II) salen complexes. Literature reveals that dinuclear Schiff base complexes of transition metal ions are more capable to act as a catalyst than the mononuclear complexes due to the synergistic effect of two metal ions.⁵⁵ This observation is justified for dinuclear complexes of Cu(II) that can act as effective catalyst in oxygen activation.⁵⁶ Literature is full of examples in which complexes of Schiff base ligands were employed as catalyst in polymerization of ethylene.⁵⁷ The ring opening polymerization of cycloalkenes is now-a-days efficiently catalyzed by Schiff base metal complexes at low temperature.⁵⁸ The ring opening of large cycloalkanes is usually difficult process but Schiff base complexes of Co(II) and Cr(III) were effective in these reactions with significant enantioselectivity.⁵⁹ In Michael addition reaction Schiff base complexes of salen type is used as an efficient catalyst. The epoxidation of non-functionalized trans-olefins is catalyzed by Cr(III) complexes.⁶⁰ The asymmetric nucleophilic ring opening reaction of meso-epoxides in the presence of benzoic acid is catalyzed by Co(II) salen complexes.⁶¹ Costa *et. al.* observed the catalytic activity of Pd(II) complexes of Schiff bases possessing nitrogen donors during hydrogenation of alkenes and alkynes under mild conditions.⁶² A very efficient catalytic activity is exhibited by mono and dinuclear Pd(II) complexes of Schiff bases possessing tert-butyl groups on the salicyl

ring with steric constraints towards reduction of cyclohexene and nitrobenzene. Thus the transition metals in combination with different Schiff base ligands showed high catalytic activities in reactions of industrial importance and academic interests.

2.4.3.2. As Electroluminescent Materials

Of late, organic electroluminescence (EL) devices have attracted large interest in recent years due to flat-panel display applications. Organic dyes, chelate metal complexes and polymers are three major categories of materials used in the fabrication of organic electroluminescent (EL) devices. Literature reveals that many salicylaldehyde-derived Schiff base metal complexes with the formation of inner complex have been investigated as EL materials. Schiff base Zn(II) complexes can act as electroluminescent materials.⁶³ Blue luminescent Schiff base Zn(II) and Be(II) complexes were prepared from calixarene by Wei *et al.*⁶⁴ Zn complex like bis[salicylidene-(4-dimethylamino)aniline]Zn(II) shows charge transporting performance in organic light emitting diodes (OLEDs).

2.4.3.3. Biological Activities

Literature shows that in many enzymatic reactions for which interaction of an enzyme with an amine or carbonyl group of the substrate is involved, Schiff base intermediates are formed.⁶⁵ Over the years, a number of transition metal complexes have been exploited for the design of new drugs due to their diverse biological activities. Schiff base ligands with various coordination modes can bind with different metals and can form many nature identical homo and heterometallic complexes with varied stereochemistry. This unique feature is used for modeling active sites in biological systems.⁶⁶ Many redox enzymes like catalase and peroxidase which are responsible of the dismutation of H₂O₂ and the reduction of alkyl hydroperoxide, respectively are made up by the combination of porphyrin group and Fe(II) or Fe(III). Wang *et al.*⁶⁷ reported that Fe(salen) can effectively catalyze the reduction of O₂ and H₂O₂. Literature survey reveals that salen type metal complexes can induce specific damages in DNA or RNA. In the middle of 1980s there was an important discovery that Schiff base transition metal complexes can show chemical nuclease activity and thereby they are vastly used in bio-engineering. Literature also reveals that Schiff base metal complexes are excellent DNA cleavers.⁶⁸ The potent biological activity can be related to the presence of nitrogen atom with a lone pair of electron in it and

that the nitrogen can participate in hydrogen bonding with –NH or –OH groups present in biomolecules.

2.4.3.4. Antimicrobial Activities

Schiff bases and their metal complexes have drawn the attention of chemists for their potential antimicrobial activities. Furyl glyoxal and *p*-toluidene made Schiff base shows antibacterial activity against *Escherichia coli*, *Staphylococcus aureus*, *Bacillus subtilis* and *Proteus vulgaris*.⁶⁹ Thallium (I) complexes of benzothiazolines shows significant antibacterial activity against the pathogenic bacteria.⁷⁰ Complexes of Mo (IV) and Mn(II) of ligands hydrazine carbonyl amide and hydrazine carbonyl thioamide exhibit significant antibacterial activity against *Xanthomonas compestris*.⁷¹ Literature reveals that tridentate Schiff base metal complexes show extensive antimicrobial activities against *E. coli*, *S. aureus*, *B. subtilis*.⁷²⁻⁷⁴ Schiff bases derived from Isatin shows excellent anti-HIV activities.⁷⁵ Various Schiff bases derived from various sources (benzimidazole, quin-azolinones, pyrazolone, thio-semi-carbazone, etc.) show good antibacterial activities.⁷⁶⁻⁷⁹ Cyclo-butane and thiazole ring contained Schiff bases exhibit various biological activities. Cu and Ni complexes of chloro-salicylidene and taurine obtained Schiff bases possess significant activities to *Colibacillus* and *Pseudomonas aeruginosa*.⁸⁰ Fe and Co containing Schiff base complexes derived from Lysine exhibit antibacterial activities towards *B. Subtilis*, *S. Aureus* and *E. coli*.⁸¹ Schiff bases obtained by the condensation of semicarbazide and furfurylidene diamine and their Zn(II), Cu(II), Cd(II) and Ni(II) complexes exhibit good antimicrobial activities. Bidentate Schiff bases containing Si(IV) having at least one nitrogen donor sites exhibit antibacterial activities.⁸²

2.4.3.5. Antifungal Activities

Literature is full of examples where Schiff bases and their metal complexes act as antifungal agents. Schiff bases obtained from thiazole and benzothiazole exhibit antifungal activities.⁸³ It is found that if any methoxy or naphthyl or halogen group is attached with the Schiff base the fungicidal activities increase.⁸⁴ Schiff bases obtained from pyrandione and quinazolinones show physiological activities against *A. niger* and *candida albican*, respectively.⁸⁵ Literature reveals that *Helminthosporium gramineum* which is responsible for strip disease in barely and *Syncephalostrum racemosus* which causes fruit rot in tomato are affected significantly by furan and various amines made Schiff bases.⁸⁶ Carbothioamide made Schiff bases and their

metal complexes exhibit fungicidal activities against *H. graminicium*.⁸⁷ *A. alternata* which is responsible for disease in brinjal can be controlled by Molybdenum and manganese Schiff base complexes.

2.4.3.6. Antiviral Activities and Synergistic Action

Schiff base metal complexes containing Ag(I) exhibit inhibition against Cucumber mosaic virus.⁸⁸ Literature reveals that glycine, salicylaldehyde made Schiff base metal complex of Ag(I) gives positive outcomes up to 74.7% towards Cucumber mosaic virus. Not only that sulfane thiadizole and salicylaldehyde made Schiff bases are quite capable of exhibiting toxicity towards insects. Experiment proves that fluorination on aldehyde part of Schiff base enhances the insecticidal activity.⁸⁹ Condensation products of thiadiazole derivatives and o-vanillin show good insecticidal activities against bollworm and enhance the cell survival rate of mung bean sprouts.⁹⁰

2.4.3.7. Other Therapeutic Activities

Literature is full of examples where Schiff bases and their metal complexes show anti-inflammatory, analgesic and anti-oxidative actions. Analgesic and anti-inflammatory activities are shown by thiazole derived Schiff bases.⁹¹ Superoxide and hydroxyl scavenging may be done by taking carboxy methylchitosan containing Schiff bases.⁹² Anthelmintic and analgesic activity is shown by furan semicarbazone made Schiff base metal complexes.⁹³ Salicylidine and anthranilic acid made Schiff bases possess antiulcer activities and if complexation is done with Cu(II) then antiulcer activity further increases.⁹⁴ Cu, Ni, Zn, Co containing Schiff bases made from salicylaldehyde and glycine exhibit antitumor activities.⁹⁵ Literature depicts that antitumor activity of metal complexes follow the order Ni > Cu > Zn > Co. Human tumor cells are also affected by Schiff bases derived from aromatic and heterocyclic amines.⁹⁶

2.5. Objective of the research work and Method of Investigations

Inspired by the varied use of Schiff bases and their metal complexes, present dissertation is mainly focused on the use of some transition metal complexes as potential micronutrient supplement for selected plants. Although only few examples of this type of works were found in the literature, some notable works have drawn our attention, *e.g.*, N-acetylated Schiff bases were reported to exhibit growth inhibitory activity with seedling of wheat, rye and barley.⁹⁷ Schiff bases were reported to initiate

the plant hormone auxin required for the root growth.⁹⁸ Therefore the main objectives of this research work are as follows:

- To synthesize polydentate Schiff base-transition metal complexes using normal conventional protocols with slight alterations as required.
- To characterize the synthesized polydentate Schiff base metal complexes with different physicochemical and spectroscopic techniques.
- To study the effect of these polydentate metal complexes on various morphological and biochemical parameters of some selected plants.
- To study whether the synthesized polydentate metal complexes can solve micronutrient deficiency in plants without hampering the environment.

The present dissertation includes a total of six chapters including this introductory one. Chapter II contains details of chemicals and the various physico-chemical techniques used. The applications of the synthesized complexes as potential micronutrient supplier on selected plants are discussed in Chapters III-V, followed by concluding remarks in Chapter VI.

References

- 1) Camp, B. Fudge, *Soil Science*, **60** (1945) 157.
- 2) G. Rout, S. Samantaray, P. Das, *Plant Sci.* **137** (1978) 89.
- 3) P. Aravind, M. Narasimha, V. Prasad, *Braz. J. Plant Physiol.* **17** (2005) 3.
- 4) Vallee, D. Auld, *Biochemistry* **29** (1990) 5647.
- 5) E. Epstein, A. Bloom, *Mineral Nutrition of Plants*, Oxford University Press, Oxford, **1** (2004) 26.
- 6) A. Das, *Bioinorganic chemistry*, Oriental publication, West Bengal, **1** (2006) 94.
- 7) W. Bettger, B. O'Dell, *Life Sci*, **28** (1990) 1425.
- 8) H. Bowen, P. Cause, J. Thick, *J. Exp. Bot.* **13** (1962) 257.
- 9) T. Bray, S. Kubow, W. Bettger, *J. Nutr.* **116** (1986) 1054.
- 10) J. Burke, M. Fenton, *Proc. Soc. Exp. Biol. Med.* **179** (1985) 187.
- 11) Cakmak, H. Marschner, *Physiol. Plant.* **70** (1987) 13.
- 12) M. Chvapil, *Life Sci.* **13** (1973) 1041.
- 13) R. Dwivedi, P. Takkar, *Plant and Soil*, **40** (2008) 170.
- 14) https://upload.wikimedia.org/wikipedia/commons/thumb/1/1f/Zincdeficient_maize_plants.jpg/1024px-Zinc-deficient_maize_plants.jpg, accessed on 1st Feb, 2021.
- 15) Tanyolac, Y. Ekmekci, S. Unalan, *Chemosphere*, **67** (2007) 89.

- 16) M. Draobzkiewicz, E. Skórzyńska-Polit, Z. Krupa, *BioMetals*, **17** (2004) 379.
- 17) <https://www.pthorticulture.com/media/1556/cu-def-rose.jpg>, accessed on 1st Feb, 2021.
- 18) P. Prarr, H. Chapman, eds., *University of California Division of Agricultural Science*, Riverside, California, **2**(1966) 480.
- 19) R. Welch, *Plant Physiol.* **51** (1973) 828.
- 20) <https://uconnladybug.files.wordpress.com/2019/07/tomato-with-magnesium-def.jpg?w=370&h>, accessed on 1st Feb, 2021.
- 21) A. Gupta, *J Trace Elem Med Biol.* **18** (2005) 325.
- 22) R. Brennan, D. Bolland, *Aust J Exp Agric.* **46** (2006) 1341.
- 23) S. Thind, D. Rowell, *Biol Fertil Soils.* **28** (1999) 162.
- 24) H. Khoshgoftarmanesh, R. Schulin, R. Chaney, B. Daneshbakhsh, M. Afyuni, *Agron Sustain Dev.* **30** (2010) 83.
- 25) A. Wallace, A. Wallace, *Iron nutrition and interactions in plants* (1982) 975.
- 26) A. Vallee, D. Auld, *Biochemistry* **29** (1990) 5647.
- 27) S. Metsarinne, T. Tuhkanen, *Chemosphere*, **45** (2001) 949.
- 28) C. Bretti, R. Cigala, C. Stefano, *Chemosphere*, **150** (2016) 341.
- 29) S. Ghasemi, A. Khoshgoftarmanesh, H. Hadadzadeh, *Journal of Plant Growth Regulation*, **31** (2012) 156.
- 30) A. Butler, C. Carrano, *Coord Chem Rev.* **109** (1991) 61.
- 31) T. Katsuki, *Coord. Chem. Rev.* **140** (1995) 189.
- 32) D. Boghaei, S. Mohebbi, *Tetrahedron* **58** (2002) 5357.
- 33) J. Geldard, F. Lions, *Inorg. Chem.* **48** (1965) 414.
- 34) Z. Li, K. Conser, E. Jacobsen, *J. Am. Chem. Soc.* **115** (1993) 5326.
- 35) P. Viago, S. Tamburini, *Coord. Chem. Rev.* **248** (2004) 2128.
- 36) N. Borisova, M. Reshetova, Y. Ustynyuk, *Chem. Rev.* **107** (2007) 79.
- 37) W. Rodriguez, J. Zugazagoitia, E. Collado, *J. Phys. Chem A*, **111** (2007) 6241.
- 38) K. Gupta, A. Sutar, *Coord. Chem. Rev.* **252** (2008) 1420.
- 39) C. Che, J. Huang, *Coord. Chem. Rev.* **242** (2003) 97.
- 40) D. Paul, S. Peter, *Coord. Chem. Rev.* **242** (2003) 125.
- 41) M. Amirasr, F. Fadaee, *Inorg. Chim. Acta.* **371** (2011) 6.
- 42) R. Holm, J. Everett, R. Chakravorty, *Inorg. Chim. Acta*, **7** (1966) 83.
- 43) A. Golcu, M. Tumer, H. Demicell, *Inorg. Chim. Acta*, **358** (2005) 1785.
- 44) A. Kumar, G. Mishra, *Trans. Met. Chem.* **28** (2003) 913.

- 45) A. Asiri, S. Khan, *Molecules*, **15** (2010) 4784.
- 46) E. Kwaitkowski, M. Kwaitkowski, *Inorg. Chim. Acta*, **117** (1986) 145.
- 47) C. Jorgensen, *Acta Chem. Scand.* **11** (1957) 73.
- 48) F. Morad, M. El-Ajaily, *J. Sci. Appl.* **1** (2007) 72.
- 49) K. Suslick, T. Reinert, *J. Chem. Educ.* **62** (1988) 974.
- 50) J. Tisato, F. Refosco, F. Bandoli, *Coord. Chem. Rev.* **135** (1994) 325.
- 51) T. Uchida, T. Katsuki, *Tetrahedron Lett.* **42** (2001) 6911.
- 52) J. Bozell, B. Hames, D. Dimmel, *J. Org. Chem.* **60** (1995) 2398.
- 53) F. Hueso- Urena, N. Illan- Cabeza, M. Moreno- Carretero, *J. Inorg. Biochem.* **94** (2003) 326.
- 54) A. Zsigmond, A. Horvath, F. Notheisz, *J. Mol. Catal. A. Chem.* **171** (2001) 95.
- 55) H. Steinhagen, G. Helmchen, *Angew. Chem.* **35** (1996) 2339.
- 56) M. Lubben, R. Hage, A. Meetsma, *Inorg. Chem.* **34** (1995) 2217.
- 57) A. Small, M. Brookhart, *J. Am. Chem. Soc.* **120** (1998) 4049.
- 58) J. Claverie, R. Soula, *Prog. Polym. Sci.* **28** (2003) 619.
- 59) M. Wu, E. Jacobson, *Tetrahedron Lett.* **38** (1997) 693.
- 60) P. Beleskaya, A. Cheprakove, *Chem. Rev.* **100** (2000) 3009.
- 61) D. Devos, P. Knops-Gerrits, D. Venoppen, *Supramol. Chem.* **6** (1995) 49.
- 62) C. Bousquet, D. Gilheany, *Tetrahedron Lett.* **36** (1995) 7739.
- 63) C. Tang, S. Vanslyke, *Applied Physics Lett.* **510** (1987) 913.
- 64) O. Kwon, Y. Kim, B. Sohn, *Cryst. Liq. Cryst.* **349** (2000) 405.
- 65) X. Wei, J. Qiao, L. Wang, *Chinese Chem. Lett.* **14** (2003) 263.
- 66) H. Mohler, E. Cordes, *Biological Chemistry*, Harper and Row, New York, **2** (1971) 45.
- 67) F. Frieden, *J. Chem. Edu.*, **52** (1975) 754.
- 68) B. Dede, I Ozmen, F. Karipcin, *Polyhedron.* **28** (2009) 3967.
- 69) C. Saxena S. Shrivastava, *J Ind Chem.Soc.* **64** (1987) 685.
- 70) C. Bhardwaj, V. Singh, *Indian J Chem.* **33** (1994) 423.
- 71) T. Bharamagouclar A. Alagawadi *Curr Sci*, **56** (1987) 889.
- 72) F. Grumus, P. Gurkah, N. Gunduz, *Farm Bilmer Derg.* **19** (1994) 5.
- 73) M. Deshmukh, D, A. Doshi, *Orient J Chem.* **11** (1995) 86.
- 74) M. Tumer, H. Koksall, S. Serin, *Trans Met Chem.* **24** (1999) 13.
- 75) P. Dholakiya, M. Patel, *Synth react Inorg Met Org Chem.* **32** (2002) 753.
- 76) R. Singh, N. Gupta, N. Fahmi, *Indian J Chem*, **38** (1999) 1150.

- 77) S. Ranga, S. Sharma, V. Chowdhary, *J Curr Bio Sci*, **5** (1988) 98.
- 78) O. Nakamoto, Z. Hidaka, *Delta J Sci*, **15** (1991) 47.
- 79) Z. Malik, S. Alam, *J Pure Appl Sci*, **17** (1984) 69.
- 80) N. Sari, P. Guerkan, S. Arslan *Met Chem*, **28** (2003) 468.
- 81) H. Singh, M. Sharma, A. Varshney, Synthesis, *Chem. Res. Commun.* **8** (1998) 35.
- 82) A. Ahmed, S. BenGujji, *RASAYAN J. Chem*, **4** (2009) 781.
- 83) R. Welch, E. Huffman, *Plant Physiology*. **52** (1973)183.
- 84) S. Prasad, R. Dwivedi, M. Zeeshan, *Photosynthetica*, **43** (2005) 177.
- 85) L. Lombardi, L. Sebastiani, *Plant Sci*. **168** (2005) 797.
- 86) M. Gorska-Czekaj, W. Borucki, *Micron*, **53** (2013) 2432.
- 87) J. Dat, S. Vandenabeele, E. Vranová, M. Van Montagu, F. Van Breusegem, *Cell Mol. Life Sci.* **57** (2000) 779.
- 88) A. Henriques, J. Chalfun, M. Aarts, *Braz. J. Plant Physiology* **24** (2012) 3.
- 89) I. Cakmak, *New Phytol.* **146** (2000) 185.
- 90) Z. Miszalski, I. Ślesak, E. Niewiadomska, R. Baćzekoxide Kwinta, U. Lüttge, R. Ratajczak, *Plant Cell Environ.* **21** (1998) 169.
- 91) N. Smirnov, P. Conklin, F. Loewus, *Annu. Rev. Plant Physiol. Plant Mol. Biol.* **52** (2001) 437.
- 92) M. Bonnet, O. Camares, P. Veisseire, *J. Expt. Bio.* **51** (2000) 945.
- 93) M. Chvapil, *Life Sci.* **13**(1973) 1041.
- 94) T. Kösesakal, M. Ünal, *Fresenius Environ Bulletin* **21** (2012) 315.
- 95) Z. Chohan, H.Prevez, K. Khan, A. Rauf, G. Maharvi, C. Supuran, *J Enzy Inhib Med Chem.* **19** (2004) 85.
- 96) R. Sharma, A. Kumar, A. Kumari, R. Kumar, *Asian J Chem.* **15** (2003) 57.
- 97) S. Huneck, K. Schreiber, H. Grimmecke, *J Plant Growth Regul.* **3** (1984) 75.
- 98) Y. Wang, B. Lu, X. Yu, S. Wang, *Chem Abstr.* **137** (2002) 109.