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Original Research Article

STUDY OF PLANT GROWTH ACTIVITY OF 2-METHOXY-6-{[2-(2-METHOXY-PHENOXY)-ETHYLIMINO]-METHYL}-PHENOL AND ITS TRANSITION METAL COMPLEXES ON *TRIGONELLA FOENUM-GRAECUM, TRITICUM AESTIVUM AND BRASSICA NIGRA*.

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Abstract: Coordination complexes of transition metals with Schiff base ligand were synthesized. The characterization of these complexes were elucidated by physical parameters and spectral analysis namely colour, melting point, IR, NMR, UV, Magnetic measurements, TGA and ESR studies.. Plant growth regulating activity on seeds of *Trigonella foenum-graecum* (Methi), *Triticum aestivum* (wheat) and *Brassica nigra* (black mustard) has been studied using standard Blotter method for evaluation of inhibitory or stimulatory effects of the synthesized compounds. The plant growth analysis was decided by measurement of parameters like percentage of germination, seedling height, shoot length, root length, root/shoot ratio and vigor index. The values of these parameters have been used to make a conclusion about plant growth regulating activity of ligand and its complexes

Keywords: Schiff bases, Metal Complexes**,** Plant growth studies, Standard Blotter method

Introduction: Research in agriculture involves production of new and better varieties of crop plants, plant protection against insects and weeds, manage soil fertility. Many substances are capable of inducing same plant responses. In this context role of coordination chemistry is significant. Many transition metal complexes are been used to produce new varieties of crops, control soil fertility, protect the plants from insects, diseases and weeds. It has been observed that on complexation, the biological activity of metal chelate changes compared to that of free metal and ligand alone [1,2,3.] The microbial activity like antifungal and antibacterial of metal complexes showing an enhanced activity as compared to free metal and ligand has been reported [4]. Transition metal complexes of substituted pyrazoles were tested for their plant growth regulating activity[5]. Piperidene-2-carboxylic acid complexes of bivalent metal ions have been found to be useful in agriculture as plant growth regulating[6].

Plant growth regulating activity of (2-chlorophenyl) (5-(2- hydroxyphenyl)-3-(pyridin-3-yl)-1H-pyrazol-4-yl) methanone and its Fe (III) and Cu (II) complexes on *Trigonella foenum-graecum* were studied[7]. Piperidene-2-

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carboxylic acid complexes with some bivalent metal ions have been reported to be useful in agriculture as plant growth regulating[8]. Many workers have studied the plant growth regulating activities of various organic ligands and their transition metal ion complexes for various plants[9-14].

Materials and Methods

Chemicals and reagents: The chemicals used are 2-(2-Methoxy-phenoxy)-ethylamine (Merck ,AR grade) and o-Vanillin (Merck ,AR grade),Ethyl alcohol (Merck ,AR grade) , Cobalt (II) chloride dihydrate (Sigma Aldrich), Nickel(II) chloride hexahydrate (Sigma Aldrich), Copper(II) chloride dihydrate (Sigma Aldrich), Zinc (II) chloride (Sigma Aldrich) , Manganese (II) chloride tetrahydrate (Sigma Aldrich)

Synthesis of Ligand (SB4): The Schiff Base ligand 2-Methoxy-6-{[2-(2-methoxy-phenoxy)-ethylimino]-methyl}-phenol (Fig 1) was synthesized by condensing amine 2-(2-Methoxy-phenoxy)-ethylamine with o- Vanillin in equimolar proportions. To an ethanolic solution (10 ml) of the amine (0.01 mole) was added o-Vanillin (0.01 mole) in ethanol (10 mL) with stirring. The mixture was then refluxed for 30 mins. The reaction mixture was then cooled which immediately gave a precipitated product. The product then obtained was filtered, washed with ethanol and then dried. The crude product was then crystallized from aqueous ethanol to give a yield of 86%.

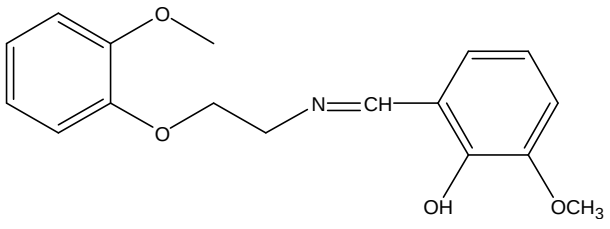

Fig 1. Structure of Ligand(SB4): 2-Methoxy-6-{[2-(2-methoxy-phenoxy)-ethylimino]-methyl}-phenol

Synthesis of metal complexes: The ligand and metal salt in the molar ratio of 2:1 was dissolved in a ethanol and the reaction mixture was heated on water bath for about one hour. It was then cooled when colored solid separated out which was washed with ethanol and dried. This is the general method employed for the synthesis of metal complexes of ligand with metal chlorides viz Ni(II), Cu(II), Co(II), Mn(II) and Zn(II).

Plant Growth Activity study: The plant growth activity studies were carried out on the seeds of three plants Trigonella foenum-graecum (Methi), *Triticum aestivum* (wheat) and *Brassica nigra* (black mustard) by standard blotter method. Metal complex solutions (5 ppm) and ligand solution (5ppm) were prepared using 20% DMSO solution in doubly distilled water. The seeds were soaked in water overnight. Healthy seeds of equal size were chosen, and then immersed in distilled water, 20 % DMSO solution, and ligand solution and complex solutions for 6 hours. The seeds soaked were taken out of each solution and washed thoroughly with distilled water. The seeds were then placed on Petri plate with 20 seeds per plate containing moistened blotters. The plates were observed for germination, root-shoot length for 10 days.

Results and Discussion: Formation of the complex was indicated by color change and melting point. Physical characteristics and yield of Schiff base and metal complexes are given in Table 1.

Table 1: Physical characteristics and Yield

Compound	Color	Yield %	M.P (^{o}C)
Ligand (SB4)	Bright yellow	86	96 ^{o}C
SB4-Ni complex	Pale green	70	257 ^{o}C
SB4-Cu complex	Blackish green	61	237 ^{o}C
SB4-Co complex	Orange	54	227 ^{o}C
SB4-Mn complex	Brownish green	71	246 ^{o}C
SB4-Zn complex	Yellow	75	240 ^{o}C

NMR and IR spectra: In NMR spectra formation of ligand was confirmed by presence of CH=N peak at 8.4 δ and OH at 5.6 δ. In the present investigation the Infra red values for major peaks are assigned. The IR spectrum of ligand gave a strong band at 1642.09 cm-1 and 2901.27cm^{-1} which are attributed to the stretching frequencies of HC=N (azomethine) and OH respectively. Complexes showed a lower shift of wave numbers for HC=N. Also IR bands were observed for M-O and M-N. All complexes showed bands 3300 cm^{-1} to 3400 cm^{-1} indicating co-ordinated H_2O moiety in the complexes. Complex of SB1-Ni showed IR bands at 1617.98 cm^{-1} and 3331.31 cm^{-1} corresponding to HC=N and H_2O , IR values of 469.582 cm^{-1} and 546.72 cm^{-1} were assigned to M-O and M-N respectively. Similarly complex of SB1-Zn complex showed bands at υ(HC=N) 1622.8 cm^{-1}, υ(H_2O) 3452.54 cm^{-1} , υ (M-O) 479.224 cm^{-1} and υ (M-N) 673.035 cm^{-1}. Similarly bands were observed for Cu complex at υ(HC=N) 1622.8cm^{-1}, υ(H_2O) 3409.86 cm^{-1} ,υ (M-O) 470.546 cm^{-1} and υ (M-N) 673.035 cm^{-1}. Co complex υ(HC=N) 1613.16cm^{-1}, υ(H_2O) 3375.81 cm^{-1} ,υ (M-O) 461.868 cm^{-1} and υ (M-N) 563.112 cm^{-1}. Mn complex υ(HC=N) 1539.88cm^{-1}, υ(H_2O) 3446.17 cm^{-1}, υ (M-O) 454.154 cm^{-1} and υ (M-N) 496.58 cm^{-1}.

Electronic absorption spectra: In the electronic spectra the ligand exhibited energy peaks at 30211cm^{-1} and 23640 cm^{-1}. The Co(II) complexes exhibited two energy peak at 18181 ,22935 and 29325 cm^{-1}, which can be assigned[15] to the transitions 4T1g(F) → 4T2g(F), 4T1g(F) → 4A2g(F) and 4T1g (F) → 4T2g (P) for a high spin octahedral geometry respectively. The electronic spectra of the Ni(II) complexes showed d–d transition at 28985, 24390 cm–1 and 22883 cm–1[15] while Mn complexes showed peaks at 30487 cm^{-1} and 24509 cm^{-1}. These are assigned to 3A2g(F) → 3T2g(F), 3A2g(F) → 3T1g(F) and 3A2g (F) → 3T2g(P) transitions, respectively. These are consistent with a well- -defined octahedral geometry. The Zn(II) complexes exhibited only a high intensity band at 26385 cm^{-1} and 29850 cm–1, which is assigned to ligand–metal charge transfer. In case of the Cu(II) complexes, a broad band at 26809, 28571 cm–1 and 27027 cm–1[15] was observed that is assigned to the 2Eg → 2T2g transition, which confirms its octahedral geometry.

Thermo Gravimetric Analysis: TGA analysis is carried out to explain the thermal stability of complexes. TGA study of complex showed weight loss in the temperature range of 110^{o}C-200 ^{o}C is due to elimination of coordinated water molecule. Also gradual decrease in mass is seen up to 300 ^{o}C due to loss of volatile matter. And a plateau observed above 350 ^{o}C respectively which corresponds to the formation of stable metal oxide.

ESR: The gll and g⊥ value for Copper complex is reported in the following Table 2. The spectrum showed asymmetric bands with two g values. The trend gll> g⊥> 2.00277, indicating that the unpaired electron lay predominately in the dx^2-y^2 orbital with possibly mixing of dz^2 orbital because of the low symmetry. The axial symmetry parameter 'G' is determined as $G = \frac{(gll - 2.00277)}{(g\perp - 2.00277)}$. G values found to be more than 4 suggesting very weak or no interaction in the solid state.

Table 2: ESR values for Copper complex

Complex	gll value	g⊥ value	g_{avg}	G
SB4 Cu complex	2.297	2.047	2.13033	6.65227

Magnetic susceptibility measurements: The effective magnetic moment values for the complexes were determined. The magnetic moment value 4.24 B.M for Co(II) complex suggests an octahedral environment[16,17]. The magnetic moment value of the Cu (II) complexes of 1.63 B.M suggests distorted octahedral geometry[18,19]. The magnetic moment value of the Ni(II) complexes 3.13 B.M suggests an octahedral geometry. Mn (II) complexes with the value of 5.64 B.M indicate octahedral geometry[20]. The Zn(II) complexes were found to

be diamagnetic, as expected for d^{10} configuration.

From the discussion of the results of various physico-chemical studies presented above, it may be concluded that the most probable geometry for the transition metal complexes with general formula $ML_2.2H_2O$ is octahedral and the bonding in the complexes can be represented in Fig 2.

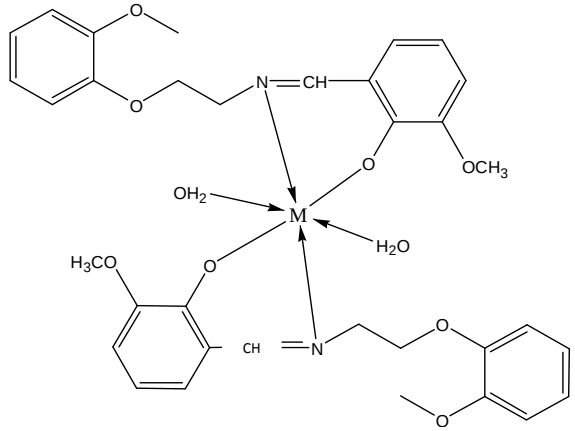

Fig : 2 Structure of complex (M= Ni, Cu, Co, Mn, Zn)

Plant growth activity: The values plant growth parameters such as percentage of germination, survival, shoot length, root length, root/shoot ratio, vigor index for *Trigonella foenum-graecum* (Methi) are reported in Table 3 , similar parameters for *Triticum aestivum* (wheat) are reported in table 4 and for Brassica nigra (black mustard) in table 5.

Vigor index was determined using equation *Vigour index = % germination x (root length + shoot length)*

The root: shoot ratio is one of the measures of overall health of the plants. Change in the root: shoot ratio over control (water) indicates change in overall health of the plant.

The root/shoot ratio was determined by using equation *root/shoot ratio = dry weight for roots/dry weight for top of plant*

The general order of plant growth activity of ligand and its complexes compared to water are shown in Table (3), Table (4) and Table (5).

Table 3: Effects of 2-Methoxy-6-{[2-(2-methoxy-phenoxy)-ethylimino]-methyl}-phenol and its Ni(II), Cu(II), Co(II), Mn(II) and Zn(II)complexes on growth parameters for *Trigonella foenum-graecum* (Methi) plant.

Parameters	Effect of		Effect of complexes				
	Water	Ligand	Ni (II)	Cu (II)	Mn (II)	Co (II)	Zn (II)
Germination seed number	20	20	20	20	20	20	20
% Germination after 7 days	85	75	60	65	55	65	55
% Survival after 10 days	100	93.33	91.66	84.61	90.90	84.61	81.81
Root length (cm)	3.0	2.1	1.0	1.4	1.3	1.1	1.3
Shoot length (cm)	4.2	3.4	2.5	2.3	2.1	2.4	2.3
Vigor index	612	412.5	210	240.5	187	227.5	198
Root-shoot ratio	0.74	0.63	0.38	0.53	0.80	0.31	0.50

Table 4: Effect of 2-Methoxy-6-{[2-(2-methoxy-phenoxy)-ethylimino]-methyl}-phenol and its Ni(II), Cu(II), Co(II), Mn(II) and Zn(II) complexes on growth parameters for *Triticum aestivum* (wheat) plant.

Parameters	Effect of		Effect of complexes				
	Water	Ligand	Ni (II)	Cu (II)	Mn (II)	Co (II)	Zn (II)
Germination seed number	20	20	20	20	20	20	20
% Germination after 7days	100	85	55	60	65	60	60
% Survival after 10 days	100	88.23	90.90	91.66	84.61	91.66	83.33
Root length (cm)	2.9	1.8	1.5	1.3	1.9	2.0	1.7
Shoot length (cm)	4.2	4.0	3.3	3.2	3.1	3.3	3.4
Vigor index	710	493	264	270	325	318	306
Root-shoot ratio	0.64	0.43	0.34	0.30	0.42	0.42	0.44

Table 5 : Effect of 2-Methoxy-6-{[2-(2-methoxy-phenoxy)-ethylimino]-methyl}-phenol and its Ni(II), Cu(II), Co(II), Mn(II) and Zn(II) complexes on growth parameters for *Brassica nigra* (black mustard) plant

Parameters	Effect of		Effect of complexes				
	Water	Ligand	Ni (II)	Cu (II)	Mn (II)	Co (II)	Zn (II)
Germination seed number	20	20	20	20	20	20	20
% Germination after 7 days	95	75	60	55	55	70	65
% Survival after 10 days	100	93.33	83.33	90.90	90.90	92.85	84.61
Root length (cm)	3.0	2.2	1.8	1.0	1.7	1.2	1.0
Shoot length (cm)	4.6	3.8	3.0	3.0	2.9	2.9	2.7
Vigor index	722	450	288	220	253	287	240.5
Root-shoot ratio	0.64	0.52	0.57	0.28	0.62	0.32	0.34

Conclusion: In present investigation it was observed that the root: shoot ratio has decreased for the complexes compared to ligand and water. Hence it was concluded that the synthesized complexes have plant inhibitory activity rather than plant growth activity. The activity can be summarized in a decreasing order as follows: Water > Ligand > Metal complexes.

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