Possible Mechanism of Inhibition of Schiff base Complexes on Gazone (Cynadon) and Cucumber (Cucumis satires)

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ABSTRACT

The divalent metal ions Mn, Cu and Zn complexes with Schiff base derived from a reaction of salicylaldehyde with L- valine amino acid (L) have been prepared and investigated by using different physicochemical techniques in terms; elemental analysis, molar conductance measurements, infrared, electronic and electron paramagnetic resonance spectroscopies. The elemental analysis exhibited the formation of 1:1 [M: L] ratio. The molar conductance measurements of the complexes indicated the presence of a non-electrolytic nature. The infrared spectral data displayed coordination sites of the free Schiff base toward the metal ions under investigation. The electronic spectral results of Schiff base and its complexes revealed the existence of π-π^* (phenyl), n-π^* (H-C =N) transitions, and these results suggest that all the complexes are octahedral. The electron paramagnetic resonance spectral data were reported. The free Schiff base, metal ions and their complexes affected on germination of root and shoot lengths of gazone (*cynadon*) and *cucumber* seeds (CuCumis satires).

KeyWords: Metal ions**,** Salicylaldehyde, Valine, Schiff base, Complexes, Gazone, Cucumber.

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INTRODUCTION:

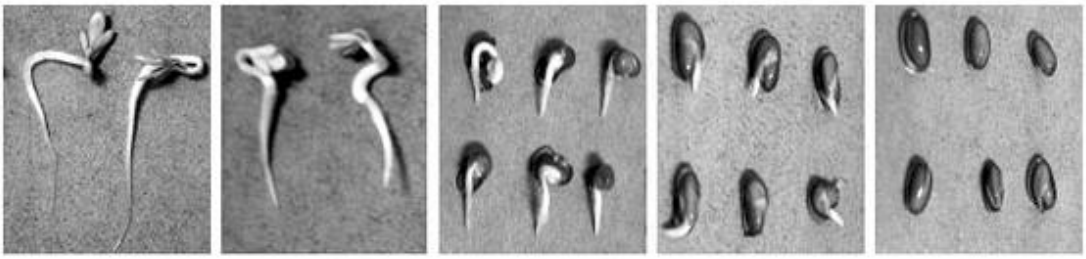
Salicylaldehyde has many applications in Chemistry and Medicine. The used ligand has a good ability to form large number of chelates with most transition and non transition metal ions.(1)

The complexes of Mn(III) with Schiff bases obtained by condensation of 2- hydroxyl-1-naphthaledehyde with glycine, L-alanine, L-phenylalanine, L-histidine, L-tryptophan and L-Therionen have been synthesized and characterized by elemental analyses, UV-vis, IR, magnetic susceptibility, thermogravimetry and nonaqueous titration.(2)

A ligand (HL) obtained from the Schiff base condensation of 4-(diethylamino) salicylaldehyde with 4-nitroaniline is reported with its nickel(II) Copper(II), and cobalt(II) complexes.(3)

Complexes of chlorosalicylalidene aniline with Co(II) and Cu(II) were synthesized and screened for antibacterial activity against several bacterial strains.(4)

It is well known that 6-methoxy-2-benzoxazolinone (MBOA) and its related compounds inhibit the germination and growth of several plant species. However, the physiological mechanism of MBOA on germination inhibition is not fully understood. MBOA inhibited the germination of cress and lettuce seeds at concentrations greater than 0.03 mM. Both inhibitions increased with increasing concentrations of MBOA, and the extent of the germination was positively correlated with the activity of alpha-amylase in the seeds. Alpha-Amylase is considered essential for seed germination because this enzyme principally triggered starch degradation in endosperm that MBOA may inhibit the germination of cress and lettuce seeds by inhibiting the induction of alpha-amylases activity. It may be one of the possible action mechanisms of MBOA on inhibition of plant germination.(5)



EXPERIMENTAL:

All chemicals used in this investigation were of analyzed grade BDH and Aldrich.

Synthesis of Schiff base:

The amino acid Schiff base was synthesized as following: NaOH (10 mmol, 0.4 g) was dissolved in methanol (30 cm^3) and the amino acid L-valine (10 mmol) was added to it the mixture was stirred magnetically at room temperature. When the mixture becomes homogenous, a solution of salicylaldehyde (10mmol, 1.22 g) in ethanol (20 cm^3) was added. After 2 minutes, the solution of was evaporated to 20% of its original volume and 1cm^3 of CH_3COOH was added immediately. After 2hours, yellow crystals appeared. The crystals were filtered and washed with ethanol. They were recrystallized form hot methanol to give yellow crystals.

Synthesis of Schiff base complexes:

The amino acid (L- valine) (1.17g) was dissolved in (50 cm^3) of methanol containing NaOH (0.8 g) in flask and stirred at temperature room. A solution of salicylaldehyde (2.44 g) in 50cm^3 of ethanol was added to the solution. After 2 minutes, the metal salts (10 mmol); ($MnCl_2.4H_2O$ or $Cu(CH_3COOH)_2.H_2O$ or $ZnCl_2$) was stirred magnetically for 3 hours. The solution volumes were reduced to 75% by evaporation and the residues were left to stand overnight, crystals were obtained and the solids were recrystallized from methanol\ ethanol (50%) mixture.

Physical techniques:

Melting points and solubility of the synthesized ligand and complexes were determined in capillary tubes using griffin apparatus and are uncorrected. The prepared Schiff base was soluble in water; ethanol and DMSO solvents. Schiff base complexes are soluble in DMSO solvent. Elemental analysis of the Schiff base and its complexes have been subjected to (C, H, and N) using 2400 elemental analyzer at Micro Analytical Center, Cairo–University, Egypt. Molar conductivity measurements of the complexes in DMSO solvent were measured using digited conductivity meter CMD 650, at Chemistry department, Faculty of science, Garyounis, University, Benghazi Libya. The infrared spectra of Schiff base and its complexes were carried out by applying the KBr disc technique using IFS-25 OPUS/IR (Bruker) spectrometer. Electronic absorption spectra of the present Schiff base and its complexes were scanned with ultraviolet and visible ranges using DMSO solvent. The absorption spectra were measured using UV-vis NIR 3101 PC Schimadzu (Japan). Electron paramagnetic resonance spectra (e.p.r) of Mn(II) and Cu(II) complexes were recorded by using EMX ESR spectrometer (Bruker) 1998Y.

Germination assay:

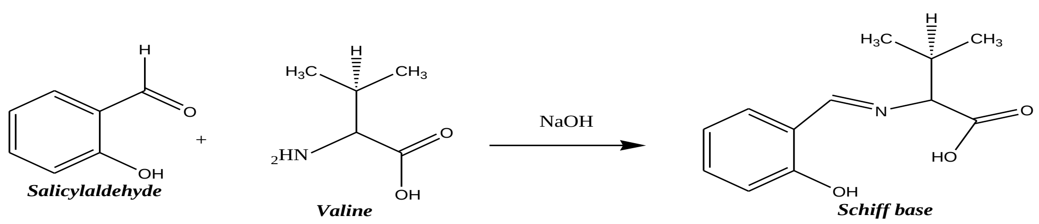
Gazone and cucumber seeds were arranged on petridishes contain two layers of filter paper (N0.1), different concentrations (0.001, 0.01, 0.1, and 0.2) g/20ml of Schiff base, its complexes MnL.4H_2O, CuL.3H_2O and ZnL.3HO_2 and its metal ions were added to the seeds on the filter paper. The control seeds were irrigated with distilled water. At the end of experiment, the number of seeds germination was counted and compared with control. Both lengths of root and shoot were measured and compared with the reference of root and shoot growth of control.

Statistical analysis:

The statistical evaluation of the results was conducted with use of SPSS-(statistical package for social science; Windows version 6.0) packed program. One- way analysis of variance (ANOVA) used to analyze the results. The level of statistical significance was set at $p < .05$.

RESULTS and DISCUSSION

The reaction of salicylaldehyde with valine in methanol yields one amino acid Schiff base compound. The chemical equation concerning the formation of the compound represented as follows:



The elemental analyses (C, H and N) of the amino acid Schiff base and their complexes are listed in Table-1. The empirical formulae of the complexes indicated a 1:1 [M:L] ratio.

Table-1: Elemental analysis and some physical properties of the Schiff base and its complexes

Schiff base \complexes	C%	H%	N%	M.P	M. wt	Λm**
L ($C_{12}H_{14}O_3N$. $2H_2O$	55.79 (56.52)	6.82 (7.03)	4.92 (5.46)	242-243	256	-
[MnL. $3H_2O$]. $2H_2O$	39.59 (39.56)	6.70 (6.57)	4.92 (5.46)	<350	364.9	14.10
[Cu L.$3H_2O$]	46.00 (46.82)	5.19 (5.92)	4.60 (4.14)	247-248	320.50	7.46
[ZnL. $3H_2O$]	41.83 (42.60)	4.95 (5.92)	4.30 (4.14)	<350	304.38	8.22

( ) Calculated values in parentheses

****Unit of molar conductance ohm^{-1} cm^{2} mol^{-1}**

Molar conductivity:

The molar conductance values of the complexes in 10^{-3} M DMSO solvent were 7.46, 8.22 and 14.10 ohm^{-1} cm^{2} mol^{-1} of Mn(II), Cu(II) and Zn(II) complexes respectively, indicating that those complexes are non-electrolytic nature.[6] These values suggest that no anions are exist outside the coordination sphere, Table (1).

Infrared spectra:

The infrared spectra of the complexes (Fig.1) exhibit of a band at 1597 cm^{-1} due to ν(-HC=N) of a zomethine. The infrared spectral data of Schiff base complexes display bands in the range of 1505-1611 cm^{-1}. A slight change is observed for ν(-HC=N) band a after complexation, indicating the involvement of the a zomethine nitrogen atom in coordination.[7]The spectrum of the Schiff base displays another band at 1595 cm^{-1} which could be attributed to the presence of $\nu(COO)^-$ group. The Schiff base complexes are proven by the bands of ν (COO^-) group of the carboxyl in the range of 1539-1646 cm^{-1} region, which indicates the participation of oxygen of carboxyl group in complexation.[8] the observed bands at 536-601 and 419-475 cm^{-1} display the presence of ν M-O and ν M-N vibrations,(9) which are not present in the free Schiff base. The IR spectra of the complexes show ν(OH) bands 3293-3648 cm^{-1} region, which indicating the presence of water molecules in complexes. [10] Table (2), Fig (1).

Table -2: Infrared band assignments (cm^{-1}) of L and its complexes.

Schiff bases / complexes	$\nu(OH)(H_2O)$	ν (C=N)	ν (COO^-)	ν (M-O)	ν (M-N)
L ($C_{12}H_{14}O_3N$. $2H_2O$	**3648**	**1595**	**1505**	___	____
[MnL.$3H_2O$]. $2H_2O$	**3445**	**1649**	**1611**	**600**	475
[Cu L.$3H_2O$]	**3292**	**1539**	**1599**	**1601**	424
[ZnL. $3H_2O$]	3446	1636	1595	536	419

Table-3: Electronic spectral data (nm, cm^{-1}) of Schiff base L and its complexes

Schiff base complexes	Wavelength (nm)	cm^{-1}
L ($C_{12}H_{14}O_3N$. $2H_2O$	**367, 625**	(272481, 16000)
[MnL.$3H_2O$]. $2H_2O$	**363**	(27458)
[Cu L.$3H_2O$]	369,274	(27100, 36496)
[ZnL. $3H_2O$]	364, 371, 271	(26945, 27472, 36900)

Electronic and electron paramagnetic resonance spectra:

The electronic spectrum of L shows two bands at 367, 625nm (27248 and 16000 cm^{-1}) which is assigned to the $\pi\rightarrow\pi^*$ (phenyl ring) and $n\rightarrow\pi^*$transitions.(11) Meanwhile, for Mn-L complex, the electronic spectrum displays a band at 363nm (27548 cm^{-1}), this band due to intraligand $\pi\rightarrow\pi^*$ and charge transfer (M→L) transitions, this information assures an octahedral geometry(12) For Cu(II) complex. the electronic spectrum displays two bands at 369, 274nm (27100 and 36496 cm^{-1} due to $^2E_g\rightarrow{}^2T_{2g}$ transition and an octahedral geometry was proposed.(13)The electronic absorption spectrum of Zn(II)-L complex which is diamagnetic exhibits three bands at 364, 371, 271nm (27473,26954 and 36900 which were less intense and a broad band results from the overlap of the energy $\pi\rightarrow\pi^*$transition mainly localized within the imine chromophore and LMCT from the lone pairs of phenolat oxygen.(14)Table (3), Fig (2). Electron paramagnetic resonance spectra of the complexes deduced to obtain further information about the stereochemistry and the sites of the metal ligand bonding and to determine the magnetic interaction in the metal complexes.(15) The spectra of Mn(II)-L_1 and Mn-L_2 complexes show geff of 2.01. The obtained data showed an octahedral geometry. For-Fe(III)-L_3 complex, the spectrum of complex shows geff of 2.02, this value corresponds to an octahedral geometry. For Cu(II)-L_2 complex, the spectrum shows g_{eff} of 2.02, this value suggests the presence of an octahedral geometry.[16] Figs (4,5).

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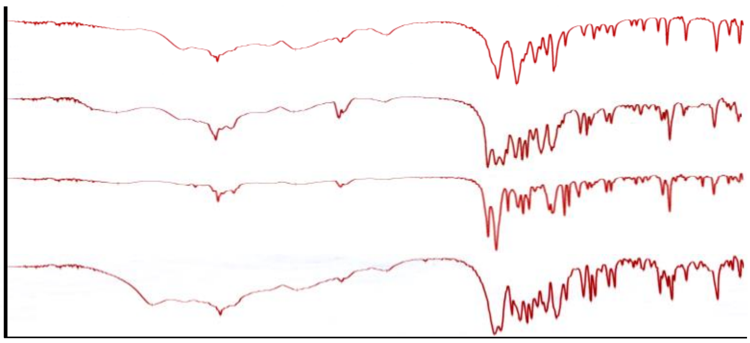
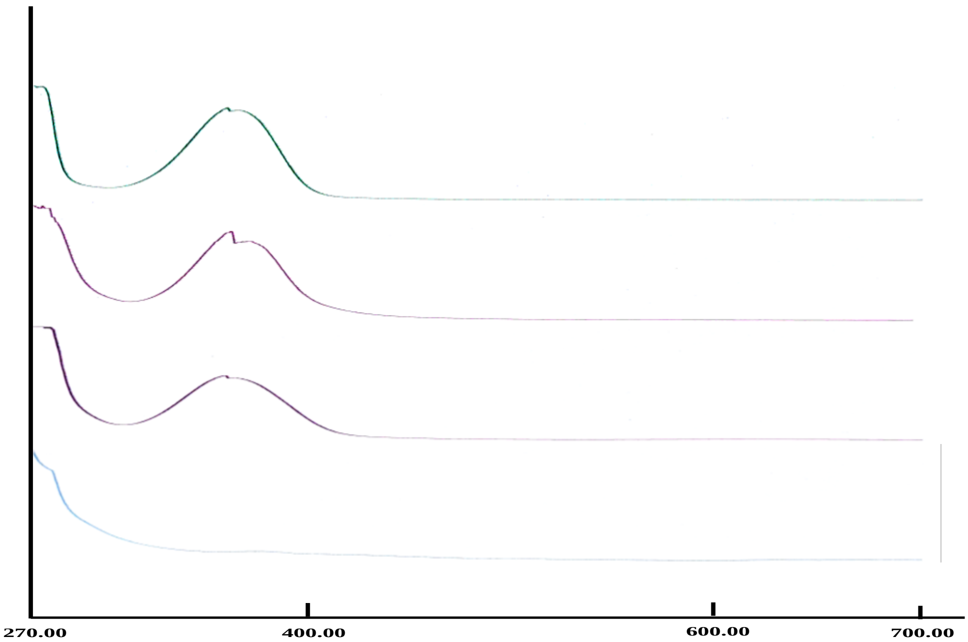


Wave number cm^{-1}

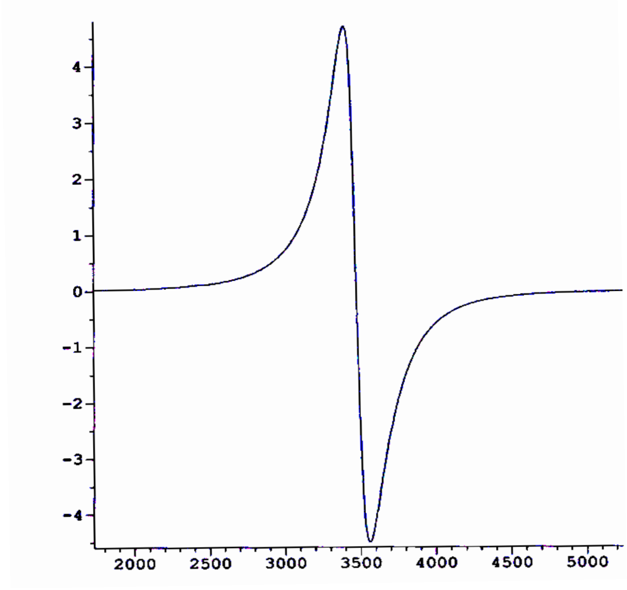
Fig(1): Infrared spectra of Schiff base and its complexes

A



Wavelength (nm)

Fig(2): electronic spectra of Mn(II), cu(II) and Zn(II)-L complexes



[G]

Fig(3): Electron paramagnetic resonance spectrum of Mn(II)

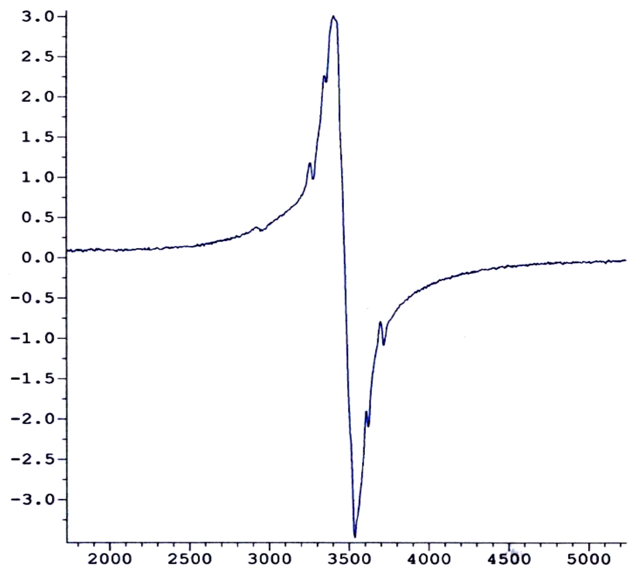
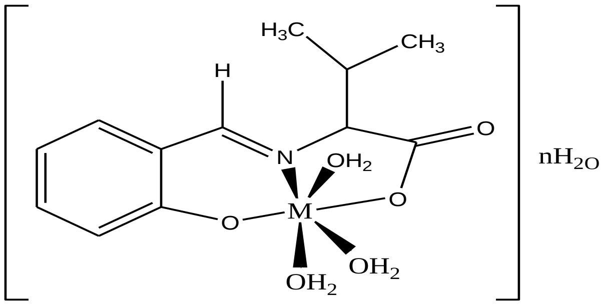


Fig. (4): Electron paramagnetic resonance spectrum of Cu(II) compound

CONCLUSION:

From the previous chemical analysis one can suggest the following chemical structure.



M = Mn(II), Cu(II) and Zn(II) [n = 0 and 3]

Seed germination, root and shoot growth

Schiff base L causes both reduction of seed germination and reduce the growth of shoot and root compared to the control. The highest effect on seed germination and root and shoot growth was observed at of (0.2 g\20ml). For The Mn-L complex was inhibited of the seed germination at higher concentration. Root and shoot lengths were decreased even reach at (0.1g\20ml) concentration to 0.1cm length and 1cm shoot length. For the Cu-L complex, the effect on seed germination and root and shoot lengths of gazon seeds is not inhibited completely at higher concentration. Root and shoot length values at this concentration are 0.1cm and 1cm of the root and shoot respectively. For the effect of Zn-L complex was partially inhibited, our results showed decreases in the root and shoot growth compared with the control. For metal ion Mn(II), the extent of inhibition of seed germination, root and shoot growth was decreased with increases of the concentration until reach 0.10cm and 1.38

cm at higher concentration for (root and shoot) lengths, respectively. For effect of Cu(II) ion the seed germination occurred only at concentration (0.001g\ 20ml), the lengths of shoot and root reach to (2.6 cm and 4.9 cm) respectively. For effect of Zn(II) ion seed germination was inhibited at concentration (0.2g\ 20ml), also for reduction of root and shoot growth was observed reach to 0.4 and 0.5cm compared to control. All results of the statistical analysis showed significant except two concentrations 0.001, 0.01) g\20ml ($p = 0.74 > 0.05$) of Mn(II) complex, between the two concentrations (0.001 and 0.01) g\20ml and two concentrations (0.1 and 0.2) g\20ml of Cu(II) complex. The effect of Mn(II) complex on seed germination, root and shoot lengths of cucumber seed had any effect on the germination. On the other hand, Root and shoot length growth was having sensitive of the increases the concentration but lees than it on the gazon plant. The statistical analysis given significant of the results. ($P < 0.05$), (Figs. 5-16).

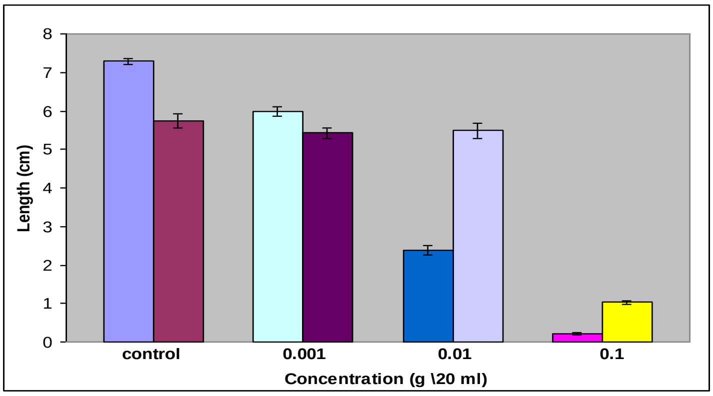


Fig (5): Effect of Schiff base on gazone seeds

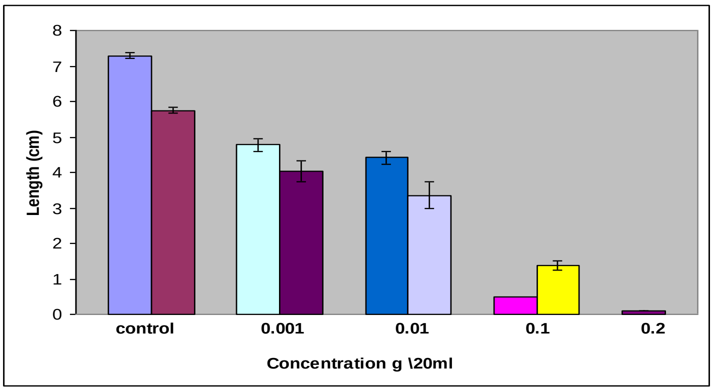


Fig.(6) Effect of Mn(II) ion on gazone seeds

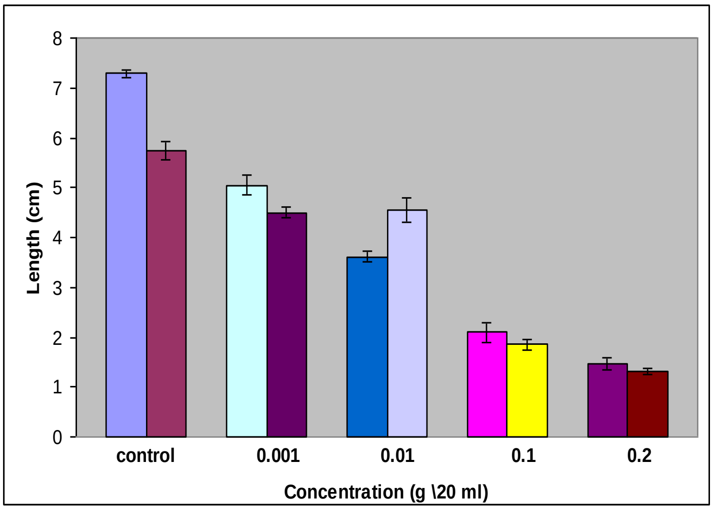


Fig.(7): Effect of Cu(II) ion on gazone seeds

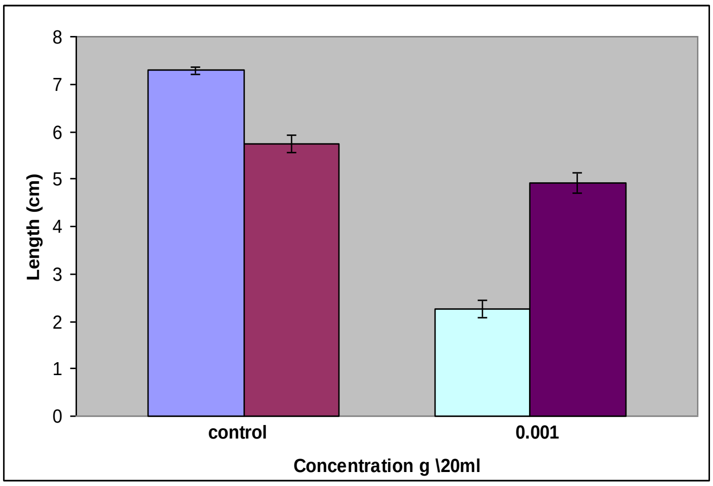


Fig.(8): Effect of Co(II) ion on gazone seeds

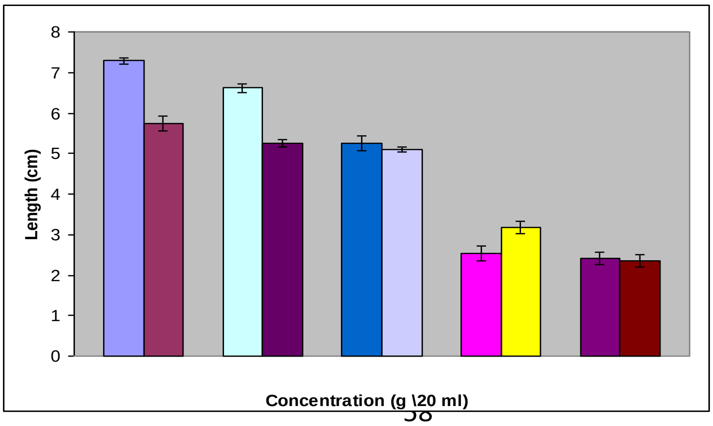


Fig.(9): Effect of Mn(II) complex on gazone seeds

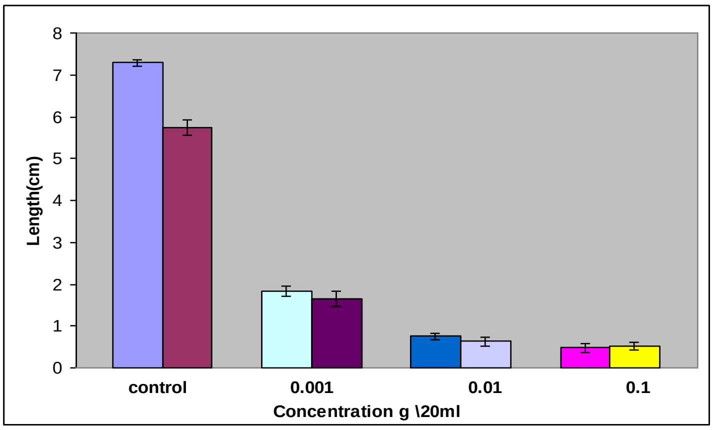


Fig.(10): Effect of Cu(II)complex on gazone seeds

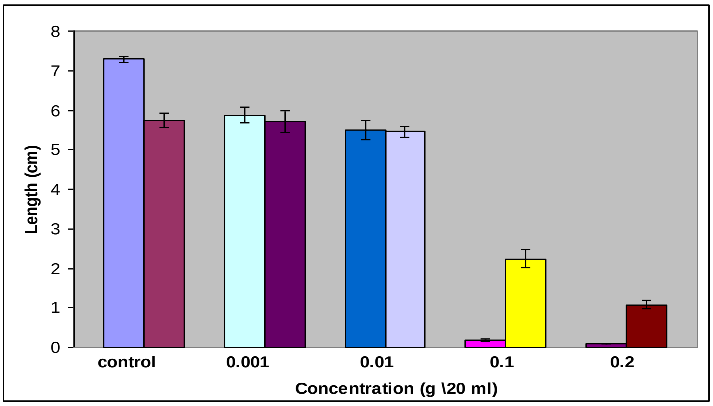


Fig.(11): Effect of Zn(II)complex on gazone seeds

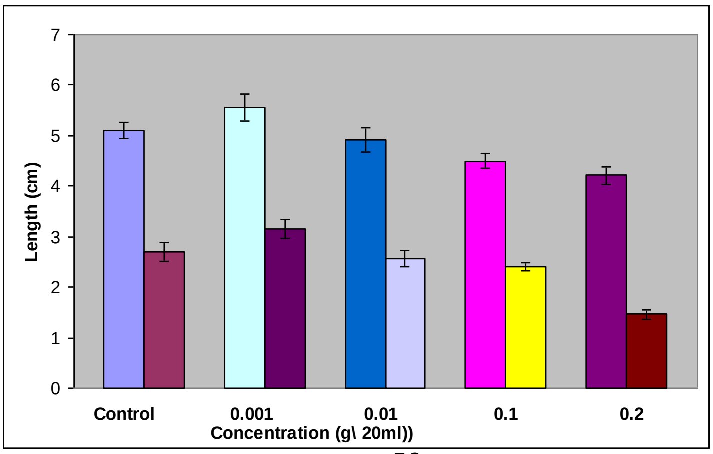
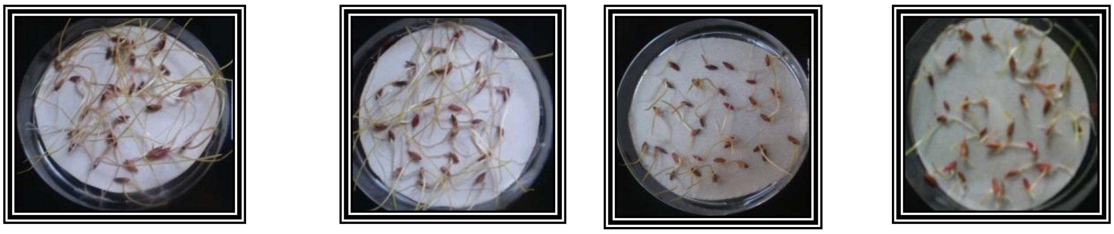


Fig.(12): Effect of Mn(II) complex on Cucumber seeds

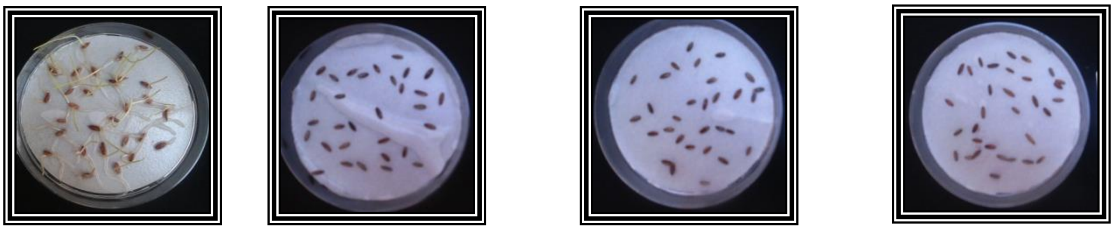
Control *(gazone)* Control *(Cucumber)*

Fig (13): Effect of the distillated water on gazone and cucumber seeds.



0.001 0.01 0.1 0.2

Fig (14): Effect of Schiff base on gazone seeds



0.001 0.01 0.1 0.2

Fig (15): Effect of Cu (II) ion on gazone seeds

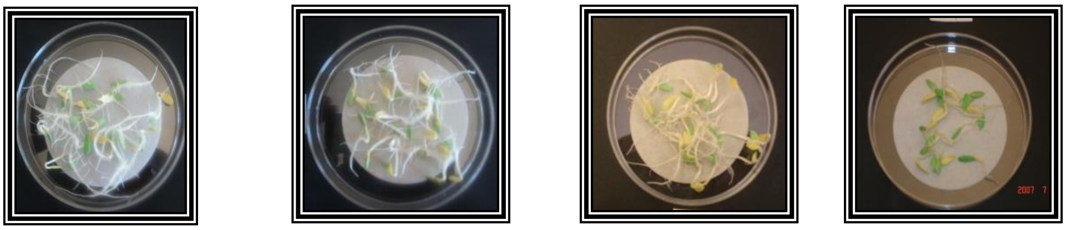


Fig. (16): Effect of Mn-L complex on Cucumber seeds

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