

# INVESTIGATION OF THE THERMAL PROPERTIES OF [Cd(hydet-en)<sub>2</sub>Pd(CN)<sub>4</sub>] AND [Zn(hydet-en)<sub>2</sub>Pd(CN)<sub>4</sub>] SINGLE CRYSTALS

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Thermal properties of the single crystals have been investigated by thermogravimetry (TG) and differential scanning calorimetry (DSC) techniques. The thermodynamic parameters such as activation energy and enthalpy and thermal stability temperature of the samples were calculated from the differential thermal analysis (DTA) and TG data. The activation energies for first peak of DTA curves were found as 496.65 (for Cd–Pd) and 419.37 kJ mol<sup>-1</sup> (for Zn–Pd). For second peak, activation energies were calculated 116.56 (for Cd–Pd) and 173.96 kJ mol<sup>-1</sup> (for Zn–Pd). The thermal stability temperature values of the Cd–Pd and Zn–Pd compounds at 10°C min<sup>-1</sup> heating rate are determined as approximately 220.7 and 203°C, respectively. The TG results suggest that thermal stability of the Cd–Pd complex is higher than that of the Zn–Pd complex.

**Keywords:** kinetics parameters, single crystal, thermal analysis

## Introduction

A lot of work has been devoted to the study of the coordination chemistry of cyanide-bridged metal complexes because of their magnetic properties especially at low temperatures, unusual electronic states, and photochemical properties [1–4]. These compounds are also interesting as ion exchangers, molecular sieves or materials for storing gases [5]. One of the most noticeable features of CN<sup>-</sup> anion is its ability to act as either a terminal or a bridging ligand. The cyanide ion may coordinate either through the C atom, acting as a monodentate ligand, or through both the C and N atoms, and acting as a bridging ligand, forming polymeric homo- and heteronuclear compounds with a one-, two- or three-dimensional network. The preparation strategy of these one dimensional (1D) compounds is based on the so-called ‘brick and mortar’ method [6, 7], where the metal cation forms a brick and cyano complex anions represent the mortar.

The thermal decomposition of the cyano-bridged polymeric complexes has been studied by several authors [8–11]. Because that the thermal data of these complexes are somewhat less abundant than the structural ones for structure determination, and they can never be of great importance for structural characterization. The thermal analysis is suitable for investigation of different application fields. The study of thermal decomposition, particularly the kinetic and thermodynamic parameters have proved to be very useful for elucidation of the thermal properties of these mate-

rials. The differential thermal analysis and other thermoanalytical methods are used to analyze the kinetic of a chemical reaction and to determine kinetic parameter such as activation energy, enthalpy, entropy and specific heat capacity. In general these 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 in which a substance is decomposed in the presence of heat, which causes bonds of the molecules to be broken [12, 13]. Differential thermal analysis (DTA) has an extensive application in materials science and condensed matter physics to determine kinetic and thermodynamic parameters of solids.

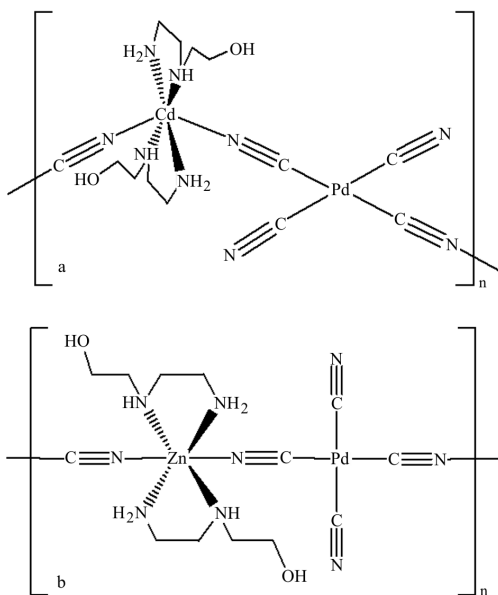
The aim of this work was to study the thermal properties of [Cd(hydet-en)<sub>2</sub>Pd(CN)<sub>4</sub>] (Cd–Pd) and [Zn(hydet-en)<sub>2</sub>Pd(CN)<sub>4</sub>] (Zn–Pd) single crystals using DTA and TG techniques.

## Experimental

### Thermal measurements

The chemical structures of the [Cd(hydet-en)<sub>2</sub>Pd(CN)<sub>4</sub>] and [Zn(hydet-en)<sub>2</sub>Pd(CN)<sub>4</sub>] (hydet-en=H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>OH) single crystals are shown in Figs 1a and b [14]. DTA and TG measurements of (Cd–Pd) and (Zn–Pd) complexes were performed using Shimadzu DTA-50 and TG-50. The DTA and TG curves were obtained at different heating rates (5, 10, 15 and 20°C min<sup>-1</sup>).

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**Fig. 1** The chemical structures of the compounds  
a – Cd(II)–Pd(II), b – Zn(II)–Pd(II)

#### Using DTA for the calculation of kinetic parameters

The classical Johnson–Mehl–Avrami (JMA) theoretical model [12], is defined as follows,

$$x = 1 - \exp[-(Kt)^n] \quad (1)$$

where  $x$  is the fraction of conversion,  $n$  is the Avrami parameter.  $K$  is the reaction rate constant, which is defined as  $K = A \exp(-E/RT)$ . In non-isothermal method, it is well known that the sample is heated at a fixed rate and heat evolved is again recorded as a function of temperature. The relation between the sample temperature and the heating rate ( $\beta$ ) is defined,  $T = T_0 + \beta t$ , where  $T_0$  is the initial temperature. The kinetic parameters are obtained by taking the derivative of  $K$  and Eq. (1). The derivative of  $K$  and  $x$  is obtained as,

$$\dot{K} = \frac{dK}{dT} \frac{dT}{dt} = \beta \frac{E}{RT^2} A \exp\left(-\frac{E}{RT}\right) = \left(\frac{\beta E}{RT^2}\right) K \quad (2)$$

and

$$\dot{x} = n(Kt)^{n-1} [K + \dot{K}t](1-x) \quad (3)$$

$$\dot{x} = n(Kt)^{n-1} K \left[1 + \frac{\beta E t}{RT^2}\right] (1-x) \quad (4)$$

Kissinger argued [15] that

$$\frac{\beta E t}{RT^2} = \frac{E}{RT} \frac{\beta t}{T} \ll 1 \quad (5)$$

which is valid if  $\beta t/T \ll 1$ . i.e., when the linear change is small compared to the actual temperature. As a result, following equation is obtained.

$$\dot{x} = nK^n t^{n-1} (1-x) \quad (6)$$

Differentiating Eq. (4) gives Eq. (7).

$$\dot{x} = n^2 K^n t^{n-2} (1-x) \left[ \frac{\beta E t}{RT^2} + \frac{n-1}{n} - K^n t^n \right] \quad (7)$$

In this equation, when  $n=1$ , which is rather frequent, this allows us to neglect the middle term and then we have the same form published in [16].

$$\begin{aligned} \dot{x} &= n^2 K^{n-1} t^{n-1} K (1-x) \left[ \frac{\beta E t}{RT^2} - K^{n-1} t^{n-1} \right] = \\ &= n^2 B K (1-x) \left[ \frac{\beta E}{RT^2} - B K \right] \end{aligned} \quad (8)$$

The maximum for what condition leads to  $\dot{x} = 0$  or

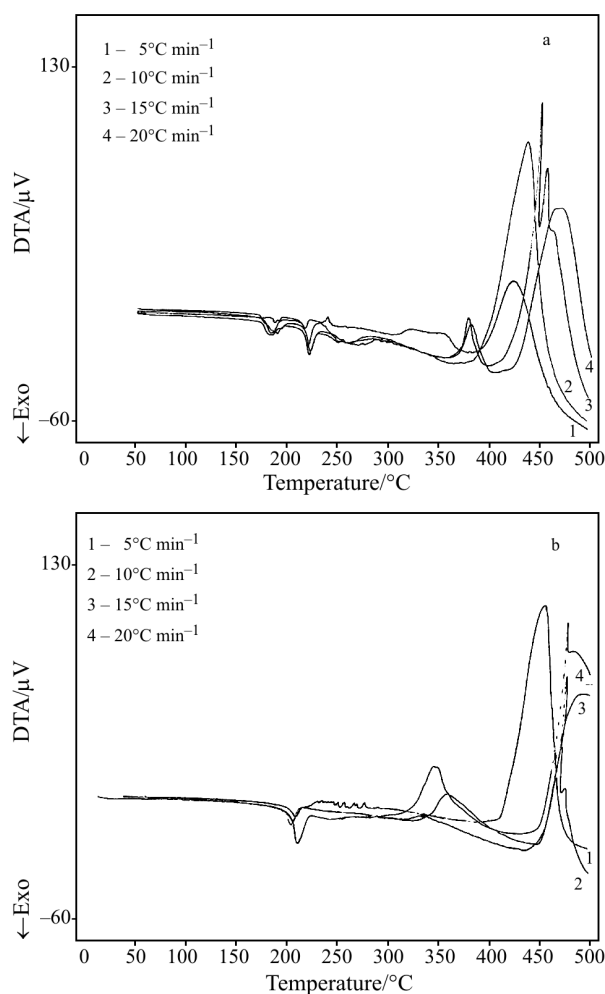
$$\frac{\beta E}{RT^2} = B K = B A \exp\left(-\frac{E}{RT}\right) \quad (9)$$

If  $T = T_p$  ( $T_p$  being the maximum peak temperature) is taken in Eq. (9), this equation can be used to obtain the activation energy using the linear relationship between  $y = \ln(\beta/T_p^2)$  and  $x = 1/T_p$ . The intercept of the straight line can be used to calculate the pre-exponential factor [17].

## Results and discussion

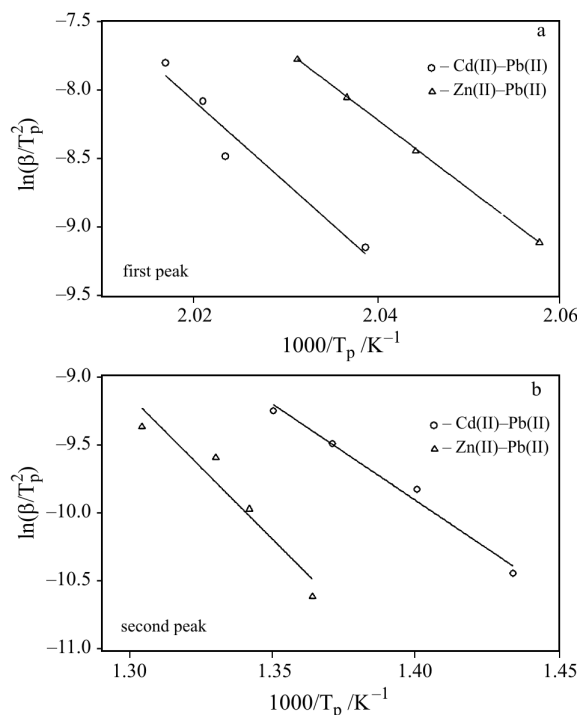
Figures 2a and b show typical DTA curves obtained under non-isothermal conditions for compounds taken different heating rates 5, 10, 15 and 20°C min<sup>-1</sup>. Three characteristic phenomena are resolved in the studied temperature region. The first peak temperature corresponds to thermal stability temperature. In the figures, the compounds were heated by a constant temperature rise and the melting of crystalline phase was appeared as exothermic process. The area of the exothermic peak corresponds to the heat of fusion and the peak temperature to the melting point. We used the Kissinger method to predict the thermal activation energy. It is important to know the activation energy of thermal properties of the compounds. It can be obtained from the dependence of the peak temperature on the heating rate, using Eq. (9). The activation energies were calculated from the slope of  $y = \ln(\beta/T_p^2)$  vs.  $1000/T_p$  plots (Figs 3a and b). The activation energies for first peak of DTA curves were found as 496.65 (for Cd–Pd) and 419.37 kJ mol<sup>-1</sup> (for Zn–Pd). For second peak, activation energies were calculated 116.56 (for Cd–Pd) and 173.96 kJ mol<sup>-1</sup> (for Zn–Pd). It is seen that activation energies obtained for first peak is higher than that of the activation energies second peak. Equation (9) can be simplified when the variation of  $\ln(\beta/T_p^2)$  vs.  $\ln\beta$  is much slower than that of  $1/T_p$  with  $\ln\beta$  and so, activation can be obtained from  $\ln\beta$  vs.  $1000/T_p$  plots. Figures 4a and b show  $\ln\beta$  vs.

$1000/T_p$  plots. The obtained activation energies for first peak of DTA curves were found as 512.03 (for Cd–Pd) and 437.78 kJ mol<sup>-1</sup> (for Zn–Pd) while for second peak, activation energies were calculated 135.78 (for Cd–Pd) and 193.58 kJ mol<sup>-1</sup> (for Zn–Pd). It is seen that activation energies obtained for first peak is higher than that of the activation energies second peak. The enthalpy values for the compounds were calculated as  $\Delta H_I$  for the first peak and  $\Delta H_{II}$  for the second peak and are given in Table 1. The enthalpy values of the Cd–Pd complex for the first peak are lower than that of the Zn–Pd complex as well as for second peak. TG curves of the samples are shown in Figs 5a and b. The thermal decomposition for each sample starts at various temperatures and apparently follows two-stage decomposition processes. The parameters related decomposition steps are given in Table 2. The decomposition process of the compounds is similar to each other. The initial decomposition temperature,  $T_s$  is defined as thermal stability of compounds.  $T_s$  values of the Cd–Pd and Zn–Pd com-

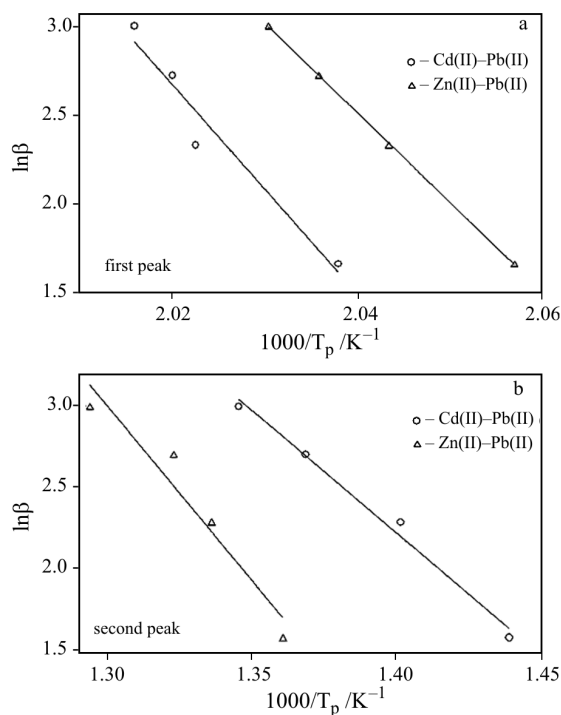


**Fig. 2** DTA curves of the samples a – Cd(II)–Pd(II), b – Zn(II)–Pd(II)

pounds at 10  $^{\circ}\text{C min}^{-1}$  heating rate are determined as approximately 220.7 and 203  $^{\circ}\text{C}$ , respectively. The results obtained suggest that thermal stability of the Cd–Pd is higher than that of the Zn–Pd. Showing that



**Fig. 3**  $\ln(\beta/T_p^2)$  vs.  $1000/T_p$  plots of the samples a – first peak, b – second peak



**Fig. 4**  $\ln\beta$  vs.  $1000/T_p$  plots of the samples a – first peak, b – second peak

**Table 1** The enthalpy values for each peak of the complexes

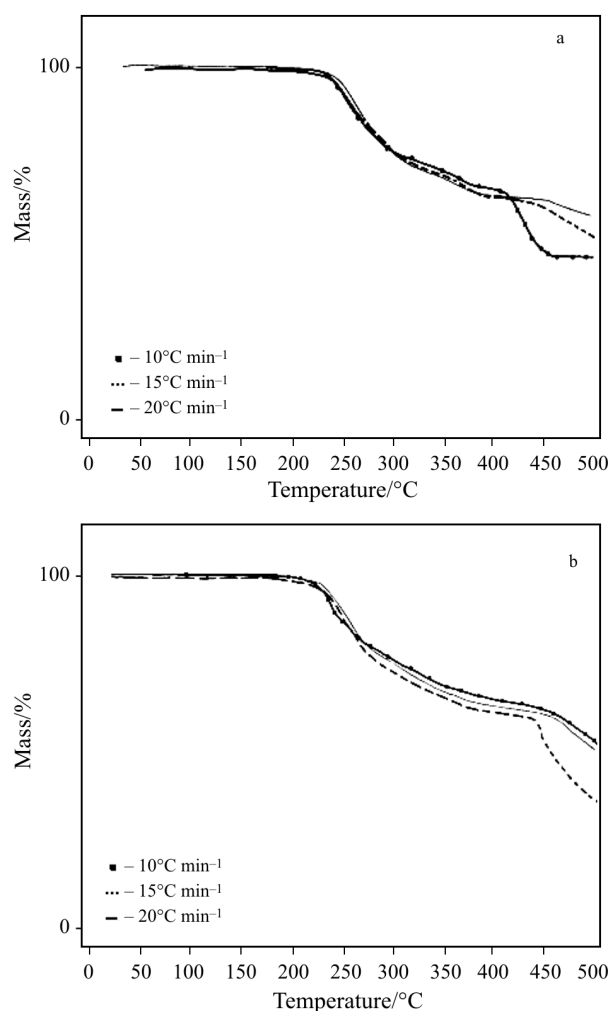
$\beta/^\circ\text{C min}^{-1}$	$\Delta H_1/\text{J g}^{-1}$ for Cd–Pd <sup>a</sup>	$\Delta H_1/\text{J g}^{-1}$ for Zn–Pd <sup>b</sup>	$\Delta H_{II}/\text{J g}^{-1}$ for Cd–Pd <sup>b</sup>	$\Delta H_{II}/\text{J g}^{-1}$ for Zn–Pd <sup>b</sup>
5	39.18	4829.77	224.93	17068.8
10	93.40	9691.88	61.11	3490.74
15	65.15	5024.52	133.55	992.12
20	43.78	2941.10	98.01	1901.37

<sup>a</sup>for first peak, <sup>b</sup>for second peak**Table 2** The TG data for Cd(II)-Pd(II) and Zn(II)-Pd(II) complexes

Complex	First step/ $^\circ\text{C}$	$\Delta m$ calc. (found)/%	Second step/ $^\circ\text{C}$	$\Delta m$ calc. (found)/%	Residue calc. (found)/%
Cd–Pd	175.0–388.0	33.19 (32.75)	388.0–419.5	19.59 (19.58)	CdO and PdO 47.22 (47.67)
Zn–Pd	188.0–460.5	36.41 (37.08)	460.5–539.3	21.49 (20.83)	ZnO and PdO 42.10 (42.09)

Cd–Pd sample is more stable. The effect of the metal coordination on thermal stability of the samples can be explained in terms of the higher attraction between metal and ligand as this attraction increases the rigid-

ity of the complex. It can be evaluated that the insertion of metal ion into ligand can change the thermal stability of the sample. This suggests that the decomposition of Cd–Pd sample takes places at higher temperatures than that of Zn–Pd.

**Fig. 5** TG curves of the samples a – Cd(II)–Pb(II), b – Zn(II)–Pb(II)

## Conclusions

Thermal properties of the single crystal materials have been investigated by TG and DTA techniques. The thermal parameters such as enthalpy, activation energy and thermal stability temperature of the organic compounds were determined from DTA and TG data. The activation energies obtained for first peak in observed in DTA curves is higher than that of the activation energies second peak. The thermal stability temperature values of the Cd–Pd and Zn–Pd compounds at  $10^\circ\text{C min}^{-1}$  heating rate are determined as approximately 220.7 and  $203^\circ\text{C}$ , respectively. The TG results suggest that thermal stability of the Cd–Pd is higher than that of the Zn–Pd.

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