Synthesis, Characterization and Thermal decomposition kinetic studies of some transition metal ion complexes of Diphenyl Glycolic acid- Leucine

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Abstract

Techniques such as elemental analysis, magnetic moment, molar conductance, UV-Vis, and FT-IR were used to characterize the recently synthesized diphenyl glycolic acid-Leucine ligand and its Cr (III), Ni (II), and Cu (II) complexes. Thermal analysis was used to determine the thermal stability and decomposition pattern of the Cr (III), Ni (II), and Cu (II) complexes. The TG curves were used to compute kinetic parameters such as activation energy (ΔE), frequency factor (A), entropy of activation (Δs), and order parameter (n) using the Coats Redfern and Horowitz Metzger equations. Nine mechanistic equations have been used to examine the reaction mechanism by employing non-isothermal approaches. The end products are discovered to be their corresponding oxides, and $[CrBL(H_2O)_2(CH_3COO)_2]$ < $[CuBL(H_2O)_2(CH_3COO)_2]$ < $[Ni(BL)_2(H_2O)_2]$ is the sequence in which they are most stable. The Cr (III) and Cu (II) complexes exhibit two-stage decomposition pattern in their TG curve whereas Ni (II) complex shows a three-stage decomposition pattern.

Keywords: Diphenyl glycolic acid; Leucine; Kinetics; TG; Decomposition mechanism.

Introduction

Coordination compounds have garnered a lot of attention lately because of their intriguing structures and useful characteristics. These materials can be employed as luminescent, optical, magnetic, catalytic, or electronic materials. When it comes to coordination compounds, the examination of their thermal characteristics is crucial as it offers insights into various physical and chemical processes that take place in the substance during its cooling or heating phases. These processes include adsorption, chemisorption, crystallization, melting, and crystal transition. These procedures have an impact on coordination compounds' characteristics and possible uses.

Transition metal complexes containing amino acids are essential to modern agriculture and medicine. Their usage as antibacterial agents is becoming more popular these days. Many studies on the structure and chemical behavior of various metal complexes have been conducted in the past few years in an effort to discover an alternative to antibiotic medications. Upon reviewing the literature on Schiff base metal complexes and their applications, a complete understanding of this class of compounds in all aspects can be gained from good review papers[1,2], with one more specifically devoted to copper complexes[3]. They include a wealth of information about the various metal complexes that are derived from Schiff bases and are widely used as enzymatic agents in biological systems, analytical chemistry, polymers, antifertility, agrochemicals, anti-inflammatory activity, and antiradical activities. Their antimicrobial, antibacterial, antifungal, anticancer, and cytotoxic

properties have been examined by a number of people[1,2]. The synthesis, characterisation, and microbiological activity of transition metal complexes of Ni, Cu, and Zn were investigated by A. S. Kuwar[4] et al. These compounds' electronic spectra and magnetic moment values show octahedral symmetry. Cu (II) complexes of salicylidene amino acid Schiff bases of the type $[Cu(sal.aa)H_2O]nH_2O$ have been described by Nathmala[5] et al.

The synthesis, characterisation, and antibacterial activity of cobalt metal complex against multidrug-resistant bacterial and fungal diseases were investigated by Subhasish Saha[6] et al. In accordance with elemental analyses, IR ^{1}HNMR, solid reflectance, magnetic moment, molar conductance, and thermal analysis (TGA), metal complexes of Schiff base derived from 2-furancarboxaldehyde and o-phenylenediamine (L1), and 2-thiophenecarboxaldehyde and 2-aminothiophenol (HL2) are reported and characterized and also their metal complexes (M=Zn(II), Fe(III), Ni(II), Cu(II), Co(II), and UO_2(II)) have also been synthesized and characterized. The synthesized ligands were further tested for their antibacterial activity against fungi (Candida) and bacterial species, including Escherichia coli, Pseudomonas aeruginosa, and Staphylococcus Pyogenes, in comparison to their metal complexes. The metal complexes are more effective antibacterials against one or more bacterial species than the parent Schiff base ligand, according to the activity data[8]. Different modifications in solids can be achieved by heating, and there are a number of thermal methods [9-11], depending on the properties that are measured and the temperature programs.

Smoothers[12] offers insightful suggestions regarding the theory, method, and tool related to thermal analysis. Wendlandt[13] has documented the use of thermoanalytical techniques for tracking the metal ion reaction mechanism during the thermal breakdown of metal chelates. Nathmala[14] has reported on a study of the thermal breakdown of Schiff base complexes of Co(II), Ni(II), and Cu(II) generated from salicylaldehyde and glycine. A recent article reports on a similar investigation conducted on the Schiff base complexes of cadmium and mercury halides[15].

Materials and Methods

By condensing an ethanolic solution of diphenyl glycolic acid with an ethanolic solution of leucine potassium salt and refluxing the mixture for three hours in a water bath, the diphenyl glycolic acid-leucine ligand was synthesized. After being left in the concentrated solution for a short while, the ligand crystallizes, is cleaned with ethanol, and is then dried on anhydrous $CaCl_2$. A melting point of 260^0C was discovered. The heated ethanolic solution of the ligand solution was mixed with the metal acetate/chloride solution drop wise to create the metal complexes. After adding a pinch of sodium acetate trihydrate, the mixture refluxed for an hour before being allowed to cool to room temperature. After gathering the crystalline precipitate, it was repeatedly cleaned with water and dried in a dessicator.

The Jasco-FT-IR-4100 model spectrophotometer was used to measure the IR spectra of the ligand and its complexes over the frequency range of 400–4000 cm^{-1} using the KBr disc method. The solid complexes' DRS UV-visible spectra were measured using a UV-VIS spectrophotometer model JascoV-550. Using Faraday's method, molar magnetic susceptibilities were measured at room temperature (298K), corrected for diamagnetism using Pascal's constants. Using a Philips conductivity bridge, the complex's molar conductance at a concentration of around 10-3M was measured at 28 ± 2^0C.
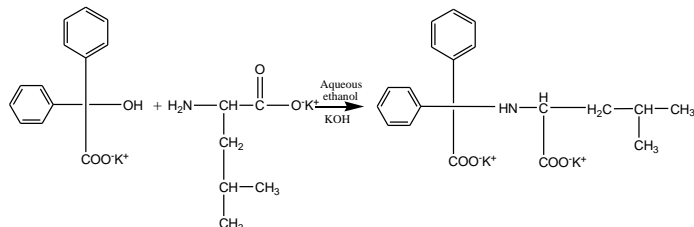
Scheme-1: The reaction pathway of the ligand HBL.

A sample mass of 2–5mg was used for the thermal decomposition investigation, which was conducted in a static air atmosphere at a heating rate of 10^0C per minute. The kinetic parameter was calculated using both mechanistic and non-mechanistic approaches. Plotting the mass loss curve using the instrumental TG values allowed for the examination of the TG curves for the complexes of Cr (III), Ni (II), and Cu (II). The TG curves were used to derive kinetic characteristics such as activation energy, frequency factor, and entropy of activation.

Results and Discussion

Characterization of ligand and its metal complexes: The structure of the newly synthesized ligand and its metal complexes was validated through a series of analytical and spectroscopic studies. Using spectral data and CHN analysis, the ligand was described. It was discovered to have a melting point of 260^0C. Micro analytical techniques were used to calculate the percentages of hydrogen, carbon, and nitrogen. The stoichiometry of all the compounds was determined to be 1:1 and 1:2. Here, diphenyl glycolic acid-leucine (HBL) functions as a bidentate ligand in the interaction with ions of typical transition metals. There was a good agreement between the observed and computed percentages of nitrogen, hydrogen, and carbon.

Electronic spectra and magnetic moments: The distinctive bands were visible in the ligand's UV and IR spectra. The complexes were found to be non-electrolytic based on their molar conductance values in methanol at a concentration of 1x 10^{-3} M at 28 ± 2^0C. The ligand in the Cr (III) combination has a magnetic moment of 1.56BM. The Cr (III) complex can be attributed to octahedral geometry since the measured μ_{eff} value falls between 1.2-2.5BM.

Depending on the size of the orbital contribution, the magnetic moment value of the Ni (II) complex is 3.2, which is extremely near to the spin-only value of octahedral complexes (2.9 – 3.4BM). Thus, the Ni (II) complex can also be given an octahedral geometry.

Cu (II) complex produces a magnetic moment value of 1.42BM, which is consistent with the octahedral shape expected for one unpaired electron in the d^9 electronic configuration. Results from measurements of magnetic susceptibility were found to be consistent with the electronic spectral data.

Chromium (III) ion is having d^3 configuration and they exhibits three spin-allowed transitions i.e. ^4A_2g (F) $\rightarrow$ ^4T_2g (F) (v$_1$), ^4A_2g (F) $\rightarrow$ ^4T_1g (F) (v$_2$), ^4A_2g (F) $\rightarrow$ ^4T_1g (P) (v$_3$) at 251nm, 430 nm and 575nm respectively suggesting the octahedral stereochemistry of the chromium complexes.

In this study nickel (II) complexes having bands in the region 666 nm and 392 nm assigned to the transition ^3A_2g (F) $\rightarrow$ ^3T_1g (P) and $\pi\rightarrow\pi^*$ transition respectively suggesting the octahedral stereochemistry of the Ni(II) chelates. The broad band in the region of 478-700nm is assignable to d-d transition which is in agreement with an octahedral geometry of the Cu (II) complex.

IR spectra of the ligand and its complexes: The characteristic IR spectra of the metal complexes of the spectra are given in Table-2. The IR band in the region 3500-3100cm^{-1} due to υ (OH) of coordinated in the metal complexes indicating that the hydrogen atom of the H_2O group is attached to the metal.

Table-1: Micro analytical, magnetic moment and conductance data of HBL ligand and its transition metal complexes.

Compound	Molecular Weight	Melting point	Colour	Yield	Ω^{-1}	μ_{eff}	M%
$C_{20}H_{23}NO_4$ (HBL)	341.41	260^0	White	80	2.8	-	-
$Cr(BL)(H_2O)_2)(CH_3COO)_2$	487.99	$>300^0$	Dark green	70	6.5	1.56	10.69(10.65)
$Ni(BL)_2(H_2O)_2$	776.69	$>300^0$	Bluish green	60	8.5	3.27	7.55(7.38)
$Cu(BL)(H_2O)_2)(CH_3COO)_2$	558.55	$>300^0$	Grey	70	7.2	1.42	11.37(11.42)

Table-2: Selected IR frequencies (cm^{-1}) of HBL ligand and its transition metal complexes.

Compound	$\upsilon(O\text{-}H)$	$\upsilon(N\text{-}H)$	$\upsilon(COO_{asymm})$	$\upsilon(COO_{symm})$	$\upsilon(H_2O)$	$\upsilon(M\text{-}O)$
$C_{20}H_{23}NO_4$ (HBL)	-	3398	1617	1388	-	-
$Cr(BL)(H_2O)_2)(CH_3COO)_2$	-	3411	1629	1385	835	543
$Ni(BL)_2(H_2O)_2$	3641	3357	1636	1409	828	547
$Cu(BL)(H_2O)_2)(CH_3COO)_2$	-	3318	1610	1396	853	571

The C-O stretch at $1172cm^{-1}$ is red shifted to $1100\text{-}1150cm^{-1}$ suggests the participation of enolic –OH in the complexation. The bands at $1617cm^{-1}$ and $1388cm^{-1}$ assigned to the $\upsilon(COO_{asymm})$ and $\upsilon(COO_{symm})$ respectively, a shift from the values indicates the binding of oxygen in carboxylate group when coordinate to the metal ion. The difference between $\upsilon(COO_{asymm})$ and $\upsilon(COO_{symm})$ is greater than $140\ cm^{-1}$ suggesting unidentate nature of acetate group. New absorption bands in the region $460\text{-}600cm^{-1}$ assigned to $\upsilon(M\text{-}O)$ stretching vibrations.

Thermal analysis of the complexes: The thermal analysis of the metal complexes was studied at a heating rate of $10^0C\ min^{-1}$ under air atmosphere and the weight loss was measured from ambient temperature to 1000^0C. Based on Coats Redfern and Horowitz Metzger methodologies, the interpretation and mathematical analysis of the thermal decomposition data are explained, along with the evaluation of the sequence of reaction, entropy change, energy of activation, and Arrhenius factor.

The nine mechanistic equations have been used to evaluate the reaction mechanism utilizing non-iso thermal approaches. Thermal experiments using non-isothermal methods were conducted on complexes of Cr (III), Ni (II), and Cu (II). Cr (III) and Cu (II) complexes show two stage decomposition, whereas Ni (II) complexes show three stages of decomposition. By using X-ray diffraction analysis, the oxides Cr_2O_3, Ni O, and Cu_2O are found to be the ultimate products of breakdown in each of these cases. From the TG curves, the total mass loss is comparable.

Two step decomposition patterns were observed for the Cr (III) complex of HBL ligand among which the first stage of decomposition stands for the removal of two coordinated acetate molecules and one coordinated water. The second stage corresponds to the removal of the one coordinated water and Diphenyl glycolic acidic part and leucine part of the HBL ligand. From the thermal data an overall weight loss of 69.37%, while the theoretical weight loss during decomposition of the complex is 71.1%. Their DTA pattern suggests an endothermic curve for the decomposition.

Two step decomposition patterns were observed for the Cu (II) complex of HBL ligand among which first stage of decomposition stands for the removal of one coordinated water. The second stage corresponds to the removal of the one coordinated water and Diphenyl glycolic acidic part and leucine part of HBL ligand. From the thermal data an overall weight loss of 69.24%, while the theoretical weight loss during decomposition of the complex is 72.50%. Their DTA pattern suggests an endothermic curve for the decomposition.

Three step decomposition patterns was observed for Ni (II) complex of HBL ligand among which first stage of decomposition stands for the removal of two coordinated water molecule. The second stage corresponds to the removal of the one coordinated water and diphenyl glycolic acidic part and leucine part of HBL ligand. From the thermal data an overall weight loss of 59.92%, while the theoretical weight loss during decomposition of the complex is 62.18%. Their DTA pattern suggests an endothermic curve for the decomposition.

The decomposition pattern of the above discussed complexes is depicted in Table-3 and their TG-DTA curve was shown in Figure-1-3.

Table-4,5 provide an overview of the kinetic parameters for these decomposition processes, which are derived from the TG curves and based on the nine mechanistic equations as well as the two non-mechanistic equations. These kinetic parameters include activation energy (ΔE), Arrhenius factor A, order parameter (n), and entropy of activation (ΔS). The relative thermal stability of the three chelates mentioned above can be expressed as follows: $[CrBL(H_2O)_2(CH_3COO)_2]$ < $[CuBL(H_2O)_2(CH_3COO)_2]$ < $[NiBL_2(H_2O)_2]$, based on experimental results from the current investigations.
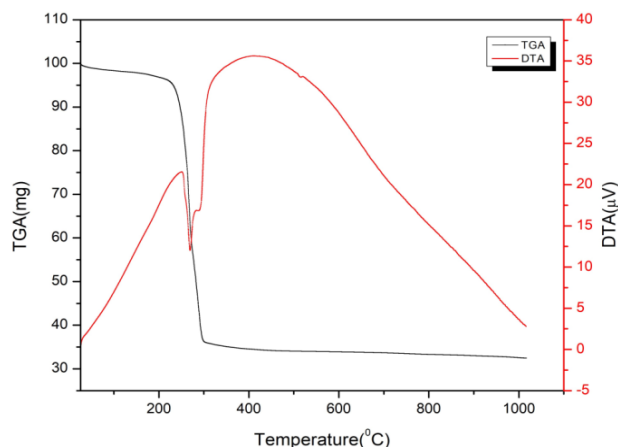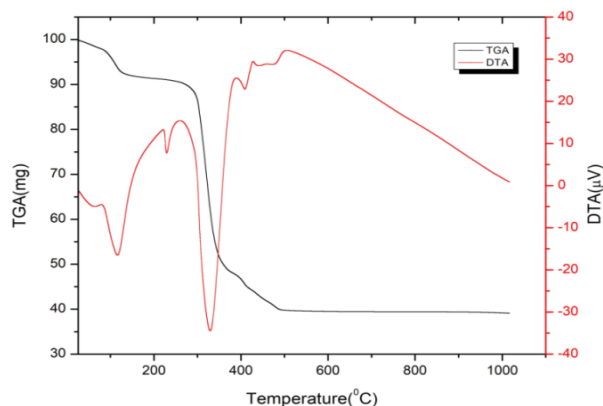

Figure- 2: TG-DTA curve of NiBL.
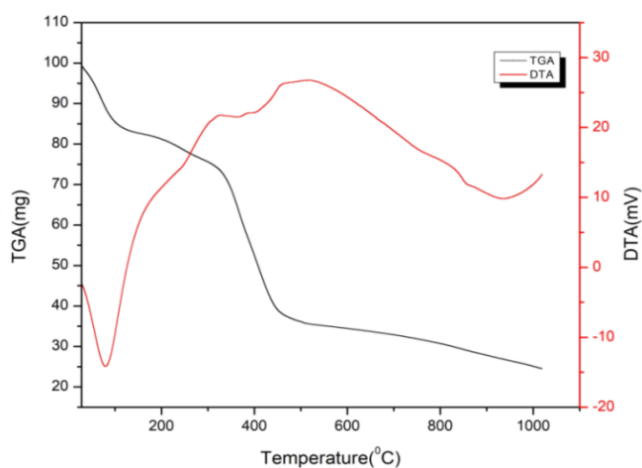

Figure- 1: TG-DTA curve of CuBL.

Figure-3: TG-DTA curve of CrBL.

Table-3: Thermal Decomposition Data of Cr (III), Ni (II) and Cu (II) Complexes of Diphenyl Glycolic Acid - L – Leucine.

Complex	Stage	Temp range	Peak temp	Loss of mass %		Probable assignment. Loss of
				TG	Theoretical	
$[CrBL(H_2O)_2(CH_3COO)_2]$ (487.99)	I	38-288	78	23.67	27.86	$2CH_3COO+1H_2O$
	II	288-798	368	45.70	46.92	$1H_2O + 2C_6H_5+2CH_3+CH+CH_2$
				69.37	71.1	$[CrBL(H_2O)_2(CH_3COO)_2]\rightarrow Cr_2O_3$
$[CuBL(H_2O)_2(CH_3COO)_2]$ (558.55)	I	36.75-186.75	46.75	2.75	3.22	$1H_2O$
	II	186.75-1016.75	266.75	67.49	69.28	$1H_2O+ 2CH_3COO$ $2C_6H_5+C+CO+2CH_3+2CH+CH_2$
				69.24	72.50	$[CuBL(H_2O)_2(CH_3COO)_2]\rightarrow Cu_2O+$ impurities
$[Ni(BL)_2(H_2O)_2]$ (487.55)	I	36.41-266.41	266.41	9.7017	10.1713	$2H_2O+2CH_3+CH$
	II	266.41-326.41	326.41	25.547	26.7803	$2C_6H_5+C+NH+CH+CH_2$
	III	326.41-486.41	336.41	24.683	25.2352	$2C_6H_5+C+2CH_3$
				59.92	62.18	$[Ni(BL)_2(H_2O)_2]\rightarrow NiO+$ impurities

Table-4: Kinetic parameters for the decomposition of Cr(III), Ni (II) and Cu (II) complexes of Diphenyl Glycolic Acid - L – Leucine from TG using mechanistic equations.

Complex		Mechanistic equations								
		1	2	3	4	5	6	7	8	9
[CrBL(H$_2$O)$_2$ (CH$_3$COO)$_2$]	E	3130.939669	3231.645846	3336.069921	3266.443603	896.2404862	896.2404862	896.2404862	817.5410375	843.5372805
	A	-12.2065042	-12.7199732	-14.0385101	-14.1622192	-12.8710073	-13.5641545	-13.9696196	-13.7039088	-14.0631624
	ΔS	-111.870472	-112.827829	-115.384572	-115.672291	-115.676337	-117.053621	-117.85928	-117.513933	-118.165571
	r	-0.74481107	-0.75277369	-0.76067151	-0.75545573	-0.51590595	-0.51590595	-0.51590595	-0.4853985	-0.49574246
[CuBL(H$_2$O)$_2$ (CH$_3$COO)$_2$]	E	2935.325342	2948.625848	2961.984923	2953.078854	740.8011639	740.8011639	740.8011639	730.7763085	734.1142586
	A	-15.9504689	-16.6192797	-18.0989264	-18.1152136	-14.8752939	-15.5684411	-15.9739062	-15.5867733	-15.9861334
	ΔS	-119.096309	-120.416253	-123.347329	-123.385675	-119.69572	-121.073003	-121.878662	-121.136501	-121.920975
	r	-0.95126108	-0.95161358	-0.9519636	-0.95173076	-0.82709369	-0.82709369	-0.82709369	-0.82368975	-0.82483377
[Ni(BL)$_2$ (H$_2$O)$_2$]	E	25923.98	27058.73038	28267.12578	27461.1777	13618.61704	13618.61704	13618.61704	12704.28413	13004.29866
	A	6.716571142	7.097722766	6.735509367	5.973946899	-2.29673548	-2.98988267	-3.39534777	-3.85364631	-3.97555924
	ΔS	-69.9368354	-69.0943612	-69.7272676	-71.2979686	-89.1253682	-90.5026516	-91.3083108	-92.3570435	-92.5529065
	r	-0.93147842	-0.9299758	-0.92836158	-0.92942902	-0.9161077	-0.9161077	-0.9161077	-0.91801556	-0.91738586

Table-5: Kinetic parameters for the decomposition of Cr (III), Ni (II), and Cu (II) complexes of Diphenyl Glycolic Acid - L – Leucine using non mechanistic equations.

Complex	Parameter	Coats Redfern	Horowitz Metziger	Mechanistic equation followed	Order of reaction
[CrBL(H$_2$O)$_2$(CH$_3$COO)$_2$]	E	843.5372805	5307.167734	Phase boundary reaction; Spherical symmetry	2/3
	A	-12.9645501	-0.5112037		
	ΔS	-58.3707238	-55.1882997		
	r	-0.49574246	0.806760129		
[CuBL(H$_2$O)$_2$(CH$_3$COO)$_2$]	E	734.1142586	4445.665138	Phase boundary reaction; Spherical symmetry	2/3
	A	-14.8875211	-2.780904		
	ΔS	-119.738032	-113.817473		
	r	-0.82483377	0.962451011		
[Ni(BL)$_2$(H$_2$O)$_2$]	E	13004.29866	17136.67431	Phase boundary reaction; Spherical symmetry	2/3
	A	-2.87694695	-0.976885		
	ΔS	-90.3699639	-112.913689		
	r	-0.91738586	0.947180588		

Conclusion

The synthesis, spectral analysis, and thermal analysis of recently synthesized transition metal ion complexes of the diphenyl glycolic acid-L-leucine molecule were reported in the current work. The coordination ability of the ligands in complexation reactions with Cr(III), Cu(II), and Ni(II) ions has been demonstrated by spectroscopic studies, and an octahedral geometry has been proposed for all of the above mentioned complexes. The thermal analysis of metal complexes revealed a three-step mechanism for the Ni(II) complex and a two-step mechanism for the Cr(III) and Cu(II) complexes. The activation energy and frequency factors were found to have the same values from both the mechanistic and non-mechanistic equations.

The stability order of the complexes is $[CrBL(H_2O)_2(CH_3COO)_2]$ $<[CuBL(H_2O)_2(CH_3COO)_2]$ $<$ $[Ni(BL)_2(H_2O)_2]$ and they are found to be highly stable in nature. The current work reveals that the two stage decomposition pattern of the $[CrBL(H_2O)_2(CH_3COO)_2]$ and $[CuBL(H_2O)_2(CH_3COO)_2]$ complexes, as well as the three stage decomposition pattern of the $[Ni(BL)_2(H_2O)_2]$ complex with n = 2/3, which is derived from the Coats – Redfern equation, have the highest correlation when explained by the R3 mechanism based on phase boundary reaction and spherical symmetry. The decomposition pattern is suggested by endothermic curves in DTA curves.

Acknowledgments

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