

Synthesis and Characterization of 2-Amino-5-benzoylbenzimidazole Complexes of Manganese(II) and Cobalt(II)

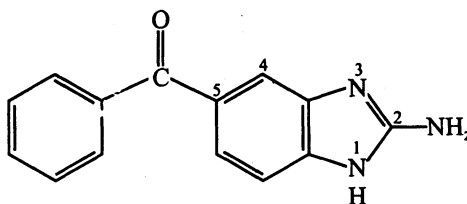
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Several complexes of 2-amino-5-benzoylbenzimidazole (ABBI) with Mn(II) and Co(II) using different anions, Cl^- , Br^- , Γ^- , NO_3^- , CH_3COO^- , HCOO^- , ClO_4^- and SO_4^{2-} have been isolated as stable, non-hygroscopic solids and characterized systematic analytical procedures such as cation-anion estimations, elemental analyses, conductivity, magnetic susceptibility and spectral studies have been employed to elucidate the structure and geometry of the complexes. The analytical data are in accordance with the composition, $[\text{M}(\text{ABBI})_2\text{X}_2]$ where $\text{M} = \text{Co(II)}$ or Mn(II) and $\text{X} = \text{Cl}^-$, Br^- , Γ^- , NO_3^- , CH_3COO^- , HCOO^- , ClO_4^- and SO_4^{2-} . The overall investigations confirm the bidenticity of the ligand, the coordinated nature of the anions and the distorted octahedral geometry of all these complexes studied.

Key Words: Synthesis, Complexes, Mn(II) and Co(II), 2-Amino-5-benzoylbenzimidazole.

INTRODUCTION

The π -acceptor capability combined with σ -donor ability of benzimidazole residue of the compound makes it a versatile ligand with significant coordination potential. In this report we present the synthesis and characterization of stable, monomeric, hexacoordinated cobalt(II) and manganese(II) complexes of this ligand using different ions Cl^- , Br^- , Γ^- , NO_3^- , CH_3COO^- , HCOO^- , ClO_4^- and SO_4^{2-} . It is found that 2-amino-5-benzoylbenzimidazole (ABBI) acts as a bidentate ligand through its $>\text{NH}$ and the $-\text{NH}_2$ groups¹.



2-Amino-5-benzoylbenzimidazole (ABBI)

EXPERIMENTAL

Standard analytical methods were used to estimate all the cations and anions except acetate, formate and nitrate for which elemental analysis was employed². The microanalytical data were obtained from a Perkin-Elmer 2400 CHN analyzer. The solid state electronic spectra in the range 450–900 nm were recorded using a Varian Cary Win spectrophotometer. The KBr technique was generally employed. The conductance measurements of 10^{-3} molar solutions of the complexes were done using Elico direct reading conductivitymeter. The magnetic susceptibility measurements at room temperature (301 ± 2) K were done using Gouy's balance. The diamagnetic corrections were computed from Pascal's constants³.

The ligand 2-amino-5-benzoylbenzimidazole is prepared by a reported procedure¹. Mebendazole (a well-known anthelmintic) methyl ester of 5-benzoylbenzimidazole-2-carbamic acid (25 g) was refluxed with 70% sulphuric acid (150 mL) for 3 h. The sulphate salt of the ligand that precipitated was decomposed with ammonia. The separated ligand was recrystallized from 25% aqueous ethanol containing activated charcoal and melting point was determined (192°C) which is in agreement with the reported value¹. The molecular weight of the compound was determined by Rast method using biphenyl as solvent⁴.

The PMR spectrum of the ligand shows a singlet at δ 5.9 ppm assignable to $>\text{NH}$ proton. The two amino protons appear as a weak singlet at δ 3.8 ppm. The aromatic protons appear as a set of four multiplets ranging from δ 7.5 to δ 7.75 ppm.

The IR spectrum of the ligand shows medium intensity bands at 3458 and 3432 cm^{-1} assignable to the symmetric and asymmetric stretch of $-\text{NH}_2$ group. The broad band centred at 3339 cm^{-1} can be assigned to $>\text{NH}$ group. The strong bands at 1648 and 1630 cm^{-1} represent the stretching modes of $>\text{C}=\text{O}$ and $>\text{C}=\text{N}$ respectively. The imidazole ring stretching frequency is observed as a strong band at 1672 cm^{-1} . These assignments are based on the published works on benzimidazole and its derivatives⁵.

The complexes except the thiocyanate complexes were prepared by a general procedure. A methanolic solution of the appropriate metal salt is added to a methanolic solution of the ligand in 1 : 2 molar ratio. The complexes are readily precipitated. The reaction mixture is kept in a water bath at 50°C to complete the reaction and then filtered, washed several times with methanol to remove the excess ligand and finally dried in vacuum over P_4O_{10} . For the preparation of the thiocyanate complexes, a stoichiometric mixture of the appropriate metal salt chloride and ammonium thiocyanate were used. The complexes are stable, non-hygroscopic solids, soluble in nitrobenzene, acetonitrile and dimethyl formamide and insoluble in benzene, carbon tetrachloride and diethylether.

RESULTS AND DISCUSSION

The analytical data (Tables 1 and 2) show that the complexes have the general formula $[\text{M}(\text{ABBI})_2\text{X}_2]$ where $\text{M} = \text{Mn}(\text{II})$ or $\text{Co}(\text{II})$ and $\text{X} = \text{Cl}^-$, Br^- , I^- , NO_3^- , CH_3COO^- , HCOO^- , ClO_4^- and SO_4^{2-} . Molar conductance values of the complexes in nitrobenzene, acetonitrile and dimethyl formamide taken using approximately 10^{-3} molar solutions are in the ranges expected for non-electrolytes⁶. The conductance values suggest that the anions are coordinated to the metal ion.

TABLE-1
ANALYTICAL, MAGNETIC SUSCEPTIBILITY, MOLAR CONDUCTANCE AND ELECTRONIC SPECTRAL DATA
OF ABBI COMPLEXES OF COBALT(II)

Complex	Colour	Cation (%)				Anion (%)				μ_{eff} at (301 ± 2) K (BM)	Molar conductance*			λ_{max} (nm)
		Observed		Calculated		Observed		Calculated			Nitro- benzene	Aceto- nitrile	Dimethyl formamide	
		Observed	Calculated	Observed	Calculated	Observed	Calculated							
[Co(ABBI) ₂ Cl ₂]	Pale blue	9.65	9.75	11.53	11.74					4.75	1.85	63	52.0	633
[Co(ABBI) ₂ Br ₂]	"	8.75	8.50	22.90	23.09					4.77	1.82	99	50.0	635
[Co(ABBI) ₂ I ₂]	"	7.32	7.49	31.98	32.26					4.69	4.87	52	46.2	633
[Co(ABBI) ₂ (NCS) ₂]	"	8.98	9.08	17.65	17.87					4.86	4.45	60	29.2	633
[Co(ABBI) ₂ SO ₄]	"	9.31	9.37	15.16	15.26					4.60	0.91	93	48.0	635
[Co(ABBI) ₂ (ClO ₄) ₂]	"	7.85	8.05	26.95	27.18					4.62	4.8	56	24.5	633
[Co(ABBI) ₂ (NO ₃) ₂]	"	8.89	8.97	C-50.1	C-51.1	H-3.34	H-3.3	N-17.1	N-17.05	4.88	12.0	14	28.5	635
[Co(ABBI) ₂ Ac ₂]	"	8.94	9.05	C-59.1	C-58.9	H-4.75	H-4.73	N-12.67	N-12.9	4.50	5.15	60	52.0	633
[Co(ABBI) ₂ (HCOO) ₂]	"	9.42	9.46	C-57.8	C-57.8	H-3.8	H-3.8	N-13.4	N-13.48	4.60	6.10	56	39.7	635

TABLE-II
ANALYTICAL, MOLAR CONDUCTANCE AND MAGNETIC SUSCEPTIBILITY DATA OF
ABBI COMPLEXES OF MANGANESE(II)

Complex	Colour	Cation (%)		Anion (%)		Conductance data			μ_{eff} (BM) at (301 ± 2) K
		Observed	Calculated	Observed	Calculated	Solvent nitro- benzene	Solvent aceto- nitrile	Solvent dimethyl formamide	
[Mn(ABBI) ₂ Cl ₂]	Light brown	9.05	9.15	10.9	11.82	4.2	82	28.4	5.82
[Mn(ABBI) ₂ Br ₂]	"	7.82	7.90	22.8	23.20	5.6	94	29.4	5.9
[Mn(ABBI) ₂ I ₂]	"	7.04	7.01	31.6	32.42	6.1	96	32.6	6.1
[Mn(ABBI) ₂ SO ₄]	"	8.10	8.79	18.1	15.36	3.6	82	41.0	5.92
[Mn(ABBI) ₂ (ClO ₄) ₂]	"	7.46	7.54	26.9	27.30	7.6	46	42.0	5.84
[Mn(ABBI) ₂ (NCS) ₂]	"	8.56	8.51	18.1	17.98	3.1	65	46.0	5.89
[Mn(ABBI) ₂ AC ₂]	"	8.32	8.49	C-59.40 H-3.39	C-59.35 H-4.30	2.1	54	42.0	5.92
[Mn(ABBI) ₂ (NO ₃) ₂]	"	8.39	8.41	N-13.10 C-49.70 H-3.29 N-17.01	N-12.90 C-51.40 H-3.30 N-17.10	5.1	84	40.0	5.96

The IR spectral studies of the ligand and the complexes show that the bands representing the symmetric and asymmetric stretch of intermolecularly hydrogen bonded —NH_2 group do not show prominent red-shift indicating the involvement of —NH_2 group in complexation. In the solid state the ligand molecules are strongly associated by hydrogen bonding⁷. But during complexation, the hydrogen bond breaks and so the increase in frequency occurring as a result of breakage of hydrogen bond is offset to a certain extent by the decrease in frequency obtained as a result of formation of coordinate bond. This is again supported by the fact that the in-plane and out-of-plane bending frequency of the N—H bond represented by the strong bands at 1672 and 883 cm^{-1} respectively undergoes prominent red-shift in all the complexes studied. The imidazole ring stretching frequency appearing at 1672 cm^{-1} also undergoes prominent redshift by about 25 cm^{-1} in all the complexes confirming its involvement in complexation. Thus the bidenticity of the ligand through its >NH and —NH_2 group is confirmed by these spectral findings. There are ample evidences in the IR spectra for the coordinated nature of the different anions also⁸.

The UV-Visible spectra of the complexes of cobalt(II) show maximum at around 635 nm representing ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ transitions as expected from cobalt(II) complexes with distorted octahedral configuration⁹. The fairly intense band observed around 320 nm may be attributed to charge transfer process. This spectral confirmation is in agreement with the results of magnetic susceptibility measurements which give a value for effective magnetic moment in the range of 4.5 to 4.88 BM, typical of distorted octahedral cobalt(II) complexes¹⁰.

The manganese(II) complexes of 2-amino-5-benzoylbenzimidazole (ABBI) give a value in the range of 5.90 BM for effective magnetic moment which are typical of spin free manganese(II) complexes. The complexes are assigned distorted octahedral structure taking into account the analytical data, the bidenticity of the ligand and the coordinated nature of all the anions.

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