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Studies on Complexes of 2-(4-Aminophenyl) Benzimidazole with Zn(II), Cd(II) and Hg(II) Salts

S. REKHA and K.R. NAGASUNDARA*
Department of Chemistry, Bangalore University, Central College Bangalore-560 001, India

Complexes of 2-(4-aminophenyl) benzimidazole with Zn(II), Cd(II) and Hg(Ii) chlorides and Cd(II) and Hg(II) bromides have been synthesized. They have been characterized by elemental analysis, conductivity measurements, IR and ^{1}H NMR spectral studies. The results show that the complexes are non-electrolytes, four coordinated and the ligand acts as a monodentate.

Key Words: Complexes, Zn(II), Cd(II), Hg(II), 2-(4-Aminophenyl) benzimidazole.

INTRODUCTION

Benzimidazole and its derivatives have been extensively studied in various fields.[1, 2] The complexes of benzimidazole and related ligands with transition metal salts exhibit anti-tumour activity[3] and anti-neoplastic property, fungicidal, insecticidal, anti-viral, anti-malarial and other pharmacological activities.[4, 5] Increased attention has been given to these complexes since they can act as molecular models to study the complex biological molecules.[6] This is possible because the metal ion sites in the complexes mimic the structure and reactivity of the biological molecules.[7] It is known that Zn(II) ion plays a variety of roles like enzyme function, gene expression, hormone receptors and in storage of proteins in the human body. Cd(II) and Hg(II) are believed 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 in coordination, kinetics and equilibria.[8]

2-(2′-Aminophenyl)-benzimidazole and its derivatives have been extensively studied for various properties.[9] It forms complexes, acting as a monodentate ligand, with various metal ions like Sn(IV), Ti(IV), V(IV), Co(II) and Fe(III)[10, 11]. Benzimidazole usually acts as a monodentate ligand coordinating through the pyridine-like nitrogen[12, 13]. In view of this, we have synthesized and characterized the complexes of 2-(4-aminophenyl) benzimidazole [4-APBI], [Fig. 1], with Zn(II), Cd(II) and Hg(II) salts. We report here the synthesis and characterization of complexes of 4-APBI with Zn(II), Cd(II) and Hg(II) chlorides and Cd(II) and Hg(II) bromides. The complexes obtained were characterized by elemental analysis, conductivity measurements, IR and ^{1}H NMR spectral studies.

†Present address: Department of Chemistry, Vidya Vardhaka Sangha First Grade College for Women, Basaveshwaranagar, Bangalore-560 079.

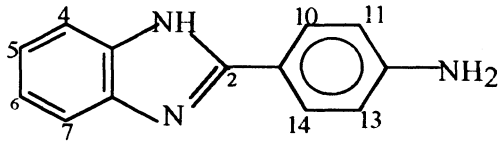

Fig. 1. 2-(4-Aminophenyl)-benzimidazole

EXPERIMENTAL

Preparation of the ligand

All the reagents used were of commercial grade. 4-APBI was prepared from *o*-phenylene diamine and 4-aminobenzoic acid in pyrophosphoric acid by following the procedure as reported in literature.[12] The percentage of elements present are calculated to be C = 74.28, N = 20.00 and H = 5.71. Experimentally determined values are found to be C = 73.90, N = 19.84 and H = 5.09.

Preparation of the Complexes

0.33 M of each of the metal salts was refluxed separately with 0.66 M of the ligand 4-APBI in 20 mL of ethanol for 4–5 h. The solvent was removed under reduced pressure. The complex obtained was washed with acetone, filtered and dried under vacuum.

The complex of $ZnCl_2$ was separated after the addition of ether and cooling overnight in a refrigerator.

Conductivity data were obtained using freshly prepared dimethyl formamide solution (10^{-3} M) at 25°C with digital conductivity meter. The C, H, N elemental analyses were carried out using Carlo Erba Strumentazione model 1106. The IR spectra in the 4000–400 cm^{-1} range were recorded with KBr pellets using Nicolet IR spectrometer. The ^1H NMR spectra was recorded on a Bruker 400 using DMSO-d_6 employing TMS as internal reference.

RESULTS AND DISCUSSIONS

The analytical data are given in Table-1. All the complexes synthesized are nearly insoluble in most common organic solvents. The conductivity measurements data in DMF solution (55–75 S cm^2 mol^{-1}) show that all the complexes are non-electrolytes.[13]

NMR spectra

The signal in the proton NMR spectrum of 4-APBI at δ 12.42 ppm corresponds to NH, δ 5.58 ppm to NH_2 and δ 7.84–6.66 ppm to the aromatic protons. The two protons on C-4 and C-7 (δ 7.48 ppm) appear as a multiplet. Similarly the two protons on C-10 and C-14 at δ 7.1 ppm appear as multiplet. The protons on C-4 and C-7 (δ 7.84 ppm) appear as a doublet with J = 8.56 Hz. Similarly the protons on C-11 and C-13 appear as a doublet at δ 6.66 ppm (refer Fig. 1).

The changes in the proton NMR spectra of the complexes compared to that of the ligand also indicate bonding between the metal and pyridine-like nitrogen. It is observed that the signals of NH, protons on C-4 and C-7 and —NH_2 show

downfield shift in the complexes (0.07–0.25). This indicates the shielding of these protons due to complexation.

TABLE-1
ANALYTICAL AND IR SPECTRAL DATA OF THE 4-APBI COMPLEXES

Complex (Colour)	Found (calcd)%			IR Spectral data (cm^{-1})		
	C	N	H	$\nu(NH_2)$	$\nu(NH)$	$\nu(C{=}N)$
4-APBI (Buff)	73.90 (74.28)	19.84 (20.00)	5.09 (5.71)	3441	3369	1632
ZnL_2Cl_2 (Grey)	53.81 (56.11)	13.98 (15.11)	3.17 (4.32)	3576	3281	1620
CdL_2Cl_2 (Brown)	49.62 (51.76)	12.17 (13.93)	3.68 (3.98)	3472	3359	1610
HgL_2Cl_2 (Pink)	45.28 (45.08)	12.19 (12.14)	3.19 (3.47)	3472	3359	1620
CdL_2Br_2 (Blackish grey)	43.36 (45.09)	11.14 (12.14)	2.93 (3.47)	3467	3359	1626
HgL_2Br_2 (Shiny grey)	38.36 (40.00)	10.91 (10.37)	2.75 (3.08)	3436	3333	1620

IR spectra

The band at 1632 cm^{-1} assigned to $\nu(C{=}N)$ in the ligand shows a downward shift of 6–27 cm^{-1} in the complexes. This suggests bonding through pyridine-like nitrogen of benimidazole. The band at 3441 cm^{-1} in the ligand assigned to the NH_2 stretching vibration[10] shifts to higher frequency by 6–35 cm^{-1} in the complexes. Similarly, the band at 3369 cm^{-1} in the ligand assigned to NH stretching mode of benzimidazole[10] shifts to lower frequency by 10–88 cm^{-1} in the various complexes. The positions of these bands also suggest bonding of the ligand to the metal through the pyridine-like nitrogen. The shift in these bands could be attributed to the intermolecular hydrogen bonding that exists in the free ligand. When the ligand coordinates to the metal through the pyridine-like nitrogen, the contribution of the resonance form 'b' as shown in Fig. 2 would increase resulting in the lowering of the NH stretching frequency. Consequently 4-APBI acts as a monodentate ligand bonding through pyridine-like nitrogen.[14]

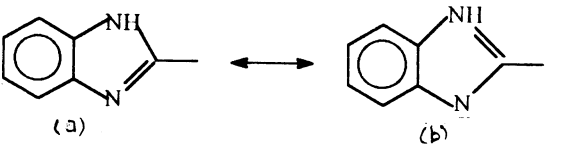

Fig. 2. Resonance forms of benzimidazole derivative

The analytical data and conductivity measurements indicate a general formula of complexes as ML_2X_2. The spectral studies indicate that the ligand is monodentate. Hence the complexes are four coordinated.

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