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Original Research Paper

Chemistry

THE EFFECTS OF SOME MANGANESE AND COBALT MIXED LIGAND COMPLEXES ON FUSARIUM OXYSPORUM F. SP. LYCOPERSICI ASSOCIATED WITH FUSARIUM WILT OF TOMATO

Gaurav Varshney Department Of Chemistry Jain Inter College Rampur

ABSTRACT Fusarium wilt of Tomato is considered as one of the most important diseases of Tomato both in field and greenhouses worldwide. In present research four fungicides [Mn(PA)2(BH)2], [Mn(PA)2(BY)2], [Co(PA)2(BH)2] and [Co(PA)2(BY)2] were evaluated for their efficacy against the disease caused by the fungus Fusarium oxysporum f. sp. lycopersici (in vitro). Five different concentrations (100, 500, 1000, 2000 and 3000ppm) were used for assessment of their inhibitory activities against the pathogen through mycelial growth innovation on Tomato. The result of tests revealed a different degree of efficacy of all tested fungicides in reducing disease infestation. Antifungal screening indicates that the complexes show enhanced antifungal activities against the fungal strains as compared with parent compound.

KEYWORDS : Mixed ligand, in vitro, Metal Complexes, Antifungal Screening, Fusarium oxysporum f. sp. lycopersici

INTRODUCTION

Fusarium wilt of Tomato caused by *Fusarium oxysporum f. sp. lycopersici* is one of the most prevalent serious diseases of Tomato[1,2]. It is economically important wilting pathogen of Tomato in India. This pathogen severely affects the Tomato crop[3]. The disease is considered as one of the main soil borne systemic disease[4,5,6]. It causes significant losses in Tomato production. Several disease management strategies are available to control Fusarium wilt. These techniques are biological control, resistant cultivers, crop rotation and chemical control[5,7] etc;. Chemical control of Tomato Fusarium wilt *in vitro* is the best method to control Fusarium wilt. It was found that mixed ligand metal complexes are effective fungicides to control Fusarium wilt. The main objective of presented paper is to evaluate the possibility of controlling Fusarium wilt of Tomato with the use of some mixed metal complexes against the growth of fungus. *Fusarium oxysporum f. sp. lycopersici* responsible for wilt disease of Tomato.

Experimental

MATERIALS AND METHODS

All the chemicals used were of AR grade. Metal salts used in the present investigation were metal di halides of Mn(II) and Co(II). Picric acid was dried over conc. H_2SO_4. Methanol, Ethanol and Benzene were further purified by double distillation. Benzoyl hydrazine was prepared by refluxing ethyl benzoate and hydrazine hydrate for about 4 hours and recrystallizing the product from hot benzene as reported in the literature[8]. 2 2' Bipyridine was used as received[9]. Picric acid was used as primary ligand whereas benzoyl hydrazine and 2,2' bipyridine were used as secondary ligands. Elements 'C', 'H' and 'N' were estimated micro analytically 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. Magnetic measurements were recorded 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. Whereas spectra in the range 4000 – 250 Cm^{-1} were recorded on a Perking Elmer infrared spectrophotometer 521 at the department of Chemistry IIT Roorkee. The electronic spectra of the compounds were recorded at CDRI Lucknow on a Schimadzu UV 1601 spectrophotometer. The antifungal activities were carried out at IIVR Varanasi and Microbiological lab IFTM University Moradabad.

RESULTS AND DISCUSSION

These complexes were solid and found to be quite stable at room temperature. They were insoluble in almost all the common organic solvents but soluble in DMF and DMSO, however very sparingly soluble in water. Low conductivity data also confirms this nature. Magnetic moment data for Mn(II) Complex (2.57 BM)[10,11,12] indicate octahedral geometry around the metal Ion. The observe magnetic moment for Co(II) Complex (2.55 BM) showed an unpaired electron and suggested a distorted octahedral geometry in terms of Jahn Teller effect[12,13]. Characterization detail is given in the Table-1

Table-1 Characterization Data of Mixed Ligand Metal Complexes

Complex	Percentage Calculated (Found)				m (ohm-1cm2mol-1)	μeff (BM)
	C	H	N	Metal		
$[Mn(PA)_2(BH)_2]$	39.85 (39.86)	2.57 (2.52)	17.87 (17.82)	7.01 (7.18)	17.55	5.89
$[Mn(PA)_2(BY)_2]$	46.67 (49.01)	2.44 (2.52)	17.01 (17.34)	6.67 (7.02)	20.98	5.82
$[Co(PA)_2(BH)_2]$	39.65 (39.78)	2.55 (2.61)	17.78 (17.88)	7.48 (8.72)	16.92	5.01
$[Co(PA)_2(BY)_2]$	46.44 (45.81)	2.44 (2.12)	16.93 (17.28)	7.12 (7.30)	26.04	5.09

IR Spectra

The IR Spectra gave the information about the bonding between metal ion and the ligand. The absence of (O-H) mode[14,15] at 3385 cm^{-1} and appearance of a medium band at about 1260 cm^{-1} in all four complexes suggest the coordination of the picrate iron in mono dentate fashion[10]. The appearance of a new medium intensity band at 1270 – 1300 cm^{-1} in the complexes is attributed to (C-O) because of coordination of the phenolic oxygen after deprotonation. This is also menifested by the appearance of new band in the region 530-550 cm^{-1} due to (M-O) vibrations[10,14,15]. In the complexes there is no change in the frequency of $-NO_2$ group of picric acid showing no involvement of $-NO_2$ group in the bond formation. In case of benzoyl hydrazine the amide-1 band occurring at 1650 cm^{-1} indicates that a strong intra molecular hydrogen bonding exist between C=O and -NH NH_2 group of the ligand in the complexes suggest the environment of oxygen of C=O and N atom of $-NH_2$ group in coordination[18]. Thus in the complexes picrate ion acts as a mono dentate ligand and benzoyl hydrazine act as bi dentate ligand. In the IR spectra of the complexes the bond due to ring vibrations of the uncoordinated 2, 2' Bipyridine observed at 1631 cm^{-1} was shifted to 1598 cm^{-1}. This shift by about 33 cm^{-1} to a lower frequency shows that 2,2' Bipyridine is coordinate to the metal enters 2-2. The strong bands at about 1598 and 770 cm^{-1} may be assigned to (C-N) and (C-H) respectively. The shifting of these bands from their position in the free ligand indicates the coordination through N atom. The intensity of the bands present in the range 765 – 775 cm^{-1} clearly indicates the environment of both the N atoms in coordination confirming the bidentate nature of the ligand 2, 2' Bipyridine[17,19].

Table-2 Main IR Spectral Bands (cm^{-1}) and Ligand Field Parameters of Metal Complexes

Complex	(C=O) or (C-O)	(M-O)	(M-N)	(M-O-C) or (M-O-N)
$[Mn(PA)_2(BH)_2]$	1300 s	540 m	440 w	360 w
$[Mn(PA)_2(BY)_2]$	1280 s	521 m	430 m	352w
$[Co(PA)_2(BH)_2]$	1275 s	545 m	735 m	370m
$[Co(PA)_2(BY)_2]$	1250 m	542 m	432 m	380 m 369 w

In vitro antifungal activity of metal complexs against fungus *Fusarium oxysporum f. sp. Lycopersici*

In vitro antifungal activity of metal complex against fungus *Fusarium oxysporum f. sp. Lycopersici* were done at the concentrations 100, 500, 1000, 2000 and 3000 ppm the results were compared with control as shown in Table-3.

Table-3

Complex	Doses (ppm)					Control	Mean
	100	500	1000	2000	3000		
$[Mn(PA)_2(BH)_2]$	40.0	35.7	32.3	29.8	18.5	62.6	36.48
$[Mn(PA)_2(BY)_2]$	42.0	30.0	29.5	20.5	19.2	62.6	33.97
$[Co(PA)_2(BH)_2]$	30.5	28.7	20.9	15.2	10.8	62.6	28.12
$[Co(PA)_2(BY)_2]$	39.5	33.5	30.0	18.5	10.5	62.6	32.43

In vitro antifungal activity of metal complex against fungus *Fusarium oxysporum f. sp. Lycopersici* (radial growth in mm).

CONCLUSION

The work described in this paper involved in the synthesis and spectroscopic characterisation of manganese and cobalt complexes with Picric Acid and Benzoyl Hydrazine or 2, 2' Bipyridine. The IR spectra revealed that picrate ions behaves as mono dentate ligand coordinated to the metal ions through the deprotonated phenolic oxygen but Benzoyl Hydrazine and 2, 2' Bipyridine as bi dentate ligands. The magnetic moment and electronic spectra confirm the octahedral geometry of the complexes. The *in vitro* antifungal activity on the radial growth of the fungus refers that the complexes have significant inhibition efficiency against fungus *Fusarium oxysporum f. sp. Lycopersici* Transition metal complexes with bioligands, represents 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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