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THERMAL DECOMPOSITION OF MIXED LIGAND COMPLEXES OF COBALT(II), NICKEL(II), ZINC(II) AND CADMIUM(II) CONTAINING 1,3-DIAMINOPROPAN-2-OL AND OXALATE

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ABSTRACT

Non-isothermal kinetics of the thermal decomposition of mixed ligand complexes of cobalt(II), nickel(II), zinc(II) and cadmium(II) have been studied using thermogravimetry (TG) and differential scanning calorimetry (DSC). The reaction in which the complex loses one molecule of the ligand is found to be first order and the activation energy was calculated using established techniques. Using Dharwadkar and Karkhanavala's method, the values obtained were 25.65, 17.32, 25.22 and 20.95 kcal mole^{-1}, respectively. Infrared spectral studies of these complexes and intermediates provided information regarding the coordinating nature of the ligand 1,3-diaminopropan-2-ol in these complexes.

INTRODUCTION

Several workers [1–5] have reported that the thermal decomposition of oxalate complexes occurs in different ways. Haschke and Wendlandt [6] have reported the decomposition of mixed ligand complexes of zinc(II) and cadmium(II) containing oxalate and ethylenediamine. In the cadmium complex ethylenediamine was lost before the rupture of the oxalate group. Previously, we have reported the thermal decomposition studies of mixed oxalates containing *N*-(2-hydroxyethyl)ethylenediamine [7]. In continuation of this work, the results of thermal decomposition studies of mixed ligand complexes containing 1,3-diaminopropan-2-ol and oxalate are presented in this paper. It is of interest to know particularly about the chelating behaviour of this ligand in these complexes as well as intermediate products of the thermal decomposition.

EXPERIMENTAL

The ligand 1,3-diaminopropan-2-ol was obtained from Fluka and it was used as such without further purification. Metal oxalates of cobalt, nickel, zinc and cadmium were prepared by adding equimolar amounts of oxalic acid solution to the solutions containing the above metal ions. Precipitates thus obtained were air dried for one day at room temperature before use. The oxalato bis(1,3-diaminopropan-2-ol) complexes were prepared from the metal oxalates employing a method similar to the one adopted for the preparation of oxalato *N*-(2-hydroxyethyl)ethylenediamine complexes as described in a previous communication [7]. The yield was approximately quantitative in all cases. Details of the complexes are given in Table 1. The percentage of the metal content present in the complexes was determined by atomic absorption spectrophotometry using a Pye Unicam SP 191 model single beam atomic absorption spectrophotometer. Amount of oxalate present in the complexes was determined by titrating an acidic solution of the complex with standard potassium permanganate solution. Analytical data for carbon and hydrogen was obtained by using a Coleman analyser. Infrared spectra of the complexes were taken as KBr pellets on a Unicam SP 1200 infrared spectrophotometer. Reflectance spectra of the solid complexes were recorded on a Unicam SP 700 spectrophotometer provided with a reflectance attachment. Thermograms of the complexes were obtained using a null type Stanton HT-D thermogravimetric analyser with a heating rate of 6°C $\min^{-1}$ in static air. The DSC curves were obtained by a DuPont differential scanning calorimeter with a heating rate of 10°C $\min^{-1}$.

Methods used for calculating the activation energy (E)

According to Coats and Redfern [8], the order of the reaction of a thermal

TABLE 1

Analytical data of complexes of 1,3-diaminopropan-2-ol and intermediates

Complex	Percent carbon		Percent hydrogen		Percent oxalate		Percent metal	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$Co(dap)_2C_2O_4$	29.36	29.10	6.16	5.89	26.90	27.23	18.01	17.52
$Ni(dap)_2C_2O_4$	29.38	29.65	6.16	6.02	26.92	26.66	17.95	17.54
$Zn(dap)_2C_2O_4$	28.79	28.44	6.04	5.88	26.38	26.72	19.59	19.16
$Cd(dap)_2C_2O_4$	25.24	24.88	5.29	5.00	23.12	22.75	29.52	29.38
$Co(dap)C_2O_4$	25.32	25.25	4.25	3.82	37.12	36.84	24.86	24.69
$Ni(dap)C_2O_4$	25.35	25.15	4.25	4.33	37.28	37.05	24.78	24.56
$Zn(dap)C_2O_4$	24.66	24.45	4.14	4.08	36.14	36.59	26.84	26.37
$Cd(dap)C_2O_4$	20.66	20.34	3.47	3.12	30.09	30.67	38.68	38.44

decomposition reaction can be calculated from the equation

$$A = \ln\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2} = \ln\left[\frac{AR}{\phi E}\left(1-\frac{2RT}{E}\right)\right]-\frac{E}{RT}$$

by plotting $\log[1-(1-\alpha)^{1-n}]/[T^2(1-n)]$ vs. $1/T \times 10^3$ where α = thermal decomposition rate of the sample calculated from the TG curve from the formula, $\alpha = (W_0 - W)/(W - W_k)$ in which W_0, W_k and W are initial weight, final weight and weight of the compound at temperature T, respectively. For a number of assumed values of n, a number of such relationships are plotted and the correct value of n for a given thermal decomposition reaction gives a straight line. These linear plots are shown in Fig. 1. If $n = 1$, then $A = -\log[-\log(1-\alpha)]/T^2]$. The activation energy, E, is calculated from the equation $E = 2.303\ mR$ where m is the slope of the straight line found and R is the gas constant.

The Horowitz and Metzger equation was modified by Dharwadkar and Karkhanavala [9] so as to yield activation energy values which do not vary much by changing sample size and heating rate. According to them, the modified equation for the first order kinetics is

$$\ln\left[\ln(1-\alpha)^{-1}\right] = \frac{E}{RT_i^2}\,\frac{100\phi}{(T_f - T_i)} + C$$

where α = fraction of the sample reacted, E = activation energy, R = gas constant, T_i = temperature of the inception of the reaction, T_f = temperature of the completion of the reaction, T_s = temperature at the inflection point of the thermogram, ϕ = difference between T_s and the temperature under consideration, C = constant.

Swarin and Wims [10] have used the equation

$$K = \frac{(A)^{n-1}\,\mathrm{d}H/\mathrm{d}t}{(A-a)^n}$$

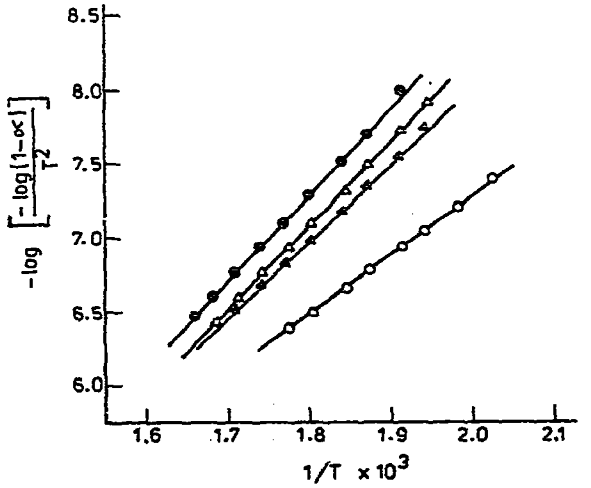


Fig. 1. Plots of $-\log[-\log(1-\alpha)/T^2]$ vs. $1/T \times 10^3$. ●, $Co(dap)_2C_2O_4$; ○, $Ni(dap)_2C_2O_4$; △, $Zn(dap)_2C_2O_4$; ▲, $Cd(dap)_2C_2O_4$.

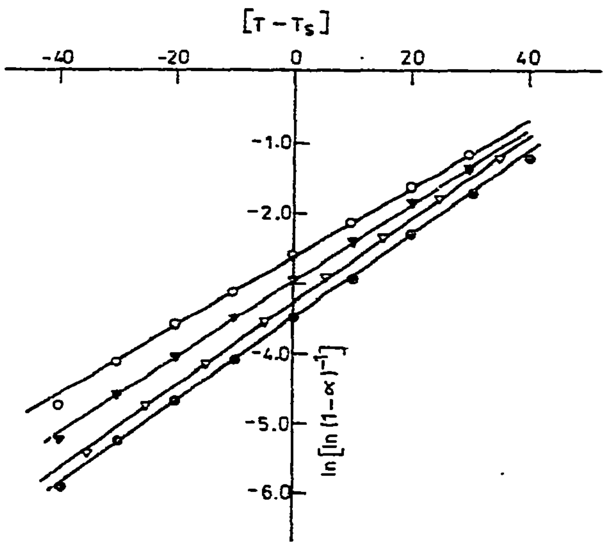


Fig. 2. Plots of $\ln\ln(1-\alpha)^{-1}$ vs. $(T-T_s)$. ●, $Co(dap)_2C_2O_4$; ○, $Ni(dap)_2C_2O_4$; △, $Zn(dap)_2C_2O_4$; ▲, $Cd(dap)_2C_2O_4$.

to determine the activation energy from the DSC curve where K = rate constant, A = total area under the DSC curve, a = area up to temperature T, n = order of the reaction.

For different values of n, plots of $-\ln K$ vs. $1/T$ are made and the correct value of n gave a straight line from which the activation energy of the decomposition reaction was calculated.

Infrared spectral studies

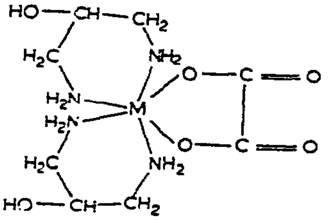
The infrared band positions and their assignments are listed in Table 2. The free ligand 1,3-diaminopropan-2-ol shows a strong broad band at 3400 to 3200 cm^{-1} indicating strong hydrogen bonding in the ligand. In diethylenetriamine, –NH stretching frequencies occur at 3360 cm^{-1} and 3280 cm^{-1}, respectively. Thus in the pure ligand 1,3-diamino propan-2-ol, –OH and –NH stretching bands get mixed up and it is not possible to use these stretching bands for ascertaining the coordination to the metal in the complexes. The metal–nitrogen stretching frequency was observed at ~495 cm^{-1}. A shift in the ν(C–N) of the ligand (~ 1085 cm^{-1}) to a lower value (~ 1050 cm^{-1}) was also observed indicating the coordination of the amino nitrogens to the metal. Oxalate coordination is also likely since the starting material for the preparation of these complexes is metal oxalate. A strong band at ~795 cm^{-1} is assigned to δ(O–C=O) + ν(M–O). These infrared bands are similar to those observed by Fujita et al. [11] for the oxalato complexes in which the oxalate acts as a bidentate ligand. Diffuse reflectance spectra of cobalt(II) and nickel(II) complexes are similar to those of octahedral complexes of cobalt(II) and nickel(II) obtained with ethylenediamine as the coordinating ligand. Since two moles of the ligand are coordinated to the metal ion in each complex, it is likely that the two amino groups

TABLE 2

IR frequencies and band assignments of mixed oxalate complexes

$Co(dap)_2C_2O_4$	$Ni(dap)_2C_2O_4$	$Zn(dap)_2C_2O_4$	$Cd(dap)_2C_2O_4$	Band assignment
3360	3360	3350	3360	$\nu(OH)$
3240	3260	3220	3240	$\nu(NH_2)$
2920, 2890	2820, 2890	2930, 2890	2920, 2885, 2840	$\nu(CH_2)$
1600	1610	1610	1620	$\nu(C=O)+\delta(NH_2)$
1440	1450	1440	1460	$\delta(CH_2)+\nu_S(CO)+\nu(C-C)$
1310	1300	1310	1310	$\nu(C-O)+\delta(O-C=O)$
1090	1095	1090	1080	$\nu(C-C)$
1045, 1030	1040, 1030	1050, 1025	1060, 1030	$\nu(C-N)$
890	895	890	900	$\nu_s(C-O)+\delta(O-C=O)$
795	795	790	795	$\delta(O-C=O)+\nu(M-O)$
540	545	555	550	$\nu(N-M-N)$
495	485	495	495	$\nu(M-N)$

are involved in coordination leaving the hydroxyl group free. These complexes will have distorted octahedral geometry with oxalate taking part in the coordination. The structure can be represented as



Infrared spectra of the intermediate complexes in which only one ligand molecule is present did not show any change in position of the hydroxyl band. So they formally appear to be four coordinated complexes. Since these intermediates are insoluble in most of the solvents, the possibility of polymerization in their case cannot be ruled out.

Thermal decomposition studies

The thermal decomposition curves of cobalt(II), nickel(II), zinc(II) and cadmium(II) complexes are given in Fig. 3. In the case of these complexes, the loss pertaining to one ligand molecule is clearly distinct. This is indicated by a definite curve plateau. On further heating, simultaneous decomposition of the ligand as well as the oxalate was observed. In the case of manganese(II) and iron(II) complexes continuous decomposition of the complex was observed in the range 220–400°C without any step. The final decomposition product in all cases is the metal oxide.

Stable intermediates in case of cobalt(II), nickel(II), zinc(II) and cadmium(II)

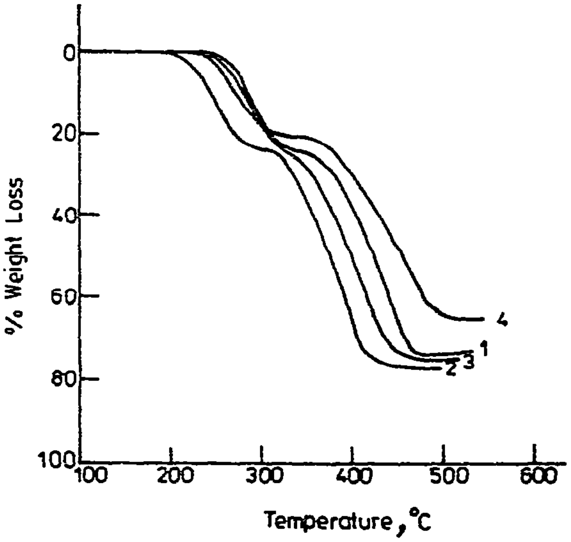


Fig. 3. Thermal decomposition curves of oxalato bis(1,3-diaminopropan-2-ol) complexes. 1, Co(dap)$_2$C$_2$O$_4$; 2, Ni(dap)$_2$C$_2$O$_4$; 3, Zn(dap)$_2$C$_2$O$_4$; 4, Cd(dap)$_2$C$_2$O$_4$.

TABLE 3

Values of activation energy (kcal mole^{-1}) calculated by different methods

Complex	Karkhanavala's method	Coats and Redfern method	DSC method
Co(dap)$_2$C$_2$O$_4$	25.65	26.93	28.55
Ni(dap)$_2$C$_2$O$_4$	17.32	17.50	19.64
Zn(dap)$_2$C$_2$O$_4$	25.22	25.85	
Cd(dap)$_2$C$_2$O$_4$	20.95	23.44	

complexes were isolated after careful heating of the complex up to the proper temperature level as ascertained by thermogram. Analytical data of carbon, hydrogen and oxalate have revealed that these intermediates are of the type M(II) (dap) C$_2$O$_4$. The decomposition temperatures for bis to mono transitions in these complexes are Co(dap)$_2$C$_2$O$_4$, 250–330°C; Ni(dap)$_2$C$_2$O$_4$, 215–290°C; Zn (dap)$_2$C$_2$O$_4$, 240–320°C and Cd(dap)$_2$C$_2$O$_4$, 235–310°C.

The activation energies for the decomposition reaction in which the complex loses one molecule of the ligand, obtained from three different methods were listed in Table 3. The deviations of these values did not differ much, considering the approximations involved in the methods applied for calculating them. From these values the decreasing order of the activation energy is

$$\mathrm{Zn(II)} \simeq \mathrm{Co(II)} > \mathrm{Cd(II)} > \mathrm{Ni(II)}$$

This trend is similar to the one observed by Horowitz and Perros [12] in the case of the thermal stability of bis(8-hydroxy-5-quinolyl) methane coordination polymers as well as the metal oxinates. Thus the high activation energy values in the case of the zinc complexes compared with nickel complexes may be attributed to the high thermal stability of the zinc complexes due to the completely filled d^{10} electron configuration. Higher values of activation energy in the case of zinc(II) and cadmium(II) complexes when compared with the corresponding mixed oxalates containing *N*-(2-hydroxyethyl)ethylenediamine [7] may be attributed to the formation of stable six membered rings due to the coordination of free amine groups of the ligand 1,3-diaminopropan-2-ol with the metal ion.

CONCLUSION

The thermal decomposition reaction in which the oxalato bis(1,3-diaminopropan-2-ol) complexes of cobalt(II), nickel(II), zinc(II) and cadmium(II) lose one molecule of the ligand is a first order reaction. Activation energies for these reactions are in the order Zn(II) $\simeq$ Co(II) $>$ Cd(II) $>$ Ni(II).

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