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Synthesis and Characterization of Some Biological Important Cobalt (II) Chelates of 2-(2′-Hydroxyphenyl) Benzimidazole

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Some new mixed ligand cobalt (II) chelates have been synthesized with 2-(2′-hydroxyphenyl)benzimidazole (HPBI) and glycine, sodium oxalate, sodium formate and phenol to form ternary metal chelates . These chelates have been characterised on the basis of their elemental analysis, conductance measurement, IR and NMR spectral studies. The metal chelates thus prepared were found to be more fungitoxic when studied against *Alternaria alternata* and *Aspergillus niger* by spore germination inhibition method as compared with Dithane M-45, a commercial fungicide.

Keywords: **Cobalt, Chelates, 2-(2′-Hydroxyphenyl) benzimidazole, Fungitoxicity.**

INTRODUCTION

2-(2′-Hydroxyphenyl) benzimidazole (HPBI) is a potent bidenate N, O- donor ligand forming a six membered chelate ring using the phenolic-O and the tertiary N of imidazole ring. The 2-substituted benzimidazole nucleus appears to be especially toxic to fungi.[1] Some transition metal chelates have been studied for their antifungal studies with 2-substituted benzimidazole and found to be more fungitoxic as compared to their parent compounds[2,3]. The fact that the mixed ligand chelates are more fungitoxic than simple compound, have promoted us to undertake the present studies. In the present communication we report the preparation of cobalt (II) chelates with 2-(2′-hydroxyphenyl) benzimidazole and ternary complexes with glycine, sodium oxalate, sodium formate and phenol and their characterization on the basis of elemental analysis, conductance measurement, IR and NMR spectral studies. Fungicidal property of these metal chelates have also been studied and reported in the present communication.

EXPERIMENTAL

All chemicals used were from BDH. The 2-substituted benzimidazole ligand 2-(2′-hydroxyphenyl) benzimidazole was prepared by the method reported in literature[4,5]. Melting points were determined in open capillaries and are uncorrected. IR spectra (KBr) were recorded on a Perkin-Elmer 577 grating IR spectrophotometer. The ^{1}H NMR spectra (chemical shift in δ ppm) were obtained from FX 90 Q JEOL spectrometer at 90 MHz in DMSO-d_6 using TMS as an internal reference. The purity of all compounds were checked by running TLC on silica gel-G using chloroform-ethyl acetate (1 : 1) mixture and spots were visualized by iodine vapours. The metal contents of the chelates were determined by standard literature procedures. The analytical data and physical properties of complexes are given in Table-1.

TABLE-1
PHYSICAL AND ANALYTICAL DATA OF LIGAND AND COMPLEXES

S.No.	m.f (colour)	Decomposition Temp. (°C)	Elemental Analysis % Found (calcd)			
			C	H	N	M
I	$C_{13}H_{10}N_2O$(HPBI) (Whitish)	242	74.18 (74.29)	4.70 (4.76)	13.22 (13.33)	—
II	Co$(HPBI)_2$ (Blue)	265	65.38 (65.41)	3.32 (3.35)	11.71 (11.74)	10.68 (10.71)
III	Co$(HPBI)_2$·(Gly) (Violet)	272	62.80 (62.88)	4.12 (4.17)	12.58 (12.68)	10.62 (10.67)
IV	Co$(HPBI)_2$·(Ox) (Dark pink)	284	59.26 (59.27)	3.50 (3.53)	9.86 (9.88)	10.32 (10.39)
V	Co$(HPBI)_2$·($(OFor)_2$) (Pink)	262	59.04 (59.06)	3.85 (3.87)	9.82 (9.84)	10.30 (10.35)
VI	Co$(HPBI)_2$·$(OC_6H_5)_2$ (Violet)	260	68.54 (68.58)	4.49 (4.51)	8.39 (8.42)	8.80 (8.86)

Attempts have been made to isolate the binary metal chelates with cobalt (II) halides and ligands *viz.* 2-(2′-hydroxyphenyl) benzimidazole, glycine, sodium oxalate, sodium formate and phenol by mixing 0.005 moles of cobalt halides in ethanol and 0.01 mole of the ligand in ethanol. The mixture was refluxed for about 4 h under suitable conditions. The compound thus separated was filtered and washed with ethanol and dried under vaccum.

Ternary metal chelates of Co(II) involving HPBI as one of the ligand and glycine, sodium oxalate, sodium formate, phenol as secondary ligand were isolated by simultaneous addition procedure and stepwise addition procedure.

Simultaneous Addition Procedure: 0.005 moles of $CoCl_2.6H_2O$ dissolved in ethanol is added to solution containing 0.01 moles of HPBI and 0.005 mole of second ligand dissolved in ethanol. The contents were refluxed for about 3 h. The complex thus separated out was filtered and washed with ethanol and dried under vaccum.

Stepwise Addition Procedure: 0.01 mole of HPBI was added to 0.005 mole of ML_2(L = Gly, OX, OF or, OC_6H_5) or 0.005 mole of Co$(HPBI)_2$ was added to 0.005 mole of ligand (L = Gly, sod.Ox, sod. OF or, OC_6H_5) in ethanol. The contents were refluxed for about 3 h the complex thus separated was filtered and washed with ethanol and dried under vacuum.

However analytical studies like colour, physical state, solubilities, decomposition temperature, conductance and IR studies have indicated that the products obtained by both the procedures are almost identical.

RESULT AND DISCUSSION

The analytical data of the complexes are reported in Table-1. The complexes are solids and are soluble in DMSO and DMF. The low value of molar conductance (10 – 20 $ohm^{-1}cm^2 mol^{-1}$) in DMF at room temperature show them to be non-electrolytic. The infrared spectrum of 2-(2′-hydroxyphenyl) benzimidazole shows a broad band in the region 3300–3200 cm^{-1}. This band has been assigned to ν_{as}(OH) stretching vibration of phenolic group. A broad absorption band at 2530 cm^{-1} is assigned to the strongly H-bonded phenolic OH[6]. As H-bonding lowers the stretching frequency of free OH, a lowering in ν(NH) may also be expected and thus a medium intensity band of ligand at 3030 cm^{-1} may be assigned to ν(NH) instead of the one at 3155 cm^{-1}. Two bands are observed at 1615 and 1665 cm^{-1} which may be assigned to δ (HOH). The other bands in the spectrum due to benzimidazole moiety appears more or less at the same position as reported in literature[7].

The band due to phenolic OH present in the ligand disappears in the spectra of the complex derivative indicating the deprotonation of —OH group and coordination of phenolic oxygen to the metal atom. The lowering in the frequency due to ν(C═N), ν(N═H) and ν(C═O) also confirms the formation of metal chelates . All other bands in the metal chelates appear in same region with slight shift due to coordination. IR spectra of other ligands and their binary metal complexes are observed in the same region as reported in literature[8, 9].

The infrared spectra of ternary complexes are non-superimpossable with those of binary complexes and thus it is assumed that new compound formed is a ternary metal complex. Further it is confirmed by the fact that the IR spectra of a ternary complex reveals the presence of the bands corresponding to the characteristic vibrations of both the ligand moiety *i.e.* 2-(2′-hydroxyphenyl) benzimidazole and the other ligand. The general feature of IR spectrum of ternary metal complex is an overlap of the spectra of two ligands. Thus presence of benzimidazole and other ligand in the ternary complexes is ascertained from the bands that appear in common absorption region of the two moieties as well as from the other bands which belong to both the ligands.

^{1}HNMR spectra of ligand and their metal complexes are recorded in d_6 DMSO solution; the chemical shifts (δ) are given in ppm downfield from tetramethyl silane. In ^{1}HNMR spectra of ligand the aromatic protons appeared as a multiplet in the region of δ 6.9–7.9 ppm. The resonance signal corresponding to —NH proton is quite broad and observed around 8.2–8.4 ppm. A broad signal which appears in the region δ10.1–10.4 ppm has been assigned to the phenolic protons. This signal is shifted downfield due to chelate ring formation with tertiary nitrogen and imino group.[10]

In metal chelate (binary and ternary) derivatives, the broad resonance signal due to—NH proton at δ 8.2–8.4 ppm remain almost at the same position indicating thereby the non-deprotonation and non-participation of this group on complexation of ligand derivatives with metal atom. The signal due to phenolic protons at δ10.4 and δ10.2 ppm disappeared in the spectra of complex derivatives suggesting the deprotonation of this group and coordination of phenolic oxygen to the metal atom.

The antifungal studies of the ligand and their corresponding binary and ternary metal complexes have been evaluated by testing these against *Alternaria alternata* and *Aspergillus niger* at different concentration. The results observed are reported in Table-2. The results of fungicidal screening show that fungicidal activity increases as the concentration increases. The metal salt has negligible activity but on complexation it is found to be active. The enhanced fungitoxicity of complexes is in accordance with the literature[11].

TABLE-2
FUNGICIDAL SCREENING DATA

Compound	Average % inhibition of spore germination after 72 h					
	Alternaria alternata (conc. in ppm)			*Aspergillus niger* (conc. in ppm)		
	100	500	1000	100	500	1000
$C_{13}H_{10}N_2O$ (HPBI)	24	36	53	22	37	53
$Co(HPBI)_2$	34	52	60	32	48	63
$Co(HPBI)_2 \cdot Gly$	37	55	66	38	50	65
$Co(HPBI)_2 \cdot (OX)$	38	55	63	35	49	64
$Co(HPBI)_2 \cdot (OFor)_2$	36	54	64	36	48	65
$Co(HPBI)_2 \cdot (OC_6H_5)_2$	34	56	66	37	49	64

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