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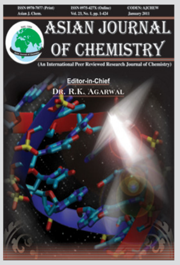

Synthesis and Characterization of Some Transitional Metal Complexes of New Polydentate Ligands Containing 1,8-Naphthyridine Moiety

S.J. SWAMY[1,*], S. RAVEENDER REDDY[2], A. DHARMA REDDY[3] and K. BHASKAR[4]

[1]Department of Chemistry, Kakatiya University, Warangal-506 009, India
[2]Department of Chemistry, L.B. College, Warangal-506 007, India
[3]Department of Chemistry, CKM College, Warangal-506 006, India
[4]Department of Chemistry, Osmania University, Hyderabad-500 007, India

*Corresponding author: E-mail: dharmareddyandru@gmail.com

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The substituted 1,8-naphthyridines, 2-hydroxy-1,8-naphthyridine-3-carboxylic acid hydrazide (HNch) and 2-hydroxy-1,8-naphthyridine-3-carboxylic acid *o*-hydroxybenzylidene hydrazide (HNCHBh) react with Ni(II), Cu(II) and Zn(II) acetate to yield complexes of definite composition. The complexes have been characterized by elemental analysis, thermal, conductance, magnetic studies and IR, electronic, NMR and ESR spectral data. The HNCh and HNCHBh form the complexes of formula [M(HNCh)$_2$] and [M(HNCHBh) (H$_2$O)$_2$], respectively.

Key Words: Ni(II), Cu(II), Zn(II), HNCh and HNCHBh.

INTRODUCTION

The interest in coordination chemistry is increasing continuously with the preparation of organic ligands containing a variety of donor atoms[1-3] and it is multiplied many folds when the ligands have biological importance[4,5]. 1,8-Naphthyridines constitute such dynamic agents whose coordination chemistry was not investigated much. We report here the chelating properties of two substituted derivatives of 1,8-naphthyridines, *viz*, 2-hydroxy-1,8-naphthyridine-3-carboxylic acid hydrozide (HNCh) and 2-hydroxy, 1,8-naphthyridine-3-carboxylic acid *o*-hydroxybenzylidine hydrazide (HNCHBh) and the characterization of their Ni(II), Cu(II) and Zn(II) complexes.

EXPERIMENTAL

All organic compounds, acids and transition metal salts used were of the analar grade and the solvents were purified by distillation before use. The C, H and N were analyzed on the Perkin-Elmer 2400 instrument. ^{1}H NMR spectra were recorded as a Brucker WP80SY instrument at institute Für Anorganische and analytische chemie der Technischen Universitat Berlin, Germany. Conductance was recorded on a Digisun DI-909 conductometer. Infrared and electronic spectra were recorded on Perkin-Elmer 283 and shimadzer UV-VIS 160 spectrometers respectively. ESR spectra were recorded at room temperature and liquid nitrogen temperature on SEOL-SES-PE-3X and Varian ESR spectrometers respectively, at RSIC, IIT, Chennai, Theromgrams were recorded on Seiko Japan DTA unit with Pt+10 % Rh Thermocouple at Instrumentation Centre, Andhra University, Warangal.

The metal contents of the complexes were determined by standard colorimetric (or) volumetric methods[6].

The ligands HNCh and HNCHBh were prepared by the methods reported elsewhere[7,8]. The compounds were crystallized from ethanol (HNCh) and methanol (HNCHBh) and the spectral properties were compared with the reported data.

Preparation of complexes: The ligands 2-hydroxy-1,8-naphthyridine-3-carboxylic acid hydrazide (HNCh-0.41 g, 2 mmol) was dissolved in 50 mL methanol and 2-hydroxy, 1,8-naphthyridine -3-carboxylic acid 0-hydroxybenzylidene hydrazide (HNCHBh-0.31g, 2 mmol) was dissolved in DMSO at 60 ºC and 1 mmol of the respective metal acetate dissolved in 20 mL methanol was slowly added with constant stirring over a period of 10 min. The reaction mixture was refluxed for 4-7 h. The volume of the solution was then reduced to half under reduced pressure and mixture was cooled at 10 ºC overnight. The crystalline solid complexes were filtered on a fine frit and recrystallized from hot methanol and dried over fused CaCl$_2$ in a desiccators (yields range 60-90 %).

TABLE-1
PHYSICAL CHARACTERISTICS OF THE METAL COMPLEXES

Sl. No.	Complexes	Elemental Analysis (%): Found (Calcd.)				Λ_M Ohm^{-1} cm^2 mol^{-1}	μ_{eff} BM
		C	H	N	M		
1	[Ni(HNCh)$_2$]	46.22 (46.48)	2.85 (3.01)	23.86 (24.10)	12.42 (12.63)	11	3.19 3.21*
2	[Cu(HNCh)$_2$]	45.65 (46.00)	2.73 (2.98)	23.76 (23.85)	13.28 (13.53)	15	1.89$ 1.93*
3	[Zn(HNCh)$_2$]	45.69 (45.82)	2.84 (2.97)	23.69 (23.76)	13.26 (13.87)	10	Diameg.
4	[Ni((HNCHBh) (H$_2$O)$_2$]	46.88 (47.34)	3.32 (3.45)	13.72 (13.81)	15.18 (15.67)	16	3.20 3.27*
5	[Cu((HNCHBh) (H$_2$O)$_2$]	46.78 (47.13)	3.28 (3.43)	13.62 (13.75)	15.76 (16.05)	8	1.89$^\$$ 1.93*
6	[Zn((HNCHBh) (H$_2$O)$_2$]	46.72 (47.13)	3.18 (3.43)	13.77 (13.75)	15.64 (16.05)	9	Diameg.

Calculated values from spectra: *Electronic spectra, $^\$$ESR spectra.

TABLE-2
ELECTRONIC SPECTRAL DATA OF COMPLEXES

Complex	Absorptions (cm^{-1})	ν_2/ ν_1	B	Dq	β
[Ni(HNCh)$_2$]	9520, 15300, 25010	1.60	783	952	0.74
[Cu(HNCh)$_2$]	14451	-	-	-	-
[Ni(HNCHBh) (H$_2$O)$_2$]	8260, 13570, 23260	1.64	803	826	0.76
[Cu(HNCHBh) (H$_2$O)$_2$]	13850	-	-	-	-

RESULTS AND DISCUSSION

All the complexes are non-hygroscopic and stable at room temperature. The complexes are soluble in methanol, ethanol, DMSO and DMF, but not in water. The characterization data are presented in Table-1. The molar conductance values of all complexes (10^{-3} M solutions in methanol) were found to be in the range 8-15 ohm^{-1} cm^2 mol^{-1}. These low values indicates that the complexes are non-ionic[9]. The thermograms of the complexes of 2-hydroxy-1,8-naphthyridine- 3-carboxylic acid hydrazide (HNCh) exhibit only one stage of decomposition in the temperature range 180-585 ºC with a corresponding exothermic curve is DSC thermograms. The residue left accounts for the metal oxides as reported above. Thus all the complexes are expected to have formula [M(HNCh)$_2$].

All the complexes of HNCHBh exhibit weight loss position at two different temperature regions 120-203 and 300-590 ºC. An endothermic peak is observed in the low temperature region in the DSC curves indicating the loss of water molecules. The loss of mass in this region was found to correspond to two water molecules. This temperature region of decomposition indicates that the water molecules are coordinated to the metal ion[10]. The endothermic peak in the high temperature region indicates the loss of organic matter and in all the cases the residue left corresponds to the percentage of their respective metal oxides. These results confirm the formula of the complexes of HNCHBh is [M(HNCHBh) (H$_2$O)$_2$].

2-Hydroxy-1,8-naphthyridine-3-carboxylic acid hydrazide (HNCh) exhibits the characteristic absorption at 1560 ν(C=N); 3600-3100 ν(O-H), 3016-2951 ν(N-H) 1699 ν(C=O), 1638 ν(N-H) and 1231 ν(C-O). In the spectra of the complexes no broad absorption is found indicating the loss of phenolic hydrogen atom and coordination of oxygen.

The low frequency shift of ν(N-H) indicates that the hydrazide-NH$_2$ group is coordinated to the metal. The high frequency shift of ν(C=N) indicating that the ring nitrogen atom is not coordinated to the metal while low frequency side shift of ν(C-O) conforming the coordination through phenolic oxygen atom.

The ligand HNCHBh shows absorption at 3600-3100 ν(O-H), 3075-2900 ν(N-H), 1693 ν(C=O) 1655 ν(C=N), 1610 ν(C=N), 1232 ν(C-O). The complexes of this ligand exhibit a broad absorption at 3600-3100 cm^{-1} attributed to coordinated water molecule. This is further confirmed with the absorption at 830-859 cm^{-1} characteristic of ν(M-OH$_2$)[11]. Slightly high frequency side shift of ν(N-H) indicating that nitrogen atom (-CO-NH) is not coordinated to the metal ion. While high frequency shift of ν(C=N) indicating that the ring nitrogen atom is not coordinated to the metal.

The coordination of oxygen and nitrogen atoms to the metal ions is evident from the low frequency vibrations in the far IR spectra[10,12,13] around 400 and 300 cm^{-1}.

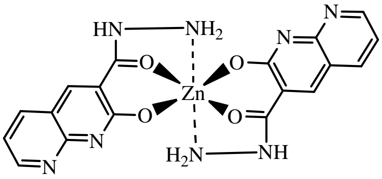
The electronic spectra of all the complexes were recorded in methanol (Table-2). High spin octahedral Ni(II) complexes are found to exhibit three transitions, *i.e.*, from the ground state $^3A_{2g}$ to the excited states $^3T_{2g}$ (F), $^3T_{1g}$ (F) and $^3T_{1g}$ (P). The parameters like β, B and Dq have been evaluated from the electronic spectral absorptions. The β values are found to be less than 1.0 indicating that the M-L bond is covalent. The magnetic moment values evaluated from the spectra[14] are in good agreement with the experimentally determined values (Table-1). The Cu(II) complexes of both ligands HNCh and HNCHBh exhibit broad absorptions centered at 14451 and 13850 cm^{-1} respectively, suggesting a distorted octahedral[15] geometry. Zn(II)-d^{10} complexes do not exhibit any characteristic *d-d* transitions and are also found to be diamagnetic.

The ESR spectra of Cu(II) complexes were recorded at liquid nitrogen temperature and the bonding parameters have been calculated using the neubuhI's approximation[16]. The g$\|$, g$^{\perp}$ and gave values are found to be 2.26, 2.19, 2.21 (Cu-HNCh) complex and 2.21, 2.17 and 2.18 (Cu HNCHBh) complex, respectively. The λ values (465 and 360 cm^{-1}) are found to be less than that of free ion value (829 cm^{-1}).

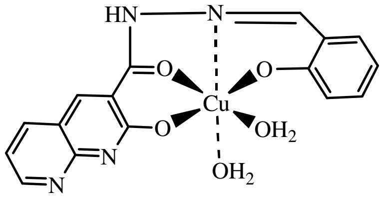
Suggesting a considerable mixing of ground and excited state terms. The same is evident from slightly higher magnetic moment values (1.91 and 1.92 BM) as compared to the spin only value of 1.73 BM.

The ^{1}HNMR spectra of diamagnetic Zn(II) complexes were recorded in DMSO-d_6. The characteristic proton resonance signals of HNCh are found at δ 12.95 (-OH), δ 10.5_{br} and (-NH/NH$_2$) δ 7.4-8.9_m (aromatic H's). In the spectrum of its Zn(II) complex, four signals at δ 64.7_{br}, δ 10.3_{br}, δ 5.5_{br} and δ 7.4-8.9_m can be attributed to the -NH/NH$_2$ and aromatic protons. The hydroxyl proton signals disappeared indicating the deprotonation and coordination of phenolic oxygen. There is no change in the resonance signals of aromatic protons on complexation but the broad signals shifted downfiled side to 5.8 and 4.8 ppm indicates the coordination of nitrogen atom of the hydrazine moiety. The ligand HNCHBh could not give signals due to poor solubility. In the spectrum of its Zn(II) complex three signals at δ 5.8_{br} (-NH/NH$_2$) δ 8.9_s and δ 6.9-8.3_m can be attributed to the -NH/NH$_2$, methyl and aromatic protons. A new signal at 3.1 ppm is observed in the spectrum of Zn(II)-HNCHBh complexe attributed to the proton resonance of coordinated water molecules.

Based on the results obtained is the investigations, it may be concluded that the ligand HNCh acts as a tridentate uninegative ligand coordinating through phenolic oxygen and hydrazene nitrogen atoms. The ligand HNCHBh acts as quadridentative uninegative ligand coordinating through phenolic oxygen carbonyloxygen and hydrogen moiety nitrogen atom. Two water molecules are further coordinated to the metal ions and the formula of complexes are [M(HNCh)$_2$] and [M(HNCHBh) (H$_2$O)$_2$]. The tentative structures of the representative complexes proposed are shown (**Structure-I**).



[Zn(HNCh)$_2$]
Tentative structure of Zn(II) complex of HNCh



[Cu(HNCHBh) (H$_2$O)$_2$]
Tentative structure of Cu(II) complex of HNCHBh

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