

X-Ray Diffraction Studies of Mn(II) and Ni(II) Complexes of Benzoyl Acetone-L-Histidine

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Benzoyl acetone-L-histidine was synthesized by refluxing benzoyl acetone with L-histidine. This benzoyl acetone L-histidine (BAH) was used to synthesize Mn(II) and Ni(II) complexes having metal to ligand stoichiometry 1:1. The ligand and metal complexes were characterized by elemental analysis, molar conductivity, electronic absorption and IR absorption spectra. The magnetic nature of the complexes was established using Gouy's balance method. The XRD data was used to index the compound for orthorhombic system.

Key Words: XRD, Mn(II) and Ni(II) complexes, Benzoyl acetone L-histidine.

INTRODUCTION

Many transition metal complexes have been synthesized for their analytical and commercial applications^{1,2}. Literature survey also reveals that the transition metal complexes generally crystallize with octahedral, tetrahedral or square planar geometry³⁻⁵. But the systematic studies on determination of lattice parameters are the short comings for most of these complexes. In continuation of our work for synthesizing and characterizing Mn(II) and Ni(II) complexes of benzoyl acetone-L-histidine an attempt was made to evaluate lattice parameters. It is also interesting to note that the above complexes exhibit very good antibacterial and antitumor properties⁶.

EXPERIMENTAL

All the chemicals for the synthesis were of AR grade. Benzoyl acetone-L-histidine (BAH) was prepared from benzoyl acetone and L-histidine following the reported procedure by Schiff. Manganese(II) and nickel(II) chelates of benzoyl acetone-L-histidine were synthesized by adding the metal salt solution in appropriate solvent to the boiling solution of the ligand. The mixture was refluxed and the separated Ni(II) chelates were filtered. Manganese(II) complex was formed only after adding the refluxed solution to distilled water with constant stirring. All the complexes were collected washed with 1:1 alcohol and dried in vacuum desiccator. The elemental analysis of ligand and complexes were carried out using reported methods⁷. The

complexes were tested for solubility using various polar and non-polar solvents. Molar conductivity of the ligand and complexes were recorded using 10^{-4} molar solution on a Toshniwal conductivity meter. The electronic absorption spectra of complexes were recorded from their aqueous solution in the UV-visible region on Shimadzu UV-1601 spectrophotometer. Infrared spectra were recorded on Shimadzu FTIR-8101 spectro photometer using KBr pellets. The X-ray diffractograms were recorded on Philips PW-712. X-ray diffractometer using $\text{CuK}\alpha$ radiations. ($\text{CuK}\alpha$, $\lambda = 1.5418 \text{ \AA}$), The X-ray diffractograms were scanned in the 2θ range of $5-60^\circ$.

RESULTS AND DISCUSSION

The results of elemental and spectral analysis are summarized in Tables 1 and 2, respectively. The complexes are anhydrous in nature and stable at room temperature. The observed values of the elemental analysis are in close agreement with the calculated values for the metal complexes. All these complexes have metal to ligand stoichiometry 1:1. The complexes are sparingly soluble in common organic solvents but are sufficiently soluble in hot distilled water. The low values of the molar conductance suggest the non-electrolytic behaviour of these complexes. The Gouy's balance method indicates that all these complexes are paramagnetic in nature and suggests an octahedral geometry for Mn(II) and Ni(II) complexes.

TABLE-1
MICRO ANALYTICAL, MAGNETIC AND CONDUCTANCE DATA OF
TRANSITION METAL CHELATES OF BENZOYL ACETONE-L-HISTIDINE ($\text{L}'\text{H}_2$)

Complex	Colour	Elemental analysis (%): Found (Calcd.)				μ_{eff} (BM)	Ω^{-1}
		M	C	H	N		
$\text{MnL}'(\text{H}_2\text{O})_3$	Dark green	13.50 (13.45)	47.52 (47.40)	5.28 (5.20)	10.35 (10.30)	5.90	2.78
$\text{NiL}'(\text{H}_2\text{O})_3$	Pale green	14.50 (14.32)	46.95 (46.86)	5.10 (5.15)	10.22 (10.25)	3.02	3.45

Calculated values are given in the parenthesis, Ω^{-1} = molar conductance in $\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

TABLE-2
CHARACTERISTIC INFRARED ABSORPTION FREQUENCIES (cm^{-1}) OF
TRANSITION METAL CHELATES OF BENZOYL ACETONE-L-HISTIDINE ($\text{L}'\text{H}_2$)

Substances	$\nu(\text{H}_2\text{O})$	$\nu_{\text{asym}}(\text{COO})$	$\nu(\text{C}=\text{N})$ azomethine)	$\nu(\text{C}=\text{N})$ in ring	$\nu_{\text{sym}}(\text{COO})$	In plane deformation	Out of plane deformation	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
$\text{L}'\text{H}_2$	–	1700s	1550m	1440m	1400	830m	760, 738m	–	–
$\text{MnL}'(\text{H}_2\text{O})_3$	3500- 3100br	1603s	1516m	1445m	1380s	830m	765, 736m	518w	410w
$\text{NiL}'(\text{H}_2\text{O})_3$	3500- 3100br	1591s	1520m	1440m	1330s	820m	771, 736m	518w	410w

The infrared spectra of the chelate indicate the absence of characteristic absorption for the -OH group and a shift in $\nu(\text{C}=\text{N})$ shows that -OH group and C=N are involved in coordination, The chelation of the carbonyl oxygen is confirmed by the shift of carbonyl stretching frequency of the carboxylate group to lower frequencies. This asymmetric and symmetric stretching vibrations of the carboxylate groups occur at *ca.* 1600 and 1400 cm^{-1} , respectively showing a difference of about 200 cm^{-1} . This indicates the monodentate behaviour of the carboxylate group^{8,9}. These two complexes show broad absorption bands between 3500-3100 cm^{-1} due to the presence of co-ordinated water molecules which is further supported by the appearance of rocking mode of medium intensity bands¹⁰ at *ca.* 860 cm^{-1} . The weak bands in the 550-500 cm^{-1} and 450-400 cm^{-1} regions exhibited by the complexes are tentatively assigned to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$, respectively¹¹.

The complexes were characterized with respect to various electronic transitions associated with it in the UV-visible spectral regions. The ligand spectrum showed two characteristic bands near 37,000 and 27000 cm^{-1} . The shift of these bands exhibited in the spectra of complexes can be taken as a proof of coordination of the ligand to metal ions. The octahedral environment¹² of ligands around Mn(II) ion is confirmed by the appearance of a broad band at 24500 cm^{-1} . The two electronic transitions bands at 10400 and 22600 cm^{-1} present in Ni(II) complex are due to ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ and to ${}^3\text{A}_{1g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ transitions. The good quality of X-ray diffractograms of Mn(II) and Ni(II) complexes indicates high crystallinity of these complexes. The powder diffraction pattern of Mn(II) complex of benzoyl acetone-L-histidine exhibited 9 peaks between 12-23°, 2θ values. Ni(II) complex recorded 13 peaks up to 43° of 2θ .

TABLE-3
X-RAY DATA OF $[\text{MnL}(\text{H}_2\text{O})_3]$

Crystal system: Orthorhombic, A = 0.012728; B = 0.0012728; C = 0.004242, a = 6.8333 Å; b = 21.655 Å; c = 11.8365 Å, Cell volume (V) = 1748.316598 Å; Density (D) = 1.2400 g/cm^3

Lines	2θ	Plane spacing (d) Å	Relative Intensity (I)	$\text{Sin}^2\theta$		hkl
				(obs.)	(calcd.)	
1	12.956	7.5892	97.3	0.01272	0.01272	100
2	13.682	7.1883	51.4	0.01418	0.01400	110
3	15.523	6.3390	48.8	0.01823	0.01824	111
4	16.641	5.9153	70.9	0.02094	0.02036	40
5	17.969	5.4807	100.0	0.02438	0.02460	41
6	20.500	4.8092	24.0	0.03166	0.03182	50
7	21.200	4.6515	25.0	0.03383	0.03309	140
8	22.700	4.3471	20.0	0.03873	0.03818	3
9	25.500	3.8751	25.0	0.04870	0.04879	52

All the reflections have been indexed for h, k, l values using methods reported in literature¹³. The 'd' values of reflexes were obtained using Bragg's equation ($\nu\lambda = 2d \sin \theta$). The two complexes have been found to be orthorhombic. The values of $\text{sin}^2\theta$ for each peak have been calculated with the help of the cell parameters and the corresponding h, k, l values. In all cases they are in good agreement with observed

$\sin^2\theta$ values as shown in Tables 3 and 4. The lattice constants, a, b and c for each unit cell have been found out and are given in Tables 3 and 4, along with the density.

TABLE-4
X-RAY DATA OF $[\text{NiL}(\text{H}_2\text{O})_3]$
Crystal system: Orthorhombic, a = 0.0082695; b = 0.003307; c = 0.0011814, a = 8.4774 Å;
b = 13.405 Å; c = 22.4289 Å, Cell volume (V) = 2548.9431 Å³; Density (D) = 1.4601 g/cm³

Lines	2θ	Plane spacing (d) Å	Relative intensity (I)	$\text{Sin}^2\theta$		hkl
				(obs.)	(calcd.)	
1	10.435	8.471	63.60	0.008269	0.00826	100
2	13.068	6.769	15.40	0.012948	0.01275	111
3	14.515	6.098	100.00	0.015950	0.01630	112
4	15.803	5.603	43.60	0.018890	0.01890	4
5	16.830	5.263	36.11	0.021410	0.02148	120
6	17.653	5.020	39.30	0.023540	0.02387	23
7	20.765	4.274	44.90	0.032470	0.03213	24
8	23.845	3.790	31.20	0.042670	0.04371	203
9	25.255	3.524	30.10	0.047790	0.04748	221
10	29.313	3.044	26.30	0.064020	0.06402	231
11	31.411	2.845	16.60	0.073270	0.07442	300
12	36.981	2.428	19.70	0.100000	0.10418	330
13	42.713	2.115	19.00	0.132610	0.13231	400

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