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Synthesis, Characterization and Biological activity of Schiff base 2-{[2-(2-Methoxy-phenoxy)-ethylimino]-methyl} - phenol and its transition metal complexes

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ABSTRACT

Coordination complexes of transition metals with Schiff base ligand were synthesized. The characterization of these complexes was 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 comlexetion, 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 studied7. Piperidene-2-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].

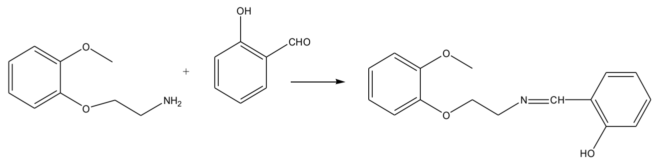
METHODOLOGY

Chemicals and reagents:

The chemicals used are 1-Naphthalen-1-yl-ethylamine (Merck, AR grade) and Salicydehyde (2-Hydroxy benzaldehyde) (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 (MPEMP-MPEMP):

The Schiff Base ligand 2-{[2-(2-Methoxy-phenoxy)-ethylimino]-methyl}- phenol (Fig 1) was synthesized by condensing amine 2-(2-Methoxy-phenoxy)-ethylamine with Salicydehyde in equimolar proportions. To an ethanolic solution (10 ml) of the amine (0.01 mole) was added Salicydehyde (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 89%.



2-(2-Methoxy-phenoxy) - ethylamine	Salicydehyde	2-{[2-(2-Methoxy-phenoxy)-ethylimino]-methyl}-phenol

Fig 1: Formation of Schiff base MPEMP-MPEMP

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, 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.

RESULT 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.

NMR and IR spectra:

In NMR spectra formation of ligand was confirmed by presence of CH=N peak at 8.7 δ and OH at 5.7 δ. In the present investigation the Infra red values for major peaks are assigned. The IR spectrum of ligand gave a strong band at 1634.77 cm-1 and 2904.61cm^{-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 1617.28 cm^{-1} and 3347.77 cm^{-1} corresponding to HC=N and H_2O , IR values of 490.7cm^{-1} and 604.67 cm^{-1} were assigned to M-O and M-N respectively. Similarly complex of SB1-Zn complex showed bands at υ(HC=N) 1629.24 cm^{-1}, υ(H_2O) 3260.38 cm^{-1} , υ (M-O) 485.87 cm^{-1} and υ (M-N) 575.59 cm^{-1}. Similarly bands were observed for Cu complex at υ(HC=N) 1598.23 cm^{-1}, υ(H_2O) 3339.22 cm^{-1} ,υ (M-O) 475.58 cm^{-1} and υ (M-N) 559.66 cm^{-1}. Co complex υ(HC=N) 1616.33 cm^{-1}, υ(H_2O) 3361.73 cm^{-1} ,υ (M-O) 461.73 cm^{-1} and υ (M-N) 607.77 cm^{-1}. Mn complex υ(HC=N) 1615.28 cm^{-1}, υ(H_2O) 3446.57 cm^{-1}, υ (M-O) 471.59 cm^{-1} and υ (M-N) 580.65 cm^{-1}.

Electronic absorption spectra:

In the electronic spectra the ligand exhibited energy peaks at 25000 cm^{-1} and 27392 cm^{-1}. The Co(II) complexes exhibited two energy peak at 27247 cm^{-1} and 23866 cm^{-1}, which can be assigned[5] 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 27248 cm^{-1} and 30487 cm^{-1} [15] while Mn complexes showed peaks at 25000 cm^{-1}, 27173 cm^{-1} and 24630 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 27777 cm^{-1} and 33444 cm^{-1}, which is assigned to ligand–metal charge transfer. In case of the Cu(II) complexes, a broad band at 23809 cm^{-1} and 30487 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 (Table 2) 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.

Magnetic susceptibility measurements:

The effective magnetic moment values for the complexes were determined. The magnetic moment value 4.12 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 3.12 B.M suggests an octahedral geometry. Mn (II) complexes with the value of 5.56 B.M indicate octahedral geometry [20]. The Zn(II) complexes were found to be diamagnetic, as expected for d10 configuration.

Conductivity measurements:

Solid complexes were dissolved in DMSO to perform conductivity experiments. Solutions of 10^{-1} M concentration were prepared and the molar conductivity of these solutions was measured at room temperature. The Molar conductance values for all the newly synthesized complexes were in the range 23 to 94 mhos cm^2 mol^{-1}, indicating very low conductance. These values indicate that the complexes are non-electrolytic nature. The conductance values of the metal complexes were given in Table3.

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.

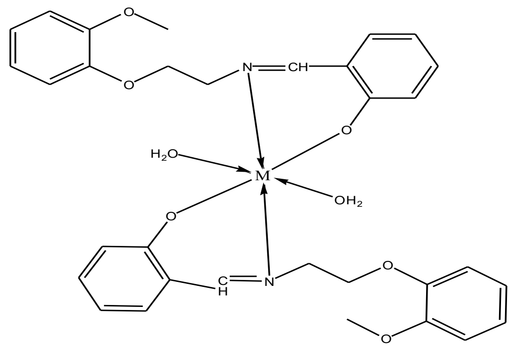


Fig: 2 Structure of complex (M= Ni, Cu, Co, Mn, Zn)

Table 1: Physical characteristics and Yield

Compound	Color	Yield %	M.P (^oC)
Ligand (MPEMP)	MPEMP	Fluoroscent light yellow	89
MPEMP-Ni complex	MPEMP Ni	Light green	78
MPEMP-Cu complex	MPEMP Cu	Brown	57
MPEMP-Co complex	MPEMP Co	Orangish brown	55
MPEMP-Mn complex	MPEMP Mn	Dirty green	70
MPEMP-Zn complex	MPEMP Zn	Light yellow	78

Table 2: Thermogravimetric Data of the Metal Complexes of MPEMP

Complexes	Temperature(°C)	Calc (%)	Obs (%)	Mass loss
MPEMP Ni	110 - 200	5.67	6.0	Mass loss due to H_2O molecules
	250 - 320	14.60	18.0	Mass loss due to volatile matter
	Above 350	11.76	12.0	Mass of the metal oxide
MPEMP Cu	110 - 200	5.62	5.0	Mass loss due toH_2O molecules
	250 - 320	15.33	17.0	Mass loss due to volatile matter
	Above 350	9.92	10.0	Mass of the metal oxide
MPEMP Co	110 - 200	5.6	5.0	Mass loss due toH_2O molecules
	275 - 320	14.69	17.0	Mass loss due to volatile matter
	Above 350	11.79	11.0	Mass of the metal oxide
MPEMP Mn	110 - 200	5.70	6.0	Mass loss due toH_2O molecules
	220 - 330	14.18	16.0	Mass loss due to volatile matter
	Above 350	11.23	11.0	Mass of the metal oxide
MPEMP Zn	110 - 200	5.6	6.0	Mass loss due toH_2O molecules
	225 - 275	15.58	16.0	Mass loss due to volatile matter
	Above 350	12.67	11.0	Mass of the metal oxide

Table 3: ESR values for Copper complex

Complex	g‖ value	g⊥ value	g_{avg}	G
MPEMP Cu complex	2.372	2.080	2.274	4.779

Table 4: Effects of MPEMP and its 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	100	85	70	70	75	85	80
% Survival after 10 days	100	94.11	85.71	85.71	86.66	94.11	93.75
Root length (cm)	2.8	2.2	1.9	1.4	1.3	1.0	0.9
Shoot length (cm)	4.0	3.4	3.0	2.8	2.1	2.2	2.7
Vigor index	680	476	343	294	255	272	288
Root-shoot ratio	0.657	0.60	0.52	0.47	0.47	0.47	0.38

Table 5: Effect of MPEMP 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	80	65	60	60	65	65
% Survival after 10 days	95	93.75	84.61	91.66	91.66	84.61	84.61
Root length (cm)	2.4	2.1	1.4	1.2	1.4	1.0	0.5
Shoot length (cm)	3.8	3.5	1.9	2.0	2.1	1.5	0.9
Vigor index	620	448	214.5	192	210	162.5	91
Root-shoot ratio	0.65	0.63	0.73	0.56	0.66	0.72	0.75

Table 6: Effect of 2-[(1-Naphthalen-1-yl-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	70	60	60	65	60	70
% Survival after 10 days	100	92.85	83.33	83.33	84.61	91.66	92.85
Root length (cm)	2.2	2.0	1.1	1.0	1.0	0.8	0.4
Shoot length (cm)	3.6	3.2	3.4	3.3	3.1	3.0	2.6
Vigor index	551	364	270	279.5	266.5	228	210
Root-shoot ratio	0.58	0.62	0.28	0.27	0.28	0.24	0.13

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 (4), similar parameters for *Triticum aestivum* (wheat) are reported in table (5) and for Brassica nigra (black mustard) in table 6. 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 (4), Table (5) and Table (6).

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.

Conflicts of interest: The authors stated that no conflicts of interest.

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