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Research Paper

Metal Complexation Studies of 1-(4-carboxy-3-hydroxy-N- ethyl phenyl Amino methyl) benzotriazole.

Chemistry

KEYWORDS : Benzotriazole, N-ethyl-4-amino salicylic acid, metal complexes, spectral studies, magnetic moment, antibacterial and antifungal activity

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ABSTRACT

Aminomethylation of benzotriazole was carried out by treating benzotriazole with formaldehyde and N-ethyl 4-aminosalicylic acid. The resultant compound namely was designed as CEPB 1-(4-caroxy-3-hydroxy-N-ethyl phenylamino methyl)benzotriazole. The transition metal complexes of Cu2+, Co2+, Ni2+,Mn2+,and Zn2+ of CEPB have been prepared and characterized by Elemental analyser, spectral studies, magnetic moment determination, molar conductivity measurement and antimicrobial activity.

Introduction:

One of the heterocyclic compound say 1-(H)-benzotriazole is found as an important heterocyclic compound. It's prime application is as corrosion inhibiters for copper or copper alloys[1,2]. Ciba Geigy has introduced benzotriazole derivative under the trade name Trinavin-p[3]. It is applied as an UV light absorber for stabilizing plastics and other organic materials against discoloration determination[3]. It is also employed as photographic emulsion stabilizer[4]. In the peptide synthesis it acts in form of an active ester[5]. 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. With this view, the present authors communicated the initial work recently[6]. In connection of this work the present paper describes the synthesis and characterization of benzotriazole, N-ethyl-4-aminosalicylic acid clubbed molecule and its metal complexes[6-9]. The work is illustrated in Scheme-1.

Experimental:

Materials

Benzotriazole was prepared by method reported in literature[10]. N-ethyl-4-aminosalicylic acid was prepared by method reported[11,12]. All other chemicals used were of analytical grade.

Synthesis of 1-(4-caroxy-3-hydroxy-N-ethyl phenylamino methyl) benzotriazole.

A mixture of 1-H Benzotriazole (0.02 mole), formaldehyde (0.02 mole) and N-ethyl-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 CEPB was isolated and dried in air. Yield was 73%. It's m.p was 206°C. (uncorrected).

Elemental analysis:

$C_{16}H_{16}N_4O_3$ (312 gm/mol)

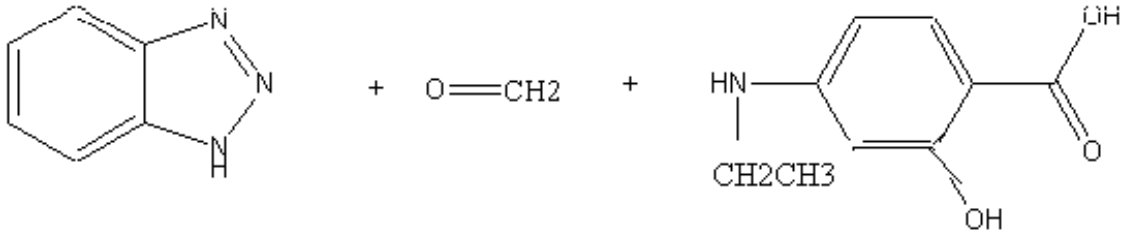
	C%	H%	N%
Calculated:	61.54	5.13	17.95
Found:	61.51	5.10	17.65

IR Features:

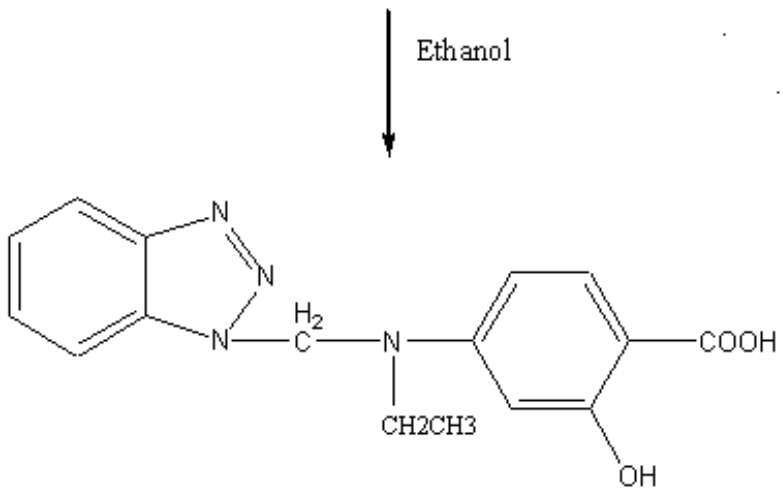
1485-1522 cm^{-1}	Benzotriazole ring	
3032,1502,1600 cm^{-1}	Aromatic	
1683 cm^{-1}	>CO of -COOH	
3200-3600 cm^{-1}	-OH	
2850,2920 cm^{-1}	$>CH_2$	

NMR (DMSO)

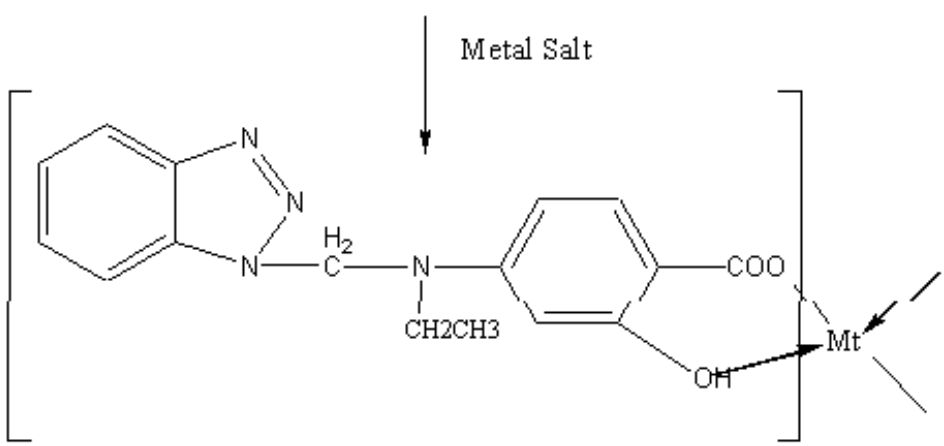
7.1-7.7 ppm	Multiplet aromatic	
2.57 ppm (2H)	Singlet ($> CH_2$)	
10.0 ppm (1H)	Singlet (-COOH)	
3.9 ppm (1H)	Singlet (-OH)	
1.13 ppm (3H)	Triplet ($-CH_3$)	
3.39 ppm (2H)	Quartet ($>CH_2$)	



Benzotriazole Formaldehyde N-ethyl p-amino salicylic acid



1-(4-carboxy-3-hydroxy-N-ethyl phenylamino methyl) benzotriazole



CEPB -Metal Complexes where Mt: Cu^{2+},Ni^{2+},Zn^{2+},Mn^{2+},CO^{2+}

Scheme-1

Synthesis of metal complexes of CEPB

Formation of CEPB metal complexes

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

To a solution of CEPB (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 of the stock solution (which contains 0.01 ml CEPB) was added drop wise to the solution of metal salt (0.005 mole for divalent metal ions and 0.0033 mole for Fe^{3+} ion) in water at room temperature. Sodium acetate or ammonia was added up to complete precipitation. The precipitation was di-

gested 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.

Measurements:

The elemental analysis for C, H, and N were carried out on elemental analyzer. IR spectra of CEPB 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 literature10. Magnetic susceptibility measurement of all the metal complex was carried out at room temperature by the Gouy method. Mercury tetrathiocynatocobaltate (II) Hg [Co (NCS)4] was used as a calibrant. The diffused reflectance spectra of solid metal complex were recorded on a Beckman-DK-2A spectrophotometer with a solid reflectance attachment, MgO was employed as the reflectance compound.

Antifungal activity:

The fungicidal activities 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[14]. 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 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 given below.

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

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 CEPB 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 the ligand was synthesized as shown in the scheme-1.

Examination of IR spectrum (not shown) of CEPB reveals that a broad band of phenolic hydroxyl stretching is observed at 3200-3600 cm^{-1} as well as additional absorption bands at 3030 cm^{-1}, 1500 cm^{-1} and 1600 cm^{-1} are characteristics of the salicylic acid [15-16]. The strong bands at 1680 cm^{-1} for C=O. The NMR data (shown in experimental part) also confirm the structure of CEPB. The metal complex of CEPB with the metal ions Cu^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, and Zn^{2+} vary in colours. On the basics of the proposed structure as shown in schme-1, the molecular formula of the CEPB ligand is $C_{16}H_{16}N_4O_3$ which 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 $[C_{32}H_{30}N_8O_6]\ M\ 2(H_2O)$ for divalent metal ions. This has been confirmed by results of elemental analysis of all the five metal 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.

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 CEPB 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 bands in the region of 3200-3600 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 [12-14]. This is explained by the fact that water molecules might have strongly absorbed to the metal chelate sample during their formation.

Table-1 Analytical data of the metal chelates of CEPB

Compound	Empirical Formula	Mol. Cal G m / mole	Yield (%)	Elemental Analysis							
				C%		H%		N%		M%	
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
CEPB	C16H16N4O3	312	73	61.54	61.51	5.13	5.10	17.95	17.65	------	-------
[Cu(CEPB)2(H2O)2]	C32H30N8O6Cu2+2(H2O)	721.54	60	53.22	53.18	4.71	4.69	15.52	15.40	8.80	8.70
[Co(CEPB)2(H2O)2]	C32H30N8O6Co2+2(H2O)	716.93	58	53.56	53.51	4.74	4.70	15.62	15.49	8.22	8.15

[Ni(CEPB)2(H2O)2]	C32H30N8O6Ni2+2(H2O)	716.69	70	53.58	53.50	4.74	4.70	15.63	15.51	8.19	8.12
[Mn(CEPB)2(H2O)2]	C32H30N8O6Mn2+2(H2O)	712.93	66	53.86	53.81	4.77	4.72	15.71	15.60	7.70	7.62
[Zn(CEPB)2 (H2O)2]	C32H30N8O6Zn2+2(H2O)	723.39	62	53.08	53.02	4.70	4.66	15.48	15.35	9.04	8.95

Another noticeable difference is that the bands due to the COO^- anion at 1600 com^{-1} in the IR spectrum of the each metal complex. The band at 1400 cm^{-1} in the IR spectrum of CEPB assigned to inplane OH determination [15-17] 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 week bands at 1105 cm^{-1} corresponding to C-O-M stretching [15-17]. 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 μeff(B.M)	Absorption band (Cm-1)	Transitons
Cu-CEPB	2.08	24381 15620	C.T 2B1g→2A1g
Ni- CEPB	3.20	22188 14125	3A2g→3T1g (P) 3A1g→3T1g (F)
Co- CEPB	4.80	24117 19720 8655	4T1g (F)→4T2g (F) 4T1g (F)→4A2g 4T1g (F)→4T2g (P)
Mn- CEPB	5.10	23987 17634 15455	6A1g →4T1g (4Eg) 6A1g →4T2g (4G) 6A1g →4T1g (4G)
Zn- CEPB	Diamagnetic	--------	---------

Tbale-3 Antifungal Activity of Ligand CEPB and its metal complexes

Sample	Zone of inhibition of fungus at 1000ppm (%)				
	PE	BT	N	T	RN
(CEPB)-Mn2+	48	45	59	58	45
(CEPB)-Co2+	61	60	68	64	70
(CEPB)-Ni2+	59	54	61	60	64
(CEPB)-Cu2+	70	66	75	79	75
(CEPB)-Zn2+	65	62	70	75	73
CEPB	65	52	48	45	55

PE= *Penicillium expansum*, BT= *Botrydepladia thiobromine*, N=*Nigrospra 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) stoichiomery in all of the complex of divalent metal ions. Magnetic moment (μeff) of each of the metal complex is given in Table-2. Examination of these data reveals that all complexes other than that of Zn2+ are paramagnetic while those of Zn2+ are diamagnetic.

The diffuse electronic spectrum of the $[Cu(CEPB)_2(H_2O)_2]$ metal complex shows broad bands at15620 and 24381 cm^{-1} due to the $^2B_{1g} \rightarrow {}^2A_{1g}$ transition and charge transfer, respectively suggesting a distorted octahedral structure[18-19] for the $[Cu(CEPB)_2(H_2O)_2]$ complex. Which is further confirmed by the higher value of μ_{eff} of the $[Cu(CEPB)_2(H_2O)_2]$ complex. The $[Ni(CEPB)_2(H_2O)_2]$ complex gave two absorption bands at 14125, 22188 corresponding to $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ and $^3A_{1g} \rightarrow {}^3T_{1g}(F)$ transitions. The $[Co(CEPB)_2(H_2O)_2]$ complex gave three absorption bands at 24177, 19720 and 8655 cm^{-1} Thus absorption bands at 24177, 19720 and 8655cm^{-1} corresponding to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}$, $^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$ the diffuse, reflectance spectra and the value of the magnetic moments (μ_{eff}) indicate and octahedral configuration for the $[Ni(CEPB)_2(H_2O)_2]$ and $[Co(CEPB)_2(H_2O)_2]$ complex. The spectra of $[Mn(CEPB)_2(H_2O)_2]$ shows weak bands at 15455, 17634 and 23987 cm^{-1} assigned to the transitions $^6A_{1g} \rightarrow {}^4T_{1g}(4G)$, $^6A_{1g} \rightarrow {}^4T_{2g}(4G)$ and $^6A_{1g} \rightarrow {}^4T_{1g}(4Eg)$ respectively suggesting an octahedral structure for the $[Mn(CEPB)_2(H_2O)_2]$ chelate. As the spectrum of the $[Zn(CEPB)_2(H_2O)_2]$ is not well resolved, it is not interpreted but it's 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 about 70%. Hence produced metal chelate can be employed as garden fungicides. Further work in the direction is in progress.

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REFERENCE

1. J.W Long, L.V Vecek, Sherwin-Williams Co. U.S. 1982, 4663914. | 2. F. Hageolorn, W. Evertz, Bayer US 1984, 4424360. | 3. Rahway N.J Mark Inded 11th Ed Merk & Co. (1981). | 4. Ullman's Encyclopedia of Ind Chem Willey Veh 1984, 26 614. | 5. D. Hadson, R.C. River, G.E Marshell, Peptides Chem. Str. & Biology Escam, Leiday | (1990). | 6. P.K.Patel and P.D.Patel, , E-Journal of chemistry, Volume.VI,2009.6(2), 475-480 | 7. P.K.Patel and P.D.Patel , Asian Journal of Chemistry Vol. 22, No. 2(2010) 1091-1096 | 8. P.K.Patel and P.D.Patel, International Journal of ChemTech Research Vol. 2, No. 2 PP | 1147-1152 April-June 2010 | 9. P.K.Patel , P.D.Patel and S.P.Patel, International Journal of Pharmaceutical and | Chemical Sciences Vol. 1 (4) Oct.-Dec. 2012 | 10. A.I. Vogel, Textbook of practical Organic Chemistry Pearson Education Ltd. New | Delhi 1st Indian Edition, 2004. | 11. P. C. Ferreira Arg. Biol. 34, 134 (1950). | 12. W.Carimme, H.Schmitz Chem. Ber. 84, 734 (1957). | 13. N. Radjohn, Org. Synthesis, Coll. Vol. IV Willey & Sons N.Y, 1963. | 14. W. R. Baily and E.G. Scott, Diagnostic Microbiology, The C.V. Moshy Co. St. Lovis | 1966, 257. | 15. R.M. Silverstein, Spectrometric Identification of organic compounds 5th Ed. John | Wiley, 1991. | 16. W. Kemp, Organic Spectroscopy, ELBS. (Macmillan' UK), 1998. | 17. K. Nakamoto, Infrared Spectra of Inorganic and Co-ordination Compound, Wiley | NY 1970. | 18. Lever. ABP, Inorganic Electronic Spectroscopy, Elsevir NY, 1968. | 19. B.N. Figgis, Introduction to Ligands Field, Wiley Estern Ltd. NY 1976. | 20. R.N. Carlin and A. Van Dryneveldt, J, Magnetic properties of Transition Metal | Compound, Springe- Verlag, NY. 1997. |