



## SYNTHESIS, CHARACTERIZATION AND ANTIFUNGAL ACTIVITY OF CR(III) AND CU(II) COMPLEXES OF 4-(PHENYLAMINO)BENZOIC ACID

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### ABSTRACT

Cr(III) and Cu(II) complexes (1–6) of general composition  $M(HL)X_2$  and  $M(HL)_2$  ( $M=Cr(III)$ ,  $Cu(II)$ ,  $X=Cl-1$ ,  $NO_3-1$ ) with ligand 4-(phenylamino) benzoic acid ( $HL_1$ ) were synthesized. The characterization of newly synthesized ligand and complexes was done by  $^1H$  NMR, UV–VIS, IR, Mass spectrophotometry and molar conductivity studies. On the basis of the spectral study, octahedral geometry was assigned to Cr(III) metal complexes. Cu(II) complexes in metal:ligand (1:1) show square planar geometry and distorted octahedral geometry in metal:ligand (1:2) complexes. Antifungal activity of the metal complexes were also investigated.

**Keywords:** Antifungal, Cr(III) & Cu(II) complexes 4-(Phenylamino)Benzoic Acid

### INTRODUCTION

Design and construction of metal-involved supramolecular architectures based on crystal engineering are currently of interest in the field of supramolecular chemistry and material science. The increasing interest in this field is justified not only by their intriguing structural motifs, but also their potential applications as luminescence, catalysis, porosity, sensors, magnetism, molecular recognition, nonlinear optics and ferroelectrics [1–4].

N-phenylanthranilic acid, an indicator to detect the vanadium among steel, is a semi-rigid V-shaped ligand composed of two phenyl moieties which are linked with an imino bridge. The two phenyl arms can rotate freely around the imino ( $-NH-$ ) groups according to the small change in the coordination environment in order to minimize steric hindrance, which promise possibilities for generating unusual frameworks. In comparison to many researches on

the N-alkyl substituted aminobenzoic acid, the N-phenyl substituted counterparts are limited. Kakas [5] and Greiner [6] pointed out that for triphenylamine and its derivatives, there is conjugation between the nitrogen lone pair electrons and the phenyl p-electrons. The whole molecule is a new chromophore with characteristic absorption and emission spectra. N-phenyl vs N-alkyl substitution of aromatic amines leads to superior performance in material chemistry viz. hyperpolarizability [8], hole transport [7,8], electroluminescence [9], etc.. 4-Aminodiphenylamine is a model of the polymer polyaniline [10] and research in [10] has been extended in another publication [11].

Therefore, it is worthwhile to carry out the synthesis and study the spectral properties of the ligand derived from the condensation of p-chlorobenzoic acid and aniline. The goal of the study presented here is to synthesize the Cr(III) and Cu(II) metal complexes of 4-(phenylamino)benzoic acid produced from condensation of p-chlorobenzoic acid and aniline and to provide a baseline of structural data using various spectroscopic techniques, and antifungal activity.

### MATERIALS AND METHODS

All the chemicals were used of Anala R grade and received from Sigma-Aldrich and Fluka. Metal salts were purchased from E. Merck and used as received.

#### Synthesis of Ligand

The Schiff base  $HL^1$  (Scheme 1) was prepared by mixing equimolar amount of p-chlorobenzoic acid (1 mmol) and aniline (1 mmol) in absolute ethanol. To this anhydrous potassium carbonate and copper oxide was added. The resulting solution was refluxed for 3–4 hours. The mixture tends to foam during the

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earlier part of heating due to evolution of carbon dioxide. The product separated out which was filtered off, washed, recrystallized with cold ethanol and dried under vacuum over  $P_4O_{10}$ .

### Synthesis of metal complexes

Hot methanolic solution (15 mL) of  $CrCl_3$  (1 mmol) was added drop wise to a magnetically stirred solution of 4-(phenylamino)benzoic acid **HL**<sup>1</sup> (1 mmol) in ethanol (20 mL) (scheme 1). The resultant mixture was refluxed for 12 h and the clear solution was allowed to cool at room temperature. The solid product precipitated out which was filtered, washed with ethanol, diethyl ether and dried under vacuum over  $P_4O_{10}$ . The same method was used for the preparation of metal complexes **2–4** in metal : ligand (1:1). The metal complexes **5–6** were synthesized by using the above mentioned same procedure by taking metal : ligand in a 1:2 molar ratio. Physical, analytical and spectral data of ligands and metal complexes are given in Table 1.

recorded on FTIR spectrum BX-II spectrophotometer. NMR spectra were recorded with a model Bruker Advance DPX-300 spectrometer operating at 400 MHz using DMSO- $d_6$  as a solvent and TMS as internal standard. The electronic spectra were recorded in DMSO on Shimadzu UV mini-1240 spectrophotometer. EPR spectra was recorded on E4-EPR spectrometer at room temperature using DPPH as standard.

### Antifungal activity

The fungicidal activity of synthesized ligand and complexes were examined by Poison food Technique [12]. The compounds were screened for antifungal activity using three fungus i.e. *Aspergillus niger*, *Fusarium oxysporum* and *Rhizoctonia bataticola*. The stock solution of the compound was directly mixed into the PDA (Potato Dextrose Agar) medium at the tested concentration. A disc of 5 mm of test fungal culture of a specific age growing on solid medium was then cut with a sterile cork borer and was

**Table 1:** Analytical data of ligand **HL**<sup>1</sup> and metal complexes **1–6**

Comp . No.	Color	Molecular Formula	Yield (%)	Elemental Analysis (%) found				Molar Conductance (Ω <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )	Meltin g Pt. (°C)
				(calc.)					
				C	H	N	M <sup>a</sup>		
HL <sup>1</sup>	White	C <sub>13</sub> H <sub>11</sub> NO <sub>2</sub>	72	73.10 (73.23)	5.22 (5.20)	6.55 (6.57)	-	-	188
1	Light Green	[Cr(HL)(Cl) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] C <sub>13</sub> H <sub>14</sub> Cl <sub>2</sub> CrNO <sub>4</sub>	63	42.12 (42.07)	3.88 (3.80)	3.72 (3.77)	14.05 (14.01)	3	>280
2	Green	[Cr(HL)(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] C <sub>13</sub> H <sub>14</sub> CrN <sub>3</sub> O <sub>10</sub>	58	35.92 (36.80)	3.31 (3.33)	10.95 (9.90)	12.36 (12.26)	4.1	>280
3	Blue	[Cu(HL)(Cl)(H <sub>2</sub> O)] C <sub>13</sub> H <sub>12</sub> ClCuNO <sub>3</sub>	65	47.48 (47.43)	3.63 (3.67)	4.22 (4.25)	19.26 (19.30)	8.6	>280
4	Light Blue	[Cu(HL)(NO <sub>3</sub> )H <sub>2</sub> O)] C <sub>13</sub> H <sub>12</sub> CuN <sub>2</sub> O <sub>6</sub>	59	43.85 (43.89)	3.43 (3.40)	7.91 (7.87)	17.81 (17.86)	5.2	>280
5	Green	[Cu(HL) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] C <sub>26</sub> H <sub>24</sub> CuN <sub>2</sub> O <sub>6</sub>	52	59.51 (59.59)	4.60 (4.62)	5.37 (5.35)	12.10 (12.13)	4.3	>280
6	Green	[Cu(HL) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] C <sub>26</sub> H <sub>24</sub> CuN <sub>2</sub> O <sub>6</sub>	52	59.55 (59.59)	4.65 (4.62)	5.42 (5.35)	12.17 (12.13)	8.1	>280

### Analysis

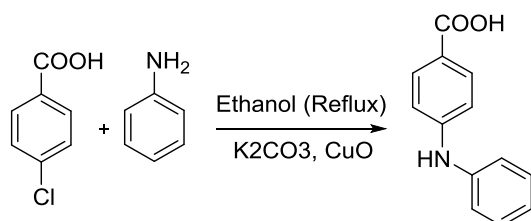
The carbon and hydrogen were analyzed on Carlo-Erba 1106 elemental analyzer. The nitrogen content of the complexes was determined using Kjeldahl's method. Molar conductance was measured on the ELICO (CM82T) conductivity bridge. ESI-MS spectra were obtained using a VG Biotech Quattrro mass spectrometer equipped with an electrospray ionisation source in the mass range of  $m/z$  100 to  $m/z$  1000. IR spectra (CsBr) were

placed at the center of the solid PDA plate with the help of inoculums' needle. The plates were sealed with Parafilm® and incubated at  $29 \pm 2^{\circ}C$  for 7 days. DMSO was used as a control and Mancozeb as a standard fungicide.

### RESULTS AND DISCUSSION

The ligand **HL**<sup>1</sup> (Scheme 1) was prepared by mixing equimolar amount of p-chlorobenzoic acid (1 mmol) and aniline (1 mmol) in absolute ethanol. To this anhydrous potassium carbonate and copper

oxide was added. The resulting solution was refluxed for 3–4 hours. The mixture tends to foam during the earlier part of heating due to evolution of carbon dioxide. The product separated out which was filtered off, washed, recrystallized with cold ethanol and dried under vacuum over  $P_4O_{10}$ . The structure of ligand thus formed was established by IR,  $^1H$  NMR and Mass spectrophotometry.

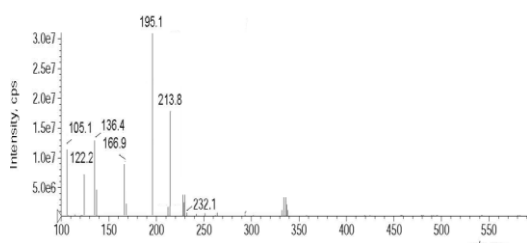


**Scheme 1:** Synthesis of ligand  $HL^1$

The synthesized ligand was further used for the complexation with Cr(II) and Cu(II) metal ions, using the following metal salt:  $CrCl_3$  for complex **1**,  $Cr(NO_3)_3$  for complex **2**,  $CuCl_2$  for complexes **3** & **5** and  $Cu(NO_3)_2$  for complexes **4** & **6**. The obtained complexes are microcrystalline solids which are stable in air and decompose above  $280^\circ C$  (Table 1). They are insoluble in common organic solvents such as acetone & chloroform, sparingly soluble in ethanol & methanol and completely soluble in DMF & DMSO. The molar conductance of the soluble complexes in DMF showed values indicating that complexes **1–6** ( $3\text{--}8.6\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ ) [13] are non-electrolytes in nature. The elemental analysis data of the ligand are in agreement with the structure of the ligand. The elemental analysis data of the ligand ( $HL^1$ ) and metal complexes (**1–6**) are given in Table 1.

### Mass Spectra

The ESI mass spectrum of ligand showed a molecular ion peak at  $m/z = 213.8$  amu corresponding to  $[M + H]^+$ , which confirms the proposed formula (Figure 1). It also shows a series of

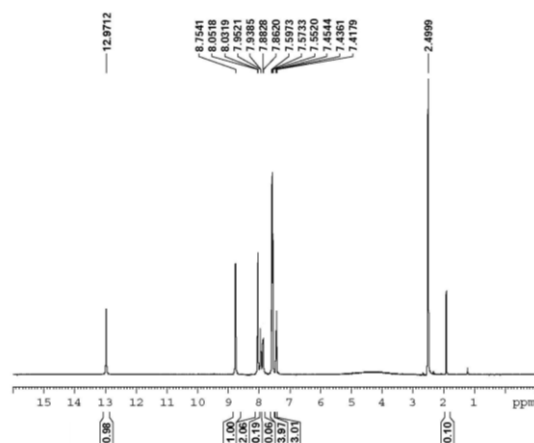


**Figure 1 :** Mass spectra of ligand  $HL^1$

peaks at 195.1, 166.9, 136.4, 122.2 and 105.1 corresponding to various fragments. The intensities of these peaks give the idea of the stability of the fragments.

### $^1H$ NMR Spectra

The  $^1H$  NMR spectra have been recorded for ligand  $HL^1$  (Figure 2). The characteristic signals, due to  $-NH$  and  $-COOH$  protons appear at 8.75 and 12.97 ppm, respectively. The aromatic region is a set of doublets, triplets and multiplets in the range 7.75–6.67 ppm for the complexes while it is 7.41–8.75 ppm for the ligand. All the proton peaks were found to be in the expected regions.



**Figure 2:** Mass spectra of ligand  $HL^1$

### IR Spectra

The IR spectrum of the ligand was compared with those of the metal complexes in order to confirm the binding mode of the ligand to the corresponding metal ion. A very broad band at  $3124\text{ cm}^{-1}$  corresponds to  $-COOH$  group in ligand  $HL^1$ . However, in metal complexes **1–6** this band disappears, which indicates that the  $-COOH$  group deprotonate and coordinates to metal ion. In metal complex **1**, The stretching bands corresponding to  $\nu_{asym}(COO^-)$  appeared at  $1532\text{ cm}^{-1}$ , while the band corresponding to  $\nu_{sym}(COO^-)$  appeared at  $1442\text{ cm}^{-1}$ . The separation value ( $\Delta\nu$ ) of  $90\text{ cm}^{-1}$  indicates bidentate binding of the carboxylato group [14]. Similarly, for metal complexes **2–6** the band for  $\nu_{asym}(COO^-)$  and  $\nu_{sym}(COO^-)$  appeared in the range of  $1540\text{--}1566$  and  $1444\text{--}1467\text{ cm}^{-1}$ , respectively. This is also supported by the appearance of band in range of  $532\text{--}554\text{ cm}^{-1}$ , which corresponds to  $\nu(M-O)$  bond [15].

**Table 2 : Magnetic Moment (B.M) and Electronic Spectral data (cm<sup>-1</sup>) and Ligand Field Parameter of the complexes**

Complex	$\mu_{\text{eff}}$ B.M.	Electronic data (cm <sup>-1</sup> )			Ligand Field Parameter			
		$\nu_1$	$\nu_2$	$\nu_3$	Dq (cm <sup>-1</sup> )	B (cm <sup>-1</sup> )	B	LFSE (kJmol <sup>-1</sup> )
1	3.72	16640	20000	24550	1664	477	0.52	238
2	3.75	17740	20533	27300	1774	394	0.43	254
3	1.74	-	-	20125	-	-	-	-
4	1.92	12287	18345	26345	-	-	-	-
5	1.78	-	-	18456	-	-	-	-
6	1.98	15103	19178	24078	-	-	-	-

The presence of bands at 1450-1410 ( $\nu_5$ ), 1348 - 1320 ( $\nu_1$ ) and 1058-1025( $\nu_2$ ) cm<sup>-1</sup>, in the IR spectra of the metal complex **2**, **4** and **6** suggests that both the nitrate groups are coordinated to the central metal ion in a unidentate fashion [16]. Furthermore, the presence of coordinated water molecules is evidenced by broad band's corresponding to O-H stretching vibration [17] at 3345–3473 cm<sup>-1</sup> in complexes **1–6**. The chloro complexes show the IR bands in the region 340-385 cm<sup>-1</sup> due to  $\nu(\text{M-Cl})$  [18]. The IR spectral data indicates that the ligand **HL**<sup>1</sup> behaves uninegative bidentately.

**Table 3 . EPR spectral data of the Cr(III) and Cu(II) complexes**

Complex	Data as polycrystalline sample			G
	$g_{\parallel}$	$g_{\perp}$	$g_{\text{iso}}$	
1	--	--	1.9704	----
2	----	---	2.1749	---
3	2.0641	2.0255	2.0384	2.5137
4	2.0773	2.0318	2.0469	2.4308
5	2.0591	2.0218	2.0289	2.6231
6	2.0771	2.0315	2.0478	2.4109

### Magnetic moments

Generally the magnetic moment of chromium(III) complexes at room temperature lies near 3.87 B.M. i.e. equal to spin-only value. For the Cr(III) compounds the magnetic moment is reduced below the spin-only value because of the (1-4  $\lambda$  /10Dq) effect. The spin-orbit coupling constant for Cr(III) is rather small. The magnetic moment of complexes

under study at room temperature lies in range of 3.72- 3.75 B.M.(Table 2) [19] corresponding to three unpaired electrons. At room temperature Cu(II) complexes show magnetic moment in the range 1.74-1.98 B.M. corresponding to one unpaired electron [20].

### Electronic spectra

For Cr(III) ( $d^3$ , the spin quantum number  $S=3/2$ ), the strong field ground configuration is  $t_{2g}^3 e_g^0$ . The excited configuration  $t_{2g}^2 e_g^1$  is six fold orbitally degenerate and the second excited configuration  $t_{2g}^1 e_g^2$  is three fold orbitally degenerate. The ground state can be written by considering a spin of 3/2 as it is an orbital singlet. The free ion split quartet term  $^4F$  and  $^4P$ . These terms in octahedral field split into  $^4A_{2g}$ ,  $^4T_{1g}$ ,  $^4T_{2g}$  and  $^4E_g$  ( $P$ ), respectively. The electronic spectra of the Cr(III) complexes **1–2** recorded in DMSO, display three bands in the range of 16640-17740, 20000-20533 and 24550-27300 cm<sup>-1</sup> (Table2). These spin allowed bands shown by six coordinated complexes having Oh symmetry could be assigned to the transitions:  $^4A_{2g}(F) \rightarrow ^4T_{2g}(F)$ ,  $\nu_1$ :  $^4A_{2g}(F) \rightarrow ^4T_{1g}(F)$ ,  $\nu_2$ :  $^4A_{2g}(F) \rightarrow ^4E_g(F)$ ,  $\nu_3$  [21].

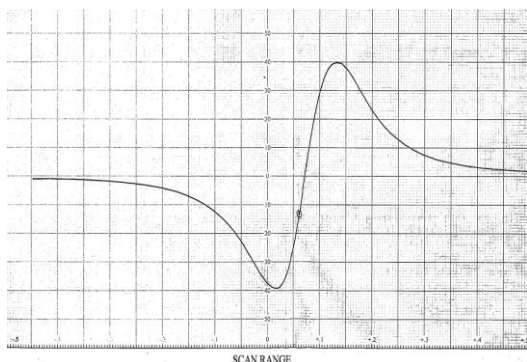
Electronic absorption spectra of the copper complexes **3** and **5** display a transition in the region 18456-20125 cm<sup>-1</sup>, which can be assigned as the  $^2B_{1g} \rightarrow ^2A_{1g}$  transition, revealing that the Cu(II) complexes exist in the square planar geometry [22]. Electronic spectra of Cu(II) complexes **4** and **6** show the d-d transition bands in the range 12,287–15,103, 18,345–19,178 and 24,078–26,345 cm<sup>-1</sup>. These bands correspond to  $^2B_{1g} \rightarrow ^2A_{1g}$  ( $d_{x^2-y^2} \rightarrow d_{z^2}$ ),  $^2B_{1g} \rightarrow ^2B_{2g}$  ( $d_{x^2-y^2} \rightarrow d_{xy}$ ) and  $^2B_{1g} \rightarrow ^2E_g$  ( $d_{x^2-y^2} \rightarrow d_{xz}$ ,  $d_{yz}$ ) transitions, respectively [23]. On the basis of

electronic transitions, a distorted octahedral geometry is suggested for complexes **4** and **6**.

Various ligand field parameters are calculated for the complexes. The energy of the first spin allowed transition i.e.  ${}^4A_g(F) \rightarrow {}^4T_{2g}$ , directly gives the value of 10 Dq ( $\nu_1=10Dq$ ). The Nephelauxetic parameter  $\beta$  is calculated by the relation  $\beta = B \text{ complex} / B \text{ free ion}$ . For Cr(III) the value of B free ion is 918 [24]. The value of  $\beta$  calculated for Cr(III) complexes lie in the range of 0.43-0.52 given in table. These values indicate that the complexes have appreciable covalent character.

### EPR spectra

The X-band EPR spectra of all the Cr(III) complexes in solid state show a broad signal (Fig. ) in the vicinity of  $g_{iso} \approx 2.0$ . Due to large line widths and dominance of  $g_{iso} \approx 2.0$  peaks, no hyperfine splitting is observed and the estimation of parameters D and E is not possible. The EPR results of Cr(III) complexes in the present study are consistent with the presence of hexacoordinated Cr(III) centers (Table 3, Figure 3).

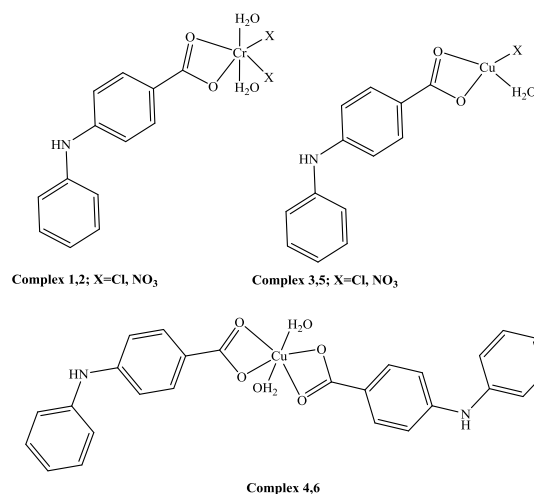


**Figure 3.** EPR spectrum of complex **1** at RT in polycrystalline form

EPR spectra of the Cu(II) complexes were recorded, at room temperature as polycrystalline samples, on the X-band at 9.1 GHz under the magnetic field range 3000 G. The trend  $g_{||} > g_{\perp} > 2.0023$ , observed for the complexes, under study, indicate that the unpaired electron is localized in the  $d_{x^2-y^2}$  orbital of the Cu(II) ion and the spectral figures are characteristic for the axial symmetry. Tetragonally elongated geometry is thus confirmed for the afore-said complexes.  $G = (g_{||} - 2) / (g_{\perp} - 2)$ , which measure the exchange interaction between the metal centers in a polycrystalline solid has been calculated. The complexes show the G values smaller

than 4 which indicate exchange interaction in the solid complexes [25].

Based on above observations following structures are proposed for metal complexes 1–6 (Figure 4).



**Figure 4.** Proposed structures of metal complexes 1–6

### Antifungal Screening

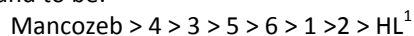
The inhibition of the fungal growth expressed in percentage terms was determined from the growth in the test plate relative to the respective control plate as given below:

$$\text{Inhibition (\%)} = (C - T) 100 / C$$

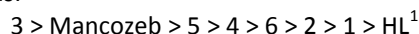
where C = diameter of fungal growth in the control plate and T = diameter of fungal growth in the test plate.

The antimicrobial screening data show that the compounds exhibit antimicrobial properties and it is important to note that the metal chelates exhibit more inhibitory effects than the parent ligand. The increased activity of metal complexes can be explained on the basis of chelation theory [26]. It has also been proposed that concentration plays a vital role in increasing the degree of inhibition; as the concentration increases, the activity increases (Table 4).

The activity order for *Aspergillus niger* was found to be:



With *Fusarium oxysporum* the order of activity was:



**Table 4.** Antifungal activities data of the ligand and complexes

Com- pounds	Fungus species (tested )	Fungal inhibition (%) Concentrations( $\mu\text{g ml}^{-1}$ ) (mm)		
		100	200	300
<b>HL<sup>1</sup></b>	<i>A. niger</i>	45 $\pm$ 4	53 $\pm$ 4	60 $\pm$ 6
	<i>F. oxysporum</i>	50 $\pm$ 2	61 $\pm$ 6	70 $\pm$ 3
	<i>R. bataticola</i>	43 $\pm$ 6	59 $\pm$ 2	64 $\pm$ 4
<b>1</b>	<i>A. niger</i>	50 $\pm$ 3	63 $\pm$ 2	71 $\pm$ 4
	<i>F. oxysporum</i>	54 $\pm$ 6	62 $\pm$ 4	75 $\pm$ 2
	<i>R. bataticola</i>	59 $\pm$ 6	67 $\pm$ 5	80 $\pm$ 3
<b>2</b>	<i>A. niger</i>	49 $\pm$ 3	58 $\pm$ 3	69 $\pm$ 4
	<i>F. oxysporum</i>	56 $\pm$ 4	67 $\pm$ 5	79 $\pm$ 2
	<i>R. bataticola</i>	52 $\pm$ 4	63 $\pm$ 5	71 $\pm$ 5
<b>3</b>	<i>A. niger</i>	55 $\pm$ 2	72 $\pm$ 6	89 $\pm$ 3
	<i>F. oxysporum</i>	76 $\pm$ 6	89 $\pm$ 4	100 $\pm$ 2
	<i>R. bataticola</i>	69 $\pm$ 2	80 $\pm$ 4	96 $\pm$ 3
<b>4</b>	<i>A. niger</i>	60 $\pm$ 3	77 $\pm$ 3	92 $\pm$ 6
	<i>F. oxysporum</i>	69 $\pm$ 4	78 $\pm$ 2	88 $\pm$ 6
	<i>R. bataticola</i>	63 $\pm$ 3	71 $\pm$ 5	89 $\pm$ 5
<b>5</b>	<i>A. niger</i>	54 $\pm$ 6	70 $\pm$ 5	84 $\pm$ 3
	<i>F. oxysporum</i>	70 $\pm$ 6	81 $\pm$ 3	92 $\pm$ 4
	<i>R. bataticola</i>	58 $\pm$ 2	67 $\pm$ 2	75 $\pm$ 6
<b>6</b>	<i>A. niger</i>	52 $\pm$ 5	65 $\pm$ 2	79 $\pm$ 4
	<i>F. oxysporum</i>	65 $\pm$ 5	71 $\pm$ 6	80 $\pm$ 3
	<i>R. bataticola</i>	61 $\pm$ 3	76 $\pm$ 4	92 $\pm$ 3
<b>Man- cozeb</b>	<i>A. niger</i>	65 $\pm$ 0	80 $\pm$ 2	97 $\pm$ 1
	<i>F. oxysporum</i>	74 $\pm$ 1	85 $\pm$ 2	96 $\pm$ 0
	<i>R. bataticola</i>	70 $\pm$ 2	82 $\pm$ 0	100 $\pm$ 1

<sup>a</sup>The results are expressed as the percentage of fungal inhibition with respect to control and are presented as mean  $\pm$  SD

The order of activity with *Rhizoctonia bataticola* was found to be:

Mancozeb > 3 > 6 > 4 > 1 > 5 > 2 > HL<sup>1</sup>

## CONCLUSION

The analytical and physico-chemical analyses confirmed the composition and the structure of the newly obtained complex combinations. On the basis of the spectral studies Cr(III) complexes were found to have a octahedral geometry whereas Cu(II) complexes has a square planar geometry in 1:1 (metal:ligand) complexes and distorted octahedral in 1:2 complexes. In all complexes the ligand HL<sup>1</sup> acts as uninegative bidentate around the metallic ion. Results of the antifungal activity revealed that metal complexes show enhanced activity in comparison to free ligand. The activity order for *Aspergillus niger* was found to be: Mancozeb > 4 > 3 > 5 > 6 > 1 > 2 >

HL<sup>1</sup>; with *Fusarium oxysporum* the order of activity was: 3 > Mancozeb > 5 > 4 > 6 > 2 > 1 > HL<sup>1</sup>; with *Rhizoctonia bataticola* the order found was: Mancozeb > 3 > 6 > 4 > 1 > 5 > 2 > HL<sup>1</sup>.

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