

## Physico-chemical Studies and Thermal Decomposition Kinetics of Some Metal Complexes of Dibenzoylmethane L-Histidine

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The complexes of Co(II), Ni(II) and Cu(II) with dibenzoylmethane L-histidine (DBMH) have been synthesized and characterized on the basis of elemental analysis, molar conductance, magnetic moment, UV-visible and IR spectra. Co(II) and Ni(II) complexes of DBMH were subjected to thermal analysis so as to understand their thermal stability and decomposition patterns. The kinetic parameters like activation energy  $E$ , frequency factor  $A$ , entropy of activation  $\Delta S$  and order parameter ( $n$ ) were calculated from the TG curves, using Coats-Redfern equation. The mechanism of decomposition has been established from thermogravimetric data. On the basis of present findings the relative thermal stabilities of the chelates can be given as  $\text{NiL}(\text{H}_2\text{O})_3 < \text{CoL}(\text{H}_2\text{O})_3$ .

**Key Words:** Dibenzoyl methane-L-histidine, Kinetics, Complexes, Thermal decomposition.

### INTRODUCTION

In recent years, Schiff base ligands and their metal complexes have come to the forefront area in coordination chemistry because of their biological significance. The marked biological activity of transition metal complexes of histidine Schiff bases as antifungal/antibacterial agents and their role in the biosystems prompted us to study the thermal decomposition and dehydration reactions of transition metal complexes of dibenzoylmethane L-histidine.

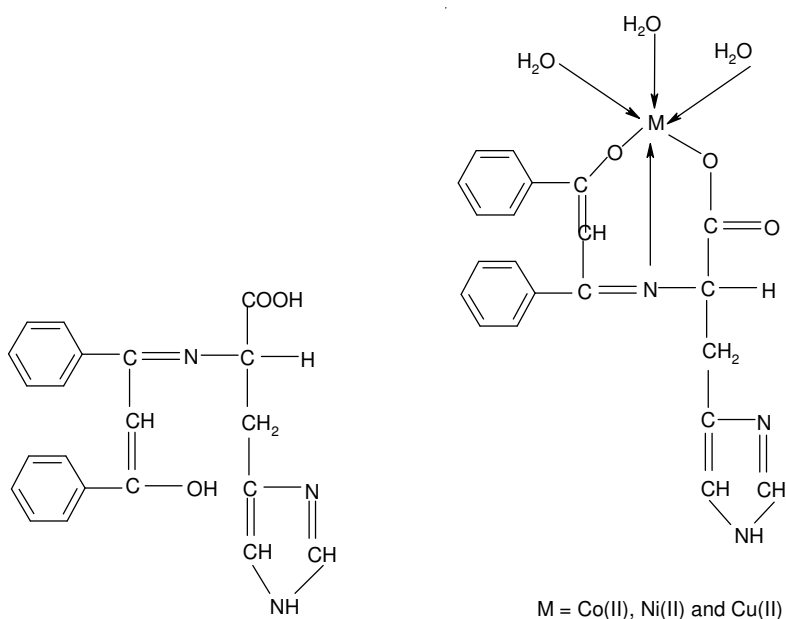
Comparatively less have been reported showing the relationship between the thermal stability of metal chelates and the structure of the chelating reagents<sup>1</sup>. Wendlandt and coworkers<sup>2-5</sup> and Hill and co-workers<sup>6,7</sup> studied the thermal properties of metal chelates with different types of complexing ligands. Such studies on thermal decomposition and kinetics of metal chelates with azo methine ligands have been carried out by a few workers<sup>8-11</sup>. In continuation of our work<sup>12,13</sup> on thermal decomposition kinetics of metal chelates, the preparation, characterization and thermo analytical data for the Co(II), Ni(II) and Cu(II) complexes of dibenzoyl methane-L-histidine are reported.

### EXPERIMENTAL

The ligand was prepared from dibenzoyl methane and L-histidine following the procedure reported by Schiff. KOH (0.56 g, 0.01 mol) dissolved in methanol

and histidine (1.55 g, 0.01 mol) in methanol were mixed and stirred vigorously. A hot methanol solution of dibenzoylmethane (2.25 g, 0.01 mol) was added to it with constant stirring. The cream coloured crystals obtained was filtered, recrystallized from methanol and dried in vacuum desiccator. Melting point was found to be 90 °C. The ligand was characterized on the basis of C, H, N analysis, UV and IR spectral data.

**Preparation of complexes:** The complexes were generally prepared by adding slowly a hot aqueous methanol solution of the metal acetate or chloride to a refluxing solution of the ligand in methanol medium. The complexes possess 1:1 stoichiometry. Co(II), Ni(II) and Cu(II) were prepared by adding slowly methanolic solution of the corresponding metal acetate (0.01 mol) to a refluxing solution of the ligand (0.01 mol) in methanol after adjusting its pH (7-7.5) with acetic acid. The precipitated complex was filtered, washed with methanol-water (1:1) mixture and dried in a vacuum desiccator. The UV and IR spectra and elemental analysis confirm the general structure of complex as Fig. 1.



Dibenzoylethyl-L-histidine (DBMH)

Fig. 1

Thermal analysis was carried out using a Perkin-Elmer-7 series thermal analysis system. A constant heating rate of 10 °C/min and a sample mass of *ca.* 5 mg were employed for the entire study. The atmosphere was static air. The fractional decomposition was determined directly from the TG curves. Computational work was performed with a Horizon III mini computer using the programming language Fortran.

The complexes were characterized on the basis of elemental analysis, spectral and thermal studies. The IR spectra of chelate indicate that -COOH, -OH and C=N are involved in coordination. Characteristic bands of H<sub>2</sub>O are present in the spectra of all the above complexes.

**Mathematical analysis of data:** TG curves of Co(II) chelate shows a 3 stage decomposition pattern, while Ni(II) chelate shows a 4 stage decomposition pattern. Mass loss considerations from TG curves indicate that the first and 2nd step of decomposition stands for removal of the water molecules. X-Ray diffraction data confirmed the products to be the corresponding oxide.

The non isothermal TG curves have been subjected to mathematical analysis using the integral methods of Coats-Redfern<sup>14</sup> and the activation parameters have been evaluated for the above complexes.

## RESULTS AND DISCUSSION

The analytical data, molar conductance and magnetic moments of the complexes are summarized in Table-1.

The very low molar conductance value of the complexes in ethanol indicates that these complexes are non-electrolytes in ethanol and neutral in nature<sup>15</sup>. The electronic spectrum of the ligand DBMH is characterized by two bands lying around 38300 and 27600 cm<sup>-1</sup>. During complex formation, a red shift is detected for these bands, which indicates the involvement of the Schiff base in coordination. The band appearing at 24810 cm<sup>-1</sup> in the electronic spectrum of Co(II) complex of the ligand DBMH gives only one characteristic band at 14900 cm<sup>-1</sup> due to <sup>4</sup>T<sub>1g</sub>(F) → <sup>3</sup>+T<sub>2g</sub>(F) transition. Ni(II) complex exhibits two *d-d* transitions in the electronic spectra at *ca.* 16,700 and 22,500 due to <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>1g</sub>(F) and <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>1g</sub>(P) transitions. The electronic spectra of Cu(II) complexes showed a broad band at 16000 cm<sup>-1</sup> which is assigned to <sup>2</sup>E<sub>g</sub> → <sup>2</sup>T<sub>g</sub> transitions indicating octahedral structure of the complex<sup>16</sup>. The IR spectrum of the ligand shows a sharp band at 3200 cm<sup>-1</sup>, which can be assigned to the hydrogen bonded OH group. On complexation this band disappears indicating that the hydrogen atom of the hydroxyl group is replaced by the metal. A broad features at 3500-3100 cm<sup>-1</sup> in the spectra of several complexes is attributed to the hydroxyl stretching mode of water molecules<sup>17-20</sup>.

In addition, a medium band approximately at 950-870 cm<sup>-1</sup> suggests that the water molecules are co-ordinated<sup>21</sup>. A strong intense band at 1460 cm<sup>-1</sup> in the spectrum of the ligand DBMH may be assigned to ν(C=N) stretch. This band shows a downward shift about 40-30 cm<sup>-1</sup> in the spectra of all the metal complexes<sup>22</sup> indicating the participation of the azomethine nitrogen in coordination with metal ions. Spectra of all the metal complexes prepared showed bands at 550-515 cm<sup>-1</sup> and 430-415 cm<sup>-1</sup> assignable to ν(M-N) and to ν(M-O) respectively.

From all the above studies, it is clear that the ligand acts as a bivalent tridentate towards transition metal ions. Based on the above observations, the structure of complexes can be confirmed to be octahedral for Co(II), Ni(II) and Cu(II) complexes.

TABLE-1  
ANALYTICAL, MAGNETIC AND CONDUCTANCE DATA OF TRANSITION METAL  
CHELATES OF DIBENZOYL METHANE-L-HISTIDINE (LH<sub>2</sub>)

Complex	Colour	Elemental analysis (%): Found (Calcd.)				$\mu_{\text{eff}}$ (BM)	$\Omega^{-1}$
		M	C	H	N		
CoL(H <sub>2</sub> O) <sub>3</sub>	Orange	11.99 (12.48)	52.98 (53.40)	4.00 (4.40)	8.10 (8.90)	4.50	4.80
NiL(H <sub>2</sub> O) <sub>3</sub>	Yellowish green	12.30 (12.44)	53.00 (53.50)	4.10 (4.50)	8.20 (8.90)	2.88	3.90
CuL(H <sub>2</sub> O) <sub>3</sub>	Pale green	12.95 (13.30)	52.10 (52.90)	4.00 (4.40)	8.40 (8.80)	2.12	5.70

$\Omega^{-1}$  = molar conductance in ohm<sup>-1</sup> cm<sup>2</sup> mol.

TABLE-2  
CHARACTERISTIC INFRARED ABSORPTION FREQUENCIES (cm<sup>-1</sup>) OF TRANSITION  
METAL CHELATES OF DIBENZOYL METHANE-L-HISTIDINE (LH<sub>2</sub>)

Substance	$\nu(\text{H}_2\text{O})$	$\nu_{\text{asym}}(\text{COO})$	$\nu(\text{C}=\text{N})$ (azomethine)	$\nu(\text{C}=\text{N})$ (in ring)	$\nu_{\text{sym}}(\text{COO})$	In plane deformation	Out of plane deformation	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
LH <sub>2</sub>	–	1635s	1460m	1440m	1420s	835m	760, 738m	–	–
CoL(H <sub>2</sub> O) <sub>3</sub>	3500-3100br	1595s	1425m	1443m	1410s	830m	789, 746m	517w	420w
NiL(H <sub>2</sub> O) <sub>3</sub>	3500-3100br	1593s	1435m	1444m	1408s	830m	790, 756m	518w	420w
CuL(H <sub>2</sub> O) <sub>3</sub>	3500-3100br	1595s	1435m	1440m	1409s	830m	790, 744m	517w	418w

TABLE-3  
THERMAL DECOMPOSITION DATA OF Co(II), Ni(II) AND Cu(II) COMPLEXES OF DIBENZOYL METHANE L-HISTIDINE

Complex	Stage	Temp. range in TG (°C)	Peak temp. in TG (°C)	DTG	DTA	Loss of mass %			Probable assignment
						From TG	Theoretical	From pyrolysis	
CoL(H <sub>2</sub> O) <sub>3</sub>	I	90-160	110	108	113	4.7	3.8	–	Loss of 1 H <sub>2</sub> O
	II	160-320	312	306	297	36.1	36.4	–	Loss of 2H <sub>2</sub> O and histidine part
	III	320-440	439	427	444	44.07 84.87	42.06 82.26	– 83	Loss of dibenzoyl methane part CoL(H <sub>2</sub> O) <sub>3</sub> → Co <sub>3</sub> O <sub>4</sub>
NiL(H <sub>2</sub> O) <sub>3</sub>	I	80-140	95	95	98	2.97	3.8	–	Loss of 1H <sub>2</sub> O
	II	140-240	213	209	--	23.6	20.8	–	Loss of 2H <sub>2</sub> O + CO <sub>2</sub>
	III	240-340	338	335	301	41.36	43.9	–	Loss of dibenzoylmethane part
	IV	340-460	420	420	424	19.46 87.39	19.5 88.0	– 85	Loss of histidine part NiL(H <sub>2</sub> O) <sub>3</sub> → NiO

The results of the studies on the thermal decomposition of Co(II) and Ni(II) complexes of dibenzoyl methane-L-histidine are given in Tables 3 and 4. Metal percentage from independent pyrolytic experiments and from thermal studies was found to be agreeable with the calculated values in the case of metal complexes of DBMH. The thermal data have supported the structure of the complexes as  $[M(\text{DBMH})(\text{H}_2\text{O})_3]$  where  $M = \text{Co(II)}$  and  $\text{Ni(II)}$ .

TABLE-4  
KINETIC PARAMETERS FOR THE DECOMPOSITION OF Co(II), Ni(II)  
COMPLEXES OF DIBENZOYLMETHANE L-HISTIDINE ( $\text{LH}_2$ )

Complex	E (kcal mol <sup>-1</sup> )	A (s <sup>-1</sup> )	$\Delta S$ (eu)	$\gamma$	Order n
$[\text{CoL}(\text{H}_2\text{O})_3]$	4.733	$9.290 \times 10^{-3}$	-114.295	0.9839	1/3
$[\text{NiL}(\text{H}_2\text{O})_3]$	3.173	$4.973 \times 10^{-3}$	-115.430	0.7929	2/3

The kinetic parameters calculated for the decomposition of Co(II) and Ni(II) complexes of dibenzoylmethane L-histidine on the basis of Coats-Redfern equation are given in Table-3. It is found that the greater the thermal stability of the complex the larger the activation energy for the decomposition. The negative  $\Delta S$  values of the decomposition stage of the complexes show that the complexes are more ordered in the activated state than the reactants and that the reactions are slower than normal. On the basis of the observations, the relative thermal stabilities of metal chelates can be given as  $[\text{Ni}(\text{DBMH})(\text{H}_2\text{O})_3] < [\text{Co}(\text{DBMH})(\text{H}_2\text{O})_3]$ .

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(Received: 15 September 2008; Accepted: 3 September 2009) AJC-7805