

SYNTHESIS OF NOVEL N₂, O₂ SCHIFF BASE ZINC (II) COMPLEXES AND THEIR EFFECT ON GERMINATION, SEEDLING GROWTH OF PLANTS

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Introduction:

Coordination chemistry is undoubtedly most active area of research in inorganic chemistry. This branch of chemistry has now leaped into many areas of science such as analytical chemistry, medicinal chemistry, metallurgy, industrial chemistry and material science. It is mainly the chemistry of metal complexes derived from various types of ligands. A large number of Schiff bases have been synthesised and used as ligands. These ligands have largely played an important role in the development of coordination chemistry [1]. They have also played important roles in biological modeling [2-4], in designing molecular ferromagnets[5,6], in the development of liquid crystals [7,8], in catalysis [9,10] and in medical imaging [11].

The –RC=N- linkage present in ligand and its metal complexes is reflected for diverse applications related to electrochemical sensing , catalytic activities, nonlinear optical activities, fluorescence properties, electroluminescent properties, organic photovoltaic materials and biological activities.

Zinc deficiency in soils and plants is a global micronutrient deficiency problem in most agricultural regions of the world as well as in India [12]. The easiest and most straight forward practice to correct micronutrient deficiency is to apply zinc fertilizers.

In comparison with inorganic fertilizers, synthetic and natural chelates have the advantages of keeping the applied nutrient in a less reactive form [13]. In contrast with inorganic salts, synthetic metal chelates are more useful to correct the metal deficiency [14] for a longer period.

In this context the research work is done to investigate the effect of Zn complexes on germination and seedling growth of papaya.

Scope:

In most agricultural regions of the World as well as in India, the micronutrient deficiency of Zinc in soils and plants is a major problem. The easiest and most suitable practice to correct micronutrient deficiency is to use zinc fertilizers. Several reviews have shown that the salen type Schiff base complexes possess excellent properties in many fields like oxygen atom transfer reaction, enantioselective epoxidation, aziridination, mediating organic redox reactions and other oxidative processes. Due to these versatility offered by the salen type ligands in this

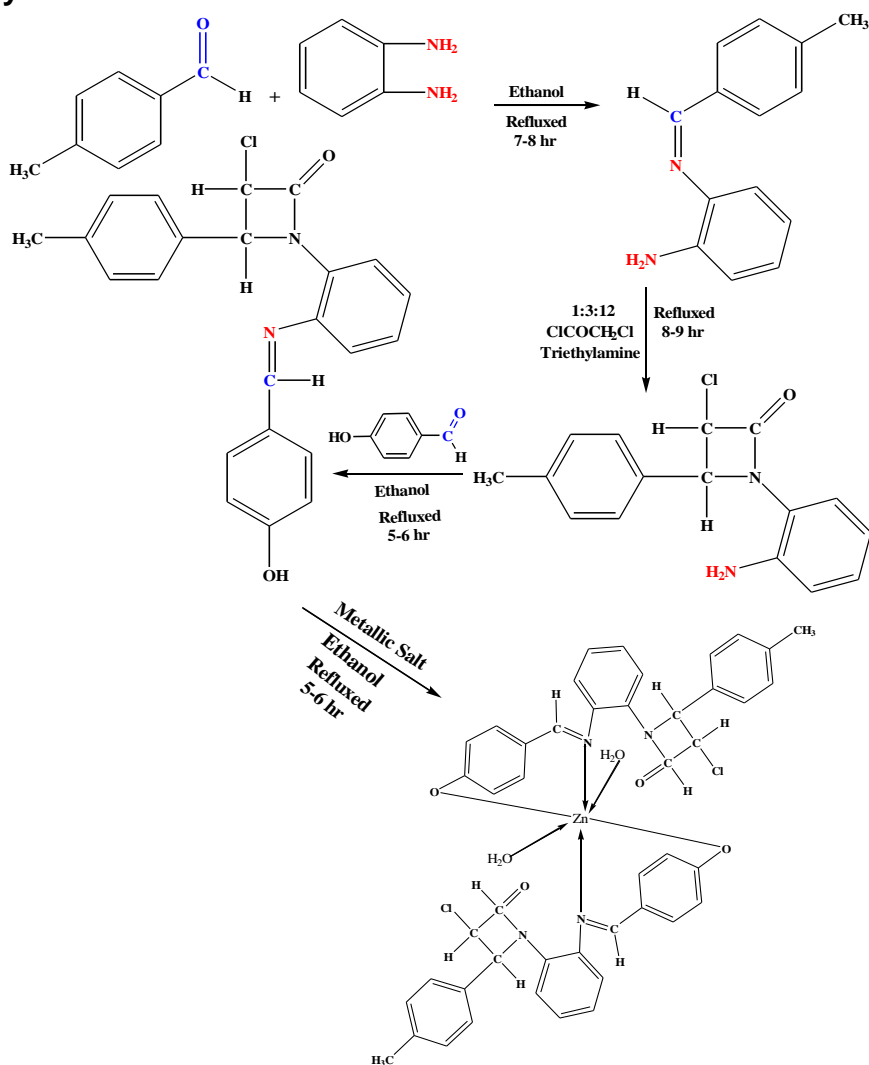
work, we have synthesized three different Zn complexes and investigated their effect on germination and seedling growth of papaya.

Objectives:

1. Synthesis of N₂, O₂ Schiff bases, and their zinc metal complexes.
2. Characterization of the synthesized compounds by UV, IR, ¹H NMR, EPR, thermal and Mass spectroscopy and, X-ray crystallography
3. Study the effect of synthesized zinc complexes on germination and seedling growth of plants.

Methodology:

Part-A - Chemistry:

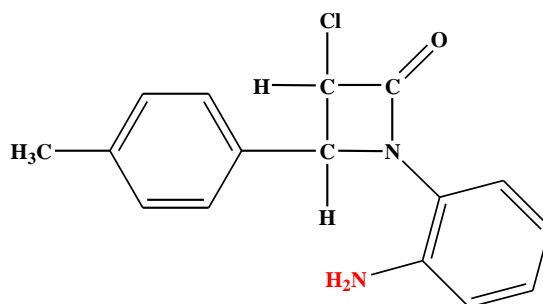


SYNTHESIS OF NOVEL N₂, O₂ SCHIFF BASE ZINC (II) COMPLEXES

a. Preparation of N-(4-Methyl-benzylidene)-benzene-1,2-diamine(iii):

The mixture of p-tolualdehyde(i) and o-Phenylenediamine(ii) taken in 1:1 ratio and dissolved in 20 ml ethanol and stirred for 1 hour and refluxed for 7-8 hours. The white crude product was filtered, washed with water, dried and recrystallized with ethanol to achieve the product (iii).

Yield: 85%, M.P: 163-165°C, IR(Nujol): 3290cm⁻¹(NH₂), 1665cm⁻¹(C=N), H¹NMR: δ 6.5-8.0(m, 8Ar-H), 7.1(s, 1H CH), 2.4(s, 3H CH₃), 4.5(s, 2H NH₂), C₁₄H₁₄N₂(210): (Anal. Cal.): C, 79.97; H,6.71; N,13.32%.Found:C,79.30; H,6.59; N,13.72%.



N-(4-Methyl-benzylidene)-benzene-1,2-diamine

b. Preparation of 1-(2-Amino-phenyl)-3-chloro-4-p-tolyl-azetid-2-one(iv):

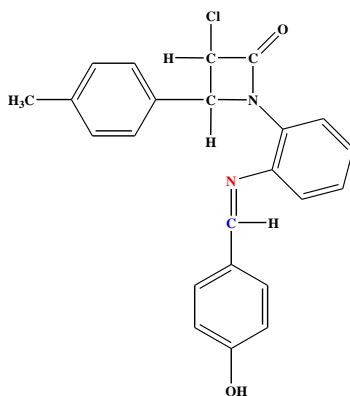
The mixture of compound [iii], Triethylamine and chloroacetyl chloride is taken in the ratio 1:3:12 and dissolved in 25 ml dioxane, stirred for 1 hour and refluxed for 8-9 hours and then cooled to room temperature. Ice cold water was added in excess to get complete precipitate. The product [iv] was filtered off and washed with ethanol. The product was recrystallized from ethanol.

Yield: 85%, M.P: 163-175°C, IR(Nujol): 3285cm⁻¹(NH₂), 1745cm⁻¹(C=O), H¹NMR: δ 6.85-7.5(m, 8Ar-H), 6.1(s, 1H CH), 2.5(s, 3H CH₃), 4.8(s, 2H NH₂), C₁₆H₁₅ClN₂O(287): (Anal. Cal.): C, 67.07; H, 5.71; Cl,12.32, N, 9.77%.Found: C, 68.07; H, 5.98; Cl,12.55, N, 9.85%.

c. Preparation of Ligand (3-Chloro-1-{2-[4-hydroxy-benzylidene)-amino]-phenyl}-4-p-tolyl-azetid-2-one)(v):

The mixture of compound [iv], salicylaldehyde taken in 1:1 ratio and catalytic amount of CAN dissolved in 25 ml ethanol and stirred for 1 hour and refluxed for 5-6 hours. The white crude product was filtered, washed with water, dried and recrystallized with ethanol to achieve the product (iii).

Yield: 85%, M.P: 175-182°C, IR(Nujol): 1670cm⁻¹(C=N), 1225cm⁻¹(C-N), 1265cm⁻¹(C=O), 3525cm⁻¹(O-H), H¹NMR: δ 6.5-7.8(m, 12Ar-H), 2.35(s, 3H CH₃), 5.1(s, 1H CH), 5.3(s, 1H CH), 7.5(s, 1H CH), 10.63(bs, 1H OH), C₂₃H₁₉ClN₂O₂(391): (Anal. Cal.): C, 70.68; H, 4.90; N, 7.17, Cl, 9.04%. Found: C, 70.33; H, 4.55; N, 7.77, Cl, 9.04%.

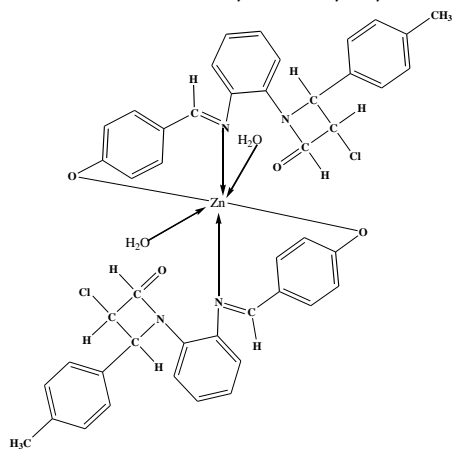


(3-Chloro-1-(2-[4-hydroxy-benzylidene]-amino)-phenyl)-4-p-tolyl-azetidin-2-one

d. Preparation of Complexes(vi):

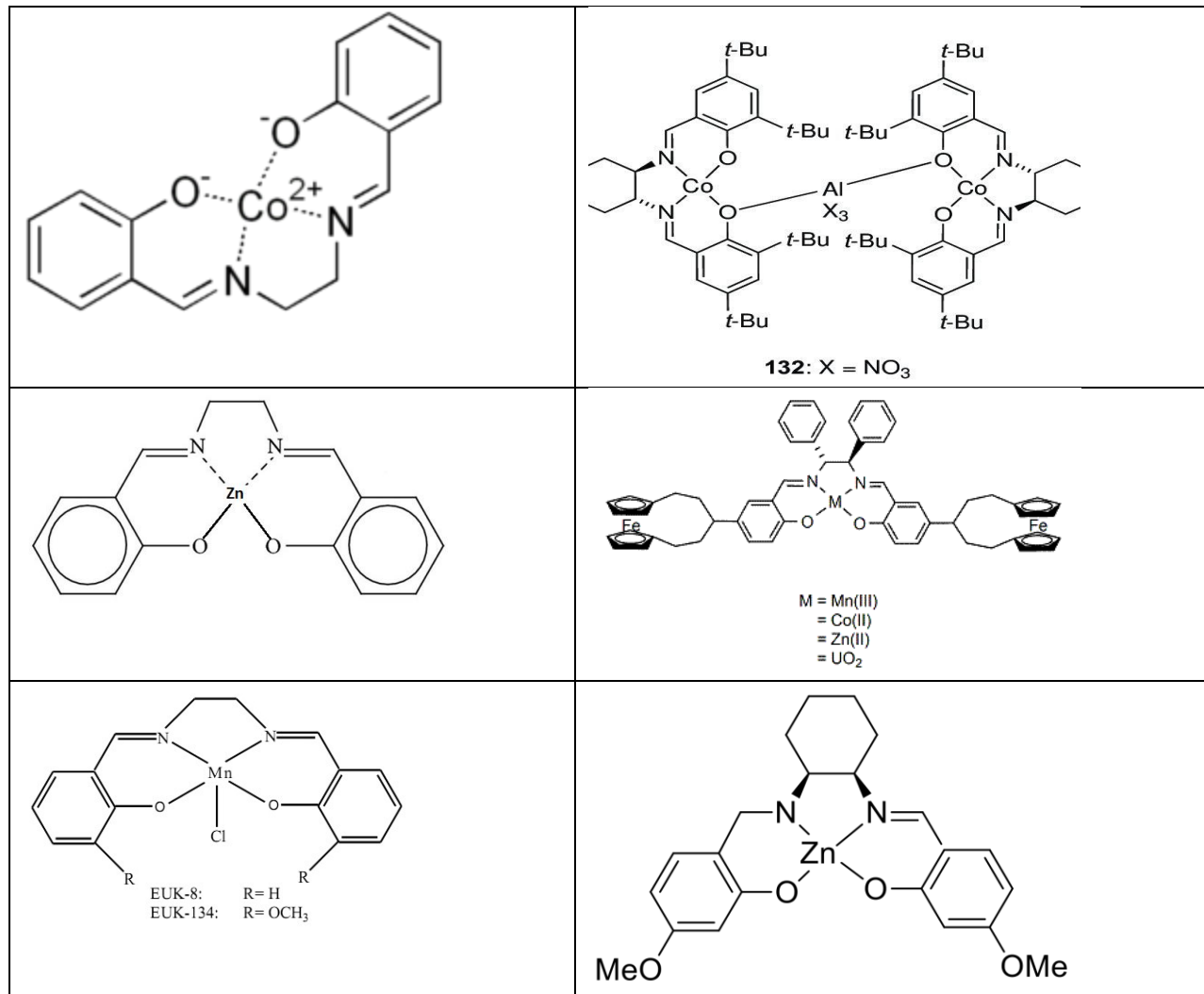
For a solution of ligand (v), metal chloride in 1:1 molar ratio in ethylalcohol was supplemented with constant stirring. The pH of the reaction system was maintained to 7-8 and kept refluxed for 6 hours. The white (vi) precipitate was collected by filtration and washed several times with hot ethyl alcohol.

Yield: 75%, M.P: >250°C, IR(Nujol): 1645cm⁻¹(C=N), 1269cm⁻¹(C=O), 1265cm⁻¹(C-O), 3455cm⁻¹(H₂O), 520cm⁻¹ (M-N), 450cm⁻¹ (M-O), H¹NMR: δ 7.0-7.8(m, 12Ar-H), 2.57(s, 3H CH₃), 5.2(s, 1H CH), 5.6(s, 1H CH), 6.2(s, 1H CH), 4.1(s, 2H H₂O), C₄₆H₃₆Cl₂N₄O₄(455): (Anal. Cal.): C, 70.68; H, 4.90; N, 7.17, Cl, 9.04%. Found: C, 70.33; H, 4.55; N, 7.77, Cl, 9.04%



Zn(II) Complex

Some of the important reported Salen types of metal complexes



Part B

Seeds of papaya are soaked with 10 ppm solutions of prepared Zn complexes and equal concentrations of ligands differently for 12 hrs. Control is made up of distilled water. An equal number of seeds are used for every solution. The seeds after soaking are transformed into a polythene container containing a growing media consisting of garden soil at a depth of 1 cm under controlled conditions in a greenhouse with light at 280 to 350 day/night temperature, and 65%-75% relative humidity. Two seeds are removed and planted in each pot. The length of seedlings, root lengths, and number of leaves are monitored at intervals of fifteen days and thirty days respectively. The observations are analyzed in a completely randomized design. Leaf morphology is compared with control sample. The chlorophyll contents of leaves are measured through spectrometer. After 15 days and 30 days intervals, leaves are plucked off. The plant leaves are dried immediately in a forced-air oven at 700 to a constant weight and ground to a fine powder. Dry samples of 1g are placed into ceramic vessels and combusted in a muffle furnace at 5500C. The ash samples are removed, cooled, and then dissolved in 2M

HCl. The final solution is diluted to follow the analytical procedures. The analysis of Zn is carried out with an AAS.

Results and Discussions:

The ligand(v) was prepared by condensation reaction of 1-(2-Amino-phenyl)-3-chloro-4-p-tolyl-azetidin-2-one (iii) with salicylaldehyde. TLC spots suggested the formation of the ligand. The complexes were formed by the direct reaction of the ligand with zinc(II) acetate. The elemental analysis of the compounds is in good agreement with their proposed formulae and the conductance values indicate the non-electrolytic nature of the complexes. The magnetic measurements of the complexes at room temperature reveal that all the complexes are paramagnetic and diamagnetic, consistent with octahedral geometry of zinc (II) complexes. All the complexes are stable at room temperature and melt with decomposition above 250°C. Unfortunately, our efforts to obtain single crystals of complexes were not successful. Therefore the ligand, and its complexes were characterized on the basis of elemental analysis, ¹HNMR, IR, magnetic susceptibility measurement, electronic spectra data, TGA/DTA, colours, melting point, partial elemental analyses and molar conductivities. FT IR spectra To determine the way of chelation of Schiff base ligand to metal(II) ion, the IR spectrum of free Schiff base ligand is compared with IR spectra of its metal(II) complexes. The IR spectra of the ligand(v) show a very strong band at 3525 cm⁻¹ was assigned to (O-H) vibration. The absence of (O-H) stretching and $\nu(\text{O-H})$ vibration in the spectra of the complexes indicated deprotonation of the –OH groups. The strong band observed in the region 1670cm⁻¹ in the ligand assigned to C=N stretching. The complexes (vi) show a strong band at 1645-1655 cm⁻¹ band at region, representing the C=N stretching moiety. This band is shifted to a lower frequency by ~ 15-30 cm⁻¹, as compared to the corresponding ligand indicating that the azomethine nitrogen of the C=N group has participated in coordination. This can be ascribed to the withdrawn of electron density from the nitrogen atom owing to coordination. The phenolic $\nu(\text{O-H})$ band is shifted from 3525 to 1265–1275 cm⁻¹ as a consequence of the delocalization of double bond in chelate rings that has increased the bond order of the phenolic C-O. The phenolic oxygen, after the loss of O-H proton gets coordinated to the metal. This is supported by shift in the stretching frequency of $\nu(\text{C-O})$ to lower wave number from its position in the free ligand. In addition all the complexes showed additional weak to

medium intensity bands in the region new 520-630 and 450-510 cm⁻¹ which were absent in the spectra of ligand, these can be attributed to $\nu(\text{M-N})$ and $\nu(\text{M-O})$ respectively. The proton NMR spectrum of the Schiff base ligand shows singlet peaks at 10.6-12.5 ppm which are corresponds to phenolic-OH groups which are absent in the spectrum of Zn(II) complexes. This indicates that the deprotonated phenolic-O atom is involved in chelation. The absence of a peak in the region 4.10–4.75 ppm reveals the absence of coordinated water molecules in the complex. The magnetic moment of the complexes were measured at room temperature. The electronic spectra of Zn(II) complexes reveal a charge transfer bands $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions in the vicinity of the Schiff base ligand at 350-375 and for complexes at 275 to 285 cm⁻¹ suggesting an octahedral structure which is common for d10 systems. Thermal Studies The study of the thermal behavior of all the complexes in air provides information about its thermal stability and nature of degradation of products produced at various

temperatures. Thermal analyses of the complexes were carried out up to 800 °C. All the complexes show a gradual mass loss indicating decomposition by fragmentation with increase in temperature and follow the similar pattern of their thermal decomposition. Thermogram of complex shows three stages of weight loss whereas Zn(II) complexes shows only two stages of weight loss. By comparison, the Zn(II) complex shows an initial weight loss at 120–250 °C which corresponds to the coordinated water molecules. The weight loss (80–82%) at 250–350 °C corresponding to continuous sublimation of organic ligand moieties and the formation of an air stable metal oxide as the end product in the range of above 400 °C. The results well agreed with the composition of the metal complexes. The decomposition was completed at ≥800 °C.

Conclusion:

The synthesized Schiff base ligand and its metal(II) complexes were characterized by micro analytical and various spectral studies. The observed molar conductance, magnetic susceptibility and spectral data confirm octahedral environment. The presence of coordinated water molecules in all the complexes further confirmed from thermal analysis.

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