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NOTE

Studies on Some Biologically Important Ternary Complexes of Nickel(II) with 2-(2′-Hydroxyphenyl) Benzimidazole and Acids

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Some new antifungal nickel(II) complexes of 2-(2′-hydroxyphenyl) benzimidazole (HPBI) and amino acid, carboxylic acid and phenol have been synthesizd and characterized on the basis of their elemental analysis, conductance measurement, IR and NMR studies. These complexes were screened for their antifungal activities against *Alternaria alternata* and *Aspergillus niger* and compared with Dithane M-45, a commercial fungicide.

Key Words: Ternary complexes, Nickel, Antifungal, Benzimidazole.

Harkins *et al.*[1] isolated some transition metal complexes of the type M(O-PhBzH)$_2$. Transition metal complexes of 2-substituted benzimidazole have been explored for their antifungal activity by few workers[2, 3]. Fungitoxicity is enhanced in mixed ligand complexes. This prompted us to prepare and characterize mixed ligand complexes of 2-(2′-hydroxyphenyl) benzimidazole (HPBI) and other ligands like amino acid, carboxylic acid and phenol and to study fungitoxicity of these complexes. These studies are reported in the present communication.

2-(2′-Hydroxyphenyl) benzimidazole was prepared by the method reported in literature.[1] M.P. 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 FX90Q JEOL spectrophotometer at 90 MHz in DMSO-d$_6$ using TMS as an internal reference. The purity of all the compounds was checked by running TLC on silica gel-G using chloroform-ethyl acetate (1 : 1) mixture and spots were visualized by iodine vapours. Fungitoxicity was determined by spore germination inhibition technique. These complexes have been screened for their antifungal activities against *Alternaria alternata* and *Aspergillus niger* in different concentrations. The metal contents of the complexes were determined by standard literature procedures.

Binary metal complex was prepared by mixing $NiCl_2 \cdot 6H_2O$ and 2-(2′-hydroxy phenyl) benzimidazole in 1 : 2 ratio in ethanol. The mixture was refluxed for 2–3 h when the product separated out was filtered, washed with ethanol and dried under vacuum. Mixed ligand complexes, *i.e.*, ternary complexes with HPBI as primary ligand and amino acid, carboxylic acid and phenol as secondary ligand were prepared by refluxing the mixture of $NiCl_2 \cdot 6H_2O$, HPBI and secondary ligand such as amino acid (glycine or alanine), formic acid and phenol in 1 : 1 : 1 ratio in ethanol for about 2–3 h. The product obtained was filtered, washed with ethanol and dried under vacuum.

The analytical data of the complexes is reported in Table-1. The complexes obtained were coloured solids and were stable to air and moisture. They decomposed at high (>200°C) temperature. These complexes were soluble in DMSO and DMF and are non-electrolytes.

TABLE-1

No.	m.f.	% Analysis: Found (Calcd.)			
		C	H	N	Ni
I.	$C_{13}H_{10}N_2O$(HPBI)	74.26 (74.29)	4.71 (4.76)	13.30 (13.33)	—
II.	$Ni(HPBI)_2 \cdot 2H_2O$	60.81 (60.85)	4.10 (4.29)	10.81 (10.92)	11.39 (11.45)
III.	$Ni(HPBI)Gly \cdot 2H_2O$	47.60 (47.66)	4.42 (4.50)	11.02 (11.12)	15.49 (15.54)
IV.	$Ni(HPBI)Ala \cdot 2H_2O$	48.82 (48.89)	5.05 (5.09)	10.64 (10.70)	14.90 (14.95)
V.	$Ni(HPBI)OFor \cdot 3H_2O$	45.76 (45.81)	4.31 (4.36)	7.59 (7.63)	15.91 (16.00)
VI.	$Ni(HPBI)OPh \cdot 3H_2O$	54.92 (54.98)	4.75 (4.82)	6.70 (6.75)	14.10 (14.15)

Gly = glycine; Ala = alanine; OFor = formic acid; OPh = phenol.

In the IR spectra of all the ligand derivatives, strong and sharp absorption band at 1650–1610 cm^{-1} assigned to $\nu(C{=}N)$ vibrations of the imidazolyl ring, shifts to lower frequency by 10–12 cm^{-1} in the spectra of corresponding complexes indicating the coordination of the ligands to the metal atom[4] through tertiary nitrogen of the imidazolyl ring. This further gets support by the band in the region of 240–237 cm^{-1} due to ν(Ni—N) bonds[5].

The bands due to ν_{asym}(NH) and δ(NH) stretching vibrations at 3200–3150 and 1420 cm^{-1} of the imidazolyl ring remain almost at the same position in the spectra of metal complexes, suggesting the non-coordination and non-deprotonation through this imino group. The absorption bands ascribed to ν_{asym}(OH) of the ligand moieties observed in the region 3450–3300 cm^{-1} disappear completely in the spectra of metal complexes indicating the deprotonation and coordination through these groups. These observations are further supported by the formation of new bands in the region 256–250 cm^{-1} and assigned to ν(Ni—O) vibrations[6]. Appearance of broad troughs in the region 3500–3450 cm^{-1} has been assigned ν(OH) vibrations of the water molecule. The δ(HOH) manifests as a shoulder in the region 1635–1615 cm^{-1} and the absorption band at 860–850 cm^{-1} has been assigned to rocking vibrations of coordinated water molecules[7]. The infrared spectra of ternary complexes are non-superimposable with those of binary complex and thus it is assumed that new complexes formed are mixed ligand complexes. Further it is confirmed by the fact that the IR spectra of ternary metal complex reveal the presence of the bands corresponding to the characteristic vibrations of both the ligand moieties.

The proposed bonding pattern is further supported by ^{1}H NMR spectra. The ^{1}H NMR spectra reveal the broad signal due to —NH proton at δ 9.3–9.6 ppm in case of the ligands, remain unperturbed and are observed almost at the same position in the spectra of complex derivatives. The —OH proton signals of the ligands observed at δ 10.1–10.2 ppm disappear completely in the spectra of the complexes supporting the above mentioned conclusions. Appearance of broad resonating signals at δ 10.8–11.0 ppm may be assigned to the water molecule. Aromatic protons appearing at δ 7.3–8.0 ppm in ligands show slight deshielding on complexation with metal ions.

All the newly synthesized ligands and their complexes were screened for their antifungal activity against *Alternaria alternata* and *Aspergillus niger* by the spore germination inhibitition technique. The results reveal that the fungitoxicity increases with the increase in concentration and it is also evident that there is a considerable increase in toxicity of complexes as compared to those of the ligands. A possible mode of enhanced toxicity of complexes could be speculated in the light of "Chelation Theory"[8].

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