

Synthesis and Characterization of Metal Complexes of 1-(4-Carboxy-3-hydroxy-N-methyl phenylamino methyl)benzotriazole

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Aminomethylation of benzotriazole was carried out by treating benzotriazole with formaldehyde and N-methyl 4-aminosalicylic acid, which yielded 1-(4-carboxy-3-hydroxy-N-methyl phenylamino methyl)benzotriazole (CMPB). The transition metal complexes of Cu²⁺, Co²⁺, Ni²⁺, Mn²⁺ and Zn²⁺ of CMPB have been prepared and characterized by elemental analysis, spectral studies, magnetic moment, molar conductivity and antimicrobial activity.

Key Words: Benzotriazole, N-methyl-4-aminosalicylic acid, Metal complexes, Spectral studies, Magnetic moment, Antibacterial and Antifungal activity.

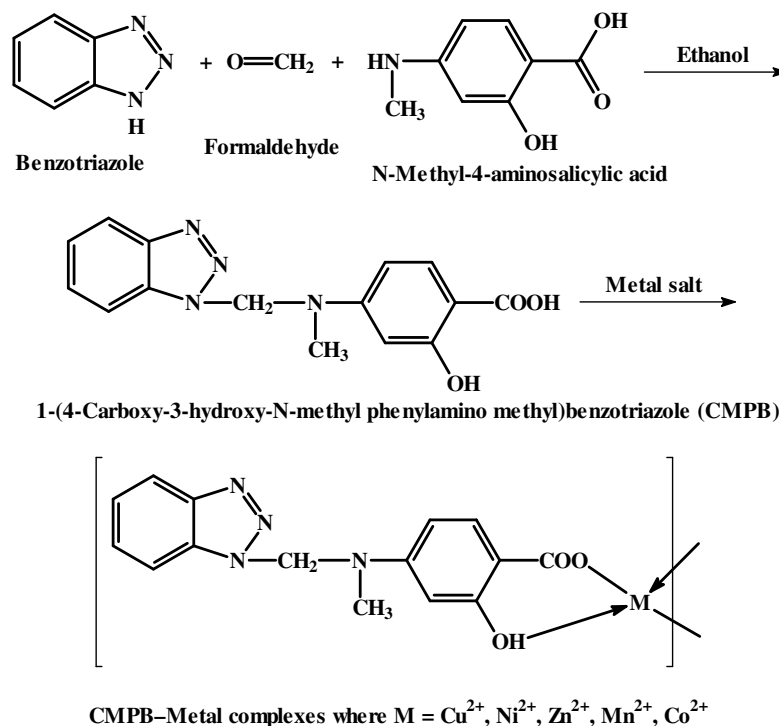
INTRODUCTION

One of the heterocyclic compounds *i.e.*, 1-(*H*)-benzotriazole is found as an important heterocyclic compound. Its prime application is as corrosion inhibitors for copper or copper alloys^{1,2}. Ciba Geigy has introduced benzotriazole derivative under the trade name Trinvin-p³. It is applied as an UV light absorber for stabilizing plastics and other organic materials against discoloration determination³. It is also employed as photographic emulsion stabilizer⁴. In the peptide synthesis it acts in form of an active ester⁵. The area in which the amino methylation of benzotriazole by using aromatic amine having metal gripping group (*i.e.*, ligand) has not been developed. With this view, the present authors communicated the initial work recently⁶. In continuation of this work⁶ the present paper describes the synthesis and characterization of 1-(4-carboxy-3-hydroxy-N-methyl phenylamino methyl)benzotriazole and its metal complexes. The work is illustrated in **Scheme-I**.

EXPERIMENTAL

Benzotriazole was prepared by method reported in literature⁷. N-Methyl-4-aminosalicylic acid was prepared by method reported⁸. All other chemicals used were of analytical grade.

Synthesis of 1-(4-carboxy-3-hydroxy-N-methyl phenylamino methyl)-benzotriazole: A mixture of 1*H*-benzotriazole (0.02 mol), formaldehyde (0.02 mol) and N-methyl-4-aminosalicylic acid was (0.02 mol) in ethanol (70 mL) was heated under reflux for 4 h. Subsequently ethanol was distilled off and the lump mass obtained. It was triturated with petroleum ether (40-60 °C). The solid designated as CMPB was isolated and dried in air. Yield *ca.* 78 %, m.p. 173 °C.



Scheme-I

Elemental analysis: $\text{C}_{15}\text{H}_{14}\text{N}_4\text{O}_3$ (m.w. 298 g/mol); Calcd. (%): C 60.40 H 4.69 N 18.79; Found (%): C 60.39, H 4.60, N 18.65; IR spectral data: 1522-1485 cm^{-1} benzotriazole ring, 3032, 1502, 1600 cm^{-1} aromatic, 1683 cm^{-1} CO of COOH, 3200-3600 cm^{-1} OH, 2850, 2920 cm^{-1} CH_2 . NMR: 7.1-7.7 ppm multiplet aromatic; (DMSO) 2.57 ppm (2H) singlet CH_2 , 10.0 ppm (1H) singlet (COOH), 3.9 ppm (1H) singlet (OH).

Synthesis of metal complexes of CMPB: All the Cu^{2+} , Co^{2+} , Ni^{2+} , Mn^{2+} and Zn^{2+} metal ion complexes of CMPB have been prepared in a similar manner. The procedure is as follow.

To a solution of CMPB (0.1 mol) in ethanol-acetone (1:1) mixture (150 mL), 0.1 N KOH solution was added drop wise with constant 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 of the stock solution (which contains 0.01 mL CMPB) was added drop wise to the solution of metal salt (0.005 mol for divalent metal ions) in water at room temperature. Sodium acetate or ammonia was added up to complete precipitation. The precipitation was digested on water bath at 80 °C for 2 h. The digested precipitates of complex were filtered washed with water and air dried. It was amorphous powder. Yield was almost quantitative. The details are given in Table-1.

TABLE-1
ANALYTICAL DATA OF THE METAL CHELATES OF CMPB

Compound [m.f.]	m.w. (g/mol) (Yield, %)	Elemental analysis (%): Calcd. (Found)			
		C	H	N	M
CMPB	298	60.40	4.69	18.79	–
[C ₁₅ H ₁₄ N ₄ O ₃]	(78)	(60.39)	(4.60)	(18.65)	
[Cu(CMPB) ₂ (H ₂ O) ₂]	693.54	51.90	3.74	16.14	9.16
[C ₃₀ H ₂₆ N ₈ O ₆ Cu·2(H ₂ O)]	(55)	(51.80)	(3.70)	(16.10)	(9.10)
[Co(CMPB) ₂ (H ₂ O) ₂]	688.93	52.25	3.77	16.25	8.55
[C ₃₀ H ₂₆ N ₈ O ₆ Co·2(H ₂ O)]	(51)	(52.24)	(3.60)	(16.21)	(8.50)
[Ni(CMPB) ₂ (H ₂ O) ₂]	688.69	52.27	3.77	16.26	8.52
[C ₃₀ H ₂₆ N ₈ O ₆ Ni·2(H ₂ O)]	(53)	(52.21)	(3.71)	(16.21)	(8.50)
[Mn(CMPB) ₂ (H ₂ O) ₂]	684.93	52.56	3.79	16.35	8.01
[C ₃₀ H ₂₆ N ₈ O ₆ Mn·2(H ₂ O)]	(56)	(51.24)	(3.72)	(16.31)	(8.00)
[Zn(CMPB) ₂ (H ₂ O) ₂]	695.39	51.76	3.73	16.10	9.40
[C ₃₀ H ₂₆ N ₈ O ₆ Zn·2(H ₂ O)]	(59)	(51.72)	(3.71)	(16.00)	(9.30)

The elemental analysis for C, H and N were carried out on elemental analyzer. IR spectra of CMPB and its metal complexes were scanned on a Nicolet 760 FTIR spectrophotometer in KBr. 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 literature⁹. Magnetic susceptibility measurement of all the metal complex was carried out at room temperature by the Gouy method. Mercury tetrathiocyanatocobaltate (II) Hg [Co(NCS)₄] was used as a calibrant. The diffused reflectance spectra of solid metal complex were recorded on a Beckman DK spectrophotometer with a solid reflectance attachment, MgO was employed as the reflectance compound.

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 method¹⁰. Each of the plant pathogenic strains on a potato dextrose agar (PDA) medium contained potato 200 g, dextrose 20 g, agar 20 g and water 1 L, 5 days old culture were employed. The compounds to be tested were suspended (1000 ppm) in a PDA medium and autoclaved 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 CMPB 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-I**.

Examination of IR spectrum of CMPB reveals that a broad band of phenolic hydroxyl stretching is observed at 3600-3200 cm^{-1} as well as additional absorption bands at 3030 cm^{-1} , 1500 and 1600 are characteristics of the salicylic acid¹¹. The strong bands at 1680 cm^{-1} for $\nu(\text{C}=\text{O})$. The NMR data also confirm the structure of CMPB. The metal complex of CMPB with the metal ions Cu^{2+} , Co^{2+} , Ni^{2+} , Mn^{2+} and Zn^{2+} vary in colours. On the basis of the proposed structure as shown in **Scheme-I**, the molecular formula of the CMPB ligand is $\text{C}_{15}\text{H}_{14}\text{N}_4\text{O}_3$ which upon complexation coordinates with one central metal atom at two coordination sites and with two water molecules. Therefore the general molecule formula of the resulting metal complex is $[\text{C}_{30}\text{H}_{26}\text{N}_8\text{O}_6]\text{M}\cdot 2(\text{H}_2\text{O})$ for divalent metal ions. This has been confirmed by results of elemental analysis of all the five metal chelate 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 complex.

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 bands in the region of 3600-3200 cm^{-1} for the metal complex as the oxygen of the O-H group of the ligands forms a coordination bond with the metal ions¹¹. This is explained by the fact that water molecules might have strongly absorbed to the metal chelate sample during their formation.

Another noticeable difference is that the bands due to the COO^- anion at 1600 cm^{-1} in the IR spectrum of the each metal complex. The band at 1400 cm^{-1} in the IR spectrum of CMPB assigned to inplane OH determination¹¹ 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 cm^{-1} corresponding to C-O-M stretching¹¹.

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 (μ_{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^{2+} are paramagnetic while those of Zn^{2+} are diamagnetic.

The diffuse electronic spectrum of the $[\text{Cu}(\text{CMPB})_2(\text{H}_2\text{O})_2]$ metal complex shows broad bands at 15532 and 22379 cm^{-1} due to the ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ transition and charge transfer, respectively suggesting a distorted octahedral structure^{12,13} for the $[\text{Cu}(\text{CMPB})_2(\text{H}_2\text{O})_2]$ complex. Which is further confirmed by the higher value of μ_{eff} of the $[\text{Cu}(\text{CMPB})_2(\text{H}_2\text{O})_2]$ complex. The $[\text{Ni}(\text{CMPB})_2(\text{H}_2\text{O})_2]$ complex gave two absorption bands at 14570, 20430 corresponding to ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ and ${}^3\text{A}_{1g} \rightarrow$

TABLE-2
MAGNETIC MOMENT AND REFLECTANCE DATA OF THE METAL COMPLEXES

Complex	Magnetic moment μ_{eff} (BM)	Absorption band (cm^{-1})	Transitions
Cu(CMPB) ₂ ·(H ₂ O) ₂	1.95	22379	C.T
		15532	² B _{1g} → ² A _{1g}
Ni(CMPB) ₂ ·(H ₂ O) ₂	3.82	20430	³ A _{2g} → ³ T _{1g} (P)
		14570	³ A _{1g} → ³ T _{1g} (F)
Co(CMPB) ₂ ·(H ₂ O) ₂	4.42	26722	⁴ T _{1g} (F) → ⁴ T _{2g} (F)
		15679	⁴ T _{1g} (F) → ⁴ A _{2g}
		8991	⁴ T _{1g} (F) → ⁴ T _{2g} (P)
Mn(CMPB) ₂ ·(H ₂ O) ₂	4.86	24341	⁶ A _{1g} → ⁴ T _{1g} (4Eg)
		18321	⁶ A _{1g} → ⁴ T _{2g} (4G)
		16831	⁶ A _{1g} → ⁴ T _{1g} (4G)
Zn(CMPB) ₂ ·(H ₂ O) ₂	Diamagnetic	–	–

³T_{1g}(F) transitions. [Co(CMPB)₂(H₂O)₂] complex gave three absorption bands at 15679, 26722 cm^{-1} . Thus absorption bands at 26740, 15688 and 8991 cm^{-1} corresponding to ⁴T_{1g}(F) → ⁴T_{2g}(F), ⁴T_{1g}(F) → ⁴A_{2g}, ⁴T_{1g}(F) → ⁴T_{2g}(P) the diffuse, reflectance spectra and the value of the magnetic moments (μ_{eff}) indicate an octahedral configuration for the [Ni(CMPB)₂(H₂O)₂] and [Co(CMPB)₂(H₂O)₂] complex. The spectra of [Mn(CMPB)₂(H₂O)₂] shows weak bands at 16831, 18321 and 24341 cm^{-1} assigned to the transitions ⁶A_{1g} → ⁴T_{1g}(4G), ⁶A_{1g} → ⁴T_{2g}(4G) and ⁶A_{1g} → ⁴T_{1g} (4Eg) respectively suggesting an octahedral structure for the [Mn(CMPB)₂(H₂O)₂] chelate. As the spectrum of the [Zn(CMPB)₂(H₂O)₂] is not well resolved, it is not interpreted but its μ_{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 chelate is more toxic than other. These compounds almost inhibit the fungi *ca.* 70 %. Hence produced metal chelate can be employed as garden fungicides.

TBALE-3
ANTIFUNGAL ACTIVITY OF CMPB AND ITS METAL COMPLEXES

Sample	Zone of inhibition of fungus at 1000 ppm (%)				
	PE	BT	N	T	RN
Mn(CMPB) ₂ ·(H ₂ O) ₂	66	70	69	71	70
Co(CMPB) ₂ ·(H ₂ O) ₂	65	63	72	71	71
Ni(CMPB) ₂ ·(H ₂ O) ₂	69	76	75	72	74
Cu(CMPB) ₂ ·(H ₂ O) ₂	83	79	81	85	78
Zn(CMPB) ₂ ·(H ₂ O) ₂	68	62	71	77	71
CMPB	60	61	63	61	65

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

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