

Non-isothermal degradation-based solid state kinetics study of copper (II) Schiff base complex, at different heating rates

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Abstract The coordination complex of Cu (II) with the Schiff base derived from 4-chloroaniline with salicylaldehyde 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 three different heating rates viz. 5, 10 and 20 °C per min. 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 method. The stoichiometry of the complexes are in 1:2 (M:L) molar ratio. Synthesized complex has been tested for their reactivity and substitution behaviour.

Keywords Thermal analyses · 4-Chloroaniline · Salicylaldehyde · Non-isothermal kinetics

Introduction

The thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) techniques are in use over many decades in studying the thermal behaviour 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 salicylaldehyde 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 [20–29]. From the survey of existing literature, it appears that 4-chlorosalicylidene aniline and metal complexes have a variety of applications in biological and industrial fields. Keeping the above facts in the mind and in continuation of the research work on transition metal complexes with Schiff bases, we report herein the bidentate Schiff bases, derived from the condensation of 4-chloroaniline with salicylaldehyde and their Cu(II) complex. The present course of study was initiated with the preparation, characterization and solid state kinetic study at different heating rates of Cu(II) complex involving nitrogen donor ligands.

Experimental

Apparatus and reagents

All the used chemicals and solvents were of A.R. grade. Copper (II) chloride was obtained from Aldrich, Fluka,

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Loba and E-Merck chemie. Elemental analysis were performed microanalytically on Elementar Vario EL III Carbo Erba 1108 model, microanalyzer. IR 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 up to 800 °C at Mettler Toledo Mumbai, India.

Synthesis of Schiff base

Schiff base has been synthesized by adding the methanolic solution of salicylaldehyde (0.06) with methanolic solution of 4-chloroaniline (0.06) in 1:1 equimolar ratio. The reaction mixture was then refluxed for 5–8 h (Scheme 1). The volume of solvent was reduced until precipitation began, and the mixture was allowed to stand overnight, after which the coloured solid was obtained. It was filtered off, recrystallized thrice with ethanol, finally washed with ether, and dried under reduced pressure over anhydrous CaCl₂ in desiccator. The purity of the synthesized compounds was monitored by TLC using silica gel-G. Schiff base (90% yield) as yellow crystalline solid and melting point is 110 °C. IR (cm⁻¹): 3421(Ph-OH), 1630(CH=N), 1310(S, CH).

Synthesis of complex

The Cu(II) metal complex has been prepared by mixing the methanolic solution of CuCl₂·2H₂O (0.005) with the methanolic solution of Schiff base (0.010 mol) in 1:2 molar ratio. The resulting mixture was refluxed on water bath for 8–9 h (Scheme 1). The volume of solvent was reduced until precipitation began, and the mixture was allowed to stand overnight, after which the coloured solid was obtained. It was filtered off, recrystallized thrice with ethanol, finally washed with ether, and dried under reduced pressure over anhydrous CaCl₂ in desiccator. The purity of the synthesized compound was monitored by TLC using silica gel-G. Metal complex; 95% yield; dusty yellow crystalline solid; decomposition temp. 148 °C. IR (cm⁻¹): 1380(M-OH), 1620(CH=N), 550(M-N) and 570(M-O).

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 shows the results of typical mass losses of the thermal degradation and non-isothermal based solid state kinetics at different heating rates viz. 5, 10 and 20 °C/min. The kinetics of the non-isothermal decomposition has been considered here, in view of the Coats-Redfern (CR) integral method.

FAB-mass

The FAB-mass spectra suggested that the complex has 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 the [Cu(L)₂]Cl₂·2H₂O complex shows a characteristic molecular ion (M⁺) peak at *m/z* = 633 amu, which corresponds to the molecular weight of the complex for a monomeric structure. The mass spectrum shows multiple peaks representing successive degradation of the complex molecule by the formation of different fragments. The spectrum of complex also shows series of peak at 616, 598, 528, 297 and 66 corresponding to various fragments. The *m/z* value 633 corresponds to nearest composition of the [Cu(L)₂]Cl₂·2H₂O and of 66 corresponds to Cu(II) with chelated N donor as ligand moiety.

FT-IR spectra

The IR spectra show that the characteristic frequencies of the complex exhibit significant changes as compared with those of the parent ligand. The IR spectra of the ligand showed the absence of bands at ~1735 and 3315 cm⁻¹ due to the carbonyl ν (C=O) and ν (NH₂) stretching

Table 1 Analytical and physical data of the metal complex and ligand

Comp.	Mol. mass/mg	Colour/yield/%	Deco. temp./°C	Found/calcd./%				Mag. condu./ Λ_m^a
				C	H	N	Metal	
(C ₁₃ H ₁₀ NOCl)	231.69	Yellow/90	110	67.39/67.46	4.35/4.31	6.05/6.07	–	–
[Cu(C ₁₃ H ₁₀ NOCl) ₂ ·Cl ₂ ·2H ₂ O	633.86	Dusty yellow/95	148	38.83/38.80	2.51/2.49	3.48/3.50	15.78/15.74	120.0

^a $\Lambda_m = \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$

Table 2 Thermal analysis and non-isothermal kinetic parameters of Cu(II) Schiff base complex at different heating rates

Heating rate/K/min	Decomposition stage/temp./°C	Mass loss/% obs./calc.	Non-isothermal kinetic parameters/J mol ⁻¹			
			<i>E</i> *	ΔS^*	ΔH^*	ΔG^*
5	I/50–250	25.80/25.70	-2.946×10^{-3}	-178.03×10^{-66}	-4351.168×10^{-6}	88756.66×10^{-72}
	II/250–320	3.55/3.53	-7.104×10^{-3}	-293.56×10^{-66}	-4937.31×10^{-6}	$169146.74 \times 10^{-72}$
	III/320–500	38.27/38.67	-9.573×10^{-3}	-197.41×10^{-66}	-6436.29×10^{-6}	$146160.87 \times 10^{-72}$
	IV/500–635	22.03/21.26	-63.759×10^{-3}	-221.91×10^{-66}	-7612.87×10^{-6}	$193879.59 \times 10^{-72}$
10	I/50–450	25.36/25.67	-4.203×10^{-3}	-154.95×10^{-66}	-6015.23×10^{-6}	$106013.63 \times 10^{-72}$
	II/450–500	10.95/10.58	-19.147×10^{-3}	-98.53×10^{-66}	-6445.87×10^{-6}	69720.91×10^{-72}
	III/500–550	22.07/22.07	-9.573×10^{-3}	-148.86×10^{-66}	-6851.99×10^{-6}	$115658.88 \times 10^{-72}$
	IV/550–650	30.18/30.06	-67.01×10^{-3}	-179.85×10^{-66}	-7740.83×10^{-6}	$158260.72 \times 10^{-72}$
20	I/50–395	25.44/25.40	-3.350×10^{-3}	-144.06×10^{-66}	-5557.10×10^{-6}	90675.58×10^{-72}
	II/395–495	8.77/8.78	-7.658×10^{-3}	-26.62×10^{-66}	-6392.81×10^{-6}	14052.58×10^{-72}
	III/495–525	10.98/10.90	-19.15×10^{-3}	-91.12×10^{-66}	-6653.72×10^{-6}	66062.44×10^{-72}
	IV/525–750	46.24/46.76	-42.12×10^{-3}	-176.24×10^{-66}	-8547.35×10^{-6}	$171746.17 \times 10^{-72}$

vibrations and a strong new bands at $\sim 1630 \text{ cm}^{-1}$ assigned to azomethine ν (HC=N) linkage, showing that amino and aldehyde moieties of the reactant are absent and have been converted into the ligand, i.e. 4-chlorosalicylidine aniline.

The comparison of IR spectra of the ligand and its Cu(II) complex indicated that the ligand is principally coordinated to the metal ion is two ways, 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 $\sim 115 \text{ cm}^{-1}$ in Cu complex, indicating participation of azomethine nitrogen with the metal ion. A broad band appearing at 3415 cm^{-1} [ν (OH)] in the ligand was no longer found in the spectra of the metal complex. A new band appeared at $\sim 1380 \text{ cm}^{-1}$, indicated deprotonation and coordination of hydroxyl oxygen with the metal ion.

Electronic spectra and magnetic moment

The electronic spectra of metal complexes were recorded in methanol solution. The nature of the ligand field around the metal ion has been deduced from the electronic spectra. The Cu(II) Schiff base complex shows a broad band at $12314\text{--}16570 \text{ cm}^{-1}$ which is attributed to ${}^2E_g - {}^2T_{2g}$ (ν_3) transition. Its magnetic moment is 1.82 B.M. Thus, the octahedral geometry has been suggested for this Cu(II) complex.

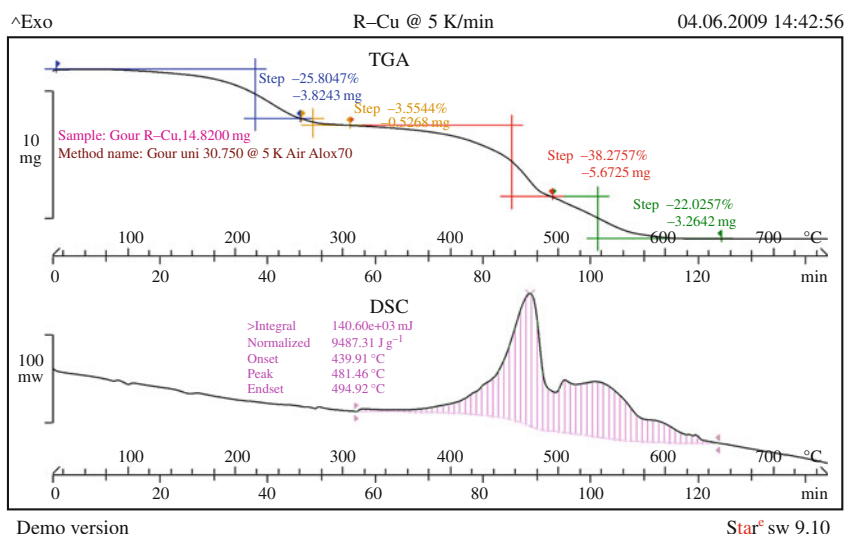
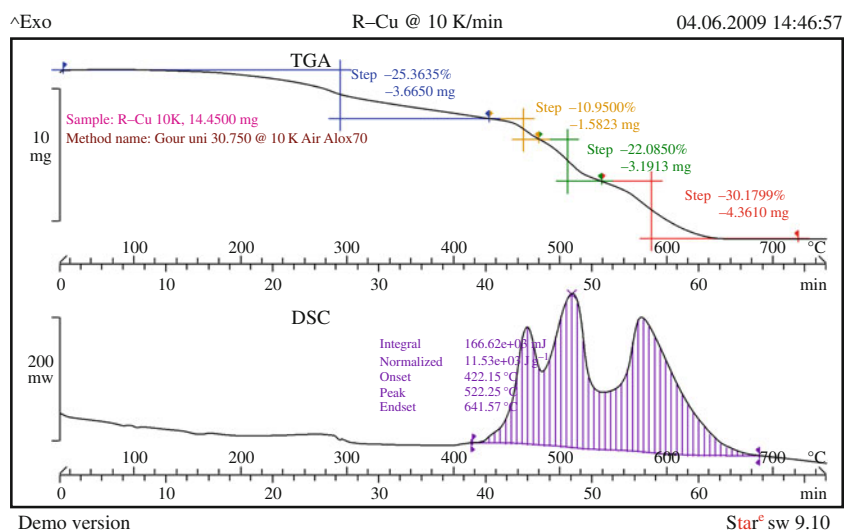
Thermal analysis

A general decomposition pattern was concluded, whereby the complex decomposed in four stages. The decomposition of complex began at 50°C . From the TG curve of Cu

(II) complex, it appears that the sample decomposes in four stages over the $50\text{--}750^\circ\text{C}$ temperature range. All data shows the first step from corresponding loss of water molecules, second step partial decomposed the organic part of complex, third step loss of metal-chloride moiety and fourth step loss of metallic and carbon residue is the final product.

The thermal degradation behaviour of the Cu(II) complex has been studied by thermogravimetric analysis at 5 K/min heating rate. The TG curve of the complex shows that the complex starts decomposition at 50°C . Elimination of lattice water molecules has been observed on increasing the temperature up to $50\text{--}250^\circ\text{C}$ (Remaining mass% obs./calc., 25.80/25.70). The complex shows loss in mass between 250 and 320°C (Remaining mass% obs./calc., 3.55/3.53). A loss in mass has been observed in general up to $320\text{--}500^\circ\text{C}$ corresponding to the loss of partially decomposed ligand part from the complex (Remaining mass% obs./calc., 38.27/38.67). A loss has been observed at $500\text{--}635^\circ\text{C}$ which corresponds to a mixture of metal oxide as an ultimate pyrolysis product (Remaining mass% obs./calc., 22.03/21.26) (Fig. 1).

The thermal degradation behaviour of the Cu(II) complex has been studied by thermogravimetric analysis at 10 K/min heating rate. The TG curve of the complex shows that the complex starts decomposition at 50°C . Elimination of lattice water molecules has been observed on increasing the temperature up to $50\text{--}450^\circ\text{C}$ (Remaining mass% obs./calc., 25.36/25.67). The complex shows loss in mass between 450 and 500°C (Remaining mass% obs./calc., 10.95/10.58). A loss in mass has been observed in general up to $500\text{--}550^\circ\text{C}$ corresponding to the loss of partially decomposed ligand part from the complex

Fig. 1 Thermogram at 5 K/min**Fig. 2** Thermogram at 10 K/min

(Remaining mass% obs./calc., 22.07/22.07). A loss has been observed at 550–650 °C which corresponds to a mixture of metal oxide as an ultimate pyrolysis product (Remaining mass% obs./calc., 30.18/30.06) (Fig. 2).

The thermal degradation behaviour of the Cu(II) complex has been studied by thermogravimetric analysis at 20 K/min heating rate. The TG curve of the complex shows that the complex starts decomposition at 50 °C. Elimination of lattice water molecules has been observed on increasing the temperature up to 50–395 °C (Remaining mass% obs./calc., 25.44/25.40). The complex shows loss in mass between 395 and 495 °C (Remaining mass% obs./calc., 8.77/8.78). A loss in mass has been observed in general up to 495–525 °C corresponding to the loss of partially decomposed ligand part from the complex (Remaining mass% obs./calc., 10.98/10.90). A loss has

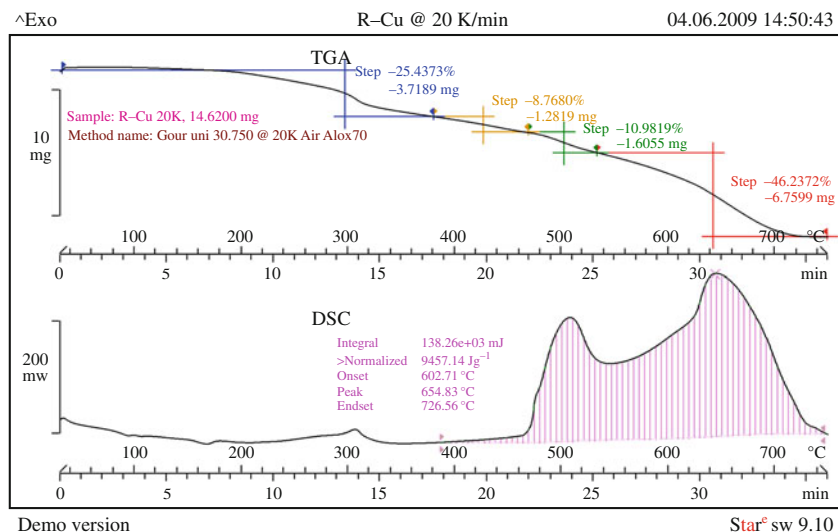
been observed at 525–750 °C which corresponds to a mixture of metal oxide as an ultimate pyrolysis product (Remaining mass% obs./calc., 46.24/46.76) (Fig. 3).

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 (ΔG^*) are calculated from the TG curves using CR equations [30].

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

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.

Fig. 3 Thermogram at 20 K/min


The degree of conversion α is measured as $\alpha = (m_0 - m_t) / (m_0 - m)$, 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. It can be seen that values of activation energy vary from -2.946×10^{-3} to -4.203×10^{-3} J mol⁻¹ for stage-I; from -7.104×10^{-3} to -19.147×10^{-3} J mol⁻¹ for stage-II; from -9.573×10^{-3} to -19.15×10^{-3} J mol⁻¹ for stage-III; from -42.12×10^{-3} to -67.01×10^{-3} J mol⁻¹ for stage-IV. The high value of the activation energies reflects the thermal stability of the complexes.

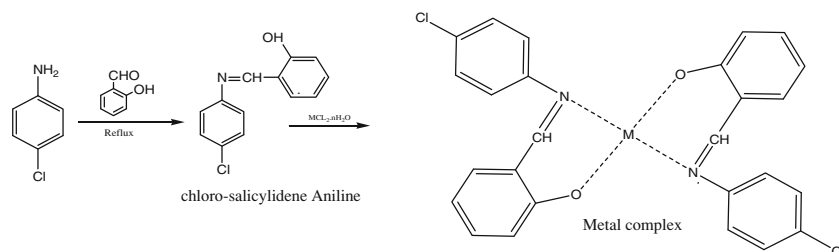
The entropy also vary from -144.06×10^{-66} to -178.03×10^{-66} J mol⁻¹ for stage-I; from -26.62×10^{-66} to -293.56×10^{-66} J mol⁻¹ for stage-II; from -91.12×10^{-66} to -197.41×10^{-66} J mol⁻¹ for stage-III; from -176.24×10^{-66} to -221.91×10^{-66} J mol⁻¹

for stage-IV. 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 vary from -4351.168×10^{-6} to -6015.23×10^{-6} J mol⁻¹ for stage-I; from -4937.31×10^{-6} to -6447.87×10^{-6} J mol⁻¹ for stage-II; from -6436.29×10^{-6} to -6851.99×10^{-6} J mol⁻¹ for stage-III; from $-76.12.87 \times 10^{-6}$ to -8547.35×10^{-6} J mol⁻¹ for stage-IV.

The Gibbs free energy vary from 88756.66×10^{-72} to $106013.63 \times 10^{-72}$ J mol⁻¹ for stage-I; from 14052.58×10^{-72} to $161946.74 \times 10^{-72}$ J mol⁻¹ for stage-II; from 66062.42×10^{-72} to $146160.87 \times 10^{-72}$ J mol⁻¹ for stage-III; from $158260.72 \times 10^{-72}$ to $193879.59 \times 10^{-72}$ J mol⁻¹ for stage-IV.

The values of obtained kinetic parameters are quite consistent which indicate that the similar types of chemical changes take place at all heating rates. 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 (Scheme 1).


Scheme 1 Synthesis of bis-[4-chloro salicylideneaniline] copper(II) complex

Conclusions

In these studies, the efforts have been to synthesize Cu(II) Schiff base complex. 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 bidentate 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 three different heating rates viz. 5, 10 and 20 K/min.

- In all heating rates the activation energy for first step is less than other steps. Same is the trend with entropy, enthalpy but Gibbs free energy shows just opposite trend.
- With increasing heating rates, the activation energy (E^*), entropy of activation (ΔS^*), enthalpy of activation (ΔH^*) and Gibbs free energy (ΔG^*) increases.

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