

# Synthesis, Characterization, Chelating Properties and Biological Activities of Benzotriazole-Salicylic acid Combined Molecule

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## ABSTRACT

Aminomethylation of benzotriazole was carried out by treating benzotriazole with formaldehyde and N-n-propyl 4-amino salicylic acid. The resultant compound was designated as 1-(4-carboxy-3-hydroxy-N-propyl phenyl amino methyl) benzotriazole. The transition metal complexes of Cu<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Mn<sup>2+</sup>, and Zn<sup>2+</sup> of 1-(4-carboxy-3-hydroxy-N-propyl phenyl amino methyl) benzotriazole have been prepared. Elemental analyser, spectral studies, magnetic moment determination, molar conductivity measurement and microbial activity of 1-[4-carboxy-3-hydroxy phenyl (N-n-propyl amino) methyl] benzotriazole and its metal complexes were carried out.

**Keywords:** Benzotriazole, N-n-propyl 4-aminosalicylic acid, metal complexes, spectral studies.

## INTRODUCTION

One of the heterocyclic compound say 1-(H)-benzotriazole is found as an important heterocyclic compound. It's prime application is as corrosion inhibitors for copper or copper alloys<sup>1,2</sup>. Ciba Geigy has introduced benzotriazole derivative under the trade name Trinvin-p<sup>3</sup>. It is applied as an UV light absorber for stabilizing plastics and other organic materials against discoloration determination<sup>3</sup>. It is also employed as photographic emulsion stabilizer<sup>4</sup>. In the peptide synthesis it act in form of an active ester<sup>5</sup>. The area in which the amino methylation of benzotriazole by using aromatic amine having metal gripping group (i.e ligand) has not been developed. Hence it was thought to undertake such work. In continuation with our previous research publications<sup>6-8</sup> and with this view, the present communication describe the synthesis and characterization of benzotriazole N-n-propyl 4-aminosalicylic acid clubbed molecule and its metal

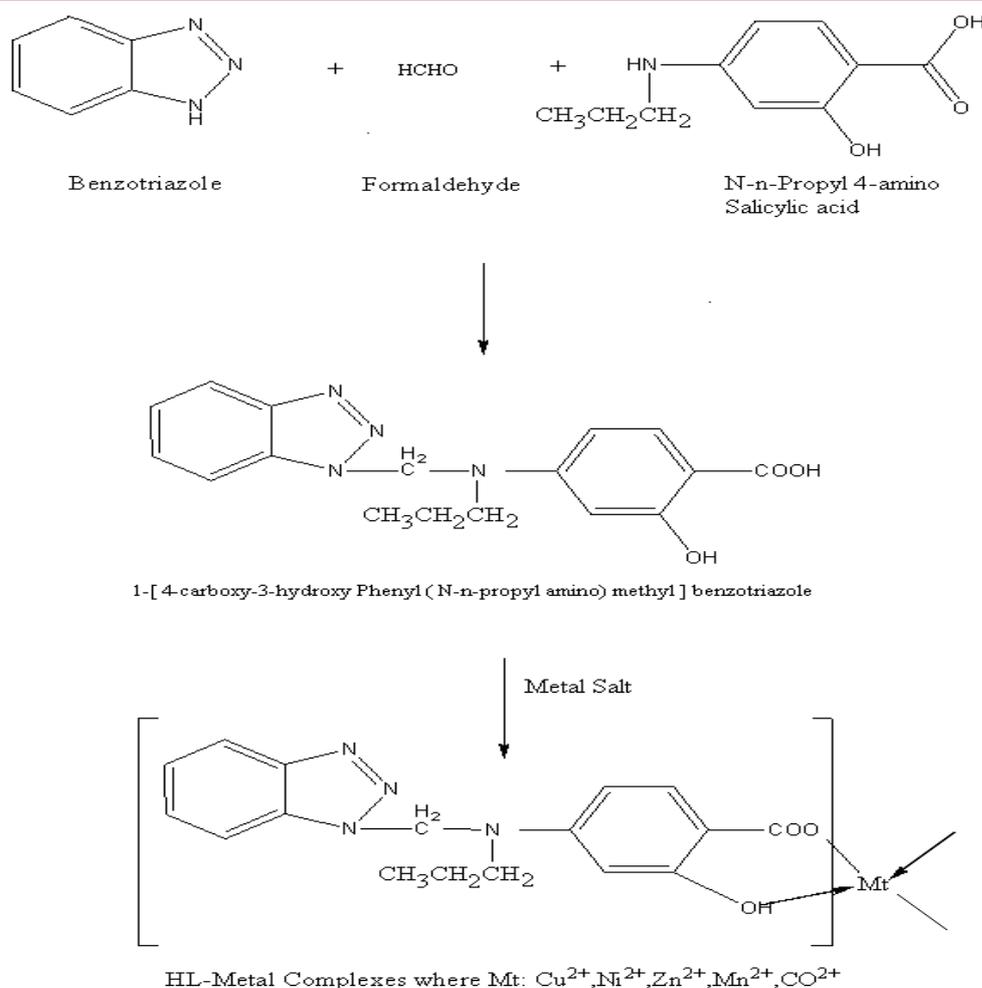
complexes. The work is illustrated in Scheme-1.

## Experimental MATERIALS

Benzotriazole was prepared by method reported in literature<sup>9</sup>. N-n-propyl 4-amino salicylic acid was obtained from local dealer. All other chemicals used were of analytical grade.

## Synthesis of 1-[4-carboxy-3-hydroxy phenyl (N-n-propyl amino) methyl] benzotriazole

A mixture of 1-H Benzotriazole (0.02 mole), formaldehyde (0.02 mole) and N-propyl 4-aminosalicylic acid was (0.02 mole) in ethanol (70 ml) was heated under refluxed for 4h. Subsequently ethanol was distilled off and the lump mass obtained. It was triturated with petroleum ether (40-60 °C). The solid designated as HL was isolated and dried in air. Yield was 70%. It's m.p was 200°C. (uncorrected).



Scheme-1

**Elemental analysis** $\text{C}_{17}\text{H}_{18}\text{N}_4\text{O}_3$  ( 326 gm/mol )

	C%	H%	N%
Calculated:	62.57	5.52	17.17
Found:	62.42	5.48	17.11

IR Features:	Wavenumber ( $\text{cm}^{-1}$ )	Assignment
	1485-1522	Benzotriazole ring
	3032,1502,1600	Aromatic
	1683	CO of COOH
	3200-3600	OH
	2850,2920	$\text{CH}_2$

NMR : (DMSO)	Chemical Shift (ppm)	Integration	Assignment
	7.1-7.7	(7H)	Multiplet aromatic
	2.57	(2H)	Singlet ( $\text{CH}_2$ )
	10.0	(1H)	Singlet (COOH)
	3.9	(1H)	Singlet (OH)
	1.1	(3H)	Triplate ( $\text{CH}_3$ )
	1.56	(2H)	Multiplate ( $\text{CH}_2$ )
	3.55	(2H)	Triplate ( $\text{CH}_2$ )

### Synthesis of metal complexes of HL

Formation of HL metal complexes

The  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Zn}^{2+}$  metal ion complexes of HL have been prepared in a similar manner. The procedure is as follow.

To a solution of HL (0.1 mole) in ethanol-acetone (1:1) mixture (150 ml), 0.1 N KOH solution was added drop wise with stirring. The pasty precipitates were obtained at neutral PH. These were dissolved by addition of water up to clear solution. It was diluted to 250 ml by water and was known as stock solution. 25ml of the stock solution (which contains 0.01 mole HL) was added drop wise to the solution of metal salt ( 0.005 mole ) in water at room temperature. Sodium acetate or ammonia was added up to complete precipitation. The precipitates were digested on water bath at 80°C for 2h. The digested precipitates of complexes were filtered washed with water and air dried. It was amorphous powder. Yield was almost quantitative. The details are given in Table-1.

### Measurements

The elemental analysis for C,H, and N were carried out on elemental analyzer. IR spectra of HL and its metal complexes were scanned on a Nicolet 760 FTIR spectrophotometer in KBr. The NMR spectrum of HL was scanned on Bruker NMR spectrometer using DMSO solvent. The metal content of the metal chelate were performed by decomposing a weighed amount of each metal complexes followed by EDTA titration as reported in literature <sup>10</sup>. Magnetic susceptibility measurement of all the metal complexes was carried out at room temperature by the Gouy method. Mercury tetrathiocyanatocobaltate (II)  $\text{Hg} [\text{Co} (\text{NCS})_4]$  was used as a calibrant. The diffused reflectance spectra of solid metal complexes were recorded on a Backman DK Spectrophotometer with a solid reflectance attachment, MgO was employed as the reflectance compound. The electrical conductivity of all the complexes was measure in acetonitrile at  $10^{-3}$  M concentration.

### Antifungal activity

The fungicidal activity of all the compounds were studied at 1000 ppm concentration in vitro plant pathogenic organisms listed in Table-3 were used. The antifungal activity of all the samples were measured by cup plate method <sup>11</sup>. Each of the plant pathogenic strains on a potato dextrose agar (PDA) medium contained potato 200gms, dextrose 20gms, agar 20gms, and water 1 litre. 5 days old culture were employed. The compounds to be tested were suspended (1000 ppm) in a PDA medium and autoclaved at 120°C for 15 min. at 15 atm pressure. These medium were poured into sterile petri plate and the organisms were incubated after cooling the petri plated. The percentage inhabitation for fungi was calculated after 5 days using the formula give below.

$$\text{Percentage of Inhibition: } \frac{100 (X-Y)}{X}$$

Where X: Area of colony in control plate

Y: Area of colony in test plate

The fungicidal activity all compounds are shown in Table-3.

### RESULTS AND DISCUSSION

The parent ligand HL was an amorphous yellow powdered, soluble in various solvents like dioxane, DMSO and DMF. The results of elemental analysis of the ligand are reported in Table-1. They are consistent with the predicted structure as shown in Scheme-1 .

Examination of IR spectrum (not shown) of HL reveals that a broad band of phenolic hydroxyl stretching is observed at 3200-3600  $\text{cm}^{-1}$  as well as additional absorption bands at 3030 , 1500 and 1600  $\text{cm}^{-1}$  are characteristics of the salicylic acid <sup>12-13</sup>. The strong bands at 1680  $\text{cm}^{-1}$  for C=O . The NMR data (shown in experimental part) also confirm the structure of HL. The metal complexes of HL with the metal ions  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Zn}^{2+}$  vary in colours. On the basis of the proposed structure as shown in schme-1, the molecular formula of the HL ligand is  $\text{C}_{17}\text{H}_{18}\text{N}_4\text{O}_3$ . This upon complexion

coordinates with one central metal atom at four coordination sites and with two water molecules. Therefore the general molecular formula of the resulting metal complex is  $[C_{34}H_{34}N_8O_6] M 2(H_2O)$  for divalent metal ions. This has been confirmed by results of elemental analysis of all the five metal chelates and their parent ligand. The data of elemental analysis reported in Table-1 are in arrangement with the calculated values of C,H and N based on the above mentioned molecular formula of parent ligand as well as metal complexes.

Inspection of IR Spectra (not shown) of metal complexes reveals that all the

spectra are identical in all respects. The comparison of IR spectrum of the parent ligand HL with that of its each metal complex has revealed certain characteristics differences.

One of the significant difference to be expected between the IR spectrum of the parent ligand and its metal complex is the presence of more broadened band in the region of  $3200-3600\text{ cm}^{-1}$  for the metal complex as the oxygen of the O-H group of the ligands forms a coordination bond with the metal ions<sup>12-14</sup>. This is explained by the fact that water molecules might have strongly absorbed to the metal chelates sample during their formation.

Table 1: Analytical data of the metal chelates of HL

Compound	Emperical Formula	Mol. Cal Gm/mole	Yield (%)	Elemental Analysis							
				C%		H%		N%		M%	
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
[CuHL (H <sub>2</sub> O) <sub>2</sub> ]	C <sub>34</sub> H <sub>34</sub> N <sub>8</sub> O <sub>6</sub> Cu <sup>2+</sup> 2(H <sub>2</sub> O)	749.54	65	54.43	54.35	4.54	4.48	14.94	14.87	8.48	8.40
[CoHL (H <sub>2</sub> O) <sub>2</sub> ]	C <sub>34</sub> H <sub>34</sub> N <sub>8</sub> O <sub>6</sub> Ni <sup>2+</sup> 2(H <sub>2</sub> O)	744.69	70	54.79	54.74	4.57	4.53	15.04	14.96	7.88	7.80
[NiHL (H <sub>2</sub> O) <sub>2</sub> ]	C <sub>34</sub> H <sub>34</sub> N <sub>8</sub> O <sub>6</sub> Mn <sup>2+</sup> 2(H <sub>2</sub> O)	740.93	67	55.06	55.00	4.59	4.55	15.12	15.10	7.41	7.38
[MnHL (H <sub>2</sub> O) <sub>2</sub> ]	C <sub>34</sub> H <sub>34</sub> N <sub>8</sub> O <sub>6</sub> Co <sup>2+</sup> 2(H <sub>2</sub> O)	744.94	65	54.77	54.71	4.56	4.54	15.03	15.00	7.91	7.88
[ZnHL (H <sub>2</sub> O) <sub>2</sub> ]	C <sub>34</sub> H <sub>34</sub> N <sub>8</sub> O <sub>6</sub> Zn <sup>2+</sup> 2(H <sub>2</sub> O)	751.39	63	54.30	54.22	4.52	4.49	14.91	14.83	8.70	8.67

Another noticeable difference is that the bands due to the COO<sup>-</sup> anion at  $1600\text{ cm}^{-1}$  in the IR spectrum of the each metal complex. The band at  $1400\text{ cm}^{-1}$  in the IR spectrum of HL assigned to inplane OH determination<sup>12-14</sup>. is shifted towards higher frequency in the spectra of the

metal complex due to the formation of metal oxygen bonds. This has been further confirmed by a weak bands at  $1105\text{ cm}^{-1}$  corresponding to C-O-M stretching<sup>12-14</sup>. Thus all of these characteristics features of the IR studies suggested the structure of the metal complex as shown in scheme-1.

Table 2: Magnetic Moment & Reflectance data of the Metal Complexes

Complex	Magnetic Moment $\mu_{\text{eff}}$ (B.M)	Absorption band (Cm <sup>-1</sup> )	Transitions
Cu-HL	1.74	24503 15652	C.T <sup>2</sup> B <sub>1g</sub> → <sup>2</sup> A <sub>1g</sub>
Ni-HL	5.03	22495 13120	<sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>1g</sub> (P) <sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>1g</sub> (F)
Co-HL	11.91	22975 19055 8540	<sup>4</sup> T <sub>1g</sub> (F)→ <sup>4</sup> T <sub>2g</sub> (F) <sup>4</sup> T <sub>1g</sub> (F)→ <sup>4</sup> A <sub>2g</sub> <sup>4</sup> T <sub>1g</sub> (F)→ <sup>4</sup> T <sub>2g</sub> (P)
Mn-HL	15.93	23401 18584 16120	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>1g</sub> ( <sup>4</sup> Eg) <sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>2g</sub> ( <sup>4</sup> G) <sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>1g</sub> ( <sup>4</sup> G)
Zn-HL	Diamagnetic	-----	-----

Table 3: Antifungal Activity of Ligand HL and its metal complexes

Sample	Zone of inhibition of fungus at 1000ppm (%)				
	PE	BT	N	T	RN
(HL)-Mn <sup>4+</sup>	47	49	64	47	47
(HL)-Co <sup>2+</sup>	69	61	71	59	56
(HL)-Ni <sup>2+</sup>	63	53	69	50	50
(HL)-Cu <sup>2+</sup>	85	86	75	73	81
(HL)-Zn <sup>2+</sup>	71	75	73	60	71
HL	53	52	48	52	49

PE= *Penicillium expansum*, BT= *Botrydoepladia thiobromine*,  
 N=*Nigrospora sp.*, T= *Trichothesium sp.*, RN= *Rhizopus nigricans*

Examination of data of the metal content in each compound revealed a 1:2 metal:ligand (M:L) stoichiometry in all of the complex of divalent metal ions. Magnetic moment ( $\mu_{\text{eff}}$ ) of each of the metal complex is given in Table-2. Examination of these data reveals that all complexes other than that of Zn<sup>2+</sup> are paramagnetic while those of Zn<sup>2+</sup> are diamagnetic.

The diffuse electronic spectrum of the [CuHL (H<sub>2</sub>O)<sub>2</sub>] metal complex shows broad bands at 15630 and 22288 cm<sup>-1</sup> due to the <sup>2</sup>B<sub>1g</sub>→<sup>2</sup>A<sub>1g</sub> transition and charge transfer, respectively suggesting a distorted octahedral structure<sup>15-17</sup> for the [CuHL (H<sub>2</sub>O)<sub>2</sub>] complex. Which is further confirmed by the higher value of  $\mu_{\text{eff}}$  of the [CuHL (H<sub>2</sub>O)<sub>2</sub>] complex. The [NiHL (H<sub>2</sub>O)<sub>2</sub>] complex gave two absorption bands at 14677, 20535 corresponding to <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>1g</sub> (P) and <sup>3</sup>A<sub>1g</sub> → <sup>3</sup>T<sub>1g</sub> (F) transitions. [CoHL (H<sub>2</sub>O)<sub>2</sub>] complex gave three absorption bands at 15688, 26740 cm<sup>-1</sup>. Thus absorption bands at 26740, 15688 and 8995 cm<sup>-1</sup> corresponding to <sup>4</sup>T<sub>1g</sub>(F)→<sup>4</sup>T<sub>2g</sub>(F), <sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>A<sub>2g</sub>, <sup>4</sup>T<sub>1g</sub>(F)→<sup>4</sup>T<sub>2g</sub>(P) the diffuse, reflectance spectra and the value of the magnetic moments ( $\mu_{\text{eff}}$ ) indicate and octahedral configuration for the [NiHL (H<sub>2</sub>O)<sub>2</sub>] and [CoHL (H<sub>2</sub>O)<sub>2</sub>] complex. The spectra of [MnHL (H<sub>2</sub>O)<sub>2</sub>] shows weak bands at 16850, 18333 and 24445 cm<sup>-1</sup> assigned to the transitions <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>T<sub>1g</sub> (4G), <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>T<sub>2g</sub> (4G) and <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>T<sub>1g</sub> (4Eg) respectively suggestion an octahedral structure for the [MnHL (H<sub>2</sub>O)<sub>2</sub>] chelate. As the spectrum of the [ZnHL (H<sub>2</sub>O)<sub>2</sub>] is not well resolved, it is not interpreted but it's  $\mu_{\text{eff}}$  value shows that it is diamagnetic as expected.

The antifungal activity of all the compounds measured for various plant

pathogens. Inspection of the result shown in Table-3 indicates that all compounds are good toxic for fungi. Out of all the compounds copper chelates is more toxic than other. These compounds almost inhibit the fungi about 70%. Hence produced metal chelates can be employed as garden fungicides. Further work in the direction is in progress.

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