

The Kinetic and Thermal Degradation Studies of N-(4-Acetyl-phenyl)-acetimidic Acid Pyridine-3-yl ester Metal(II) Complexes

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Schiff base complexes of transition metals are of particular interest to inorganic chemists because of their structural, spectral and chemical properties, which are often strongly dependant on the nature of the ligand structure. Large number of metal(II) complexes with Schiff-base ligands has been extensively studied for their interesting structural specialties, applications and properties. The coordination complexes of $[\text{Co}(\text{C}_{15}\text{H}_{15}\text{N}_2\text{O}_2)_2(\text{H}_2\text{O})_2] \cdot \text{Cl}_2 \cdot 2\text{H}_2\text{O}$ and $[\text{Cu}(\text{C}_{15}\text{H}_{15}\text{N}_2\text{O}_2)_2(\text{H}_2\text{O})_2] \cdot \text{Cl}_2$ with the Schiff base N-(4-Acetyl-phenyl)-acetimidic acid pyridine-3-yl ester derived from 4-aminoacetophenone with 3-acetoxypyridine have been synthesized and characterized by micro analytical data; FT-ir, UV-Vis, FAB- mass and thermal analysis studies. Thermal data show degradation of complexes. We carried out thermal analysis at 10 °C. The activation thermodynamic parameters, such as activation energy (E^*), entropy of activation (ΔS^*), enthalpy of activation (ΔH^*) and Gibbs free energy (ΔG^*) have been calculated with the help of TG, DTA and DTG curves using Coats-Redfern (C-R) method. The stoichiometry of the complexes are in 1:2 (M:L) molar ratio. Synthesized complex has been tested for their reactivity and substitution behavior.

Keywords: Thermal analyses, 4-Aminoacetophenone, 3-Acetoxypyridine and N-(4-acetyl-phenyl)-acetimidic acid pyridine-3-yl ester complex

INTRODUCTION

The thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) techniques are in use over many decades in studying the thermal behavior and properties of various types of materials and in evaluating the solid state kinetic parameters [1,2]. The evaluation of the kinetic parameters has often been done by using a single thermogravimetric curve (TG curve) recorded at a certain heating rate. Some recent results on thermal and thermo-oxidative degradation of polymeric materials/metal complexes/medicinal plants studied by thermo analytical methods (TG, DTG, DTA and DSC) have been reported [3, 4]. These reports show that these kinetic parameters evaluated for each step of degradation processes have been

carried out by using the integral methods based on a reaction order model for a single TG curve [5]. Schiff base complexes of transition metals are of particular interest to inorganic chemists because of their structural, spectral and chemical properties, which are often strongly dependant on the nature of the ligand structure. Large number of metal(II) complexes with Schiff-base ligands has been extensively studied for their interesting structural specialties [6-12], applications and properties [12-19]. The thermal decomposition of transition metal complexes with Schiff-base ligands have been extensively studied in recent years [5-9]. From the survey of existing literature, it appears that Schiff base and metal complexes have a variety of applications in biological and industrial fields. Keeping the above facts in the mind and in continuation of our research work on transition metal complexes with Schiff bases, we report herein the bi-dentate N-(4-acetyl-phenyl)-acetimidic acid pyridine-3-yl ester Schiff bases, derived from the

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Table 1. Analytical and Physical Data of the N-(4-Acetyl-phenyl)-acetimidic Acid Pyridine-3-yl ester Metal(II) Complexes

Comp.	Mw./[Mp./ Decomp. Temp. °C]	Color/Yield (%)	Elemental% [obs./calc.]				Molar Conduc. (S ⁻¹)
			C	H	N	Metal	
[C ₁₅ H ₁₅ N ₂ O ₂] (AAP)	255/100	Wine red/90	70.69 (70.60)	5.92 (5.95)	10.90 (10.82)	-	-
[Co(AAP) ₂ (H ₂ O) ₂].Cl ₂ .2H ₂ O	746/160	Coffee/83	48.30 (48.20)	5.13 (4.97)	7.51 (7.59)	7.87 (7.68)	107.3
[Cu(AAP) ₂ (H ₂ O) ₂].Cl ₂	678/178	Brown/88	53.14 (52.91)	5.05 (5.16)	8.26 (8.29)	9.37 (9.29)	120.5

condensation of 4-aminoacetophenone with 3-acetoxypyridine and their Co(II) and Cu(II) complex. The present course of study is initiated with the preparation, characterization and Solid state kinetic study at 10 °C heating rate.

EXPERIMENTAL

Apparatus and Reagents

All the used chemicals and solvents were of A.R. grade. Metal(II) chloride was obtained from Aldrich, Fluka, Loba and E-Merck chemie. Elemental analysis were performed microanalytically on Elementar Vario EL III Carbo Erba 1108 model, microanalyzer. I.R. spectra were recorded on Perkin Elmer RX-I spectrophotometer as KBr pellets and UV-Vis absorption spectra were obtained in methanol by Perkin Lambda-2B Spectrophotometer in the range 900-400 nm. FAB-mass spectra were recorded on a JEOL SX 102/DA 6000 Mass Spectrometer using argon/xenon (6 kV, 10 mA) as the FAB gas. Thermal studies of the complex were carried out on Perkin Elmer Thermal Analyzer upto 750 °C I.I.T Roorkee, India.

Synthesis of Schiff Base

The N-(4-acetyl-phenyl)-acetimidic acid pyridine-3-yl ester Schiff base (AAP) has been synthesized by adding the methanolic solution of 4-aminoacetophenone (0.06) with methanolic solution of 3-acetoxypyridine (0.06) in 1:1 equimolar ratio. The reaction mixture was then refluxed for 5-6 h. The volume of solvent was reduced until precipitation began, and the mixture was allowed to stand overnight, after which the colored solid was obtained. It was filtered off, recrystallized thrice with ethanol, finally washed with ether, and dried under reduced pressure over anhydrous CaCl₂ in desiccators. The purity of the synthesized compounds was monitored by TLC using silica gel-G. Schiff base (90% yield) as wine red crystalline solid and melting point is 100 °C.

Synthesis of Complex

The metal(II) complexes have been prepared by mixing the methanolic solution of MCl₂.nH₂O (0.005) with the methanolic solution of Schiff base (0.010mole) in 1:2 molar ratio. The resulting mixture was refluxed on water bath for 8-9 h. The volume of solvent was reduced until precipitation began, and the mixture was allowed to stand overnight, after which the colored solid was obtained. It was filtered off,

recrystallized thrice with ethanol, finally washed with ether, and dried under reduced pressure over anhydrous CaCl_2 in desiccators. The purity of the synthesized complexes was monitored by TLC using silica gel-G.

RESULT AND DISCUSSION

The metal complex is coloured, solid and stable towards air and moisture at room temperature. They decompose on heating at high temperature, more or less soluble in common organic solvents. Analytical data of the compounds, together with their physical properties are consistent with proposed molecular formula (Table 1). The metal chelates have 1:2 (metal:ligand) stoichiometry. The observed molar conductance of the complexes in methanol at room temperature is consistent with the electrolytic nature of the complexes. Table 2 and Table 3 shows the results of typical mass losses of the thermal degradation and non-isothermal based solid state kinetics at $10\text{ }^\circ\text{C min}^{-1}$ heating rate. The kinetics of the non-isothermal decomposition has been considered here, in view of the Coats-Redfern integral method.

FAB-mass Spectra

The FAB-mass spectra suggested that the complexes have a monomeric nature. These complexes show molecular ion peaks in good agreement with the empirical formula suggested by elemental analyses.

The FAB-mass spectrum of $[\text{Co}(\text{C}_{15}\text{H}_{15}\text{N}_2\text{O}_2)_2(\text{H}_2\text{O})_2].\text{Cl}_2.2\text{H}_2\text{O}$ complex (Fig. 2) has been recorded. The FAB-mass spectrum of the complex $[\text{Co}(\text{AAP})_2(\text{H}_2\text{O})_2].\text{Cl}_2.2\text{H}_2\text{O}$ exhibited the molecular ion (M^+) peak at m/z 746. Other important peaks observed at m/z 670, 654, 630, 381 and 129 correspond to the fragmented species after the successive removal of different groups. The m/z value 746 correspond to composition $[\text{Co}(\text{AAP})_2(\text{H}_2\text{O})_2].\text{Cl}_2.2\text{H}_2\text{O}$ and 129 to Co with some chelated-N and -O ligand moiety. The FAB-mass spectrum of the complex $[\text{Cu}(\text{C}_{15}\text{H}_{15}\text{N}_2\text{O}_2)_2(\text{H}_2\text{O})_2].\text{Cl}_2$ (Fig. 3) exhibited the molecular ion (M^+) peak at m/z 678. Other important peaks observed at m/z 600, 589, 568, 315 and 90 correspond to the fragmented species after the successive removal of different groups. The m/z value 678 correspond to composition of $[\text{Cu}(\text{AAP})_2(\text{H}_2\text{O})_2].\text{Cl}_2$ and 120 to Cu with some chelated-N

and -O ligand moiety.

FT-IR Spectra

A careful comparison of spectra of ligand with its complexes results the following information, regarding coordination of various groups. The IR spectra show that the characteristic frequencies of the complexes exhibit significant changes as compared with those of the parent ligand. The IR spectrum of the ligand showed the presence of bands at ~ 1650 and $\sim 3090\text{ cm}^{-1}$ due to the carbonyl ν (C=O) and ν (C-H) stretching vibrations and a strong new bands at $\sim 1630\text{ cm}^{-1}$ assigned to azomethine ν (HC=N) linkage, showing that free amino and ketone moieties of the reactant are absent and have been converted into the Schiff base ligand.

The comparison of IR spectra of the ligand and its metal(II) (Fig. 1) complexes indicated that the ligand is coordinated to the metal ion at two positions, thus acting as a bidentate ligand. The band appearing at $\sim 1630\text{ cm}^{-1}$ due to azomethine has shifted to a lower frequency by $\sim 10\text{-}15\text{ cm}^{-1}$ in complexes, indicating participation of azomethine nitrogen with the metal ion. The band at $\sim 1200\text{ cm}^{-1}$ due to ν (C-O) stretching vibration has shifted to higher frequency by $\sim 8\text{-}10\text{ cm}^{-1}$ in complexes. The complexes show H_2O stretching at $3423\text{-}3430\text{ cm}^{-1}$. A medium intensity band at $847\text{-}854\text{ cm}^{-1}$ (ν -rocking) suggests the presence of coordinated water in complexes. These spectra show M-O and M-N coordination bands at $541\text{-}592$ and $450\text{-}482\text{ cm}^{-1}$.

Electronic Spectra and Magnetic Measurements

The electronic spectra of complexes were recorded in methanol.

The electronic spectrum of $[\text{Co}(\text{C}_{15}\text{H}_{15}\text{N}_2\text{O}_2)_2(\text{H}_2\text{O})_2].\text{Cl}_2.2\text{H}_2\text{O}$ complex shows two bands of appreciable intensity at 12484 cm^{-1} and 19607 cm^{-1} ; these have tentatively been assigned to ${}^4\text{T}_{1g}(\text{F})\text{-}{}^4\text{A}_{2g}(\text{F})$ (ν_2) and ${}^4\text{T}_{2g}(\text{F})\text{-}{}^4\text{T}_{1g}(\text{P})$ (ν_3) respectively. First band ν_1 could not be observed here due to instrumental limitations. The various ligand field parameters *viz.* 10 Dq , B , β , $\beta\%$, λ , ν_2/ν_1 and LFSE have been calculated and values are as: 6935 cm^{-1} , 1029 cm^{-1} , 0.91, 8.12, (-512), 2.2 cm^{-1} and 66.28 kJ mol^{-1} , respectively. The magnetic moment value for Co(II)-complex is 5.07 B.M., which favors octahedral geometry. The electronic spectrum of $[\text{Cu}(\text{C}_{15}\text{H}_{15}\text{N}_2\text{O}_2)_2(\text{H}_2\text{O})_2].\text{Cl}_2$ complex shows

Table 2. Non-isothermal Kinetic Parameters of N-(4-Acetyl-phenyl)-acetimidic Acid Pyridine-3-yl Ester Metal(II) Complexes

Com.	Decom. step/ Temp. (°C)	Non-isothermal kinetic parameters (J mol ⁻¹)			
		E*	ΔS*	ΔH*	- ΔG*
Co(AAP)	I/50-299	2.457	-301.018 × 10 ⁻³	-4.753	167.429 × 10 ⁻³
	II/299-481	7.249	-304.316 × 10 ⁻³	-6.262	223.193 × 10 ⁻³
	III/481-750	31.002	-328.395 × 10 ⁻³	-8.474	327.474 × 10 ⁻³
Cu(AAP)	I/50-300	2.464	-300.690 × 10 ⁻³	-4.761	167.534 × 10 ⁻³
	II/300-500	8.291	-305.624 × 10 ⁻³	-6.418	229.828 × 10 ⁻³
	III/500-750	34.054	-330.652 × 10 ⁻³	-8.471	329.785 × 10 ⁻³

Table 3. Thermal Degradation of N-(4-Acetyl-phenyl)-acetimidic Acid Pyridine-3-yl Ester Metal(II) Complexes

Complex	TG-range (°C)	Remaining wt. loss (%) Obs./cal.	DTA- peak (°C)	DTG-peak (°C)
	100-198	90.1/90	-	-
	198-299	77.3/77.5	-	-
	299-399	63.8/63.0	303-Exothermic	-
	399-481	56.3/56.8	-	-
	481-601	47.3/47.6	-	492
	601-712	16.8/16.5	658-Exothermic	662
Cu(AAP)	23-184	99.0/99.1	-	-
	184-215	90.1/90.1	202-Exothermic	204, 205
	215-300	59.1/59.3	269-Exothermic	-
	300-401	50.4/50.8	-	-
	401-500	46.5/46.8	-	-
	500-600	25.1/25.6	578-Exothermic	509, 577
	600-651	9.6/9.11	614-Exothermic	-
	651-709	8.8/8.3	-	-

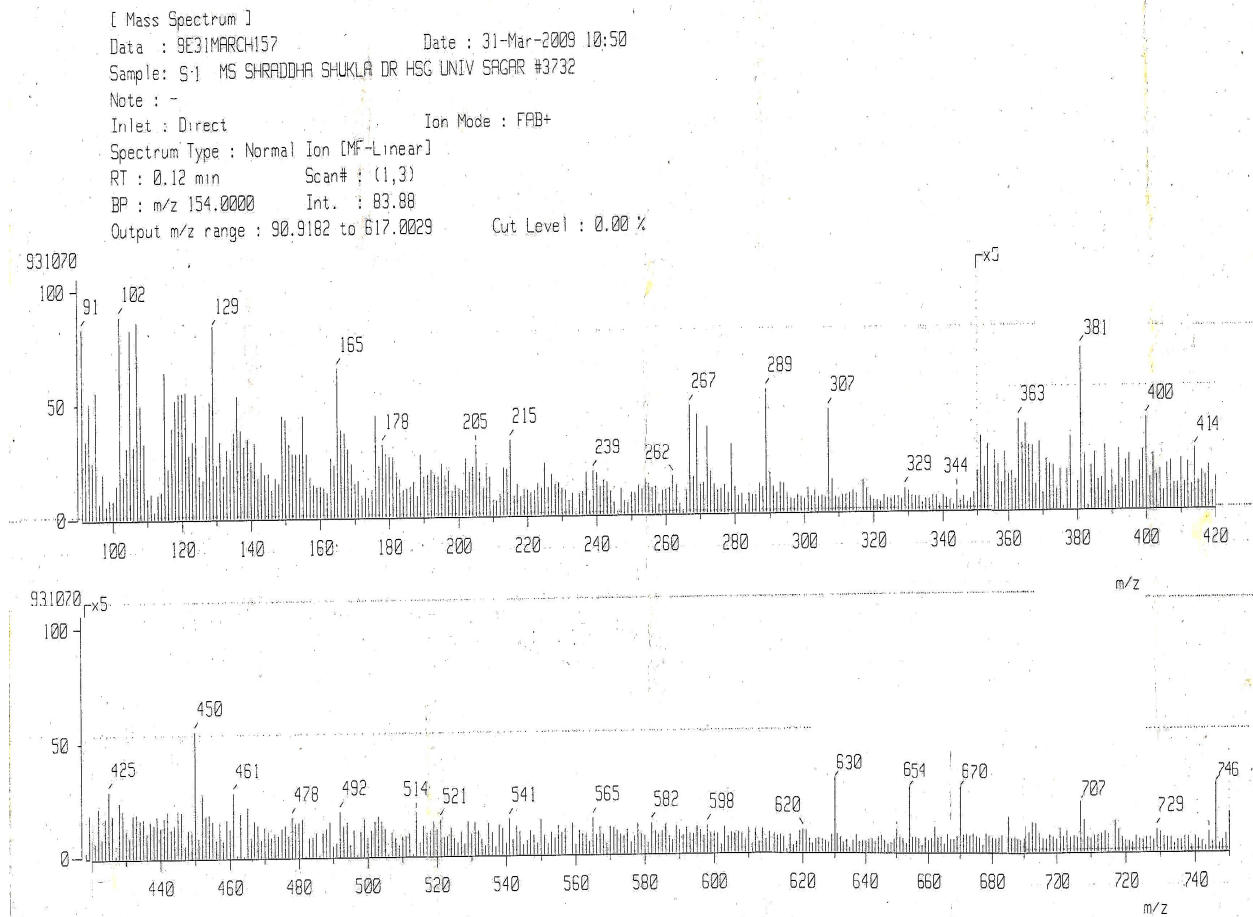


Fig. 2. FAB-MASS Spectrum of Co(AAP) complex.

a single broad band at $12314\text{--}16570\text{ cm}^{-1}$, corresponding to transitions ${}^2E_g\text{--}{}^2T_{2g}$ respectively. The various ligand field parameters *viz.* $10 Dq$, λ and LFSE have been calculated and values are as: 12314 cm^{-1} , $(-678)\text{ cm}^{-1}$ and 86.05 kJ mol^{-1} respectively. The magnetic moment value for Cu(II) complex is 1.92 B.M., nature of spectrum and other parameters suggest the geometry to be distorted octahedral.

Thermal Analysis

A general decomposition pattern was concluded, whereby the complex decomposed in four stages. The decomposition of complex began at $50\text{ }^\circ\text{C}$. From the TG curve of $[\text{Co}(\text{C}_{15}\text{H}_{15}\text{N}_2\text{O}_2)_2(\text{H}_2\text{O})_2]\cdot\text{Cl}_2\cdot 2\text{H}_2\text{O}$ and

$[\text{Cu}(\text{C}_{15}\text{H}_{15}\text{N}_2\text{O}_2)_2(\text{H}_2\text{O})_2]\cdot\text{Cl}_2$ complex, it appears that the sample decomposes in three stages over the $50\text{--}750\text{ }^\circ\text{C}$ temperature range. All data shows the first step from corresponding loss of water molecules, second step partial decomposed the organic part of complex and loss of metal-chloride moiety and third step loss of metallic and carbon residue is the final product. All data are summarized in Table 2 and 3.

Activation Thermodynamic Parameters

The thermodynamic activation parameters of decomposition processes of dehydrated complexes, such as activation energy (E^*), entropy of activation (ΔS^*), enthalpy of activation (ΔH^*) and Gibbs free energy

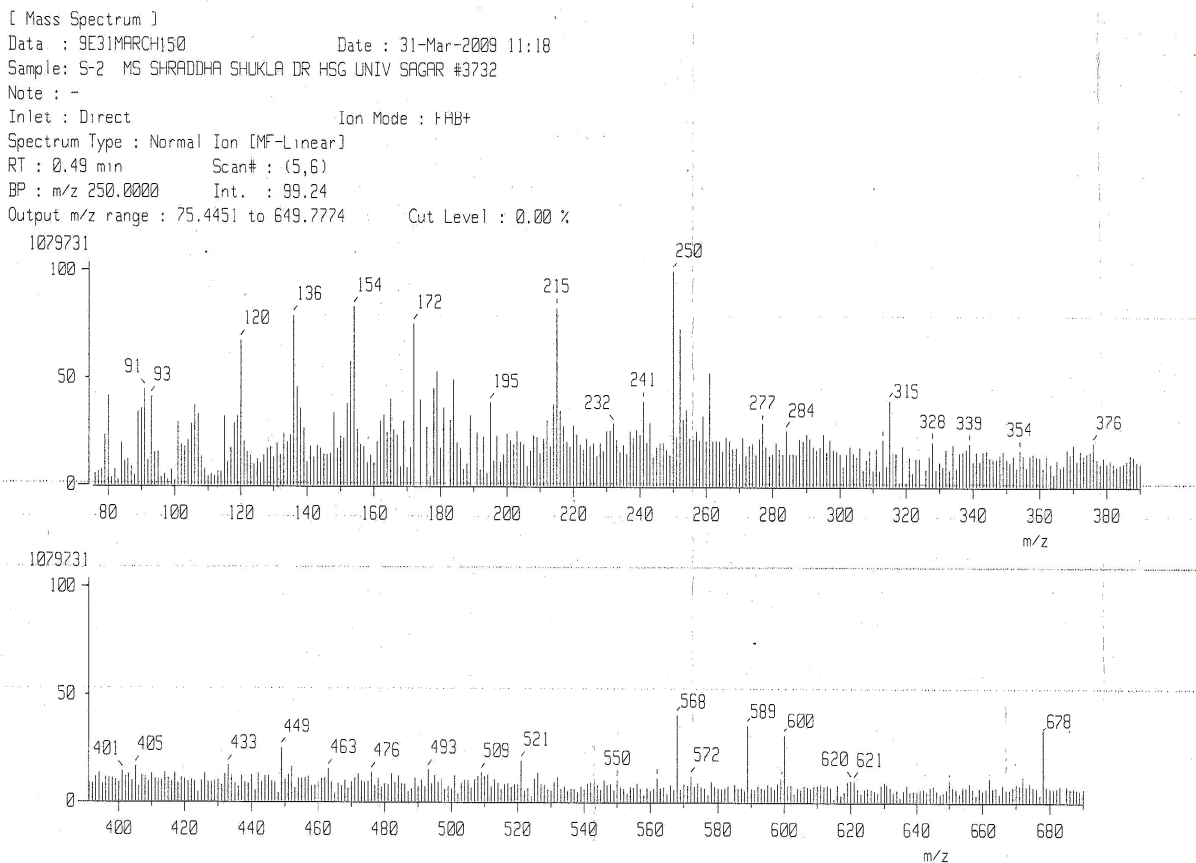


Fig. 3. FAB-MASS Spectrum of Cu(AAP) complex.

(ΔG^*) are calculated from the TG curves using Coats-Redfern (C-R) equation [21,22].

$$\log(\alpha)/T^2 = \log[-\ln(1-\alpha)/T^2] = E/2.303 RT$$

The function $g(\alpha)$ is defined as $g(\alpha) = \ln(1 - \alpha)$. The symbol α denotes the fraction decomposed at any temperature, β is the heating rate and T is temperature in $^{\circ}\text{K}$. The degree of conversion α is measured as $\alpha = m_0 - m_t / m_t - m_{\infty}$. Where m_0 , m_t and m_{∞} are the actual, the initial and the final mass loss of the sample up to temperature.

$$E^* = -\text{slope}(2.303R)$$

$$\Delta S^* = 2.303[\log(zh/kT)]R$$

$$\Delta H^* = E^* - RT$$

$$\Delta G^* = \Delta H^* - T\Delta S^*$$

Where h = plank constant = 6.6×10^{-37} , k = boltzman constant = 1.38×10^{-26} , R = gas constant = 8.314×10^{-3} , Z = arrhenius factor.

The data are summarized in Table 2. The Co(II)-shiff base complex (Fig. 4) shows difference of I-step to III-step. The $[\text{Co}(\text{C}_{15}\text{H}_{15}\text{N}_2\text{O}_2)_2(\text{H}_2\text{O})_2] \cdot \text{Cl}_2 \cdot 2\text{H}_2\text{O}$ complex shows difference in I-step to III-step. It can be seen that values of activation energy vary from 2.457 to 31.002 J mol^{-1} . The high value of the activation energies reflects the thermal stability of the complexes. The entropy also varies from -301.018×10^{-3} to $-328.690 \times 10^{-3} \text{J mol}^{-1}$. The entropy of activation had negative values in all stages, which indicates

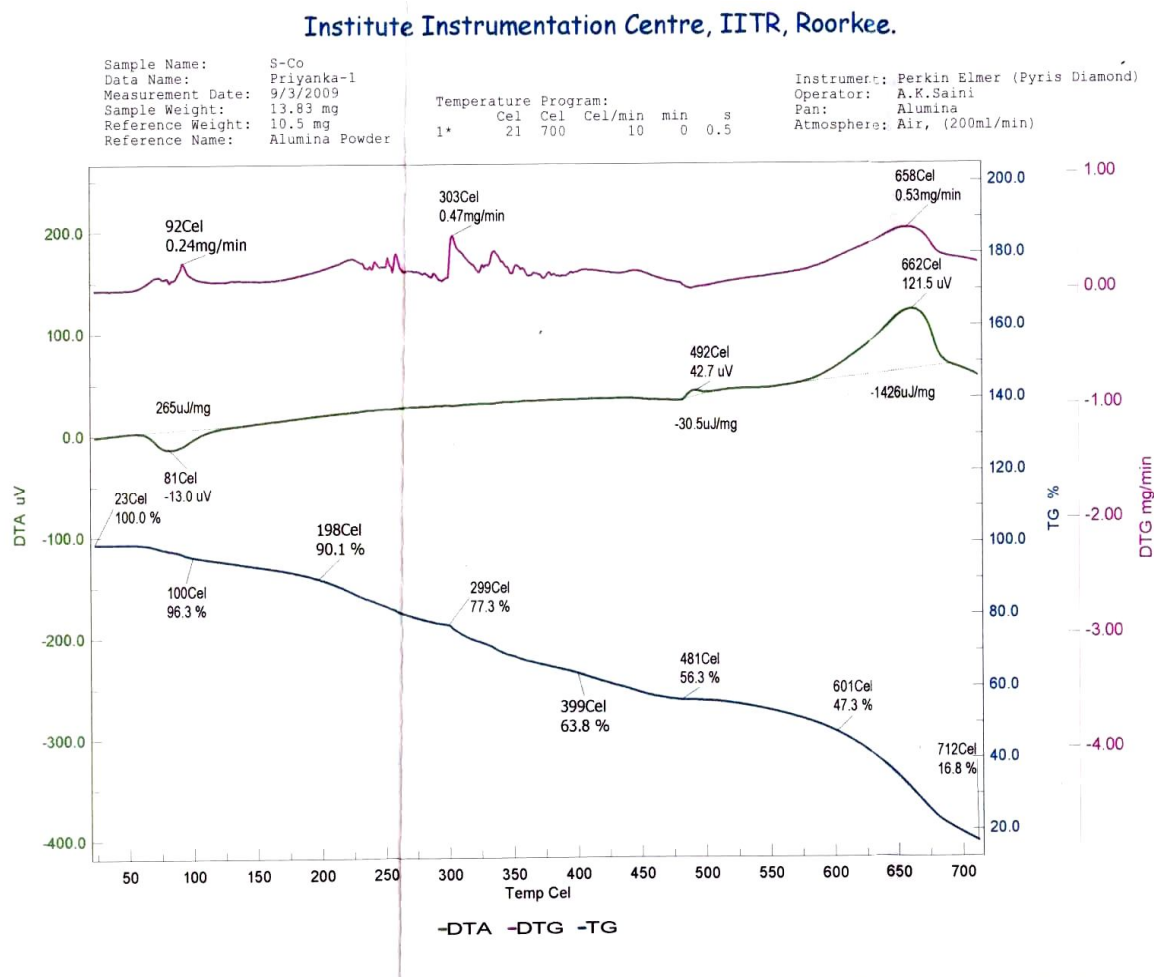


Fig. 4. DTA-DTG-TG curve of Co(AAP) complex.

that the decomposition reactions proceed with a lower rate than the normal ones. The enthalpy varies from -4.758 to $-8.474 \text{ J mol}^{-1}$. The Gibbs free energy varies from 167.429×10^{-3} to $327.474 \times 10^{-3} \text{ J mol}^{-1}$. The $[\text{Cu}(\text{C}_{15}\text{H}_{15}\text{N}_2\text{O}_2)_2(\text{H}_2\text{O})_2] \cdot \text{Cl}_2$ complex (Fig. 5) also shows difference of I-step to III-step. It can be seen that values of activation energy vary from 2.464 to $34.054 \text{ J mol}^{-1}$. The high value of the activation energies reflects the thermal stability of the complexes. The entropy also varies from -300.69×10^{-3} to $-330.652 \times 10^{-3} \text{ J mol}^{-1}$. The entropy of activation had negative values in all stages, which indicates that the decomposition reactions proceed with a lower rate than the normal ones. The enthalpy varies from -4.761 to $-8.471 \text{ J mol}^{-1}$. The Gibbs free energy varies from $167.534 \times$

10^{-3} to $329.785 \times 10^{-3} \text{ J mol}^{-1}$.

The values of obtained kinetic parameters are quite consistent which indicate that the similar types of chemical changes. Generally with decreasing value of E , the value of Z increases. The higher value of activation energy suggest the higher stability. Higher value of E and lower value of Z favours the reaction to proceed slower than normal. The large negative values of entropy of activation and enthalpy suggest that the transition state is a highly ordered state than the individual reactants.

Electron Spin Resonance Spectrum

The ESR spectrum (Fig. 6) of metal complex provides information on the basis of hyperfine and super hyperfine

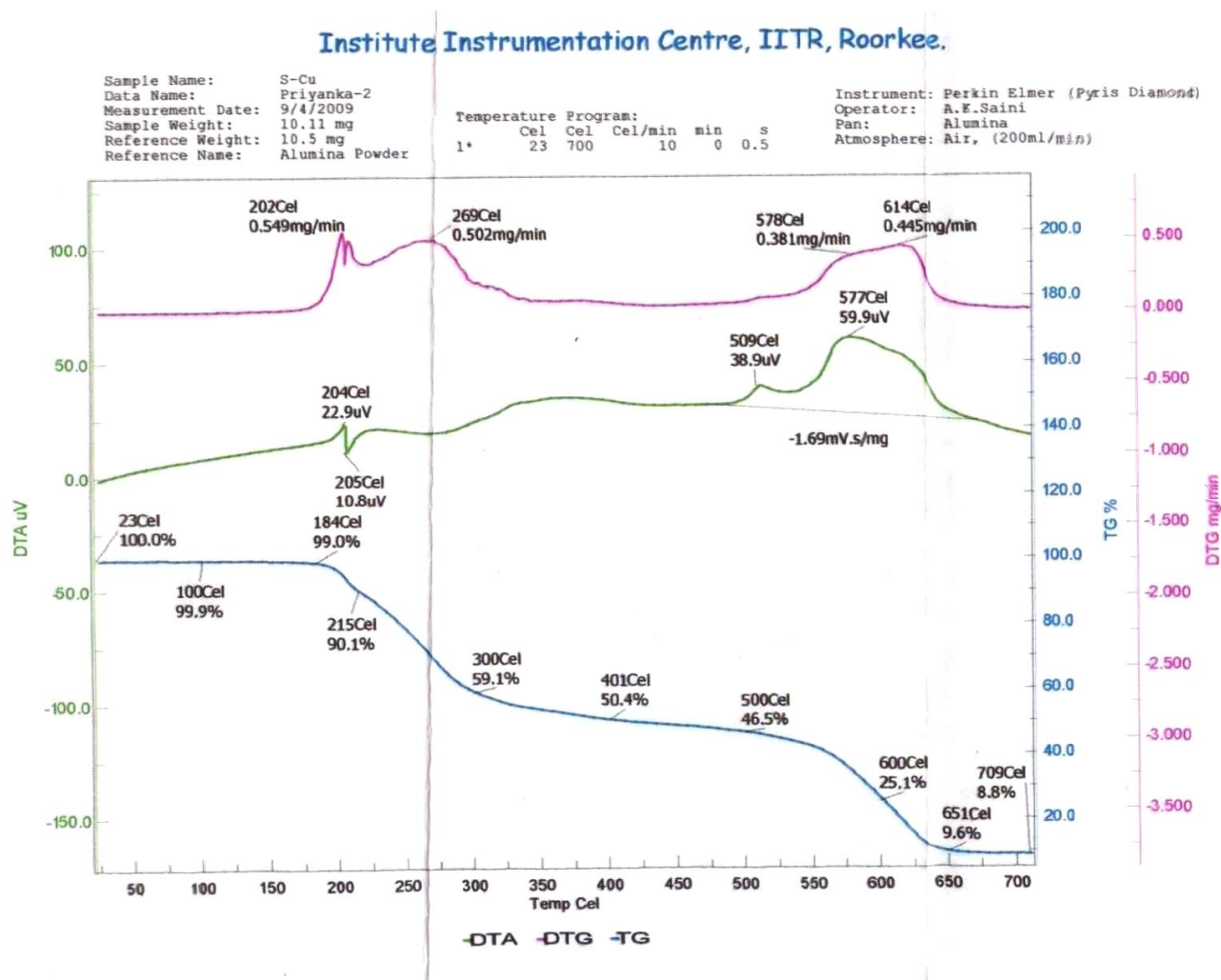


Fig. 5. DTA-DTG-TG curve of Cu(AAP) complex.

structures. This tells about the environment of the metal ion within the complexes *i.e.* the geometry and nature of the ligating sites of the Schiff bases and corresponding metal ions. For Cu(II) in most environments, the ground state magnetism is essentially spin only and the orbital motion is said to be "quenched". Since Cu(II) has one unpaired electron in its $3d^9$ configuration, the "effective" spin is equal to the actual spin of the free ion $S = 1/2$. The Zeeman splitting, or g factors are shifted from the free-electron value of 2.2-0.09 by spin-orbit coupling of the ground state to excited states. The ESR spectrum of $[\text{Cu}(\text{C}_{15}\text{H}_{15}\text{N}_2\text{O}_2)_2(\text{H}_2\text{O})_2] \cdot \text{Cl}_2$ complex has been recorded on X-band. The value of ESR parameters of Cu(II)-AAP

complex, g_{\parallel} , g_{\perp} , g_{av} , Δg and G are given in Table 4. The parameter g_{av} was obtained by equation $[g_{av} = (1/3 g_{\parallel} + g_{\perp})]$. The $g_{\parallel} > g_{\perp}$ indicates covalent character of the metal-ligand bond. The G value indicates the pressure of significant exchange coupling and misalignment of molecular axes [24-27]. The covalent nature of the metal-ligand bond in the complex is further supported by the G value which is < 4.0 , the value $g_{\parallel} > g_{\perp}$ is well consistent with a primarily dx^2-y^2 ground state having elongated tetragonal or square planar structure.

According to Hathway [23,28], if the value of G is greater than four ($G > 4$), the exchange interaction is negligible; whereas when the value of G is less than 4 ($G <$

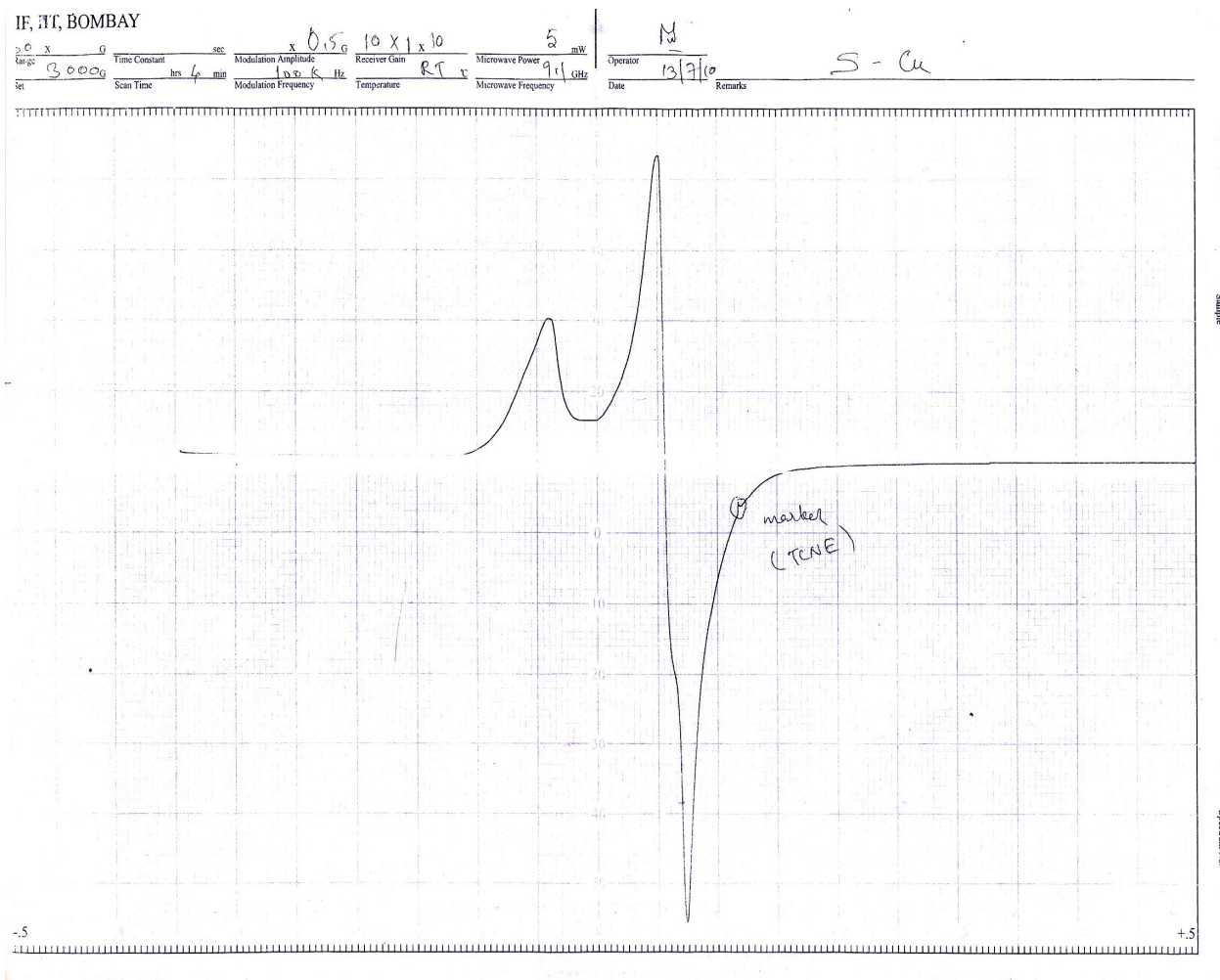


Fig. 6. ESR Spectrum of Cu(AAP) complex.

Table 4. Electronic Spin Resonance Parameters of N-(4-Acetyl-phenyl)-acetimidic Acid Pyridine-3-yl Ester Cu(II) Complexes

Complex	g_{\parallel}	g_{\perp}	g_{av}	Δg	G
Cu(AAP)	2.213	2.123	2.153	0.09	1.74565

4) a considerable exchange interaction is indicated in the complex. The G value of 1.7 indicates considerable exchange interaction in the complex.

CONCLUSIONS

In the present studies, our efforts have been to

synthesize metal(II) Schiff base complexes. These synthesized compounds have been characterized by various physicochemical and spectral analyses. The IR data of both the Schiff base and its metal complex show that the Schiff base are coordinated to the metal ion in bi-dentate manner with N donor sites of azomethine nitrogen and pyrimidine nitrogen. FAB-mass data shows degradation pattern of the complexes. Thermogravimetric studied of the complex also helped to characterize the complex and calculated for non-isothermal kinetics at heating rates $10\text{ }^{\circ}\text{C min}^{-1}$ heating rate. The metal(II) Schiff base complexes are showing that the activation energy for first step is less than other steps. Same is the trend with entropy, enthalpy and Gibbs free energy. With increasing temperature the activation energy (E^*), entropy of activation (ΔS^*), enthalpy of activation (ΔH^*) and Gibbs free energy (ΔG^*), increases.

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