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Complexes of N-(4-Methoxy-benzilidene)-2-(4-aminophenyl) Benzimidazole with Zn(II), Cd(II) and Hg(II) Halides

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The synthesis and characterization by elemental analysis, conductivity measurements, IR and proton NMR spectroscopy of complexes of the Schiff base derived from 2-(4-aminophenyl) benzimidazole and 4-methoxy benzaldehyde with Zn(II), Cd(II) and Hg(II) halides have been reported.. Mercury halides yield complexes with the general formula $[Hg(POM4APBI)_2X_2]$; X = Cl, Br. Zinc and cadmium halides yield binuclear complexes with the general formula $[(POM4APBI)X_2]$; M = Zn, X = Cl; M = Cd, X = Cl, Br. The complexes are all non-electrolytes and the ligand acts as a monodentate.

Key Words: 2-(4-Aminophenyl) benzimidazole, 4-Methoxy-benzaldehyde, Schiff bases, Complexes.

INTRODUCTION

Schiff bases constitute an interesting class of compounds due to their ability to act as chelating agents forming mononuclear as well as polynuclear metal complexes[1, 2]. The Schiff base complexes also find application in analytical chemistry and serve as biochemical models[3, 4]. Schiff bases derived from 2-aminomethylbenzimidazole, 2-aminobenzimidazole and 2-aminophenylbenzimidazole are known to form chelates acting as bidentate ligands[5–7]. In view of this, we have synthesized a Schiff base derived from 2-(4-aminophenyl) benzimidazole and 4-methoxy benzaldehyde [POM4APBI] (Fig. 1). It has been discovered that the Zn(II) ions play a variety of roles like enzyme function, gene expression, hormone receptors and in storage proteins in the human body. Cd(II) and Hg(II) are known to be toxic to the human body due to their interference in the Zn(II) biological pathway. The toxicity is caused due to the change of coordination, kinetics and equilibria[8].

In continuation of our studies on the coordination chemistry of the post-transition metals[9] Zn, Cd and Hg, the synthesis of the complexes of POM4APBI with Zn(II), Cd(II) and Hg(II) halides and their characterization by elemental analysis, conductivity measurements, IR and proton NMR spectroscopic studies have been reported.

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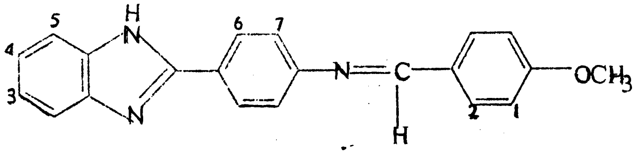


Fig. 1. POM4APBI

EXPERIMENTAL

Preparation of the ligand: All the reagents used were of highest purity chemicals. 2-(4-aminophenyl)-benzimidazole (4-APBI) was prepared as reported in an earlier paper[9]. The ligand POM4APBI was prepared by refluxing equimolar mixture of 4-APBI with 4-methoxybenzaldehyde in ethanol for 8 h. The solvent was evaporated in vacuum to obtain the ligand. It was recrystallized from ether. Calculated for $C_{21}H_{17}N_3O$: C = 76.82%, H = 5.49%, N = 12.80%. Experimental: C = 75.17%, H = 5.44%, N = 12.04%.

Preparation of the complexes: The metal halides and the ligand were taken in 1 : 2 molar ratio. 0.33 Mol of each of the metal salts were refluxed separately with 0.66 mol of the ligand POM4APBI in 20 mL of ethanol for 4–6 h. The solvent was evaporated under reduced pressure. The complex obtained was washed with acetone, filtered and dried under vacuum. The complexes of Cd and Hg bromides separated after the addition of ether and cooling in a refrigerator overnight. In the preparation of the $ZnCl_2$ complex, the ligand was refluxed with $ZnCl_2$ in equal volume of ethanol and water in the molar ratio of 1 : 2.

Conductivity data were obtained using freshly prepared dimethylformamide solution (10^{-3} M) at 25°C with digital conductivity meter. The elemental analyses were carried out using a Carlo-Erba Strumentazione model 1106.

The IR spectra in the 4000–400 cm^{-1} range were recorded with KBr pellets using a Nicolet Impact 400D spectrometer. The IR spectra in the range 400–200 cm^{-1} were recorded using a Thermo Nicolet model IR 100 spectrometer. The ^1H NMR spectra were recorded using a Bruker-400 instrument using DMSO-d_6 as solvent employing TMS as internal reference.

RESULTS AND DISCUSSION

The analytical data are given in Table-1. All the complexes synthesized are almost insoluble in common organic solvents. The conductivity measurements in DMF solution (55–75 S cm^2 mol^{-1}) show that all the complexes are non-electrolytes[10].

TABLE-1
ANALYTICAL DATA FOR THE COMPLEXES OF POM4APBI

Compound	Colour	% Elemental analysis: Found (Calcd.)		
		Carbon	Nitrogen	Hydrogen
POM4APBI	Brown	75.17 (76.82)	12.04 (12.80)	5.44 (5.49)
$ZnLCl_2$	Pale yellow	55.94 (54.42)	8.90 (9.07)	3.66 (3.67)
$CdLCl_2$	Buff	50.13 (49.37)	8.86 (8.23)	3.88 (3.33)
$CdLBr_2$	Buff	43.93 (42.05)	8.71 (7.03)	3.48 (2.84)
HgL_2Cl_2	Reddish brown	52.34 (54.37)	8.95 (9.05)	3.53 (3.88)
HgL_2Br_2	Yellow	47.34 (49.70)	8.95 (8.28)	3.53 (3.35)

NMR Spectra

The signals in the proton NMR spectra of the ligand POM4APBI are assigned as: δ 12.88 ppm (s, —NH), δ 8.64 ppm (s, —N═CH—), δ 8.21 ppm (d, Ar—H_1, J = 8.52 Hz), δ 7.93 ppm (d, Ar—H_2, J = 8.76 Hz), δ 7.67 ppm (d, Ar—H_3, J = 7.44 Hz), δ 7.53 ppm (d, Ar—H_4, J = 7.16 Hz), δ 7.41 ppm (d, Ar—H_5, J = 8.52 Hz), δ 7.2 ppm (m, Ar—H_6), δ 7.1 ppm (d, Ar—H_7, J = 8.72 Hz), δ 3.85 ppm (s, —OCH_3). The PMR signals indicate a shift of 3 ppm for —NH proton (δ 9.88 ppm) in the complexes. The aromatic protons and —OCH_3 protons show no change. This indicates the complexation of the ligand with the metal through the imidazole nitrogen. It also shows that the ligand is monodentate.

IR Spectra

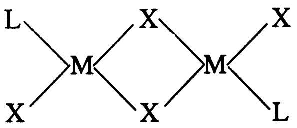
The IR spectral data in the range (4000–200 cm^{-1}) are given in Table-2.

TABLE-2
SELECTED IR BANDS IN cm^{-1} OF THE LIGAND POM4APBI AND ITS COMPLEXES

Compound	ν(NH)	ν(OCH_3)	ν(N═CH)	ν(C—N)	ν(M—N)	ν(M—X) (t)	ν(M—X) (b)
POM4APBI	3328	2769	1920	1688	—	—	—
$ZnLCl_2$	3369 3219	2753	1910	1683	355 (m) 307 (w)	282 (m) 256 (s)	206 (w) 173 (w)
$CdLCl_2$	3384 3343	2748	1910	1631	349 (m) 317 (s)	277 (w)	252 (m)
$CdLBr_2$	3353 3214	2748	1910	1678	359 (m) 294 (w)	274 (w)	136 (s)
HgL_2Cl_2	3379	2753	1910	1631	355 (w) 305 (s)	242 (m)	—
HgL_2Br_2	3322	2888	1910	1610	339 (w) 248 (s)	181 (w)	—

4000–400 cm^{-1} range: The absorption at 3328 cm^{-1} assigned[1] to the NH stretching of benzimidazole shows a shift of about 50 cm^{-1} in the complexes. The absorptions due to the stretching of N═CH and C—N of benzimidazole also show a shift of 10 cm^{-1} and 50–10 cm^{-1} respectively in the complexes. These shifts indicate the bonding of imidazole nitrogen of benzimidazole[5].

400–200 cm^{-1} range: The absorptions due to the stretching modes of metal-nitrogen bond and metal-halogen terminal bond are observed in all the complexes in the region as reported in the literature[11]. The complexes of zinc and cadmium halides show an additional band due to the metal-halogen bridge. This suggests the formation of binuclear metal complexes of zinc and cadmium halides. Elemental analyses suggest the molecular formula of the complexes as follows:



where M = Zn, Cd and X = Cl, Br and L = POM4APBI.

Since the mercury complexes do not show any absorption due to metal-halogen bridge, a square planar configuration is suggested for these complexes.

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