



Synthesis and Characterization of Manganese (II), Cobalt (II), Complexes of New Polydentate Ligands Containing 1,8-Naphthyridine Moiety

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ABSTRACT

The substituted 1,8-naphthyridines, 2-hydroxy-1,8-naphthyridine-3-carboxylic acid hydrazide (HNCh) and 2-hydroxy-1,8-naphthyridine-3-carboxylic acid 0-hydroxybenzylidene hydrazide (HNCHBh) react with acetates of Mn(II), Co(II) metal ions 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 $[M(\text{HNCh})_2]$ and $[M(\text{HNCHBh})(\text{H}_2\text{O})_2]$ respectively.

Key words: Mn(II), Co(II), HNCh, HNCHBh.

INTRODUCTION

The interest in coordination chemistry is increasing continuously with the preparation of organic ligands containing a variety of donor atoms¹⁻³ and it is multiplied many folds when the ligands have biological importance⁴⁻⁵. 1,8-naphthyridines constitute such dynamic agents whose coordination chemistry was not investigated much. We report here in the results of our studies on chelating properties of two substituted derivatives of 1,8-naphthyridines, viz, 2-hydroxy-1,8-naphthyridine-

3-carboxylic acid hydrazide (HNCh) and 2-hydroxy, 1,8-naphthyridine-3-carboxylic acid 0-hydroxybenzylidene hydrazide (HNCHBh) and the characterization of their Mn(II), Co(II) complexes.

Chemicals and solvents

All organic compounds, acids and 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. ¹HNMR spectra were recorded as a Bruker WP80SY instrument at institute Für

Anorganische and analytische chemie der Technischen Universität Berlin, Germany. Conductance was recorded on a Digisun DI-909 conductometer. Infrared and electronic spectra were recorded on Perkin-Elmer 283 and Shimadzu 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. Thermograms were recorded on Seiko Japan DTA unit with Pt+10% Rh thermocouple at instrumentation centre, Andhra University, Waltair.

The metal contents of the complexes were determined by standard colorimetric (or) volumetric methods⁶.

Preparation of ligands

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 hydrazido (HNCh-0.41g, 2mmol) was dissolved in 50 ml methanol, and 2-hydroxy, 1,8-naphthyridine-3-carboxylic acid 0-hydroxybenzylidene hydrazide (HNCHBh-0.31g, 2mmol) was dissolved in DMSO at 60°C, and 1mmol 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°C overnight. The crystalline solid complexes were filtered on a fine frit and recrystallized from hot methanol and dried over fused CaCl₂ in a desiccator. The yields of the complexes were in the range 60-90%.

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

Table 1: Characterization data of the complexes

S. No.	Complexes	Found (Calc.), %				Ohm ⁻¹ cm ² mol ⁻¹	μ_{eff} BM
		C	H	N	M		
1	[Mn(HNCh) ₂]	46.12 (46.86)	2.88 (3.04)	23.92 (24.30)	11.48 (11.92)	9	5.91
2	[Co(HNCh) ₂]	46.18 (46.46)	2.84 (3.01)	23.75 (24.09)	12.06 (12.67)	9	5.10 5.12*
3	[Mn(HNCHBh) (H ₂ O) ₂]	47.88 (48.37)	3.31 (3.52)	13.92 (14.10)	13.63 (13.84)	8	5.95
4	[Co(HNCHBh) (H ₂ O) ₂]	47.56 (47.89)	3.23 (3.49)	13.58 (13.97)	14.15 (14.70)	8	4.95 5.16*

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

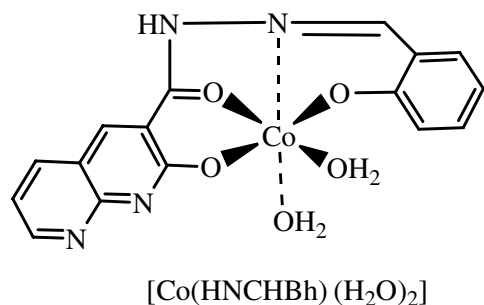
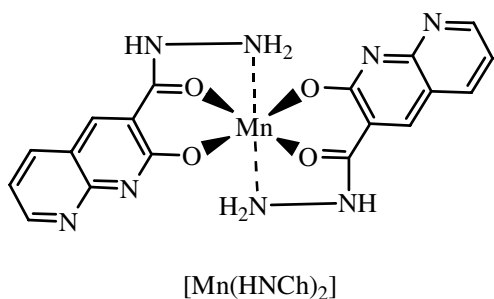
Table 2: Electronic spectral data of complexes

Complex	Absorptions, cm ⁻¹	ν_2/ν_1	B	Dq	β
[Mn(HNCh) ₂]	18518, 19685, 20746 23529, 26666	-	-	-	-
[Co(HNCh) ₂]	8928, 18392, 21568	2.06	925	1016	0.95
[Mn(HNCHBh) (H ₂ O) ₂]	19231, 19960, 21008 22222, 23810, 26316	-	-	-	-
[Co(HNCHBh) (H ₂ O) ₂]	9174, 18898, 22124	2.06	948	1044	0.97

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 $8-15 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$. These low values indicate that the complexes are non-ionic⁹.

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 $180-585^\circ\text{C}$ with a corresponding exothermic curve. DSC thermograms. The residue left accounts for the metal oxides as reported above. Thus all the complexes are expected to have formula $[\text{M}(\text{HNCh})_2]$ the ligand HNCh acts as a tridentate ligand.

All the complexes of HNChBh exhibit weight loss position at two different temperature regions $120-203^\circ\text{C}$ and $300-590^\circ\text{C}$. 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 tentative structures of complexes

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 $[\text{M}(\text{HNChBh})(\text{H}_2\text{O})_2]$. Thus, HNChBh is expected to act as a quadridentate ligand and the coordination number of the metal ions is six.

2-hydroxy-1,8-naphthyridine-3-carboxylic acid hydrazide (HNCh) exhibits the characteristic absorption at $1560 \text{ v} (\text{C}=\text{N})$; $3600-3100 \text{ v} (\text{O}-\text{H})$, $3016-2951 \text{ v} (\text{N}-\text{H})$, $1699 \text{ v} (\text{C}=\text{O})$, $1638 \text{ v} (\text{N}-\text{H})$ and $1231 \text{ v} (\text{C}-\text{O})$. 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 $\nu(\text{N}-\text{H})$ indicates that the hydrazide $-\text{NH}_2$ group is coordinated to the metal. The high frequency shift of $\nu(\text{C}=\text{N})$ indicating that the ring nitrogen atom is not coordinated to the metal while low frequency side shift of $\nu(\text{C}-\text{O})$ conforming the coordination through phenolic oxygen atom.

The ligand HNChBh shows absorption at $3600-3100 \text{ v} (\text{O}-\text{H})$, $3075-2900 \text{ v} (\text{N}-\text{H})$, $1693 \text{ v} (\text{C}=\text{O})$, $1655 \text{ v} (\text{C}=\text{N})$, $1610 \text{ v} (\text{C}=\text{N})$, $1232 \text{ v} (\text{C}-\text{O})$. The complexes of this ligand exhibit a broad absorption at $3600-3100 \text{ cm}^{-1}$ attributed to coordinated water molecule. This is further confirmed with the absorption at $830-859 \text{ cm}^{-1}$ characteristic of $\nu(\text{M}-\text{OH}_2)$ ¹¹. Slightly high frequency side shift of $\nu(\text{N}-\text{H})$ indicating that nitrogen atom ($-\text{CO}-\text{NH}$) is not coordinated to the metal ion. While high frequency shift of $\nu(\text{C}=\text{N})$ 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). The high spin d^5 Mn(II) octahedral complexes (μ_{eff} 5.89 B.M) exhibit complex spin forbidden transitions from the ${}^6\text{A}_{1g}$ ground state. The Mn(II) complexes of HNCh and HNChBh show five or six absorptions

characteristic of electronic transitions to the excited states ${}^4T_{1g}$, ${}^4T_{2g}$, ${}^4T_{2g}$, (D) ${}^4E_{1g}$ (D) and ${}^4T_{1g}$ (P). High spin octahedral Co(II) complexes are found to exhibit three transitions, i.e., to the excited states of ${}^4T_{1g}$ (F), ${}^4T_{2g}$ (F) and ${}^4T_{2g}$ (P) from the ground state ${}^4T_{1g}$ (F) in the case of Co(II) complexes. The parameters like \hat{a} , B and Dq have been evaluated from the electronic spectral absorptions. The \hat{a} values are found to be less than 1.0 indicating that the M-L bond is covalent. The magnetic moment values evaluated from the spectra¹⁴ are in good agreement with the experimentally determined values (Table-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 B.M.

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 hydrogen nitrogen atoms. The ligand HNCHBh acts as quadridentate uninegative ligand coordinating through phenolic oxygen carbonyloxygen and hydrazene moiety nitrogen atom. Two water molecules are further coordinated to the metal ions and the formula of complexes are $[M(\text{HNCh})_2]$ and $[M(\text{HNCHBh})(\text{H}_2\text{O})_2]$. The tentative structures of the complexes proposed are shown (structure-I).

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