

## NOTE

**Synthesis and Antifungal Activity of Some Metal Complexes of 2-(2'-Hydroxybenzylidene)aminophenyl benzimidazole**

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Some new metal complexes of 2-(2'-hydroxybenzylidene)aminophenyl benzimidazole (HBAPBI) with Pd(II), Pt(II), Pr(III), Nd(III) VO(II) and UO<sub>2</sub>(II) have been synthesized. These metal complexes have been characterized on the basis of their elemental analysis, conductance measurement, IR and NMR spectral studies. The metal complexes 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.

**Key Words:** Synthesis, Characterization, 2-(2'-Aminophenyl) benzimidazole, 2-(2'-hydroxybenzylidene)aminophenyl benzimidazole, Fungitoxicity, Pd(II), Pt(II), Pr(III), Nd(III), VO(II), UO<sub>2</sub>(II).

Many benzimidazoles/Schiff's bases and their metal complexes show fungitoxicity and other biocidal properties<sup>1</sup>. Srivastava<sup>2</sup> studied the antifungal activity of transition metal chelates of 2-(2'-hydroxybenzylidene)aminobenzimidazole. In continuation of our earlier studies on the metal complexes of substituted benzimidazoles, we report here preparation of some metal complexes of 2-(2'-hydroxybenzylidene)aminophenyl benzimidazole (HBAPBI) with Pd(II), Pt(II), Pr(III), Nd(III), VO(II) and UO<sub>2</sub>(II) and their characterization on the basis of elemental analysis, conductance measurement, IR and NMR spectral studies. The ligand (HBAPBI) and its metal complexes were screened for their toxicity against *Alternaria alternata* and *Aspergillus niger*.

All chemicals used were from Merck. 2-(2'-Aminophenyl)benzimidazole (APBI) was prepared according to the reported method<sup>4</sup>. Its Schiff bases with salicylaldehyde was prepared by the condensation of the reactants, viz., APBI and salicylaldehyde in 1 : 1 molar ratio in absolute ethanol. To prepare complexes, a mixture of the requisite metal salt and ligand HPAPBI was refluxed in 1 : 1 molar ratio in absolute alcohol for 5–6 h. The complexes separated on cooling were washed with absolute ethanol and dried in vacuum. Melting points were determined in open capillaries and are uncorrected. IR spectra (KBr) were recorded on a Perkin-Elmer 577 spectrophotometer and <sup>1</sup>H NMR spectra

(DMSO- $d_6$ ) on a JEOL FX 90 Q spectrometer (90 MHz) using TMS as an internal reference. The purity of all the compounds was checked by TLC. The metal contents were determined by standard procedure.

The analytical data and physical properties of complexes are given in Table-1

TABLE-1  
ANALYTICAL AND PHYSICAL DATA OF LIGAND AND COMPLEXES\*

S. No.	Compound	Colour	Decomposition temperature	Metal( %) Found (Calcd.)
	HBAPBI (C <sub>20</sub> H <sub>15</sub> N <sub>3</sub> O)	Yellow	282	—
1.	Pd(C <sub>20</sub> H <sub>14</sub> N <sub>3</sub> O)Cl	Brown	290	23.37 (23.44)
2.	Pt(C <sub>20</sub> H <sub>14</sub> N <sub>3</sub> O)Cl	Red	272	35.87 (35.95)
3.	Pr(C <sub>20</sub> H <sub>15</sub> N <sub>3</sub> O)(NO <sub>3</sub> ) <sub>3</sub> ·2H <sub>2</sub> O	Yellow	274	20.76 (20.85)
4.	Nd(C <sub>20</sub> H <sub>15</sub> N <sub>3</sub> O)(NO <sub>3</sub> ) <sub>3</sub> ·2H <sub>2</sub> O	Yellow	280	21.08 (21.20)
5.	UO <sub>2</sub> (C <sub>20</sub> H <sub>15</sub> N <sub>3</sub> O)(NO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O	Orange	252	32.76 (32.82)
6.	[VO(C <sub>20</sub> H <sub>15</sub> N <sub>3</sub> O)SO <sub>4</sub> ] <sub>2</sub>	Green	262	10.29 (10.32)

\*All compounds gave satisfactory C, H and N analyses.

The complexes (Table-1) are solid and soluble in DMSO and DMF. The low values of molar conductance ( $10\text{--}20 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ) in DMF at room temperature revealed their non-electrolytic nature.

IR spectra of HBAPBI showed bands at 1640 (acyclic  $\text{—N=C}$ ) and 1610  $\text{cm}^{-1}$  ( $\text{—N=C}$  bond in the heterocyclic ring)<sup>5</sup>. Both of these bands shifted to lower wavenumbers appearing at 1625 and 1600–1595  $\text{cm}^{-1}$  respectively, in the spectra of the metal complexes, indicating the coordination of metal through tertiary and azomethine nitrogen. It is further supported by the band at 550–360  $\text{cm}^{-1}$  (M—N)<sup>6</sup>. The broad band observed at 3140–3050 due to  $\nu_{\text{asym}}(\text{NH})$  and 1420  $\text{cm}^{-1}$  due to  $\delta(\text{NH})$  in the imidazolyl ring remained unaltered in the spectra of the complexes. The ligand band at 3420–3350  $\text{cm}^{-1}$  assigned for  $\nu_{\text{asym}}(\text{OH})$  of the substituted phenyl ring) disappeared in the spectra of the complexes (S.No. 1–2), indicating the deprotonation and coordination through oxygen of phenolic group<sup>7</sup>. The lowering of  $\nu_{\text{asym}}(\text{OH})$  (25–30  $\text{cm}^{-1}$ ) showed the coordination of phenolic oxygen without deprotonation in complexes (Sl. Nos. 3–6). These observations are confirmed by the appearance of bands due to (M—O) at the same position as reported in literature<sup>8</sup>.  $\nu(\text{M—Cl})$  stretching frequencies are observed in the region 325–310  $\text{cm}^{-1}$  in complexes (Sl. Nos. 1–2) whereas bands due to monodentate coordinated nitrate group<sup>9</sup> are observed in the region 1500–1485 and 1295–1280  $\text{cm}^{-1}$  in complexes (Sl. Nos. 3–5). The bands at 1150, 995, 650 and 470  $\text{cm}^{-1}$  found in the spectrum of complex (Sl. No. 6) are due to bidentate coordinated sulphate. The bands due to coordinated water molecules in complexes (Sl. Nos. 3, 4, 5) appeared in the region 3500–3450  $\text{cm}^{-1}$  ( $\nu_{\text{asym}}(\text{OH})$ ) and 1635–1620 and 860–850  $\text{cm}^{-1}$  (rocking mode of coordinated water molecules)<sup>1</sup>. The characteristic bands observed at 975  $\text{cm}^{-1}$  (apical

$\nu(\text{V}=\text{O})$  in complex (Sl. No. 6)) and at 910 and 815  $\text{cm}^{-1}$  (stretching vibration of  $\text{U}=\text{O}$  bond of  $\text{O}=\text{U}=\text{O}$  moiety) in complex (Sl. No. 5).

In the  $^1\text{H}$  NMR of the ligand, the aromatic protons appeared as a multiplet in the region of  $\delta$  6.9–7.9 ppm. The resonance signal corresponding to —NH proton is quite broad and not clear and observed at  $\delta$  8.5 ppm. However, the downfield shift is explained in view of tertiary nitrogen and other functional groups of the phenyl group substituted at the 2 position of benzimidazolyl moiety<sup>11</sup>. The signal at  $\delta$  8.2 ppm is assigned to azomethine protons. The signal at  $\delta$  10.1–10.2 ppm is due to phenolic proton. The phenyl protons<sup>12</sup> are observed in the region  $\delta$  7.2–8.0 ppm. The broad signal due to —NH proton of imidazolyl ring remains unperturbed and observed almost at the same position in the spectra of the complexes indicating thereby the non-deprotonation and non-participation of this group on complexation. The —OH proton signal of the ligand disappeared completely in the spectra of complexes (Sl. No. 1–2) while in Sl. Nos. 3–6 shifted slightly downfield due to deshielding on complexation with metal ions. The resonance signal due to azomethine proton is shifted further in the spectra of corresponding metal complexes substantiating the coordination of azomethine nitrogen to the metal atom. The aromatic proton shifted slightly downfield on complexation.

All the complexes and ligands were screened for their antifungal activity against *Alternaria alternata* and *Aspergillus niger* by spore germination inhibition method at concentrations 100, 500 and 1000 ppm using Dithane M-45 as standard. It is evident from the data that the metal chelates (inhibition 29–45%) are more fungitoxic in comparison to parent compound (26–27%).

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