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THERMAL DECOMPOSITION KINETICS OF POLYMERIC COMPLEXES OF NICKEL(II), ZINC(II) AND CADMIUM(II) WITH *N,N′*-BIS(DITHIOCARBOXY)PIPERAZINE

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ABSTRACT

The polymeric complexes of Ni(II), Zn(II) and Cd(II) with *N,N′*-bis(dithiocarboxy)-piperazine are subjected to thermal decomposition studies in air using TG, DTG and DTA techniques. The kinetic parameters (non-isothermal method) for their decomposition have been evaluated by graphical and weighted least-squares methods using the equations of Freeman–Carroll, Horowitz–Metzger and Coats–Redfern. The results indicate that the values of E^*, A and ΔS^* obtained are comparable and that the decompositions follow a random nucleation mechanism.

INTRODUCTION

The thermal study of metal complexes with sulphur-containing ligands, in particular those with dithiocarbamates, has evoked considerable interest [1–4] from the point of view of obtaining information on the thermal stability of these important compounds [5–7]. Thermal studies on these complexes are also of interest in the preparation of sulphides and in the search for new classes of volatile compounds [8,9]. However, compared to the thermal decomposition studies of metal complexes with Schiff bases [10,11] and amines [12], studies on the thermal behaviour of metal dithiocarbamate complexes are scarce. In this paper we describe the thermogravimetric analysis and kinetics of the thermal decomposition of polymeric complexes of Ni(II), Zn(II) and Cd(II) with *N,N′*-bis-(dithiocarboxy)piperazine (L).

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EXPERIMENTAL

The ligand was synthesized as its disodium salt using the published procedure [13]. The metal complexes were prepared by adding an aqueous solution of the disodium salt of the ligand dropwise with constant stirring, to an aqueous solution of the respective metal chloride until the metal to ligand ratio reached 1 : 1. The solid complexes were filtered, washed several times with water and then with methanol and dried in vacuum over P_4O_{10}. The purity of the complexes was determined using standard elemental analysis [14] and they were found to have the formulae $M(L)H_2O$, where M = Ni(II) or Zn(II), and Cd(L). They were further characterized by spectral and magnetic studies [15].

Apparatus

The thermogravimetric measurements (TG and DTA) were determined on a Dupont 990 thermal analyser system using a heating rate of 10 K min^{-1} with a sample size of 2–6 mg in an atmosphere of static air and using a platinum crucible. The thermogravimetric data were analysed using a program written in BASIC for an HCL microcomputer.

The final decomposition products in air were examined by independent pyrolysis experiments, in which the samples were heated for 2 h in silica crucibles to ~ 650°. *

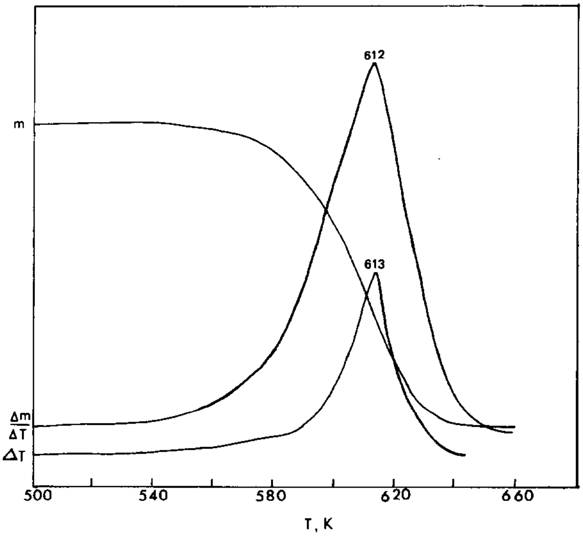

Fig. 1. TG, DTG and DTA traces of $Ni(L) \cdot H_2O$.

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* All temperatures are in degrees Kelvin.

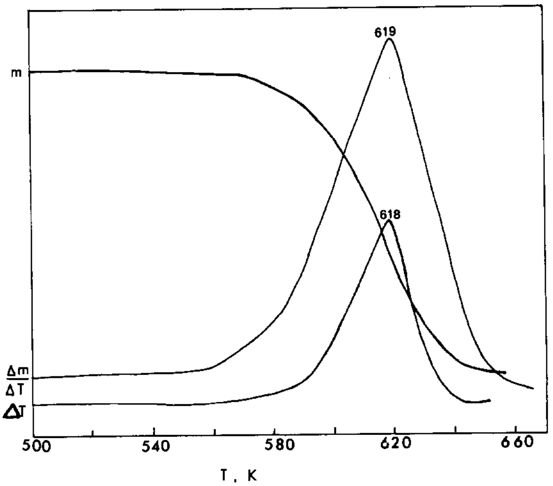

Fig. 2. TG, DTG and DTA traces of Zn(L)·H_2O.

Treatment of data

The TG curves were studied in greater detail. The instrumental thermogravimetric traces were redrawn as the fraction decomposed (α) against temperature (T) curves (TG), and also as the derivative mass loss ($\mathrm{d}m/\mathrm{d}T$) against temperature curves (DTG). The instrumental DTA curves were used as such. The TG, DTG and DTA traces are given in Figs. 1–3. The decomposition reactions of the three metal complexes were studied using non-isothermal kinetic studies. The overall order of reaction (n) and the

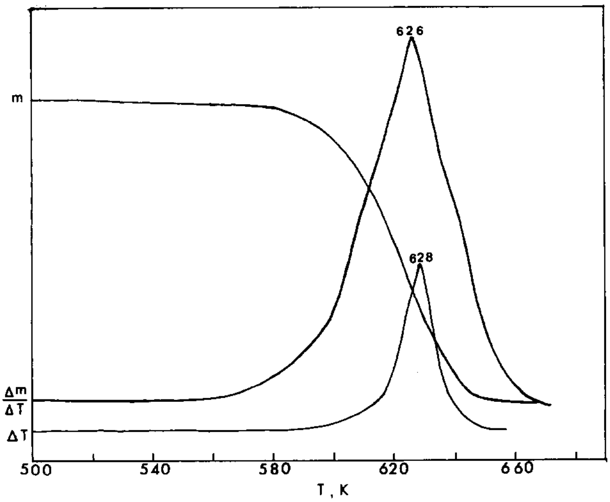

Fig. 3. TG, DTG and DTA traces of Cd(L).

kinetic parameters such as the apparent activation energy (E^*), the entropy of activation (ΔS^*) and the pre-exponential factor (A) were evaluated.

Basic theory

The integral form of the non-isothermal kinetic equation is

$$\ln g(\alpha) = M/T + B \tag{1}$$

where α is the fraction decomposed at temperature T, $g(\alpha)$ is the function of α which depends on the mechanism of decomposition, $M = (-E^*/R)$, $B = \ln(AR/qE)$, R is the gas constant and q represents the constant rate of heating.

The above form of representation is similar to the $y = ax + b$ model of the least-squares method (LSM). The least-squares analysis is based on the observation that, often, random experimental errors closely follow a Gaussian distribution. In the above equation, the errors in $g(\alpha)$ are likely to follow a Gaussian distribution, but those in ln $g(\alpha)$ are definitely not, because using the logarithmic function tends to compress the high values while expanding the low values. This defect can be remedied by using weighted LSM. It has been shown [16] that the best fit of experimental and calculated data was obtained using weighted LSM. The weights used most often are the inverse of the deviation of the dependent variable [17]. It has been shown [16] that the deviation, S_α^2 of the variable α is equal to $1 + \alpha^2$. Transforming α into y [i.e. ln $g(\alpha)$] one should also correspondingly transform S_α^2 into S_y^2. The deviation of y is calculated from the transformed formula

$$S_y^2 = S_\alpha^2 \left(\frac{y}{\partial \alpha} \right)^2 \tag{2}$$

and the following is used as weights (w) for the calculation of slope and intecept

$$w = 1/S_y^2 \tag{3}$$

Determination of the order of reaction (n)

We have adopted the following two different methods for the determination of the overall order of reaction. (i) The Freeman–Carroll equation [18] was used in the following form

$$\frac{\Delta \ln(\mathrm{d}W/\mathrm{d}t)}{\Delta \ln W_\mathrm{r}} = \frac{-E^*/R\ \Delta(1/T)}{\Delta \ln W_\mathrm{r}} + n \tag{4}$$

where W is the total loss in weight up to time t, $W_\mathrm{r} = W_\mathrm{f} - W$ and W_f is the weight loss at the completion of the reaction.

The weight–temperature gradient (dW/dT) can be obtained from the TG curve by employing Stirling's central difference formula for six points [19]. The temperature slopes, dW/dT, were converted to time slopes, dW/dt, using the equation

$$(\mathrm{d}W/\mathrm{d}t) = (\mathrm{d}W/\mathrm{d}T)(\mathrm{d}T/\mathrm{d}t) = (\mathrm{d}W/\mathrm{d}T)q \qquad (5)$$

It is evident from eqn. (4) that if a plot is made of $\Delta(1/T)/\Delta \ln W_r$ against $\Delta \ln(\mathrm{d}W/\mathrm{d}t)/\Delta \ln W_r$, a straight line with slope of $-E^*/R$ and intercept n should be obtained. (ii) The order of reaction was also obtained using the following relation suggested by Horowitz and Metzger [20]

$$1 - \alpha_s = n^{[1/(1-n)]} \qquad (6)$$

where α_s is the fraction of the substance decomposed at T_s, the DTG peak temperature.

A 'master curve' representing different values of $1 - \alpha_s$ against n was constructed, as reported earlier [21], and the value of n corresponding to the experimentally determined value of $1 - \alpha_s$ was read off from the curve for all the three complexes.

Evaluation of the kinetic parameters

Three different methods are used for the evaluation of kinetic parameters.

The differential method of Freeman and Carroll [18]

By combining the usual first-order equation with the Arrhenius equation,

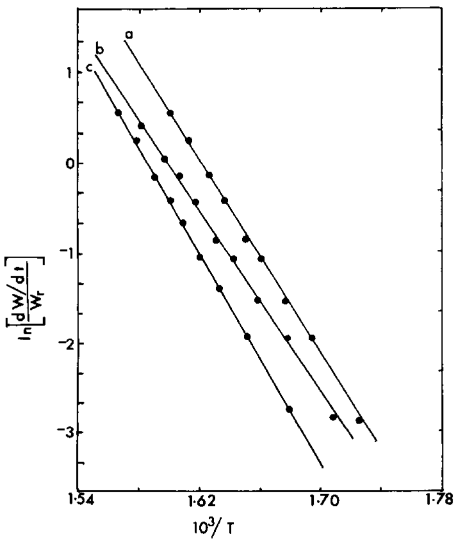

Fig. 4. Freeman–Carroll plot for a = Ni(L)·H_2O, b = Zn(L)·H_2O and c = Cd(L).

one gets

$$\ln\left[\frac{dW/dt}{W_r}\right] = \frac{-E^*}{RT} + \ln A \tag{7}$$

A plot of $\ln[(dW/dt)/W_i]$ against $1/T$ was found to be linear, as shown in Fig. 4. E^* was calculated from the slope, A was calculated from the intercept and ΔS^* was calculated from the following equation

$$A = \frac{kT_s}{h} \exp(\Delta S^*/R) \tag{8}$$

where k is the Boltzmann constant and h is the Planck constant. The kinetic parameters were also evaluated using the weighted LSM.

The approximation method of Horowitz and Metzger [20]

The equation suggested by Horowitz and Metzger for first-order reaction is in the form

$$\ln[-\ln(1-\alpha)] = \frac{E^*\theta}{RT_s^2} \tag{9}$$

where $\theta = T - T_s$.

A plot of $\ln[-\ln(1-\alpha)]$ against θ was found to be linear (Fig. 5), from the slope of which E^* was calculated. A was calculated from the equation

$$\frac{E^*}{RT_s^2} = \frac{A}{q\exp(E^*/RT_s)} \tag{10}$$

The entropy of activation, ΔS^*, was calculated using eqn. (8). The kinetic

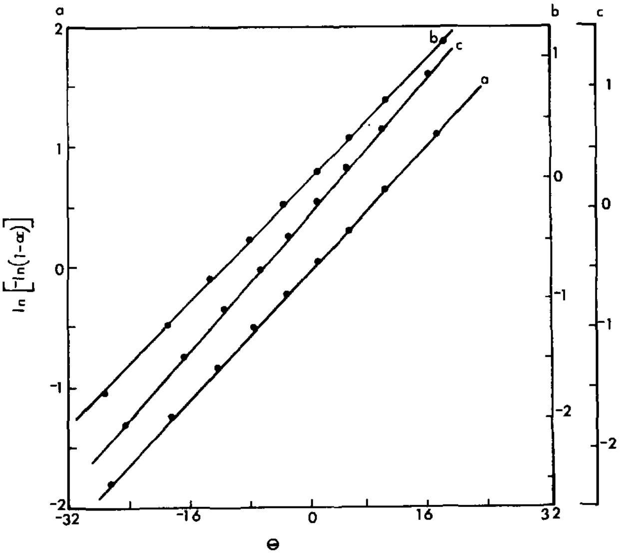

Fig. 5. Horowitz–Metzger plot for a = Ni(L)·H_2O, b = Zn(L)·H_2O and c = Cd(L).

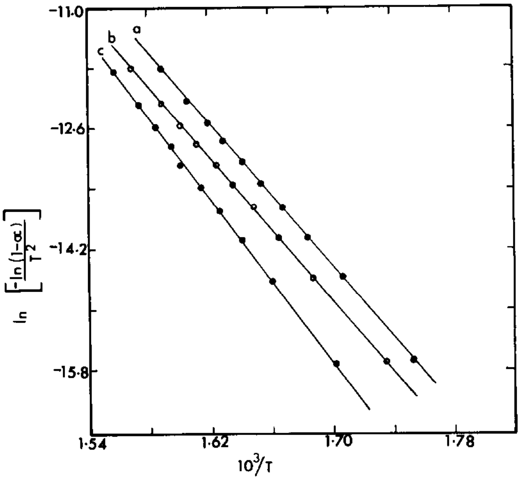

Fig. 6. Coats–Redfern plot for a = Ni(L)·H_2O, b = Zn(L)·H_2O and c = Cd(L).

parameters were also evaluated from the values of slope and intercept obtained by using weighted LSM.

The integral method of Coats and Redfern [22]

For first-order reactions, the Coats–Redfern equation may be written in the form

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]=\frac{M}{T}+B \tag{11}$$

The slope (M) and intercept (B) of the above equation were obtained from a plot of $\ln[-\ln(1-\alpha)/T^2]$ against $1/T$ (shown in Fig. 6). E^* was calculated from the slope and A was calculated from the intercept. The entropy of activation, ΔS^*, was calculated using eqn. (8). The kinetic parameters were also evaluated using weighted LSM.

Evaluation of enthalpy (ΔH) terms

It has been stated [23] that the DTG peak temperature, T_s may be identified as the thermodynamic decomposition temperature. On this basis, the ΔH terms may be approximately derived from the Gibbs–Helmholtz equation

$$\Delta G=\Delta H-T_s\,\Delta S \tag{12}$$

At the temperature at which decomposition becomes thermodynamically possible, $\Delta G=0$ and $\Delta H=T_s\,\Delta S$ from which the enthalpy (ΔH) terms were calculated.

RESULTS AND DISCUSSION

The general thermal behaviour of the complexes, including the stability ranges, peak temperatures, mass loss data, etc. are listed in Table 1. The values of the kinetic parameters, enthalpy terms and correlation coefficients are given in Table 2.

Thermal behaviour

Usually, in thermogravimetric studies, more importance is given to the temperature ranges, i.e. the initial temperature (T_i) and the final temperature (T_f) than to the peak temperatures (T_s), as the latter are dependent on variables such as sample size, surface area and rate of heating [24,25]. However, we are of the opinion that as TG and DTA are obtained simultaneously, the DTG and DTA peaks obtained under identical conditions can be compared.

The Ni(II) and Zn(II) complexes decompose in a two-stage process. They are stable up to around 363°. The elimination of the lattice-held water molecules takes place in the first step, shown by the DTG peaks around 368° and the corresponding endothermic DTA peaks around 370°. The initial mass loss in TG for these complexes agrees well with the theoretically expected loss due to the elimination of one molecule of water. The main decomposition steps of these complexes occur between 530° and 640°. The DTG peak at 612° and exothermic DTA peak at 613° for $Ni(L) \cdot H_2O$ and the DTG peak at 619° and exothermic DTA peak at 618° for $Zn(L) \cdot H_2O$ represent this stage. After the complete decomposition of the complexes, the mass loss data show that the residues are oxides of the general formula MO, where M = Ni(II) or Zn(II).

The cadmium complex, Cd(L) is stable up to 503° and decomposes in a single step which is represented by the DTG peak at 626° and corresponding exothermic DTA peak at 628°. The mass loss in this step corresponds to the formation of CdO which is stable beyond 650°.

TABLE 1

Thermal decomposition data

Complex	Stability range in TG (K)	Peak temperature in DTG (K)	Peak temperature in DTA (K)	Loss of mass (%)		
				From TG	Theoretical	From independent pyrolysis
$Ni(L) \cdot H_2O$	535	612	613	76.18	76.14	75.89
$Zn(L) \cdot H_2O$	531	619	618	74.77	74.55	74.58
Cd(L)	503	626	628	63.03	63.19	63.11

TABLE 2

Kinetic data

Equation	Complex	From graphical method				From weighted LSM				
		E^*	A	ΔS^*	ΔH	E^*	A	ΔS^*	ΔH	—
Freeman–Carroll	Ni(L)·H_2O	218.4	9.55×10^{17}	11.22	6.87	215.6	1.07×10^{18}	11.34	6.94	0.9994
	Zn(L)·H_2O	210.1	8.64×10^{17}	11.11	6.88	213.0	9.17×10^{17}	11.17	6.91	0.9998
	Cd(L)	240.3	1.42×10^{19}	13.90	8.70	238.5	1.26×10^{19}	13.78	8.63	0.9997
Horowitz–Metzger	Ni(L)·H_2O	208.3	5.99×10^{17}	10.76	6.59	213.2	1.08×10^{18}	11.35	6.95	0.9998
	Zn(L)·H_2O	205.6	1.43×10^{17}	9.31	5.76	212.2	5.40×10^{17}	10.64	6.59	0.9999
	Cd(L)	235.8	3.46×10^{19}	14.79	9.26	238.7	6.10×10^{19}	15.36	9.62	0.9999
Coats–Redfern	Ni(L)·H_2O	208.9	1.21×10^{18}	11.46	7.01	213.2	9.30×10^{17}	11.20	6.85	0.9999
	Zn(L)·H_2O	202.0	8.94×10^{17}	9.27	5.74	207.8	7.57×10^{17}	10.98	6.80	0.9999
	Cd(L)	220.7	1.60×10^{19}	14.02	8.78	224.4	1.25×10^{19}	13.78	8.63	0.9999

Units: E^* = kJ mol^{-1}; $A = \mathrm{s}^{-1}$; ΔS^* = J K^{-1} mol^{-1}; ΔH = kJ mol^{-1}.

The observations from thermogravimetric studies agree well with the mass loss data obtained in independent pyrolysis experiments (Table 1). The final decomposition products were analysed and found to be NiO, ZnO and CdO for the Ni(II), Zn(II) and Cd(II) complexes, respectively.

Decomposition kinetics

The analysis of data obtained from using the Freeman–Carroll and Horowitz–Metzger equations showed that the overall order of decomposition of all three complexes varies from 0.94 to 1.12 and therefore the average value of n may be taken as 1.0. We have also computed the values of the correlation coefficient (r) using weighted LSM, for the equations suggested by Coats and Redfern [22] (with $n = 0$, 1/2, 2/3 and 1) and found a maximum value (0.9999) for the equation with $n = 1$.

Based on this value of reaction order, the kinetic parameters were evaluated using the above-mentioned three equations by graphical means as well as by weighted LSM, and are listed in Table 2. The satisfactory values of correlation coefficients (≈ 1) in all cases indicate good agreement with experimental data. The values of kinetic parameters obtained from different equations are reasonable and in good agreement. The entropy of activation varies from 10 to 16 J K^{-1} mol^{-1}. The enthalpy terms, which vary from 6 to 9 kJ mol^{-1}, have the expected order of magnitude.

It is observed that the values of E^* and A increase in the order $Zn(L) \cdot H_2O < Ni(L) \cdot H_2O < Cd(L)$. Because of their similar structures [15], all three complexes show similar thermal behaviour as evidenced by their peak temperatures and comparable values of E^* and A. Finally, it may be concluded that the decomposition of these complexes involves a random nucleation mechanism [26,27].

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