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Synthesis and Spectral Studies of Cu(II) Complexes with Amide Group Containing 1,8-Naphthyridine Ligands

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Complexes of copper(II) with 2-amino-1,8-naphthyridine-3-carboxamide (ANC), 2-amino-N-phenyl-1,8-naphthyridine-3-carboxamide (APNC), 2-amino-N-(*p*-methyl phenyl)-1,8-naphthyridine-3-carboxamide (AMPNC), 2-amino-N-(*p*-bromo phenyl)-1,8-naphthridine-3-carboxamide (ABPNC), 2-amino-N-(*p*-chloro phenyl)-1,8-naphthyridine-3-carboxamide (ACPNC), 2-amino-N-(*p*-methoxy phenyl)-1,8-naphthyridine-3-carboxamide (AMYPNC), 2-methyl-N-O-carboxy phenyl-1,8-naphthyridine-3-carboxamide (MCNC) and 2-phenyl-N-O-carboxyphenyl-1,8-naphthyridine, 3-carboxamide (PCNC) have been prepared and characterized by elemental analysis, conductance, thermal, magnetic, IR, electronic and ESR.

Key Words: Copper(II) complexes, 1,8-Naphthyridine.

INTRODUCTION

An amide group offers two potential binding atoms, the oxygen and nitrogen, for complexation of metalions. A number of complexes have been reported with amide group ligands which exhibit diverse coordinating behaviours with different metal ions[1-4]. However, studies on the metal complexes of the derivatives of amide groups are limited. Pannu *et al.*[5] have proposed the structure for this complex with oxygen, but not nitrogen, of the amide group coordinating. On the other hand, Wiersema and Windle[6] on the basis of ESR spectra of Cu(II) salicylamide complexes, have reported that the salicylamide coordinates through nitrogen of the amide group. The majority of amide ligands form monomeric complexes with Cu(II) showing a doublet state. But the ESR spectra of Cu(II) cyclic and amide complexes are of a dimeric species, in which the two metal ions are exchange, coupled, leading to a paramagnetic triplet state. In view of these differences, investigation of the coordinating behaviour of the amide group containing ligands is worthwhile.

EXPERIMENTAL

All the chemicals used were of AR grade, 2-amino-1,8-naphthyridine-3-carboxamide (ANC), 2-amino-N-phenyl-1,8-naphthyridine-3-carboxamide (APNC), 2-amino-N-(*p*-methyl phenyl)-1,8-naphthyridine-3-carboxamide (AMPNC), 2-amino-N-(*p*-bromo phenyl)-1,8-naphthridine-3-carboxamide (ABPNC), 2-amino-N-(*p*-chloro phenyl)-1,8-naphthyridine-3-carboxamide (ACPNC), 2-amino-N-(*p*-methoxy phenyl)-1,8-naphthyridine-3-carboxamide (AMYPNC)[7], 2-methyl-N-O-carboxy phenyl-1,8-naphthyridine-3-carboxamide (MCNC)[8] and 2-phenyl-N-O-carboxyphenyl-1,8-naphthyridine, 3-carboxamide (PCNC)[8] were prepared by the literature methods. The purity of these compounds was checked by TLC and melting point determination.

Preparation of complexes: The complexes were prepared by mixing methanolic solution of cupric acetate (0.001 mmol) was dissolved in methanol. To this solution (30 mL) of ligand solution (0.002 mmol) was added with constant stirring over a period of 15 min then the reaction mixture was refluxed on a water bath for 4-5 h or until a solid separated out. The solids were suction filtered and purified by repeated washing with 1:1 diethyl ether, methanol and dried in vacuum over fused $CaCl_2$ in a desiccator.

The percentage of carbon, hydrogen and nitrogen present in organic compounds (ligands) and metal complexes were carriedout at Central Drug Research Institute, Lucknow using Elementar Vario EL III Carlo Erba 1108. Copper is estimated iodometry using sodium thiosulphate in the complexometric titrations.

The magnetic susceptibility measurements were made at room temperature were obtained using CAHN 2000 Faraday balance (using $Hg[Co(CNS)_2]\chi_g = 16.44 \times 10^{-6}$ g cc^{-1} as standard). Molar conductivities of the complexes in DMF were measured using a digisun digital conductivity meter, model DI 909 with 0.1 M KCl solution was employed for conductivity measurements. The thermal data of the complexes were obtained using Mettler-Toledo, DSC and TGA 822e series, at Central Instrumentation Centre, Kakatiya University, Warangal. The IR spectra of ligands and metal complexes were recorded in KBr pellets or Nujol mulls (using CsI plates in far-IR region) on Perkin Elmer-BX system. The scanning time was 6 min in the range of 4000-200 cm^{-1}. The electronic spectra of complexes in solutions of DMF were recorded on Shimadzu UV-Vis spectrophotometer model 2401 PC. The ESR spectra of Cu(II) complexes were recorded at liquid nitrogen temperature on Jeol-JES-PE-3X and Varian ESR spectrometers, respectively at RSIC, Indian Institute of Technology, Madras, Chennai.

RESULTS AND DISCUSSION

All the copper(II) complexes are crystalline powders their colour being green or light green. All the complexes are slightly soluble in methanol and freely soluble in DMF and DMSO. The analytical data of the complexes are presented in Table-1. The metal chelates are found to have 1:2 (metal: ligand) stoichiometry. The molar conductance values of the complexes in DMF at 10^{-3} M concentration, the results indicate that the complexes are non-electrolytes.

TABLE-1
ANALYTICAL AND PHYSICOCHEMICAL DATA OF Cu(II) COMPLEXES

Complex (m.w.)	Yield (%) / DT (°C)	Found (calcd.) %				$\lambda_M{}^{\#}$	μ_{eff} (BM)
		C	H	N	M		
[Cu(ANC)$_2$(OAc)$_2$]	87	47.99	4.02	19.95	11.97	4.7	1.92
(**1**) (557.98)	(>360)	(47.35)	(3.98)	(20.07)	(11.38)		(1.93)
[Cu(APNC)$_2$(OAc)$_2$]	79	56.93	3.92	16.22	9.25	5.9	1.91
(**2**) (710.18)	(>360)	(57.49)	(4.26)	(15.77)	(8.94)		(1.90)
[Cu(AMPNC)$_2$(OAc)$_2$]	86	59.02	5.07	14.82	8.02	5.6	1.90
(**3**) (738.24)	(>360)	(58.56)	(4.65)	(15.17)	(8.60)		(1.92)
[Cu(ABPNC)$_2$(OAc)$_2$]	55	46.84	3.77	13.05	7.96	7.1	1.93
(**4**) (867.96)	(>360)	(47.04)	(3.25)	(12.90)	(7.32)		(1.92)
[Cu(ACPNC)$_2$(OAc)$_2$]	67	51.92	2.98	15.01	8.72	5.5	1.90
(**5**) (779.12)	(>360)	(52.41)	(3.62)	(14.37)	(8.15)		(1.92)
[Cu(AMYPNC)$_2$(OAc)$_2$]	79	56.67	4.87	14.02	8.54	6.7	1.92
(**6**) (770.24)	(>360)	(56.13)	(4.45)	(14.54)	(8.24)		(1.93)
[Cu(MCNC)$_2$(H$_2$O)$_2$]	84	57.02	3.47	11.02	8.17	6.1	1.90
(**7**) (712.16)	(>350)	(57.33)	(3.97)	(11.79)	(8.92)		(1.93)
[Cu(PCNC)$_2$(H$_2$O)$_2$]	68	62.91	3.54	9.82	7.07	6.9	1.91
(**8**) (836.3)	(>350)	(63.18)	(3.86)	(10.04)	(7.59)		(1.93)

DT = Decomposition temperature.

Thermal analysis: The TGA and DTA thermograms were recorded all the complexes between 200-800 ºC in nitrogen atmosphere. Thermograms of Cu(II) complexes, **1** to **6** are thermally stable upto 200 ºC and them undergo decomposition in one step. The decomposition occurs between 200-800 ºC with a weight loss of 86.11 to 90.17 corresponding to the loss of two acetate ions and two ligand molecules. The weight of the residue left suggests the formation of CuO. Which agrees with the weight of the residue 13.89 to 9.83 and coincide with the calculated values.

Thermograms of Cu(II) complexes, **7** and **8** show initial weight loss in the temperature rang of 180-200 ºC corresponding to two water molecues. The expulsion of water molecules in the above temperature rang indicates that they are coordinated[9]. The weight loss of $[Cu(MCNC)_2(H_2O)_2]$ 88.67 and $[Cu(PCNC)_2(H_2O)_2]$ 90.52 correspond to the loss of two water molecules and two ligand molecules. The weight of the residue left suggests the formation of CuO and agrees with the weight of the residue 11.33 and 9.48 and coincides with the calculated values.

The results of the thermal analyses confirm the formulae of the complexes to be $[Cu(ANC)_2(OAc)_2]$ $[Cu(APNC)_2(OAc)_2]$, $[Cu(AMPNC)_2(OAc)_2]$, $[Cu(ABPNC)_2(OAc)_2]$ $[Cu(ACPNC)_2(OAc)_2]$, $[Cu(AMYPNC)_2(OAc)_2$, $[Cu(MCNC)_2(H_2O)_2]$ and $[Cu(PCNC)_2(H_2O)_2]$ as supported by elemental analyses.

IR spectra: The characteristic infrared absorption of Cu(II) complexes are presented in Table-2. The selected ligands exhibit ν(C=O) vibration at 1671 (ANC), 1673 (APNC), 1670 (AMPNC), 1672 (ABPNC), 1674 (ACPNC), 1670 (AMYPNC), 1685(MCNC) and 1680 cm^{-1} (PCNC). The $\nu(NH_2)$ frequency in ligands 1-6 appears at 3447 (ANC), 3450 (APNC), 3427 (AMPNC), 3428 (ABPNC), 3460 (ACPNC) and 3480 cm^{-1} (AMYPNC). The amide ν(NH) frequency shows up in ligands 2-8 around 3240, 3250, 3215, 3270, 3368, 3300 and 3250 cm^{-1}, respectively. The ν(OH) of carboxylic group absorbs in the range 2500-2700 cm^{-1} in MCNC and PCNC. The data presented in the Table-2 indicate that the coordinating atoms are amide oxygen and amine nitrogen in the case of 1-6 ligands. The ligands 7 and 8 bond through carboxylate oxygen (on deprotonation) and amide nitrogen.

TABLE-2
INFRARED SPECTRAL DATA (cm^{-1}) OF Cu(II) COMPLEXES

Complex	$\nu(NH_2)$	ν(N-H)	ν(C=O)	ν(C-N)	$\nu(M\text{-}OH_2)$	ν(M-O)	ν(M-N)
$[Cu(ANC)_2(OAc)_2]$	3082	3245	1636	1457	–	530	429
$[Cu(APNC)_2(OAc)_2]$	3065	3255	1668	1447	–	528	409
$[Cu(AMPNC)_2(OAc)_2]$	3025	3220	1634	1441	–	520	436
$[Cu(ABPNC)_2(OAc)_2]$	3087	3276	1661	1442	–	547	425
$[Cu(ACPNC)_2(OAc)_2]$	3067	3373	1621	1447	–	565	407
$[Cu(AMYPNC)_2(OAc)_2]$	3016	3354	1667	1438	–	530	403
$[Cu(MCNC)_2(H_2O)_2]$	–	3462	1626	1442	847	529	415
$[Cu(PCNC)_2(H_2O)_2]$	–	3452	1618	1462	845	535	418

The IR spectra of all Cu(II) complexes show a shift in the absorption to low frequency side [$\nu(NH_2)$ group and ν(C=O)[10,11]].

In addition to these charges, the spectra of Cu(II) complexes in far-IR region exhibit ν(Cu-O)[12,13] and ν(Cu-N)[14,15] absorptions around 520 to 565 cm^{-1} and 403 to 436 cm^{-1}, respectively.

Electronic spectra: The electronic spectra of Cu(II) complexes were recorded in methanol. The magnetic moment studies indicate that the Cu(II) ion in the complexes is in octahedral environment. The electronic spectral investigations also support the assignment of appropriate geometry to the transition metal complexes. Cu(II) with d^9 confirugration can be thought of as an inversion of d^1 and is expected to give simple electronic spectrum. A majority of Cu(II) complexes are blue or green because of a single broad absorption band in the region 11000-16000 cm^{-1}. The lack of definite statements present difficulty in assignments of the transitions. Further, Cu(II) species frequently exists in high distorted stereochemistries[16-18].

The Jahn-Teller effect operating on the ^2Eg ground term of an octahedral structure leads to distortion. Six coordinated tetragonal Cu(II) ion is expected to exhibit three absorptions due to the crystal field splitting of ^2D term of the free ion All Cu(II) complexes presented exhibit a single broad band centered at 15786, 14875, 15832, 15639, 14952,15071, 15679 and 15621 cm^{-1}, respectively in Cu(II) complexes of all ligands suggesting a distorted octahedral geometry[19] and this supports the conclusion from the magnetic moment data.

Magnetic moments: The magnetic moments of Cu(II) complexes at room temperature are given in Table-1. The Cu(II) complexes with all the ligands are paramagnetic, μ_{eff} value corresponding to the presence of one unpaired electron.

ESR spectra: The electron spin resonance spectra of Cu(II) complexes in solid state have been recorded at liquid nitrogen temperature and the bonding parameters have been calculated using the Kneubuhl's approximation[20]. The results are listed in Table-3.

TABLE-3
ESR SPECTRAL DATA OF Cu(II) COMPLEXES

Complex	$g_{\parallel}$	$g_{\perp}$	g_{ave}	$A_{\parallel} \times 10^4$ (cm^{-1})	$A_{\perp} \times 10^4$ (cm^{-1})	$A_{ave} \times 10^4$ (cm^{-1})	α^2	β^2	γ^2	$\lambda\,(cm^{-1})$
$[Cu(ANC)_2(OAc)_2]$	2.29	2.04	2.12	155	49	84	0.81	0.82	0.6	551
$[Cu(APNC)_2(OAc)_2]$	2.25	2.04	2.11	169	52	91	0.83	0.69	0.6	478
$[Cu(AMPNC)_2(OAc)_2]$	2.28	2.06	2.13	141	39	73	0.76	0.86	0.88	541
$_t[Cu(ABPNC)_2(OAc)_2]$	2.24	2.06	2.12	160	52	88	0.84	0.67	0.79	466
$[Cu(ACPNC)_2(OAc)_2]$	2.26	2.05	2.12	135	46	76	0.76	0.81	0.75	512
$[Cu(AMYPNC)_2(OAc)_2]$	2.3	2.05	2.13	149	38	75	0.77	0.88	0.78	566
$[Cu(MCNC)_2(H_2O)_2]$	2.29	2.03	2.11	137	31	66	0.67	0.96	0.57	535
$[Cu(PCNC)_2(H_2O)_2]$	2.21	2.06	2.11	183	39	87	0.76	0.67	0.66	432

The solid state spectra of all the complexes are anisotropic, each consisting of only one signal. The hyperfine coupling with Cu nucleus (I= 3/2) is expected to result in four peaks in the ESR spectrum. But, owing to the phenomenon of overlapping (or poor resolution) less number of peaks are detected in a large number of Cu(II) complexes. The ESR spectra of Cu(II) complexes investigated in the present study exhibit only one absorption probably due to the reason mentioned above[21].

The $g_{\parallel}$ and $g_{\perp}$ values obtained from the spectra recorded at liquid nitrogen temperature. The g_{ave} values have been evaluated using the equation.

$$g_{ave} = 1/3\ (g_{\parallel} + 2g_{\perp})$$

Because of the poor resolution of the peaks even at the liquid nitrogen temperature the $A_{\parallel}$ and $A_{\perp}$ values (the parallel and perpendicular components of copper hyperfine splitting) could not be evaluated.

The electronic spectral absorption have been utilized along with the information from ESR spectra to complete the spin-orbit coupling constant of Cu(II) ion in the complex. The equation used for the purpose is

$$g_{\parallel} = 2.0023 - (8\lambda/\Delta E)$$

The values of λ are found to be negative indicating the shell is more than half-filled. The magnetic moment values of Cu(II) complexes have been evaluated using the equation.

$$\mu^2 = \tfrac{3}{4}\ g^2_{ave}$$

The magnetic moment obtained from the spectra agree well with the experimentally determined values. In view of the close similarity of the ESR spectra of Cu(II) complexes investigated, it is worthwhile examining the systems to determine whether the local environment around Cu(II) is same or not. The g-values obtained by Kneubuhl's method[20] are subject to inaccuracies, in as much as they ignore the effect of hyperfine coupling constants, but in the present cases, that within closely related series of complexes, this effect is likely to be same in each complex and the relative g-values may have some significance, although the absolute values may be substantially in error. The factors which influence the relation between the g-values of the local Cu(II) ion environment and the g-values of the bulk crystal are determined by the interactions between the separate Cu(II) ions in these magnetically non-dilute systems. There are three possible types of interactions[22,23].

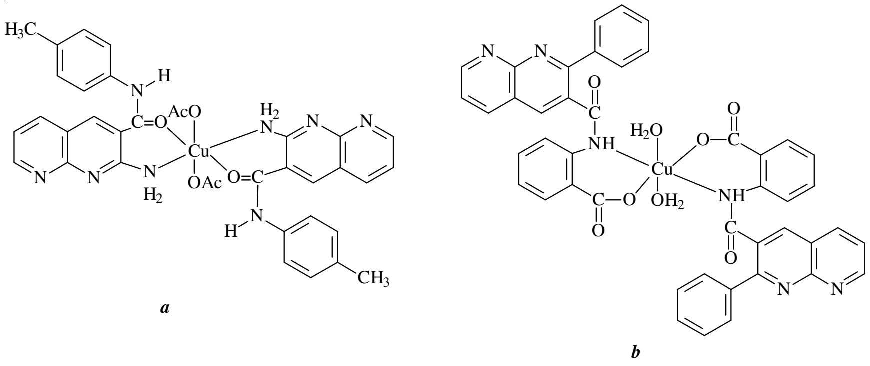
In the case of the complexes studied, this interaction does not reduce the magnetic moment below the spin-only value. Further, no isotropic spectrum was observed. If exchange coupling between non-crystallographically equivalent ions is present, then the observed $g_{\perp}$ might have been larger than the local $g_{\perp}$ and the observed $g_{\parallel}$ would have been smaller than the local $g_{\parallel}$. This should then be reflected in the values of $G \leq 4$.

g-Value is very consistent with the $g_{\perp}$ values between 2.03 and 2.06 and the $g_{||}$ values between 2.21 and 2.30, yielding value of $G > 4.0$. From this it could be proposed that the Cu(II) ions are crystallographically equivalent sites. An attempt is made to correlate the ESR parameters with the electronic spectral data. Since, one to three absorption was found, the parameters like α^2 (σ-bonding parameters), β^2 (in-plane π-bonding parameters) and γ^2 (out-of-plane p-bonding parameters) values are presented.

The spin-orbit coupling constant (λ) of Cu(II) ion in the complex has been evaluated using the equation

$$g_{||} = 2.0023 - (8\lambda/\Delta E)$$

The λ values of all the Cu(II) complexes prepared in the present investigation are found to be lower than that of the free ion value ($\lambda_0 = -829\ \text{cm}^{-1}$). This suggests that there is a considerable mixing of ground and excited state terms. This is also reflected in the magnetic moment values which are slightly greater than the spin-only value of Cu(II), *i.e.*, 1.73 BM. From the analytical, thermal and spectral (IR, electronic and ESR) information obtained and in analogue with structures proposed for Co(II) and Ni(II) complexes the geometry of the Cu(II) complexes may be proposed as tetragonally distorted octahedron. The structure of 2-amino-N-(*p*-methyl phenyl)-1,8-naphthyridine-3-carboxamide (AMPNC) and 2-phenyl-N-O-carboxyphenyl-1,8-naphthyridine-3-carboxamide (PCNC) complexes are presented in Fig. 1.



a

b

Fig. 1. Cu(II) complexes of (a) AMPNC and (b) PCNC

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