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PREPARATION, CHARACTERIZATION AND COMPARISON OF ANTIFUNGAL ACTIVITIES OF MIXED LIGAND METAL COMPLEXES OF NI(II) AND CU(II) AGAINST FUNGUS CAUSING WILT DISEASE IN LYCOPERSICON ESCULENTUM

Chemistry

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ABSTRACT

The present study includes Preparation, Characterization and Comparison of Antifungal Activities of Mixed Ligand Metal Complexes of Ni(II) and Cu(II) with some biologically important ligands. The synthesised complexes can be formulated as $[Ni(PA)_2(BH)_2]$, $[Ni(PA)_2(BY)_2]$, $[Cu(PA)_2(BH)_2]$ and $[Ni(PA)_2(BY)_2]$. Where PA is Picric acid, BH is Benzoyl Hydrazine and BY is 2, 2' Bipyridine. The magnetic moment values and spectral data indicates that the complexes have octahedral geometry. The complexes are quite stable coloured solid but sparingly soluble in water. These complexes were screened against the fungus *Fusarium oxysporum f. sp. lycopersici* causing wilt disease in *Lycopersicon esculentum* and it was found that complexes were more active against the fungus as compared to their parent compounds.

KEYWORDS

Mixed Ligands, Antifungal, Picric Acid, Benzoyl Hydrazine, Bipyridine, Wilt Disease

INTRODUCTION

The soil borne fungus *Fusarium oxysporum f. sp. lycopersici* is one of the most damaging fungus of *Lycopersicon esculentum*. The disease is called Fusarium Wilt. The disease is favoured by high temperature and humidity. Antifungal studies of transition metal complexes have been an active field of research[1,2,3,19]. It has been observed that metal complexes with ligands picric acid, Benzoyl Hydrazine, 2, 2' Bipyridine etc. are chemically more significant than the metal ions and ligands as original. Present study includes the comparison of effect of Ni(II) and Cu(II) complexes using mixed ligands Picric Acid, 2,2' Bipyridine and Benzoyl Hydrazine on wilt diseases in tomato crop.

Experimental

MATERIALS AND METHODS

All the chemicals used were of AR grade. Metal salts used in the present investigation were metal di halides of Ni(II) and Cu(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[4]. 2 2' Bipyridine was used as received[5]. 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 Ni(II) Complex (2.98 BM)[6,7,8] indicate octahedral geometry around the metal Ion. The observe magnetic moment for Cu(II) Complex (1.78 BM) showed an unpaired electron and suggested a distorted octahedral geometry in terms of Jahn Teller effect[8,9]. Characterization detail is given in the Table-1

Table-1 Characterization Data of Mixed Ligand Metal Complexes

Complex	Percentage Calculated (Found)				Λm (ohm^{-1}cm^{2}mol^{-1})
	C	H	N	Metal	
[Ni(PA)2(BH)2]	39.67 (39.79)	2.56 (2.48)	17.79 (17.92)	7.45 (7.22)	25.34
[Ni(PA)2(BY)2]	46.46 (45.98)	2.44 (2.01)	16.93 (16.52)	7.09 (6.89)	29.45
[Cu(PA)2(BH)2]	39.42 (39.61)	2.54 (2.64)	17.68 (17.88)	8.02 (7.86)	21.22
[Cu(PA)2(BY)2]	46.19 (45.92)	2.42 (3.10)	16.83 (16.99)	7.64 (8.02)	25.56

IR spectra

The IR Spectra gave the information about the bonding between metal ion and the ligand. The absence of ν(O-H) mode[15,16] 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 ν(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 ν(M-O) vibrations[4,15,16,17,18]. 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. 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 ν(C-N) and ν(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[18].

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

Complex	ν (C=O) or (C-O)	ν (M-O)	ν (M-N)	ν (M-O-C) or (M-O-N)
[Ni(PA)2(BH)2]	1274 s	530 m	430 w	360 m
[Ni(PA)2(BY)2]	1280 s	592 w 585 m	437 m	310w 350 m
[Cu(PA)2(BH)2]	1270 s	535 m	445 m	365 w
[Cu(PA)2(BY)2]	1250 m	568 m	432 m	374 m 350 m

Electronic Spectra

Electronic spectra of Ni(II) complex showed three transitions at 9900(9910), 16090and 25315 cm^{-1} as ν and ν_3 due to $^3A_2g \rightarrow {}^3T_2g$, $^3A_2g \rightarrow {}^3T_1g(F)$ and $^3A_2g \rightarrow {}^3T_1g(P)$ respectively. The ν_2/ν_1 value for the present compound is in the usual range (1.60-1.82) reported for majority of octahedral Ni(II)[11,12] complex the Cu(II) complex shows

one broad band at 14410 cm^{-1} and 15260 cm^{-1} which may be due to $^2Eg \rightarrow {}^2T_2g$ transition showing distorted octahedral geometry[13,14].

Table-3

Complex	10 Dq cm^{-1}	B cm^{-1}	β	β ^{0}
[Ni(PA)2(BH)2]	9900	780.33	0.757	24.3
[Ni(PA)2(BY)2]	9910	796.00	.0772	22.8
[Cu(PA)2(BH)2]	14410	------	------	------
[Cu(PA)2(BY)2]	15260	------	------	------

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 3000ppmthe results were compared with control as shown in Table-4.

Table-4 In vitro antifungal activity of metal complex against fungus *Fusarium oxysporum f. sp. Lycopersici* (radial growth in mm).

Complex	Doses (ppm)					Control	Mean
	100	500	1000	2000	3000		
[Ni(PA)2(BH)2]	20.5	18.9	16.0	15.0	5.0	62.6	23.00
[Ni(PA)2(BY)2]	36.7	28.9	20.2	15.2	10.2	62.6	28.96
[Cu(PA)2(BH)2]	12.5	11.5	9.7	6.5	5	62.6	17.97
[Cu(PA)2(BY)2]	30.5	25.6	20.5	18.2	10.1	62.6	27.92

CONCLUSION

The work described in this paper involved in the synthesis and spectroscopic characterisation of nickel and copper complexes with Picric Acid and Benzoyl Hydrazine or 2, 2' Bipyridine.The ir spectra revealed that picrate ions behaves as monodentate ligand coordinated to the metal ionsthrough 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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