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Synthesis and Characterization of Copper(II), Cobalt(II) and Manganese(II) Complexes of 2-(2′-hydroxynaphthylazo)-5-benzoylbenzimidazole

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Seven complexes of copper(II) with the ligand 2-(2′-hydroxynaphthylazo)-5-benzoylbenzimidazole (NABBI) with the composition $[Cu(NABBI)_2X_2]$ where X = Cl^-, Br^-, NO_3^-, ClO_4^-, CH_3COO^-, $HCOO^-$ or $½SO_4^{2-}$ and nine complexes each of cobalt(II) and manganese(II) having the composition $[M(NABBI)_2X_2]$ where M = Co(II) or Mn(II) and X = Cl^-, Br^-, NO_3^-, ClO_4^-, CH_3COO^-, $HCOO^-$, NCS^- or $½SO_4^{2-}$ have been synthesized and characterized. Systematic analytical methods such as cation-anion estimations, elemental analyses, molar conductance and magnetic susceptibility measurements and IR and UV-Vis spectral studies were made use of in arriving at the conclusions regarding the structure of the complexes. Investigations confirm the identity of the ligands and the distorted octahedral geometry of the complexes studied.

Key Words: Synthesis, Copper(II), Cobalt(II), Manganese(II), Complexes, 2-(2′-hydroxynaphthylazo)-5-benzoylbenzimidazole.

INTRODUCTION

This part of our work stems from our interest in studying the coordination behaviour of benzimidazole derivatives. Our previous works on the coordination behaviour of 2-amino-5-benzoyl benzimidazole (ABBI) have already been communicated. Literature survey reveals that ABBI can be diazotised in strongly acidic medium to give the corresponding diazonium salt which can be coupled with 2-naphthol to give the azo compound, NABBI.[1] The coordination aspects of this new ligand is investigated by synthesising 1:2 complexes with the transition metal ions, Cu(II), Co(H) and Mn(II).

EXPERIMENTAL

The compound 2-amino-5-benzoylbenzimidazole (ABBI) (Fig. 1) was prepared by a reported procedure[2]. Mebendazole (a well-known anthelmintic), methyl ester of 5-benzoylbenzimidazole-2-carbamic acid (25 g), was refluxed with 70% sulphuric acid (150 mL) for 6 h. The sulphate salt of ABBI formed was decomposed with ammonia. The compound ABBI that separated was filtered and recrystallized from 25% aqueous ethanol containing activated charcoal and melting point was determined, which is in agreement with the reported value (192°C). The compound NABBI (Fig. 2) was prepared by diazotizing ABBI with $NaNO_2$ and 1 : 1 HCl at 0°C followed by coupling with 2-naphthol. The reddish brown compound obtained (NABBI) was recrystallized from methanol and the melting point determined (132°C). The molecular weight of the new ligand was determined by Rast's micro

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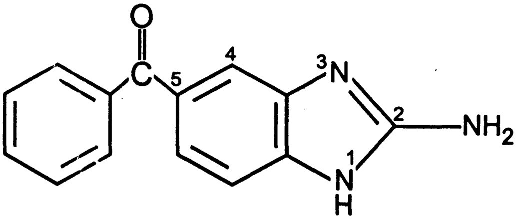

Fig. 1. 2-Amino-5-benzoylbenzimidazole (ABBI)

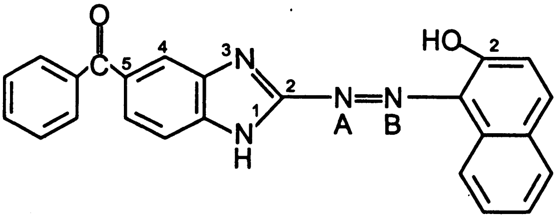

Fig. 2. 2-(2′-Hydroxynaphthylazo)-5-benzoylbenzimidazole (NABBI)

method using biphenyl as solvent. Molar conductances in the three solvents, nitrobenzene, methanol and acetonitrile were determined using Elico direct reading conductivity meter. IR spectral measurements in the range 4000–400 cm^{-1} (KBr pellets) were made using Brucker IFS 66v FT-IR spectrometer. UV spectra were recorded using a Varian Cary Win UV spectrophotometer. Magnetic susceptibility measurements at room temperature were made by Gouy's method.

The following general procedure was employed for the preparation of all the complexes except the thiocyanate complexes. A methanolic solution of the appropriate metal salt was added to a methanolic solution of the ligand in 1 : 2 molar ratio. The complexes precipitated immediately. The reaction mixture was kept in a water-bath at 50°C for 30 min to complete the reaction, filtered, washed several times with methanol to remove the excess ligand and then dried in vacuum over P_4O_{10}. For the preparation of the thiocyanate complexes, the appropriate metal chloride was added to a mixture of the ligand and ammonium thiocyanate taken in stoichiometric proportions, all in methanolic medium. The complexes are non-hygroscopic stable solids soluble in polar solvents like methanol, chloroform etc. but insoluble in non-polar solvents like carbon tetrachloride, benzene etc. Microanalyses were carried out for the estimation of nitrate, acetate and formate in the complexes. For the estimation of other anions and metals in the respective complexes, standard analytical methods were employed[3].

The PMR spectrum of the compound taken in a mixture of $CdCl_3$ and DMSO shows a signal centred at δ 17.5 ppm which may be assigned to >NH proton (the shift may be due to the proton exchange with the solvent). All the protons corresponding to the naphthol part and the imidazole part are observed in the aromatic region. The signal due to —OH proton is observed at δ 6.5 ppm.

RESULTS AND DISCUSSION

The analytical data, along with molar conductance values, magnetic moments and electronic spectral data for the three series of complexes, are presented in Tables 1–3.

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

Complex	Colour	Cu (%)	Anion (%)	Molar conductance data			μ_{eff} (BM) 301±2 K	λ_{max}
				nitrobenzene	methanol	acetonitrile		
$[Cu(NABBI)_2Cl_2]$	Coffee brown	6.88 (6.90)	7.68 (7.72)	4.00	17.20	44	2.07	690
$[Cu(NABBI)_2Br_2]$	,,	6.14 (6.30)	15.56 (15.80)	4.10	18.20	42	1.99	685
$[Co(NABBI)_2SO_4]$	,,	6.78 (6.74)	9.98 (10.17)	4.60	12.60	49	2.01	680
$[Cu(NABBI)_2(ClO_4)_2]$	,,	6.42 (6.53)	18.60 (19.00)	4.01	16.60	48	1.90	685
$[Cu(NABBI)_2(NO_3)_2]$	,,	6.42 (6.53)	C: 58.5 (59.3) H: 3.2 (3.29) N: 14.0 (14.4)	4.20	12.42	46	2.19	690
$[Cu(NABBI)_2AC_2]$	,,	6.49 (6.57)	C: 64.5 (64.62) H: 3.8 (3.9) N: 11.0 (11.6)	4.10	16.20	43	2.10	680
$[Cu(NABBI)_2(HCOO)_2]$	,,	6.66 (6.77)	C: 63.8 (64.0) H: 3.5 (3.6) N: 12.1 (11.9)	3.80	11.60	52	2.01	680

TABLE-2
ANALYTICAL, MOLAR CONDUCTANCE, MAGNETIC SUSCEPTIBILITY AND ELECTRONIC SPECTRAL DATA OF NABBI COMPLEXES OF Mn(II)

Complex	Colour	Cation (%)	Anion (%)	Molar conductance data			μ_{eff} (BM) 301±2 K
				nitrobenzene	methanol	acetonitrile	
[Mn(NABBI)$_2$Cl$_2$]	Black	5.99 (6.03)	7.8 (7.79)	2.0	23.80	44.0	5.78
[Mn(NABBI)$_2$Br$_2$]	,,	5.45 (5.49)	15.9 (16.10)	2.4	24.20	48.1	5.80
[Mn(NABBI)$_2$I$_2$]	,,	5.01 (5.02)	22.9 (23.20)	2.8	22.90	56.1	5.67
[Mn(NABBI)$_2$(NCS)$_2$]	,,	5.71 (5.75)	11.99 (12.14)	2.6	30.92	—	5.92
[Mn(NABBI)$_2$(SO$_4$)]	,,	5.79 (5.87)	9.96 (10.26)	2.1	23.10	39.8	5.81
Mn(NABBI)$_2$(ClO$_4$)$_2$]	,,	5.12 (5.29)	18.95 (19.16)	2.5	24.40	49.2	5.90
[Mn(NABBI)$_2$AC$_2$]	,,	5.65 (5.74)	C: 65.4 (65.20) H: 4.1 (3.97) N: 11.4 (11.70)	1.9	19.20	58.4	5.81
[Mn(NABBI)$_2$(NO$_3$)$_2$]	,,	5.67 (5.70)	C 59.8 (59.81) H: 3.31 (3.30) N: 14.56 (14.53)	2.6	24.20	43.2	5.84
[Mn(NABBI)$_2$(HCOO)$_2$]	,,	5.83 (5.90)	C: 63.8 (64.90) H: 3.5 (3.60) N: 11.9 (12.05)	1.8	25.10	50.2	5.72

TABLE-3
ANALYTICAL, MOLAR CONDUCTANCE, MAGNETIC SUSCEPTIBILITY AND ELECTRONIC SPECTRAL DATA OF NABBI COMPLEXES OF Co(II)

Complex	Colour	Cation (%)	Anion (%)	Molar conductance data			μ_{eff} (BM) 301±2 K	Max (nm)
				nitrobenzene	methanol	acetonitrile		
[Co(NABBI)$_2$Cl$_2$]	Violet	6.45 (6.44)	7.72 (7.76)	3.1	16.80	76.20	4.63	585
[Co(NABBI)$_2$Br$_2$]	,,	5.85 (5.87)	15.95 (15.96)	4.6	17.10	79.21	4.56	590
[Co(NABBI)$_2$I$_2$]	,,	5.27 (5.37)	22.99 (23.14)	3.2	18.20	69.50	4.57	580
[Co(NABBI)$_2$(NCS)$_2$]	,,	6.01 (6.14)	12.33 (12.09)	4.2	22.30	82.30	4.59	550
[Co(NABBI)$_2$(SO$_4$)]	,,	6.19 (6.20)	09.98 (10.20)	4.2	16.80	82.90	4.42	585
Co(NABBI)$_2$(ClO$_4$)$_2$]	,,	5.67 (5.65)	19.05 (19.09)	6.2	32.90	79.90	4.57	575
[Co(NABBI)$_2$(NO$_3$)$_2$]	,,	6.05 (6.09)	C: 58.1 (59.56) H: 3.2 (3.3) N: 11.1 (11.65)	3.7	16.40	86.90	4.61	580
[Co(NABBI)$_2$AC$_2$]	,,	6.15 (6.13)	C: 64.9 (64.93) H: 3.89 (3.95) N: 11.9 (11.65)	3.4	18.20	85.60	4.60	590
[Co(NABBI)$_2$(HCOO)$_2$]	,,	5.67 (5.63)	C: 63.9 (64.3) H: 3.59 (3.64) N: 11.9 (12.0)	3.9	20.60	82.30	4.58	585

The 1 : 2 metal-ligand ratio is established by analytical data which shows that the Co(II) and Mn(II) complexes may be represented by the composition [M(NABBI)$_2$X$_2$] where M = Co(II) or Mn(II) and X = Cl$^-$, Br$^-$, I$^-$, NO$_3^-$, ClO$_4^-$, CH$_3$COO$^-$, HCOO$^-$, NCS$^-$ or ½SO$_4^{2-}$ and copper(II) complexes may be represented by the general formula [Cu(NABBI)$_2$X$_2$] where X = Cl$^-$, Br$^-$, NO$_3^-$, ClO$_4^-$, CH$_3$COO$^-$, HCOO$^-$ or ½SO$_4^{2-}$. Molar conductances taken using 10^{-3} molar solutions in the three solvents, nitrobenzene, methanol and acetonitrile, are in the range expected for non-electrolytes which show that the different anions lie inside the coordination sphere of the metal ion[4].

IR spectrum of the ligand shows a medium intensity band at 2880 cm^{-1} representing the stretching vibration of intramolecularly hydrogen bonded —OH group which disappears in the IR spectra of all the complexes. Instead, a new band appears at around 3420 cm^{-1} which can be assigned to the stretching mode of free —OH group. In the solid state the —OH group is intramolecularly hydrogen bonded to N$_B$, while on complexation, the hydrogen bond breaks, —OH is released as a free group, which is responsible for the observed increase in frequency. But this frequency is lower than that expected for free —OH group which confirms the involvement of —OH group in complexation. The strong band observed at 1526 cm^{-1} assignable to the azo group vibration undergoes prominent red shift in the IR spectra of the complexes confirming its involvement in complexation. Thus the ligand behaves as a bidentate one through N$_B$ of the azo group and —OH group of 2′-naphthol residue, forming stable 5-membered chelate ring in the complexes. The C═N stretching-bands observed at 1620 cm^{-1} and carbonyl stretching frequency observed at 1650 cm^{-1} in the ligand are not affected in the complexes which shows that the tertiary nitrogen of the benzimidazole moiety and the C═O group are not involved in coordinate bond formation. There are evidences for the uncoordinated nature of NO$_3^-$, ClO$_4^-$, CH$_3$COO$^-$, HCOO$^-$, NCS$^-$ and the chelating bidentate nature of the sulphate group in the respective complexes[7].

The electronic spectra of the Cu(II) complexes show broad band in the region, 600–700 nm typical of distorted octahedral complexes. There are no bands above 1000 nm ruling out tetrahedral coordination[8, 9]. This observation is also supported by magnetic susceptibility measurements which give values around 2.1 BM[10]. Thus the overall investigations indicate that the copper(II) complexes are monomeric and have a distorted octahedral configuration. The distortion might have arisen by virtue of the dissimilar coordinating groups and Jahn-Teller Effect.

The electronic spectra of the cobalt(II) complexes show absorption maxima in the range 585 nm typical of cobalt(II) complexes with distorted octahedral geometry. This conclusion is supported by magnetic susceptibility measurements which give values in the range 4.42–4.63 BM[11].

The magnetic susceptibility measurements of manganese(II) complexes show values for magnetic moments in the range 5.67–5.92 BM showing that the complexes are of high spin type[11]. On the basis of the IR spectral evidences, analytical and conductance measurements, the complexes can be assigned a distorted octahedral geometry. The distortion may be due to dissimilar nature of the coordinating species involved.

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