

Reactions of 1-*p*-Dimethylaminobenzyl-2-*p*-Dimethylaminophenylbenzimidazole with Cobalt(II), Zinc(II) and Cadmium(II) Salts

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Synthesis of 1-*p*-dimethylaminobenzyl-2-*p*-dimethylaminophenylbenzimidazole (dmabdmabp, L) and its complexes of cobalt(II), $[\text{CoX}_2\text{L}_2]\cdot n\text{H}_2\text{O}$ (X = Cl, n = 3; X = Br, n = 0), $\text{CoL}_2(\text{OH})_2$, zinc(II) and cadmium(II), $\text{MX}_2\text{L}_2\cdot n\text{H}_2\text{O}$ (M = Zn, X = Cl, n = 0; X = Br, n = 3; X = I, n = 1; M = Cd, X = Cl, Br, I), $[\text{ZnL}(\text{OH})_2](\text{ClO}_4)_2\cdot 3\text{H}_2\text{O}$ and $[\text{CdL}_{1.5}(\text{OH})_2]_2(\text{ClO}_4)_4$ is described. They have been characterized by IR, UV-visible and ^1H NMR spectra and magnetic susceptibility measurements. The electronic and magnetic susceptibility studies suggest a tetrahedral geometry for CoX_2L_2 (X = Cl, Br), zinc(II) and cadmium(II) complexes and a trigonal bipyramidal geometry for $\text{CoL}_2\text{L}(\text{OH})_2$.

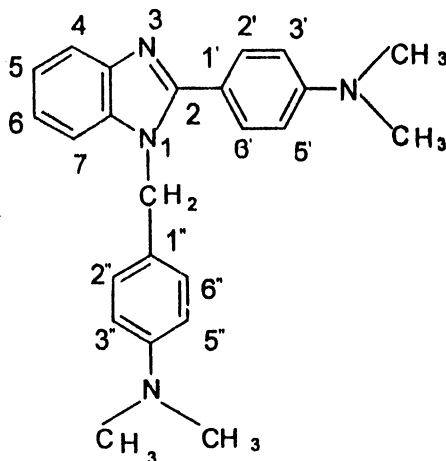
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INTRODUCTION

Benzimidazole and its derivatives play an important role in catalysis and in several biochemical reactions. Benzimidazole as its 5,6-dimethyl derivative occurs in vitamin B₁₂. In addition to this, benzimidazole derivatives exhibit antibacterial, anthelmintic and insecticidal activities,¹⁻⁵. Transition metal complexes containing benzimidazoles are widely used as catalysts for hydrogenation, hydroformylation, oxidation and other reactions⁶⁻⁹. We report here the synthesis and characterization of 1-*p*-dimethylaminobenzyl-2-*p*-dimethylaminophenyl benzimidazole (dmabdmabp; L) and its complexes with cobalt(II), zinc(II) and cadmium(II) salts.

EXPERIMENTAL

p-Dimethylaminobenzaldehyde, *o*-phenylenediamine, hydrated CoCl_2 , ZnCl_2 and CdCl_2 were obtained from BDH and SDS fine chemicals. Bromide, iodide and perchlorate of cobalt(II), zinc(II) and cadmium(II) were prepared by dissolving the corresponding carbonates in 1 : 1 aqueous hydrobromic, hydroiodic and perchloric acids respectively and evaporating the resulting solution to dryness under reduced pressure.



(dmabdmapb; L)

The IR spectra were recorded on a Nicolet FT-IR instrument using nujol mull method. The electronic spectra were recorded on a Hitachi 150-20 in solid state as nujol mulls or in DMF. The ^1H NMR spectra in DMSO-d_6 were recorded at ambient temperatures on a Bruker AMX 400 MHz spectrometer with TMS as the internal reference. Conductivity measurements were made using an Elico model CM-82T Conductivity Bridge with conventional dip type conductivity cell. Magnetic susceptibility measurements were carried out using solid samples on a Gouy balance at room temperature. Micro analyses were carried out at the microanalytical laboratories of CDRI, Lucknow and the Indian Institute of Science, Bangalore.

Synthesis of 1-*p*-dimethylaminobenzyl-2-*p*-dimethylaminophenyl benzimidazole

A mixture of *o*-phenylenediamine (0.1 mol) and *p*-dimethylaminobenzaldehyde (0.2 mol) in benzene (100 mL) was refluxed for 2 h on a steam bath. On leaving overnight yellow crystalline solid got separated. It was recrystallised from ethanol to get pale yellow crystals (yield 80%).

Complexes

$[\text{CoL}_2\text{X}_2] \cdot n\text{H}_2\text{O}$ ($\text{X} = \text{Cl}$, $n = 3$; $\text{X} = \text{Br}$, $n = 0$; $\text{X} = \text{I}$, $n = 1$): A solution of cobalt(II) halide hexahydrate (1 mmol) in acetone/ethanol (20 mL) was added to the ligand (2 mmol) in acetone/ethanol and the mixture was refluxed for about 4 h when a blue and green solid got separated. The solid was washed with ethanol/acetone and dried *in vacuo* (yield 70–75%).

$[\text{MX}_2\text{L}_2] \cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Zn}$, $\text{X} = \text{Cl}$, $n = 0$; $\text{X} = \text{Br}$, $n = 3$; $\text{X} = \text{I}$, $n = 1$; $\text{M} = \text{Cd}$, $\text{X} = \text{Cl}$, Br , I , $n = 0$): Zinc(II)/cadmium(II) halide (1 mmol) in acetone/ethanol was added to the ligand (2 mmol) in ethanol. The separation of a white solid takes place immediately in the case of zinc(II) complexes. The cadmium(II) solution was refluxed for 4 h during which a solid separates. It was collected, washed with acetone/ethanol and dried *in vacuo* (yield 60–70%).

TABLE-1: PHYSICAL PROPERTIES, ANALYTICAL AND IR SPECTRAL DATA OF COMPLEXES OF DMABDMABP

Compound	Colour	mp/dp (°C)	Λ^a	Found/Calcd. (%)				IR spectra (cm ⁻¹)			
				C	H	N	v(O—H) of H ₂ O	v(C=N) & v(C=C)	N—CH ₃ deformation mode	In-plane C—H deformation and P-substituted benzene	v(ClO ₄)
dmabdmabpzi	Yellow	178	—	77.63 (77.80)	7.07 (7.07)	14.79 (15.12)	—	1616	1400	1233	—
[CoCl ₂ L ₂].3H ₂ O	Blue	>230	26.4	61.91 (62.33)	5.70 (6.32)	10.72 (12.11)	3462	1610	1400	1176	—
[CoBr ₂ L ₂]	Blue	>230	112.4	59.77 (60.06)	5.06 (5.46)	10.94 (11.67)	—	1610	1403	1171	—
[CoL ₂ L ₂ (OH) ₂]	Green	>230	116.9	53.26 (53.79)	5.05 (5.07)	10.34 (10.45)	3431	1616	1409	1171	—
ZnCl ₂ L ₂	Ivory	>230	104.4	65.35 (65.71)	6.43 (5.97)	12.50 (12.77)	—	1610	1409	1171	—
[ZnBr ₂ L ₂].3H ₂ O	Ivory	>230	2.3 ^b	56.32 (56.50)	5.38 (5.13)	11.08 (10.98)	3480	1616	1403	1711	—
[ZnL ₂ L ₂].H ₂ O	White	240	113.2	53.95 (53.46)	5.09 (4.86)	10.89 (10.39)	3480	1610	1409	1171	—
[ZnL(OH ₂) ₃ (ClO ₄) ₂ .3H ₂ O* White	White	210	—	38.89 (38.80)	4.13 (5.16)	6.13 (7.15)	3441	1616	1415	1161	1098, 628
CdCl ₂ L ₂	Ivory	>220	19.3 ^c	62.19 (62.37)	5.89 (5.67)	12.52 (12.2)	—	1616	1414	1176	—
CdBr ₂ L ₂	Ivory	230	1.9 ^b	57.07 (56.89)	5.43 (5.17)	11.67 (11.06)	—	1610	1409	1166	—
CdI ₂ L ₂	White	220	3.6 ^b	52.11 (52.06)	4.81 (4.73)	10.69 (10.12)	—	1616	1409	1166	—
[CdL _{1.5} (OH ₂) ₂ (ClO ₄) ₄]	Pale-Yellow	210	45.7 ^b	47.85 (47.83)	4.43 (4.49)	10.83 (9.30)	3450	1615	1410	1170	1100, 625

dp = Decomposition point, ^aMolar conductance of ca. 10⁻³ M solution in DMF, ^bNitrobenzene, ^cDMSO *Insoluble

[ZnL(OH₂)₃](ClO₄)₂·3H₂O and [CdL_{1.5}(OH₂)₂](ClO₄)₄: The complexes of zinc(II) and cadmium(II) perchlorate were prepared by adopting a similar procedure as above but keeping the metal salt and the ligand ratio both as 1 : 1 and 1 : 2 in acetone/ethanol-triethylorthoformate. The resultant solution was refluxed for 4 h during which a solid separates. It was collected, washed with acetone/ethanol and dried *in vacuo* (yield 60%).

RESULTS AND DISCUSSION

The analytical data of the complexes are presented in Table-1. The ligand reacts with cobalt(II) halides to give blue/green coloured compounds of the type [CoX₂L₂] \cdot nH₂O [X = Cl, n = 3; X = Br, n = 0; X = I, n = 1]. Both 1 : 1 and 1 : 2 metal to ligand ratio gave the same composition for the complexes. The complexes are soluble in DMF and DMSO and insoluble in other solvents. The chloro complex behaves as a non-electrolyte in DMF, whereas in the bromo and iodo complexes, as evidenced by the colour change and conductivity data, DMF replaces the halide ions.

The reactions of zinc(II) and cadmium(II) halides and perchlorate, with the ligand produced ivory/white coloured complexes of the formulae MX₂L₂ \cdot nH₂O (M = Zn, X = Cl, n = 0; X = Br, n = 3; X = I, n = 1; M = Cd, X = Cl, Br, I, n = 0), [ZnL(OH₂)₃](ClO₄)₂·3H₂O and [CdL_{1.5}(OH₂)₂](ClO₄)₄. Zinc(II) complexes are insoluble in common organic solvents and are sparingly soluble in DMF. The chloro and iodo complexes seem to exchange halide ions with DMF as evidenced by their conductivity data (Table-1). The bromo complex behaves as a non-electrolyte in nitrobenzene. The perchlorate complex is insoluble even in DMF. The bromo, iodo and perchlorate cadmium(II) complexes are soluble in common organic solvents and the chloro complex is soluble in DMF and DMSO. The halo complexes are non-electrolytes in nitrobenzene and DMSO, while the perchlorate complex shows uni-bivalent electrolytic behaviour in nitrobenzene.

The IR spectra (in nujol mull) of the complexes are almost similar to that of the uncoordinated ligand except for minor shifts in the position of some of the peaks. The band at 1616 cm⁻¹ may be assigned to (C=N) and (C=C) stretching vibrations. The band at 1400 cm⁻¹ may be assigned to (N—CH₃) deformation vibration. The bands at 1284, 1016, 602 and 457 cm⁻¹ are assignable to benzimidazole ring vibrations. The (C—N) stretching band^{9, 10} is found at 1320 cm⁻¹. The IR spectrum of cadmium(II) perchlorate complex shows peaks due to perchlorate in addition to coordinated ligand peaks. The bands observed around 1100 (ν₃) and 625 cm⁻¹ (ν₄) are indicative of the presence of perchlorate ion, which is supported by the electrolytic behaviour¹¹. The broad band at 3450 cm⁻¹ attributed to OH stretching of the coordinated water molecule is also observed.

TABLE-2: ¹H SPECTRAL DATA (δ in ppm) OF LIGAND AND ITS METAL COMPLEXES

Compound	Phenylene ring CH ₃	Benzyl ring CH ₃	CH ₂	H-2'', 6''	H-3'', 5''	H-2', 6'	H-3', 5'	H-4	H-5, 6	H-7
dmabdmabpzl	2.82 d	2.97 d	5.42 s	6.87 d	6.63 d	7.60 m	6.81 d	8.00 d	7.17 m	7.37 d
ZnCl ₂ L ₂	2.83 d (0.01)	2.98 d (0.01)	5.42 s	6.87 d	6.63 d	7.60 m	6.82 d (0.01)	7.99 d (-0.01)	7.17 m	7.37 d
[ZnBr ₂ L ₂]-3H ₂ O	2.85 d (0.03)	2.99 d (0.02)	5.43 s (0.01)	6.87 d	6.63 d	7.60 m	6.82 d (0.01)	7.99 d (-0.01)	7.18 m (0.01)	7.37 d
[ZnI ₂ L ₂]-H ₂ O	2.83 d (0.01)	2.98 d (0.01)	5.43 s (0.01)	6.87 d	6.63 d	7.60 m	6.82 d (0.01)	7.99 d (-0.01)	7.19 m (0.02)	7.38 d (0.01)
CdCl ₂ L ₂	2.83 d (0.01)	2.98 d (0.01)	5.43 s (0.01)	6.87 d	6.63 d	7.60 m	6.82 d (0.01)	7.99 d (-0.01)	7.18 m (0.01)	7.39 d (0.02)
CdBr ₂ L ₂	2.82 d	2.98 d (0.01)	5.42 s	6.87 d	6.68 d (0.05)	7.60 m	6.81 d	7.90 d (-0.10)	7.17 m	7.37 d
CdI ₂ L ₂	2.82 d	2.98 d (0.01)	5.42 s	6.87 d	6.63 d	7.60 m	6.81 d	7.90 d (-0.10)	7.17 m	7.38 d (0.01)

Spectra recorded in DMSO-d₆

s = singlet, d = doublet, m = multiplet

Values in parantheses are coordination induced shifts (c.i.s.) = δ complex-δ ligand

The electronic absorption spectrum (in DMF) of the ligand exhibits two bands at 31,200 and 27,000 cm^{-1} . They may be assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions¹². The solid state electronic spectra of the blue-coloured CoX_2L_2 ($\text{X} = \text{Cl}, \text{Br}$) complexes display multiple absorption bands in the region 11,000 and 16,000 cm^{-1} . These bands may be ascribed to the ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{F})$ (ν_2) and ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{F})$ (ν_3) transition respectively of pseudo tetrahedral cobalt(II) complexes. The electronic spectrum of the iodo complex exhibits three bands in the region 14,500, 20,400 and 22,000 cm^{-1} , which are assigned to ${}^4\text{A}_2''(\text{F}) \rightarrow {}^4\text{E}'(\text{F})$, ${}^4\text{A}_2'(\text{P})$ and ${}^4\text{E}'(\text{P})$ transitions respectively of the trigonal-bipyramidal geometry around the metal ion^{13, 14}. The room temperature magnetic measurements for the complexes CoX_2L_2 ($\text{X} = \text{Cl}, \text{Br}$) as well as $\text{CoI}_2\text{L}_2(\text{OH}_2)$ gave magnetic moments in the range 4.5–4.8 B.M. The values are in the range expected for tetrahedral and trigonal-bipyramidal complexes^{15, 16}.

The ${}^1\text{H}$ NMR spectra of the ligand and its zinc(II) and cadmium(II) complexes in DMSO- d_6 (Table-2) exhibited resonances due to the phenyl and benzimidazole ring protons. The resonances due to $\text{N}-\text{CH}_3$ are observed as a doublet near 3.00 ppm. The resonance at 5.42 ppm arises from the methylene protons of the benzyl ring while the phenylene protons of the benzyl ring are observed in the range 7.20–8.21 ppm. The signals due to the phenyl ring protons are observed between 6.63–7.60 ppm. The spectra of the complexes revealed both positive and negative coordination induced shifts (c.i.s. = $\delta_{\text{complex}} - \delta_{\text{ligand}}$).

Stereochemistry

The CoL_2X_2 ($\text{X} = \text{Cl}, \text{Br}$) and $[\text{CoI}_2\text{L}_2(\text{OH}_2)_2]$ complexes possess distorted tetrahedral and trigonal bipyramidal structures respectively. The ligand coordinates through the imidazole nitrogen of the benzimidazole. The halo complexes of zinc(II) and cadmium(II); $\text{MX}_2\text{L}_2 \cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Zn}, \text{X} = \text{Cl}, n = 0; \text{X} = \text{Br}, n = 3; \text{X} = \text{I}, n = 1; \text{M} = \text{Cd}, \text{X} = \text{Cl}, \text{Br}, \text{I}$) are expected to have tetrahedral geometry. For the complex $[\text{ZnL}(\text{OH}_2)_3](\text{ClO}_4)_2$ the IR spectrum indicates the non-coordination of the perchlorate groups, where the ligand (L) is monodentately coordinated through the imidazole nitrogen of benzimidazole and hence a four coordinated tetrahedral geometry is suggested. In the case of $[\text{CdL}_{1.5}(\text{OH}_2)_2]_2(\text{ClO}_4)_4$ complex, the conductivity and IR spectral data suggest non-coordination of perchlorate groups but coordination of water molecules, one of the ligands is bonded through imidazole nitrogen and the other ligand forms a bridge between two cadmium ions. Hence a binuclear structure with tetrahedral geometry around the metal ion is suggested as shown in Fig. 1.

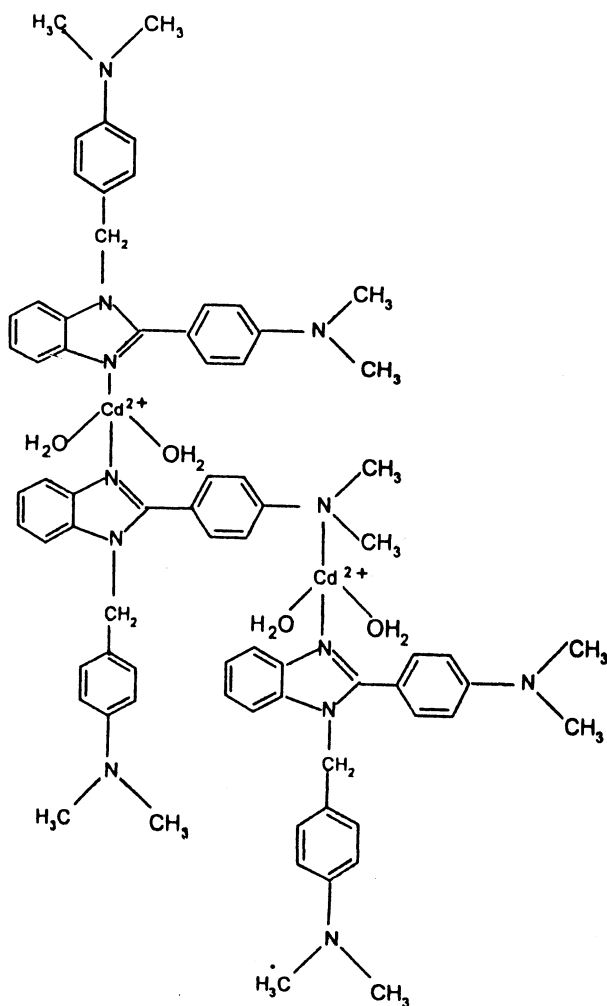


Fig. 1. Structure of $[CdL_{1.5}(OH_2)_2](ClO_4)_4$

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