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THERMAL ANALYSIS STUDY OF SOME TRANSITION METAL COMPLEXES BY TG AND DSC METHODS

M. Sekerci[1] *and F. Yakuphanoglu*[2*]

[1]Firat University Faculty of Arts and Sciences, Department of Chemistry, Elazig, Turkey
[2]Firat University Faculty of Arts and Sciences, Department of Physics, Elazig, Turkey

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Abstract

The thermodynamic and thermal properties of $[Cu(L)_2\cdot Cl_2]$, $[Ni(L)_2]\cdot Cl_2$, $[Co(L)_2\cdot Cl_2]$; L=1,2-bis(*o*-aminophenoxy)ethane (BAFE), complexes have been investigated. The thermal decomposition of the complexes took place in two distinct steps in endothermic reaction up to 700°C. The activation energy E, the entropy change $\Delta S^{\#}$, enthalpy ΔH change and Gibbs free energy change $\Delta G^{\#}$ were calculated from the results of thermogravimetry analysis (TG) and heat capacity from the results of differential scanning calorimetry (DSC). It was found that the thermal stabilities and activation energies of the complexes follow the order Ni(II)>Cu(II)>Co(II) and $E_{Co}<E_{Ni}<E_{Cu}$, respectively.

Keywords: thermal analysis, thermodynamic parameters, transition metal complexes

Introduction

The thermal analysis techniques were extensively applied in studying of the thermal behavior of metal complexes [1–9]. The preparation and characterization of metal complexes by elemental analysis, IR spectroscopy, UV-visible spectroscopy and magnetic susceptibility studies were reported earlier [1–7]. In the literature, their thermal decomposition behavior occurred in one or more steps depending on the type of the complexes investigated and decomposition ends with the formation of the metal oxides. It is also found that thermal behavior of the complexes investigated is related to the decomposition of the ligand molecule. In order to check the thermal stability of the complexes in solid state, initial temperatures of the decomposition of the complexes were compared. The main basic of these studies is to determine the thermal behavior of the metal complexes. Thus, the differential thermal analysis and other thermoanalytical methods are used to determine kinetic parameters of thermal decomposition such as activation energy, enthalpy, entropy and heat capacity. In general thermoanalytical methods are used to constantly measure the changes occurring in the physical properties of a material, such as mass as a function of temperature or time. Thermogravimetry is a process

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[*] Author for correspondence: E-mail: fyhanoglu@firat.edu.tr

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Akadémiai Kiadó, Budapest
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in which a substance is decomposed in the presence of heat, which causes bonds the molecules to be broken [10, 11]. Differential scanning calorimetry (DSC) method have been widely used to determine non-isothermal transformation kinetics. Differential thermal analysis (DTA) and DSC are of particular importance. Both procedures permit the amount of heat to be determined that are taken up from or emitted to the surroundings per unit time during isothermal procedures or during heating and cooling. In this manner heat capacities, melt enthalpies, transition temperatures, etc., can be measured and from this information further indications regarding phase transitions, crystallization processes etc. can be derived. The thermodynamic parameters are very important for the studying of heat transport phenomena mechanism in various solid state compounds.

In this study, we have investigated thermal and thermodynamic properties of synthesized complexes to understand the mechanism of decomposition and thermodynamic parameters.

Experimental

Synthesis of the Cu(II), Ni(II) and Co(II) complexes

The 1,2-bis(*o*-aminophenoxy)ethane (0.43 g, 0.02 mol) ligand (L) [12] was dissolved in 10 mL of absolute ethanol in a 50 mL round-bottom flask. A solution of metal salts of $CuCl_2{\cdot}6H_2O$ (0.24 g, 0.01 mol), $NiCl_2{\cdot}6H_2O$ (0.24 g, 0.01 mol), $CoCl_2{\cdot}6H_2O$ (0.24 g, 0.01 mol), in 5 mL of absolute ethanol was added dropwise with continuous stirring at room temperature for 15 min and the reaction continued for 12 h at room temperature. The resulting precipitates were filtered off, washed with absolute ether and dried at room temperature. The synthesized complexes $[Cu(L)_2{\cdot}Cl_2]$, $[Ni(L)_2]{\cdot}Cl_2$, $[Co(L)_2{\cdot}Cl_2]$ were characterized by ^{1}H-NMR, FT-IR, UV spectroscopy and elemental analysis and were described elsewhere [12, 13]. Their structural formulas are given in Figs 1a–c.

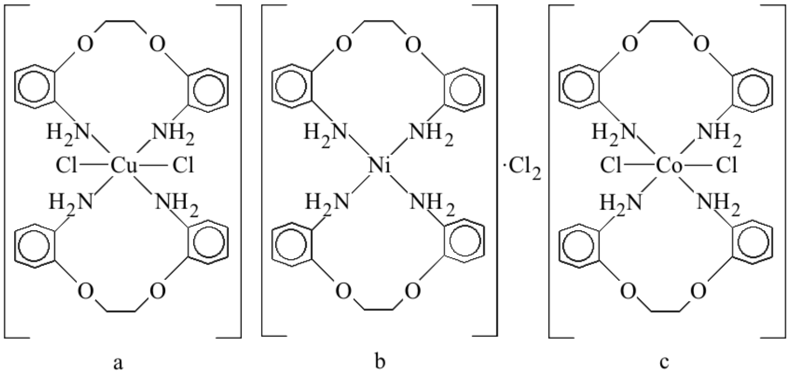

Fig. 1 The structural formulas of the complexes. a – $[Cu(L)_2{\cdot}Cl_2]$, b – $[Ni(L)_2]{\cdot}Cl_2$ and c – $[Co(L)_2{\cdot}Cl_2]$

Thermal analysis

The DSC and TG curves were obtained using DSC-50 and TG-50 Schimadzu apparatus (heating rates of 10 and 20°C min^{-1}, aluminum crucible, mass 20 mg, in nitrogen atmosphere) respectively. In TG apparatus, the aluminum crucible is then adjusted to another crucible support platform, which gives a proportional signal to the recorder and computer interface to plot the mass loss of complex *vs.* temperature.

Results and discussion

Thermodynamic and thermal studies

Figure 2 shows DSC curves of the complexes. The complexes exhibited an endothermic process. The area of the endothermic peak corresponds to the heat of fusion and the peak temperature corresponds to the melting point. The melting (T_p) and transition temperatures (T_1, T_2) of the complexes are given in Table 1. The heat capacities C_p of the complexes were calculated from DSC results and are given in Table 1.

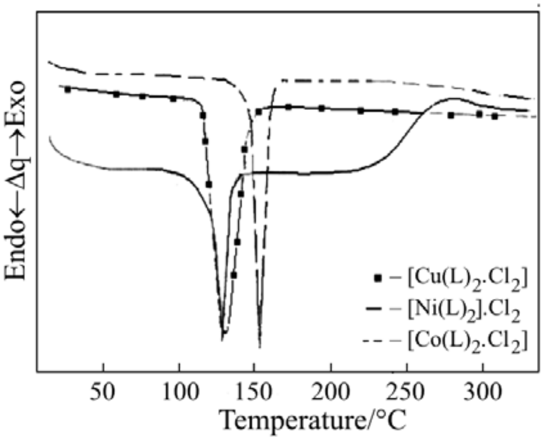

Fig. 2 The DSC curves of the complexes

The TG curves of the complexes are shown in Fig. 3. The complexes are thermal stable up to (T_s) temperature (Table 1). Co(II) complex starts to decompose at 132°C and this step continues up to 382.6°C. The second step starts after 500°C and was completed at 619.4°C. The final solid product of thermal decomposition is CoO (calc./found: 7.71/11.46%) (Table 2).

The Ni(II) complex was stable up to 209.5°C. The first step of thermal decomposition was completed at 377.2°C. The next decomposition step starts at 557.7 and continues up 623.1. The stable oxide NiO is formed after 623.1°C (calc./found: 8.75/12.09%) (Table 2).

Table 1 The thermodynamic and decomposition parameters for Cu(II), Ni(II) and Co(II) complexes

Complex	C_p/ kJ g^{-1} °C^{-1}	T_s/ °C	T_1/ °C	T_2/ °C	T_p/ °C	ΔH/ kJ mol^{-1}	$\Delta S^{\#}$/ J mol^{-1} K^{-1}	$\Delta G^{\#}$/ kJ mol^{-1}	E/ kJ mol^{-1}
$[Co(L)_2\cdot Cl_2]$	2.44	132.0	146.3	181.6	167.8	86.44	−8.83	91.67	91.38
$[Ni(L)_2]\cdot Cl_2$	3.29	239.5	119.0	149.5	133.7	100.39	−17.47	111.74	103.53
$[Cu(L)_2\cdot Cl_2]$	4.15	215.2	108.8	143.3	131.8	143.38	−16.28	153.66	148.87

L=1,2-bis(*o*-aminophenoxy)ethane

Table 2 The TG data for Cu(II), Ni(II) and Co(II) complexes

Complex	First step/ °C	Mass loss, Δm calc./found/%	Second step/ °C	Residue	Calc./found/ %
$[Cu(L)_2{\cdot}Cl_2]$	215.2–358.6	88.00 (87.22)	400–569.2	CuO	12.00 (12.78)
$[Ni(L)_2]{\cdot}Cl_2$	239.5–377.2	91.25 (87.91)	557.7–623.1	NiO	8.75 (12.09)
$[Co(L)_2{\cdot}Cl_2]$	132–382.6	92.29 (88.54)	500–619.4	CoO	7.71 (11.46)

The Cu(II) complex was stable up to 215.2°C and decomposition started at this temperature and was completed at 358.6°C. The second step temperatures are in the range of 400 and 569.2°C. The solid residue was CuO (calc./found: 12.00/12.78%) (Table 2).

The kinetic of heterogeneous condensed phase reactions that occur in non-isothermal conditions is usually described by equation:

$$\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}=A_{\mathrm{f}}(\alpha)\exp\left(-\frac{E}{RT}\right) \tag{1}$$

where α is the degree of conversion, β is the linear heating rate, and $A_{\mathrm{f}}(\alpha)$ is the differential conversion function.

For calculate kinetic parameters, the different reaction models may be used. The fraction mass loss (α) and corresponding $(1–\alpha)^{\mathrm{n}}$ are calculated from TG curves, where n depends upon the reaction model. We choose Coats–Redfern model and it may be expressed by the following relation [14–16],

$$\ln\left[\frac{1-(1-\alpha)^{1-\mathrm{n}}}{T^2(1-n)}\right]\equiv\ln\frac{AR}{\beta E}\left[1-\frac{2RT}{E}\right]-\frac{E}{RT} \tag{2}$$

A graphical representation of $\ln[-\ln(1-\alpha)/T^2]$ function of $1/T$ gives a straight line with inclination $-E/R$. The activation energies of the complexes were calculated from Fig. 4 and given in Table 1.

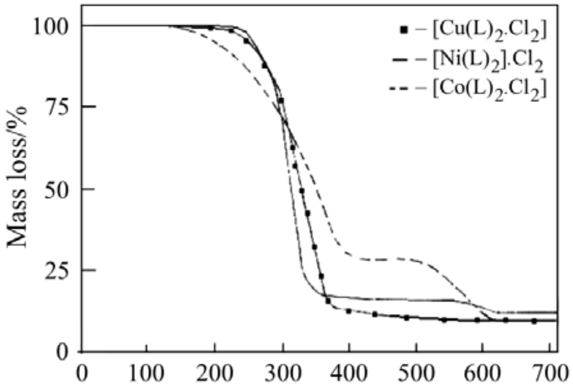

Fig. 3 The TG curves of the complexes

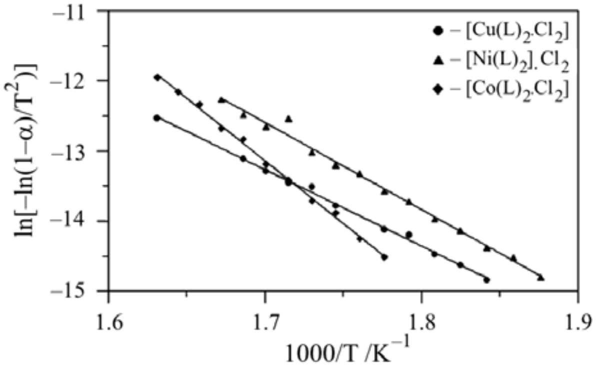

Fig. 4 Coats and Redfern plots for the complexes

The enthalpy ΔH, activation entropy $\Delta S^{\#}$, and the free energy of activation $\Delta G^{\#}$, of the complexes were calculated using the following relations [17]:

$$\Delta S^{\#}=2.303\lg\left(\frac{Ah}{kT}\right)R \tag{3}$$

$$\Delta H=E-RT \tag{4}$$

$$\Delta G^{\#}=\Delta H-T\Delta S^{\#} \tag{5}$$

where h is the Planck constant and T is the temperature, A is the Arrhenius constant. The thermodynamic parameters calculated were reported in Table 1.

The kinetic parameters, especially activation energy E and activation entropy $\Delta S^{\#}$ are helpful in assigning the strength of the bonding of ligand moieties with the metal ion [17]. The activation energies corresponding decomposition steps are in the range of 91.38–148.87 kJ mol^{-1} which indicates bonding degree of ligand bound to metal ion. It was found that the thermal stability increases in this order: Ni(II)>Cu(II)>Co(II). It is also found that all the complexes have a negative entropy, which indicates that the studied complexes have more ordered systems than reactants. The activation energy and Gibbs free energy of the complexes also increase due to increase of atomic number in the 3rd series of the *d*-block elements.

The experimental data suggest that studied complexes decompose in two-step process. All the complexes show almost a similar decomposition when heated above 600°C. The solid products of thermal decomposition were metal oxides (CuO, NiO and CoO).

Conclusions

The complexes prepared with different metals decompose in two-step process. The kinetic parameters in non-isothermal conditions are investigated and thermodynamic parameters such as enthalpy, entropy and specific heat capacity of the complexes were calculated. The highest thermal stability is displayed by the Ni(II) complex and thermal stabilities of the complexes follow the order Ni(II)>Cu(II)>Co(II). In literature, it is found by Arshad *et al*. that thermal stabilities of 1,2-dipiperidinoethane complexes of cobalt, nickel, copper, zinc and cadmium, increase in the following sequence: Ni(II)<Co(II)<Cu(II)<Zn(II)<Cd(II) [8]. On the other hand, in another study, the thermal stabilities of metal complexes of the 6-(2-pyridylazo-acetamidophenol were found as Ni(II)>Cu(II)>Zn(II)>Fe(II)>Co(II)>Cd(II) [9]. Consequently, it is evaluated that the coordination of metal ion to ligand is responsible for thermal stabilities of the metal complexes.

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