



# Effects of Some Mixed Ligand Metal Complexes Against the Fungal Disease of Tomato Caused by *Fusarium oxysporum* F. Sp. *Lycopersici* in Natural Epiphytotics.

## KEYWORDS

Mixed ligand, phenanthroline, *Fusarium oxysporum* f. sp. *lycopersici*, antifungal screening.

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**ABSTRACT** A series of mixed ligand transition metal complexes of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) with ligands picric acid and 1, 10 phenanthroline have been designed, synthesised and screened individually on fungal pathogen *Fusarium oxysporum* f. sp. *lycopersici*, an important multi drug resistant pathogenic species which attacks on tomato plants. The general composition of these complexes is  $MX_2Y_2$ . Where M stands for bivalent metal ion, X for picrate ion and Y for phenanthroline. All the metal complexes were characterized by elemental analysis, molar conductance, magnetic susceptibility measurements, electronic spectra and IR spectroscopy. Cu (II) complexes were additionally characterized by EPR spectral studies. On the basis of spectral studies octahedral geometry has been assigned to these complexes. To achieve a better pharmacological profile *in vitro* and *in vivo* antifungal screening of these complexes were done. Antifungal screening indicates that the complexes show enhanced antifungal activities against the fungal strains as compared with parent compounds.

## Introduction

Plant diseases constitute an emerging threat to global food security. Fungal plant diseases are a significant concern for the commercial productivity of vegetables, fruits and crops which are responsible for serious economic losses. Wilt disease is one of the most destructive soil borne disease of tomato caused by *Fusarium oxysporum*<sup>1,2</sup> under field conditions not only in India but also in other countries. The pathogen causes infection on leaves, stem, petiole, twig and fruits as well as leads to the defoliation, drying of twigs and premature fruit drop which ultimately reduce the yield. The disease is favoured by high temperature and humidity (crowded plantation, high rain fall and extended period of leaf wetness from dew). *Fusarium* wilt has been considered as the most common and serious disease of tomato<sup>3-5</sup> and causes heavy loss in quality of the fruits, thus rendering large quantity of tomato fruits unfit for consumption. There is, therefore, an urgent need for developing new agrochemicals to control plant diseases effectively. Chemical control measures have been tested and found effective in the control of diseases. Therefore, in the present investigation, emphasis is given to the designing, development and characterization of modern effective fungicides, inhibition of mycelial growth and spore germination of an important fungus, *F. oxysporum* exposed to different concentrations of synthesized transition metal complexes were studied. As a part of our ongoing work<sup>6</sup> on mixed ligand transition metal complexes, the present study communicates the synthesis, characterization and antimicrobial activity of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) ions with picric acid and 1, 10 phenanthroline as primary and secondary ligands respectively.

In the present investigation we have also screened our synthesized complexes against *F. oxysporum* fungal growth (*in vitro*) and for suppression of wilt disease of tomato (*in vivo*) to develop the agriculture science by protecting crops and vegetables for the production of a plentiful supply of high quality and affordable food.

## Experimental

### Materials and methods

All the chemicals used in the synthesis of transition metal complexes were of analytical grade. Metal salts used in the present study were metal di chlorides. Used picric acid was of highest purity. 1, 10 phenanthroline was used as received. Methanol, ethanol and benzene were further purified by double distillation. Mixed ligand transition metal complexes were prepared as reported by Sharma et al<sup>7</sup>.

Carbon, hydrogen and nitrogen were estimated microanalytically on EURO VECTOR EA 3000 elemental analyzer at CDRI Lucknow. Conductivity measurements were made on ELICO EQ 660 Conductivity Bridge using DMF as a solvent. Metal contents were estimated by standard methods<sup>8</sup>. Magnetic susceptibility measurement were made at room temperature by Gouy's method using  $Hg[Co(SCN)_4]$  as calibrant. The diamagnetic correction of metal ligand system was calculated using Pascal's constant. The purity of metal complexes was checked by TLC method along with standard ligands. IR spectra in the range 4000-400  $cm^{-1}$  were recorded at CDRI Lucknow on a Shimadzu FTIR 8201 P C spectrometer where as spectra in the range 4000-250  $cm^{-1}$  were recorded on a Perkin Elmer infra red spectrophotometer 521 at the department of chemistry IIT Roorkee. The electronic spectra of the compounds were recorded at CDRI Lucknow on a Scbimadzu UV 1601 spectrophotometer. The X-band EPR spectrum of the copper (II) at room temperature was recorded at IIT Mumbai, using TCNE (tetracyanoethylene) as the g-marker. The antifungal activities (*in vitro* and *in vivo*) were carried out at IIVR Varanasi and Microbiological Lab IFTM University Moradabad.

### Fungi and cultures

The fungus *Fusarium oxysporum* f sp. *lycopersici* was obtained from the fungal collection of the laboratory of IIVR Varanasi. All strains were selected for their aggressiveness among tomato. The pathogenic fungus were cultured and purified on potato dextrose agar medium (PDA): Extract of boiled potatoes (200 ml) dextrose(20 gm), agar(20 gm) and distilled water(1000 ml) at 28°C for seven days.

### *In vitro* antimicrobial activity (Fungi proliferation)

The method used is that described by Olajire and Olu-

vemisi experiment<sup>9</sup>. The medium was prepared by mixing infusion of 200 g peeled potato: 20 g dextrose in 1000 ml distilled water. After cooking the medium was poured in to 125 ml conical flasks at the rate of 50 ml per flask and were sterilized by autoclaving at 121°C, for 20 minutes. When the medium was cool down 1 ml of chloramphenicol (1%) was aseptically added. Mixed ligand transition metal complexes were introduced separately in to the flasks containing PDB at concentrations of 100, 500, 1000, 2000, 3000 ppm respectively. Flasks without fungicides used as control. The flasks were inoculated with mycelia discs of 5 days old and incubated at 28°C for seven days. At the end of incubation, the cultures in all flasks were filtered separately through pre-weighted filter paper. Dry weight of mycelium was obtained by subtracting weight of filter paper from weight of filter paper with mycelium. Inhibition of mycelia dry weight was determined by comparing growth in control flasks following the formula<sup>10</sup>.

$$\text{Percentage mycelia growth inhibition} = \frac{C-T}{C} \times 100$$

Where C represents the weight of fungi growth on untreated PDB and T represents the weight of fungi on treated fungi.

#### In vivo antimicrobial activity

The experiment was conducted at Indian Institute of Vegetable Research farm during 2013 crop season in randomized block design with three replications using 'DVRT-1' variety of tomato. Healthy tomato seeds were surface sterilized in 0.5% sodium hypochlorite solution for three minutes and rinsed with sterilized distilled water. The seeds were sown in sterilized soil mixed with sand 80:20 and were grown in seedling plug trays (plug size 3.4cm×3.4cm×5cm, 64 plugs). Trays were maintained under the glass house conditions at 23-28°C and relative humidity 60-70%. After 21 days, plugs containing tomato plants (three true leaves) were transplanted in to plots of size 4.5×3.6 m<sup>2</sup> containing sterile soil infested with *F. oxysporum* f. sp *lycopersici* at a rate of 10<sup>6</sup> CFU/ gm soil, and row to plant spacing was 60×45 cm<sup>2</sup>. Recommended dose of fertilizers 120:80:60 as NPK/ha respectively was applied before transplanting. All metal complexes were sprayed with same volume of solutions of concentration 0.2% on tomato plants per plot (25 plots). Control plants were similarly treated with sterile distilled water and inoculated with pathogen (without fungicides).

Disease severity was recorded using 0-5 rating scale<sup>11</sup>. First observation on disease severity was recorded before the beginning of first spray of fungicides, and subsequent observations were recorded before each spray, and finally disease severity was recorded 10 days after last spray.

#### Results and discussion

Elemental analysis data, magnetic moment and molar conductivities of different complexes are given in Table-1

**Table-1 Characterization data of mixed ligand metal complexes.**

Complex	Percentage Calculated (Found)				Λ <sub>m</sub>
	C	H	N	Metal	
MnX <sub>2</sub> Y <sub>2</sub>	49.61 (49.52)	2.31 (2.51)	16.07 (16.29)	6.30 (6.43)	20.42

Complex	Percentage Calculated (Found)				Λ <sub>m</sub>
	C	H	N	Metal	
Co X <sub>2</sub> Y <sub>2</sub>	49.38 (49.62)	2.30 (2.42)	16.00 (16.18)	6.73 (6.99)	27.08
Ni X <sub>2</sub> Y <sub>2</sub>	49.40 (49.48)	2.30 (2.45)	16.00 (15.87)	6.70 (7.01)	26.45
Cu X <sub>2</sub> Y <sub>2</sub>	49.13 (49.16)	2.29 (2.34)	15.91 (16.18)	7.22 (6.99)	23.13
Zn X <sub>2</sub> Y <sub>2</sub>	49.02 (48.82)	2.28 (2.46)	15.88 (16.01)	7.41 (7.59)	27.02

Where Λ<sub>m</sub> is calculated in ohm<sup>-1</sup>cm<sup>2</sup> mol<sup>-1</sup>

All the complexes are coloured solid which are quite stable at room temperature. The complexes were found stable up to 250°C. But above this they dissociates. The complexes are insoluble in common organic solvents but completely soluble in DMSO and DMF. However the complexes are very sparingly soluble in water. Conductivity data also confirm this nature. The purity of complexes was checked by TLC. On the basis of elemental analysis/characterization data the complexes are formulated as [MX<sub>2</sub>Y<sub>2</sub>], where M stands for bivalent metal ion, X for picrate ion and Y for phenanthroline.

#### Magnetic properties

Room temperature magnetic susceptibility measurements indicate paramagnetic nature for Mn, Co, Ni and Cu complexes. The magnetic moment observed for Mn (II) complex is 5.86 BM which is consistent with the octahedral geometry of the complex<sup>12</sup>. The six co-ordinate Co (II) complex exhibit magnetic moment of 4.98 BM suggesting octahedral geometry for Co (II) complex<sup>13</sup>. Ni (II) complex showed magnetic moment 3.42 BM slightly higher than the spin only value, indicating an octahedral environment around Ni (II) ion<sup>14</sup>. The observed magnetic moments for Cu (II) complex is 1.81 BM suggesting a distorted octahedral geometry around Cu (II)<sup>15</sup>. The Zn (II) complex was found to be diamagnetic, while all other complexes were paramagnetic with magnetic moment values close to the spin only values<sup>16</sup>.

#### Electronic spectra

Electronic spectra of Mn (II) mixed ligand complexes showed  $\nu_2/\nu_1$  and  $\nu_3$  transitions at 15000, 18200 and 24500 cm<sup>-1</sup> respectively which may be attributed to  ${}^4A_{1g} \rightarrow {}^4T_{1g}$  (G),  ${}^6A_{1g} \rightarrow {}^4T_{2g}$  (G) and  ${}^6A_{1g} \rightarrow {}^4A_{1g}$  (G) respectively. The  $\nu_2/\nu_1$  value is in accordance with Mn (II) octahedral complexes<sup>17</sup>. In Co (II) complexes the bands observed at 9010, 18300 and 20500 cm<sup>-1</sup> may be due to  ${}^4T_{1g}$  (F)  $\rightarrow$   ${}^4T_{2g}$  (F),  ${}^4T_{1g}$  (F)  $\rightarrow$   ${}^6A_{2g}$  (F) and  ${}^4T_{1g}$  (F)  $\rightarrow$   ${}^4T_{1g}$  (P) charge transfer transitions respectively in an octahedral field<sup>18</sup>. Ni (II) complex showed three transitions at 9905, 16255 and 25400 cm<sup>-1</sup> as  $\nu_1$ ,  $\nu_2$  and  $\nu_3$  due to  ${}^3A_{2g} \rightarrow {}^3T_{2g}$ ,  ${}^3A_{2g} \rightarrow {}^3T_{1g}$  (F) and  ${}^3A_{2g} \rightarrow {}^3T_{1g}$  (P) respectively. The  $\nu_2/\nu_1$  value for the present compound is in the usual range (1.60-1.82) reported for majority of octahedral Ni (II) complexes<sup>18,19</sup>. Ligand field parameters 10 Dq, B, β and β<sup>2</sup> have been calculated from the electronic spectra of the complexes and are given in Table-2.

Table-2 Ligand field parameters.

Complex	10Dq (cm <sup>-1</sup> )	B (cm <sup>-1</sup> )	$\beta$	$\beta^\circ$
MnX <sub>2</sub> Y <sub>2</sub>	14900	626.66	0.728	27.2
CoX <sub>2</sub> Y <sub>2</sub>	9010	784.66	0.808	19.2
NiX <sub>2</sub> Y <sub>2</sub>	9905	796.00	0.772	22.8
CuX <sub>2</sub> Y <sub>2</sub>	15265	----	----	----

These data are in accordance with the octahedral/ distorted octahedral geometry of complexes as reported earlier. The copper (II) complex showed one broad band at 15265 cm<sup>-1</sup>. Which may be due to <sup>2</sup>E<sub>g</sub> → <sup>2</sup>T<sub>2g</sub> transition showing distorted octahedral geometry<sup>16,17,20</sup>.

### IR spectra

The infrared spectroscopy is a powerful and useful unambiguous tool of structural determination for complexes of transition metals. A large number of co-ordination compounds are being investigated using infrared methods. When a ligand is co-ordinated to the metal ion, the metal atom or ion is introduced in to the ligands vibrating system and the infrared spectrum of the co-ordinated ligand will thus be different from that of the free ligand. In the present investigation the infrared spectra of the mixed ligand complexes of bivalent '3d' transition metal ions with picric acid and phenanthroline have been recorded. The proposed assignments of the IR spectral bands of the synthesized metal (II) picrate complexes are given in the Table-3.

Table-3 Important IR spectral bands (cm<sup>-1</sup>) of mixed ligand complexes.

Complexes	MnX <sub>2</sub> Y <sub>2</sub>	CoX <sub>2</sub> Y <sub>2</sub>	NiX <sub>2</sub> Y <sub>2</sub>	CuX <sub>2</sub> Y <sub>2</sub>	ZnX <sub>2</sub> Y <sub>2</sub>
v(C=N) or v(C=C)	1625sbr	1607sbr	1632s	1593s	1597s
v(NO <sub>2</sub> )	1492m	1498s	1490m	1478m	1490m
v(C-O)	1296m	1268sbr	1271s	1265m	1284m
v(C-H)	779m	777m, 724s	778m	772m	788m, 726m
v(M-O)	550w	529m	540m	550m	585m, 540m
v(M-N)	431w	439w	435m	430m	440w
v(M-O-N)	374w	373w	380w	375m, 350m	378m,360m

The two significant absorption bands at 500 and 3385 cm<sup>-1</sup> in the picric acid may be due to  $\nu_{as}$  (NO<sub>2</sub>) and  $\nu$  (O—H) (hydrogen bonded) respectively. The absence of  $\nu$  (O—H) mode<sup>21, 22</sup> at 3385 cm<sup>-1</sup> and appearance of a medium band at 1260 cm<sup>-1</sup> in all the complexes suggest the co-ordination of picrate ion in a monodentate fashion. The appearance of a new medium intensity band in the range 1260-1296 cm<sup>-1</sup> is attributed to  $\nu$  (C—O) because of co-ordination of phenolic oxygen after deprotonation<sup>23</sup>. The mode of co-ordination through the deprotonated phenolic oxygen is further manifested by appearance of new bands

in the region 529-585 cm<sup>-1</sup> due to  $\nu$  (M—O) vibrations<sup>24-26</sup>. In the IR spectra of 1, 10 phenanthroline the band around 3467 cm<sup>-1</sup> has been assigned to the O—H stretching vibration of water, but in the complexes the band is not observed. The band around 2613 cm<sup>-1</sup> has been assigned to the C—H stretching vibration, which was shifted to lower frequencies on complexation. The aromatic ring stretching vibration found at around 1638 cm<sup>-1</sup> also shifted to lower frequencies on complexation suggesting that both the nitrogen atoms of the 1, 10 phenanthroline are co-ordinated to the metal ion<sup>27</sup>. The C—H deformation band around 900 cm<sup>-1</sup> in the ligand moved to lower frequency in the complexes. In the complexes two significant bands are observed at 1610 and 1040 cm<sup>-1</sup>. These may be assigned to ring  $\nu$  (C=N) and ring breathing modes respectively. This suggests the bidentate (N, N) co-ordination of phenanthroline in the complex. In all the complexes new bands observed in the far infra red region at 529-585, 430-440 and 350-380 cm<sup>-1</sup> are probably due to the formation of  $\nu$  (M—O)<sup>24-26</sup>,  $\nu$  (M—N)<sup>28,29</sup> and  $\nu$  (M—O—C) bands respectively<sup>30,31</sup>.

### Electron paramagnetic resonance study

The EPR spectrum of copper (II) complex provides information of importance in studying the metal ion environment. The X-band EPR spectrum of the copper (II) at room temperature exhibit an isotropic signal, without any hyperfine splitting as shown in Figure 1.

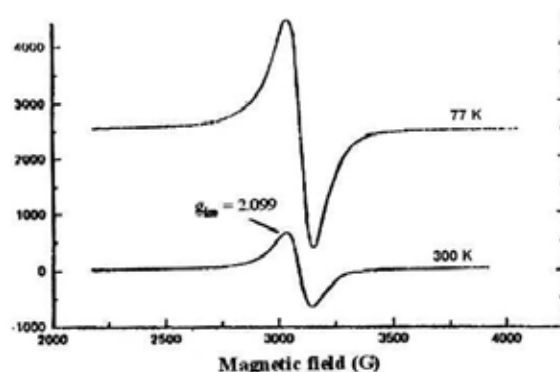


Figure 1- Powder X-band EPR spectrum of the Cu (II) complex at room temperature (300 K)

The room temperature spectra of powdered samples were recorded at 9450 MHz. Both parallel and perpendicular features of copper are resolved in the spectra, which are characteristic of axial symmetry. The  $g_{||}$  and  $g_{\perp}$  component for the complex were calculated as 2.22 and 2.04. The  $g$ -value of the copper (II) complex is found to be 2.1095, reported for a number of distorted copper (II) complexes. Moreover, the observed  $g$ -value is less than 2.3, suggesting a covalent nature of metal-ligand bonds in the complex<sup>32,33</sup>.

The lines of this type are observed usually due to either to the intermolecular spin exchange, which may broaden the lines, or to the occupancy of the unpaired electron in the degenerate orbitals. The nature and the pattern of the EPR spectra suggest an octahedral environment around the copper (II) complex.

### Antifungal activity

#### In vitro antifungal activity

In vitro antifungal activity of metal complexes were tested against fungus *Fusarium oxysporum* f sp. *lycopersici*. The compounds were screened at the concentrations 100, 500,

1000, 2000 and 3000 ppm for fungicidal activity, and compared with control as shown in Table-4.

**Table 4- In vitro antifungal activity of metal complexes against FOL (radial growth in mm).**

Complexes		MnX <sub>2</sub> Y <sub>2</sub>	CoX <sub>2</sub> Y <sub>2</sub>	NiX <sub>2</sub> Y <sub>2</sub>	CuX <sub>2</sub> Y <sub>2</sub>	ZnX <sub>2</sub> Y <sub>2</sub>
Doses (ppm)	100	42.0	40.5	13.46	13.5	45.5
	500	32.9	33.4	11.86	10.0	40.5
	1000	30.9	28.5	10.4	9.7	35.9
	2000	23.2	24.9	8.6	5.0	32.5
	3000	22.7	22.0	7.5	5.0	30.9
Control		62.6	62.6	62.6	62.6	62.6
Mean		35.72	34.97	19.09	17.63	41.32
CD 5%		2.0	2.0	1.53	1.45	2.0
CV		4.30	4.30	6.15	6.34	4.30

From Table-4, it is clear that the inhibition by metal chelates is higher under identical experimental conditions. The results are in good agreement with previous findings with respect to comparative activity of free ligand and its complexes. Comparison of activities of different metal chelates showed that the copper complex is approximately found to be more active. The nickel complex shows the activity comparable to copper complex. However cobalt and manganese complexes show less activity against *F. oxysporum* f sp. *lycopersici*. The activity of these complexes follow the order Cu complex > Ni complex > Co complex > Mn complex > Zn complex.

**In vivo antifungal activity**

Application of metal complexes reduces fusarium wilt severity on tomato plants inoculated under the field conditions. The results of performed tests indicates that, copper and cobalt complexes are the most effective fungicides against the pathogen *in vivo*, followed by nickel, manganese and zinc as shown in Table-5.

Copper complex reduces wilt infection on tomato plants both prior and after inoculation. Reduced disease and increased yield were observed in all synthesized complexes. Disease reduction caused by fungicides spray led to the increase of height of the tomato plants.

**Table 5- In vivo antifungal activity of metal complexes (different treatments) against Fusarium oxysporum f.sp. lycopersici on tomato crop.**

Treatment of Complexes		MnX <sub>2</sub> Y <sub>2</sub>	CoX <sub>2</sub> Y <sub>2</sub>	NiX <sub>2</sub> Y <sub>2</sub>	CuX <sub>2</sub> Y <sub>2</sub>	ZnX <sub>2</sub> Y <sub>2</sub>	Control
Doses %		0.2	0.2	0.2	0.2	0.2	
Symptoms after spraying	10 <sup>th</sup> Day	++	--	++	--	++	
	20 <sup>th</sup> Day	++	--	++	--	++	
	30 <sup>th</sup> Day	+++	++	+++	--	+++	

Treatment of Complexes	MnX <sub>2</sub> Y <sub>2</sub>	CoX <sub>2</sub> Y <sub>2</sub>	NiX <sub>2</sub> Y <sub>2</sub>	CuX <sub>2</sub> Y <sub>2</sub>	ZnX <sub>2</sub> Y <sub>2</sub>	Control
Infected fruits (g/plot)	4975.00	2951.60	3952.66	1651.60	6051.63	8628.50
Total yield (g/plot)	39938.50	40024.36	47563.00	77076.93	41236.00	18628.50

**Conclusions**

The work described in this paper involved the synthesis and spectroscopic characterization of manganese, cobalt, nickel, copper and zinc complexes with picric acid and 1, 10 phenanthroline ligands. These complexes were characterized by using different physicochemical techniques. The IR spectra revealed that picrate ions behaves as monodentate ligand co-ordinated to the metal ions through the deprotonated phenolic oxygen and 1, 10 phenanthroline ligand co-ordinate through both the nitrogen atoms to the metal ion. The magnetic moment and electronic spectra confirm the presence of octahedral geometry of the complexes. The nature and the pattern of the EPR spectra suggest an almost octahedral environment around the copper (II) complex. The *in-vitro* antifungal activity on the radial growth of the fungus refers that the complexes have significant inhibition efficiency against *F. oxysporum* f. sp. *lycopersici*. *In vivo* studies shows that the spray of synthesized complexes not only decreases fusarium wilt severity on tomato plants but also led to the increase of height of the tomato plants as well as the amount of healthy fruits. Transition metal complexes with bioligands represent a novel group of antimicrobial agents with potential application for the control of fungal infections and are used to treat the drug resistant fungal pathogens.

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