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Synthesis and Characterization of Cu(II), Ni(II) Co(II) and Zn(II) Complexes with 2-Amino-4-*p*-bromophenyl Oxazole

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Metal complex of Cu(II) Ni(II) Co(II) having general composition [ML_2X_2] where L = 2-amino-4-*p*-bromophenyl oxazole (ABPO) and X = H_2O. The characterization of ligand as well as metal complexs have been made on the basis of elemental analysis, magnetic susceptibility, infrared red spectra and magnetic moment data, on the basis of above observation, the ligand ABPO has been found to act in a bidentate manner coordinating to the metal ion through the nitrogen and oxygen atom of the ligand. The remaining vacant sites are occupied by water molecules. On the basis of magnetic susceptibility the geometry of the complex was observed to be octahederal.

Key Words: Cu(II), Ni(II), Co(II) Complexes, 2-Amino-4-*p*-bromophenyl oxazole.

INTRODUCTION

The chemical property of oxazole and their derivative have been reported due to their pharmacological activity[1,2]. Analytical application and chelating capacity[3]. The complex of phenyl derivative have been reported due to their medicinal and antibacterial values[4,5] keeping the above facts in mind and previous research work[6-8] on transition metal complex of 3*d* series, the present paper reported the synthesis and characterization of Co(II), Ni(II), Cu(II) and Zn(II) complexes with ligand 2-amino-4-*p*-bromophenyl oxazole (ABPO) are reported.

EXPERIMENTAL

All the reagent used were of AnalR grade.

Preparation of 2-amino-4-*p*-bromophenyl oxazole (ABPO): *p*-Bromo acetophenone was added to bromine (8 mL) in dry benezene (40 mL) and the mixture was vigorously shaken in sunlight till the colour due to bromine was disharged. To this solution urea (15 mg) was added. The flask was refluxed in a water bath using double surface water condenser for about 27 h. The reaction product was cooled and extrated with ether and continous removal of unreacted ketone and bromine. The product was basified with concenteated ammonia and kept over night. It was then filtered and the product was repeatedly washed with water and dried in vacuum. The yield was 67 %, m.p. 336 ºC.

Preparation of the complexes: The complexes have been synthesized by mixing ethanolic solution of ligand of (0.03 M) with (0.01 mol) of Cu(II), Co(II) and Ni(II) salts in ethanol with continous stirring and refluxing then for 2 h. The contents were concentrated and cooled to obtain brownish black crystals. The process carried out in each case was of similar in nature with slight variation of timing of reflux. On the basis of analytical data the complexes were found to possess the molecular formulae ML_2X_2. where M = Cu(II), Co(II), Ni(II) and X = pyridine.

The metal complexes were analyzed using standard procedure[9]. The infrared spectra of the ligand and metal complex were recorded on IR-20 spectrophotometer employing KBr pellets. The electronic spectra were recorded on cary-2390 spectrophotometer. Magnetic susceptibility were measured by Guoy method using mercury tetraisothiocyanato Co(II) as calibrant. Analytical data, magnetic moment and electronic spectra are recorded in Table-1.

RESULTS AND DISCUSSION

From the elemental analysis in all cases the stoichiometry ratio comes out to be 1:2.

Vibrational spectra of the ligand with that of metal complexes has been recorded in Table-2. It is observed that ν(C-N) stretching frequency observed at 3450 cm^{-1} in the free ligand practically remain unchanged after complexation, they show that ring nitrogen is not taking part in formation. The antisymmetric and symmetric ν(NH) stretching frequencies appeared in the region 3440-3400, 3340-3300 cm^{-1} in the free ligand get shifted to lower frequency after complexation. This shows that nitrogen of the amino group is taking part in complexation. In all the complexes a band appeared in the region 375-280 cm^{-1} assigned to ν(M-O) bond. This shows that oxygen of the oxazole ring is taking part in complexation. The characteristic band of oxazole system were observed in the region 1640-1600, 1595-1580 and 1560-1530 cm^{-1}. In the ligand as well as in all the complexes a band appeared in the region 600-500 cm^{-1}. This is due to ν(C-Br) band.

Electronic spectra and magnetic moment data: In the case of Co(II) nitrate, chloro and acetato complexes bands are observed in the range 8000-8500, 15000-18000, 20000-23000 cm^{-1}. These bands are assigned to $^4A_2(F) \rightarrow {}^4T_2$ (ν_1), $^4T_1(F)$ (ν_2) and $^4A_2(F) \rightarrow {}^4T_1(P)$ (ν_3), respectively[10]. The magnetic moment value 4.0-4.42 BM and spectral data suggest tetrahedral structure[9]. In acetato complexes bands are observed at 8600, 17000, 21000 cm^{-1} assigned to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1) $\rightarrow {}^4A_{2g}(F)$ (ν_2) and $^4T_{1g}(P)$, respectively. The magnetic moment were observed 5.0 BM confirming octahederal geometry.

TABLE-1

ANALYTICAL MAGNETIC MOMENT ELECTRONIC SPECTRA AND CONDUCTIVITY MEASUREMETS DATA OF Co (II), Ni (II) AND Cu (II) COMPLEXES OF 2-AMINO-4-*p*-BROMOPHENYL OXAZOLE (ABPO)

Compound	Elemental analysis %: Found (calcd.)					μ_{eff} (BM)	λ_{max} (electronic cm^{-1})
	C	H	N	M	Br		
$[Co(C_9H_7N_2OBr)_2]Cl_2\cdot 2H_2O$	33.50 (33.55)	2.72 (2.79)	8.62 (8.69)	9.12 (9.15)	24.80 (24.82)	4.00	8000 (8500)
$[Co(C_9H_7N_2OBr)_2](NO_3)_2\cdot 2H_2O$	31.18 (31.00)	2.60 (2.58)	12.08 (12.05)	8.48 (8.45)	22.92 (22.93)	4.42	15000 (18000)
$[Co(C_9H_7N_2OBr)_2](CH_3COO)_2\cdot 2H_2O$	3830 (38.21)	3.52 (3.47)	8.20 (8.10)	8.45 (8.53)	23.18 (23.13)	5.00	20000 (23000)
$[Ni(C_9H_7N_2OBr)_2]Cl_2\cdot 2H_2O$	34.50 (34.53)	2.50 (2.55)	8.90 (8.95)	9.32 (9.38)	25.50 (25.54)	2.90	85000 (9000)
$[Ni(C_9H_7N_2OBr)_2](NO_3)_2\cdot 2H_2O$	31.80 (31.83)	2.38 (2.35)	12.32 (12.38)	8.62 (8.65)	23.50 (23.55)	3.10	14000 (15750)
$[Ni(C_9H_7N_2OBr)_2](CH_3COO)_2\cdot 2H_2O$	39.22 (39.25)	3.32 (3.27)	8.30 (8.32)	8.70 (8.72)	23.72 (23.76)	3.20	24050 (24200)
$[Cu(C_9H_7N_2OBr)_2]Cl_2\cdot 2H_2O$	35.24 (35.27)	2.22 (2.28)	9.10 (9.14)	10.35 (9.58)	26.10 (26.09)	4.79	15500 (16000)
$[Cu(C_9H_7N_2OBr)_2](NO_3)_2\cdot 2H_2O$	32.40 (32.46)	2.18 (2.10)	12.68 (12.62)	9.58 (9.65)	24.06 (24.01)	4.81	18500
$[Cu(C_9H_7N_2OBr)_2](CH_3COO)_2\cdot 2H_2O$	40.08 (40.04)	3.08 (3.03)	8.45 (8.49)	9.68 (9.63)	24.28 (24.23)	4.82	18900 (20500)

TABLE-2

IR SPECTRAL DATA (cm^{-1}) OF LIGAND AND ITS METAL COMPLEXES

	ν(NH) (Asym) (sym)	ν(CH) Vib.	ν(C=C-N=C)	ν(C=N) Vib.	ν(C=C) Vib.	Five Membered oxazole ring	ν(C-Br) Vib.	ν(C-O) Vib.	ν(M-N) *Str.*	ν(M-Br) *Str.* Vib.	ν(M-O) *Str.* Vib.
ABPO	3500 (3400)	3000	1680	1630	1600	1560 (1500)	1160	650			
$[Co(C_9H_7N_2OBr)_2]Cl_2\cdot 2H_2O$	3265 (3248)	2995	1675	1631	1620	1542 (1410)	1152	630	333	292	268
$[Ni(C_9H_7N_2OBr)_2](NO_3)_2\cdot 2H_2O$	3270 (3254)	3015	1670	1632	1620	1525 (1400)	1155	610	330	275	230
$[Cu(C_9H_7N_2OBr)_2]Cl_2\cdot 2H_2O$	3268 (3256)	3012	1655	1634	1588	1550 (1466)	1145	615	325	290	250

The electronic spectra of Ni(II) complexes show three sharp and broad absorption band in the region 8500-9000, 14000-15750 and 24050-24200 cm^{-1} characteristic of octahederal Ni(II) ion. These observed energy of three spin allowed transition $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ agree well with octahederal geometry. The μ_{eff} value between 2.90-3.20 BM confirm high spin octahederal structure. The electronic spectra of Cu(II) complexes show absorption band in the region 15500-16000, 18500-20000 cm^{-1} assignable to $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transition, respectively. A unique peak is also obtained in all the cases around 14000 cm^{-1} this is characteristic of planar geometry. The Cu(II) complexes are paramagnetic in nature and are having magnetic moment value suggest square planar configuration of Cu(II) complexes.

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