

THERMAL DECOMPOSITION OF MIXED LIGAND COMPLEXES OF MANGANESE(II), NICKEL(II), COPPER(II), ZINC(II) AND CADMIUM(II) CONTAINING TRIETHANOLAMINE AND OXALATE

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ABSTRACT

The kinetics of thermal decomposition of mixed ligand complexes of Mn(II), Ni(II), Cu(II), Zn(II) and Cd(II) containing triethanolamine and oxalate have been studied using thermogravimetry (TG) and differential scanning calorimetry (DSC). The decomposition reaction in which the complexes lose one molecule of triethanolamine was found to be first order and the activation energy and pre-exponential factors were calculated using established techniques. The values of E_a obtained for these reactions using a modified form of the Horowitz and Metzger equation were 27.75, 20.54, 18.33, 25.32 and 23.25 kcal mole⁻¹, respectively. Infrared spectral data of these complexes and the intermediates gave additional information about the coordinating nature of the ligands in these complexes.

INTRODUCTION

The decomposition of mixed ligand complexes of various metals containing oxalate has been studied by several workers [1–5]. Haschke and Wendlandt [6] studied the thermal decomposition of several ethylenediamine complexes of metal oxalates by TG, DTA and diffuse reflectance spectroscopy. Langfelderova et al. [7] have carried out thermal decomposition studies of mixed ligand complexes of copper(II) containing amine and oxalate. Decomposition of mixed ligand complexes containing *N*-(2-hydroxyethyl)ethylenediamine and 1,3-diaminopropan-2-ol was reported by us earlier [8,9]. Since the ligand triethanolamine can act as a bi-, tri- or tetradentate ligand, it was considered of interest to study the chelating behaviour of this ligand in these complexes through thermal decomposition and infrared spectral studies.

EXPERIMENTAL

Triethanolamine was obtained from B.D.H. and was used without further purification. Oxalate complexes of triethanolamine were prepared by adopt-

ing a method similar to the one used for the preparation of oxalato-hydroxyethylethylenediamine complexes [8], but the triturated mixture was heated on a water-bath for 1 h. The amount of metal present in the prepared complexes was estimated by complexometric titrations with EDTA after decomposing the complex with aqua regia. These results were confirmed by using a Pye Unicam SP 191 model single beam atomic absorption spectrophotometer. The percentage of oxalate present in the complexes was estimated by titrating the acidic solution of the complexes with standard potassium permanganate solution. The carbon and hydrogen analyses were obtained employing a Coleman analyser. Infrared spectra of the complexes were taken using KBr pellets on a Unicam SP 1200 infrared spectrophotometer. Thermograms of the complexes were obtained using a null-type Stanton HT-D thermogravimetric analyser with a heating rate of $6^{\circ}\text{C min}^{-1}$ in static air. The DSC curves were obtained using a duPont differential scanning calorimeter with a heating rate of $10^{\circ}\text{C min}^{-1}$.

Manganese(II), nickel(II), copper(II), zinc(II) and cadmium(II) complexes of the type MX_2Y (X = triethanolamine, Y = oxalate) and iron(II) and cobalt(II) complexes of the type MXY were obtained. Analytical results of these complexes along with the intermediates are given in Table 1 and they agree with the proposed stoichiometric ratio. The methods used for calculating the activation energy were discussed in detail in a previous paper [9].

Infrared spectral studies

Infrared band positions of the complexes and their tentative assignments are listed in Table 2. The $-\text{OH}$ stretching frequency in the free ligand triethanolamine was observed as a broad band at 3450 cm^{-1} . This was shifted to a lower frequency in the complexes indicating coordination of the hydroxyl group to the metal. A shift in the $\text{C}-\text{N}$ stretching frequency of the free ligand ($\sim 1080\text{ cm}^{-1}$) to a lower value ($\sim 1050\text{ cm}^{-1}$) was also observed in all the complexes indicating coordination of the nitrogen atom of the ligand to the metal ion. The metal-oxygen stretching frequency was observed at $\sim 790\text{ cm}^{-1}$ as a strong band which could be coupled with $\delta(\text{O}-\text{C}=\text{O})$. These infrared bands are similar to those observed by Fujita et al. [10] for the oxalato complexes in which the oxalate acts as a bidentate ligand.

While the diffuse reflectance spectra of oxalato(triethanolamine) complexes of nickel(II) and copper(II) agreed with those of the corresponding reported octahedral complexes, the reflectance spectrum of cobalt(II) differed greatly from the reported spectra of cobalt(II) complexes. Since it is a mono-ligand complex, it may be either a four- or five-coordinated complex. From the infrared and reflectance spectral data, it is presumed that all the bis-ligand complexes have a distorted octahedral structure.

TABLE I
Analytical data of oxalato 'tea' complexes and intermediates

Sl. No.	Complex	Carbon		Hydrogen		Metal		Oxalate	
		Found(%)	Calcd.(%)	Found(%)	Calcd.(%)	Found(%)	Calcd.(%)	Found(%)	Calcd.(%)
1	[Mn(tea) ₂ C ₂ O ₄]	37.75	38.10	6.68	6.85	12.31	12.45	19.63	19.94
2	[Fe(tea)C ₂ O ₄]	32.39	32.78	4.99	5.16	18.74	19.05	29.75	30.03
3	[Co(tea)C ₂ O ₄]	32.16	32.44	4.93	5.10	18.80	18.85	29.46	29.72
4	[Ni(tea) ₂ C ₂ O ₄]	37.43	37.77	6.52	6.79	13.01	13.19	19.52	19.77
5	[Cu(tea) ₂ C ₂ O ₄]	37.06	37.37	6.51	6.72	14.08	14.12	19.32	19.56
6	[Zn(tea) ₂ C ₂ O ₄]	36.84	37.21	6.45	6.69	14.22	14.47	19.16	19.48
7	[Cd(tea) ₂ C ₂ O ₄]	33.44	33.71	5.81	6.06	22.35	22.53	17.41	17.64
8	[Mn(tea)C ₂ O ₄]	32.53	32.88	4.99	5.17	18.48	18.80	29.72	30.13
9	[Ni(tea)C ₂ O ₄]	32.25	32.47	4.84	5.11	19.66	19.84	29.53	29.74
10	[Cu(tea)C ₂ O ₄]	31.55	31.94	4.75	5.03	20.87	21.12	29.04	29.26
11	[Zn(tea)C ₂ O ₄]	31.38	31.75	4.76	4.99	21.39	21.60	28.76	29.09
12	[Cd(tea)C ₂ O ₄]	27.12	27.48	4.13	4.32	32.00	32.15	24.85	25.17

TABLE 2

Infrared spectral data of oxalato 'tea' complexes

Complex no. ^a							Band assignments
1	2	3	4	5	6	7	
3380	3400	3380	3420	3360	3360	3360	$\nu(\text{OH})$
2920	2930	2920	2920	2920	2930	2920	$\nu(\text{CH}_2)$
2880	2880	2860	2840	2860	2860	2880	
1620	1600	1630	1600	1600	1610	1610	$\nu(\text{C}=\text{O})$
1440	1440	1460	1480	1460	1475	1460	$\delta(\text{CH}_2) + \nu_s(\text{C}=\text{O})$
1300	1310	1300	1300	1310	1320	1310	$\nu(\text{C}=\text{O}) + \delta(\text{O}-\text{C}=\text{O})$
1080	1090	1090	1095	1110	1090	1095	$\nu(\text{C}-\text{C})$
1045	1060	1065	1045	1050	1050	1055	$\nu(\text{C}-\text{N})$
1020	1030	1050				1025	
890	895	890	890	895	895	895	$\nu(\text{C}=\text{O}) + \delta(\text{O}-\text{C}=\text{O})$
790	790	795	795	790	790	790	$\delta(\text{O}-\text{C}=\text{O}) + \nu(\text{M}-\text{O})$
485	465	520	520	490	495	495	$\nu(\text{M}-\text{N})$
440	420	425	430	430	445	425	$\nu(\text{M}-\text{O})$

^a Complexes numbered as in Table 1.*Thermal decomposition studies*

Thermal decomposition curves of mono-ligand complexes of iron(II) and cobalt(II) did not show any plateaux that could be attributed to formation of a stable intermediate. Oxalato-bis-(triethanolamine) complexes of manganese(II), nickel(II), zinc(II) and cadmium(II) did show a stable intermediate in the TG curve after losing the weight which corresponds to the loss of one molecule of the ligand in the first step (Fig. 1). The decomposition temperatures for bis- to mono-transitions in these complexes lie in the ranges 160–240, 190–250, 190–240, 170–220 and 185–240°C, respectively. The intermediate compounds were isolated after careful heating of the complex up to the proper temperature level as ascertained from the TG curves. Analytical data of these intermediates indicate that these are mono-ligand complexes. Further heating of the intermediates did not yield any stable plateaux and the final product in all the cases was the metal oxide.

It is worthwhile to mention here the thermal decomposition of the mixed complexes of diethylenetriamine (dien) and oxalate [11]. These complexes do not follow the same pattern as 'heen' [8], 'dap' [9] and 'tea' complexes. Complexes of these three ligands lose one ligand molecule in the first step of thermal decomposition. But the dien complexes appear to lose only a part of the ligand molecule in the first step of the thermal decomposition process, since the weight loss in the first step does not correspond to the removal of the ligand as a whole. The complexes $\text{Ni}(\text{dien})_2\text{C}_2\text{O}_4$ and $\text{Cu}(\text{dien})_2\text{C}_2\text{O}_4$ lost

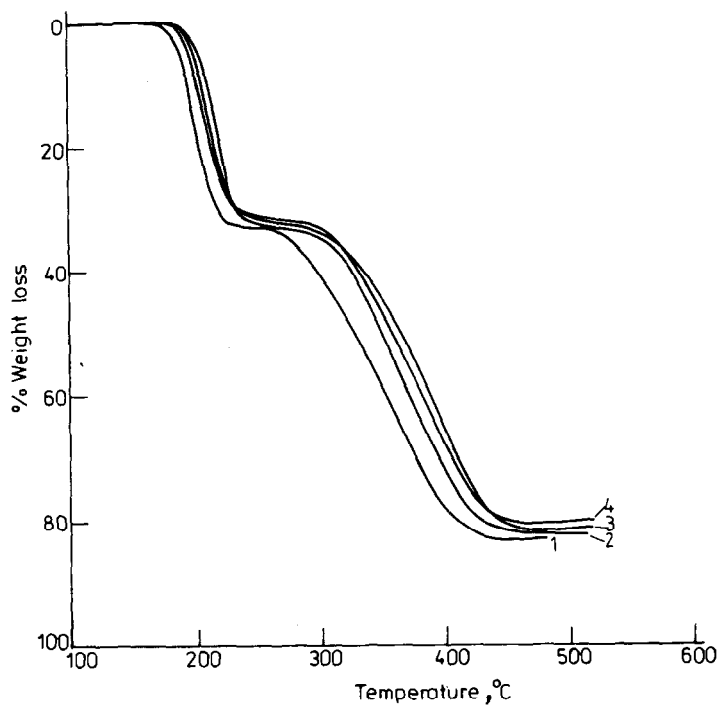


Fig. 1. TG curves of mixed ligand complexes. 1, $\text{Mn}(\text{tea})_2\text{C}_2\text{O}_4$; 2, $\text{Ni}(\text{tea})_2\text{C}_2\text{O}_4$; 3, $\text{Cu}(\text{tea})_2\text{C}_2\text{O}_4$; 4, $\text{Zn}(\text{tea})_2\text{C}_2\text{O}_4$.

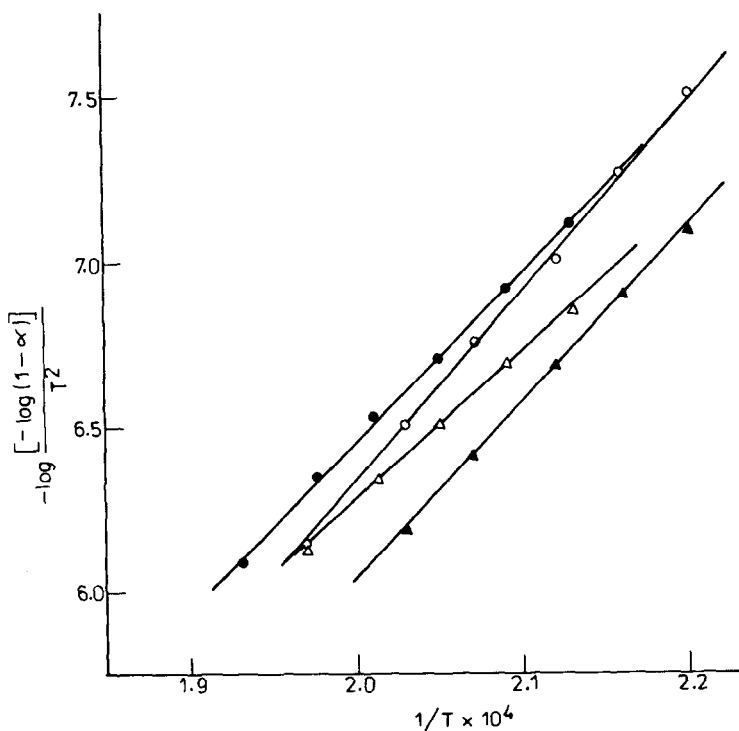


Fig. 2. Linear plots for determination of the activation energy ($n=1$) using the Coats and Redfern equation. \circ , $\text{Mn}(\text{tea})_2\text{C}_2\text{O}_4$; \bullet , $\text{Ni}(\text{tea})_2\text{C}_2\text{O}_4$; Δ , $\text{Cu}(\text{tea})_2\text{C}_2\text{O}_4$; \blacktriangle , $\text{Zn}(\text{tea})_2\text{C}_2\text{O}_4$.

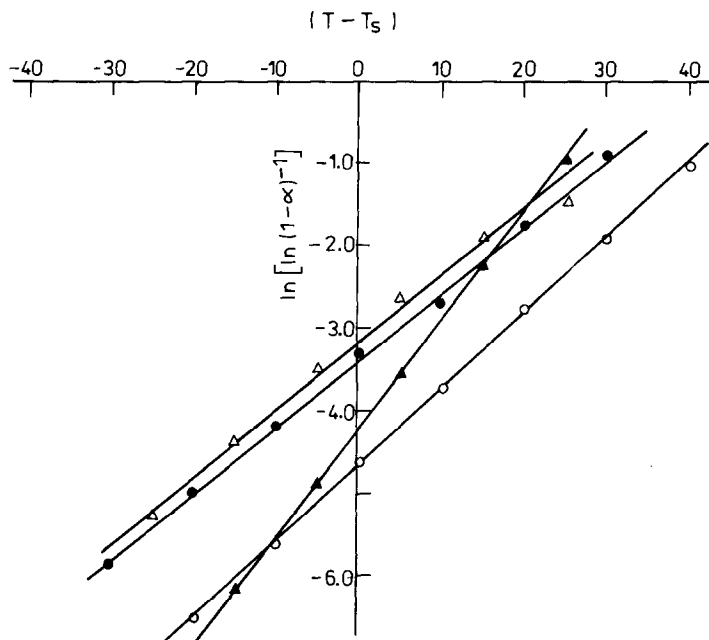


Fig. 3. Linear plots for determination of the activation energy using the Dharwadhar and Karkhanavala equation. ○, $\text{Mn}(\text{tea})_2\text{C}_2\text{O}_4$; ●, $\text{Ni}(\text{tea})_2\text{C}_2\text{O}_4$; △, $\text{Cu}(\text{tea})_2\text{C}_2\text{O}_4$; ▲, $\text{Zn}(\text{tea})_2\text{C}_2\text{O}_4$.

one molecule of the 'dien' in two steps. The possibility of oxalate decomposition in the first two steps has been ruled out from the oxalate analysis data of the intermediates. Data regarding the mixed complexes of dien and oxalate are not given as they are not useful in kinetic analysis. The difference in the behaviour may be due to the difference in the type of binding of dien to the metal complexes. As one molecule of triethanolamine is lost in the first step of the thermal decomposition of the oxalatobis-triethanolamine

TABLE 3

Activation energy values calculated by different methods

Sl. No.	Complex	Activation energy (kcal mole^{-1})			Pre-exponential factor (A) ($\times 10^8$)
		Karkhanavala method	Coats and Redfern method	DSC method	
1	$[\text{Mn}(\text{tea})_2\text{C}_2\text{O}_4]$	27.75	26.90	30.24	8.2
2	$[\text{Ni}(\text{tea})_2\text{C}_2\text{O}_4]$	20.54	20.85	24.21	2.4
3	$[\text{Cu}(\text{tea})_2\text{C}_2\text{O}_4]$	18.33	19.08	23.52	0.9
4	$[\text{Zn}(\text{tea})_2\text{C}_2\text{O}_4]$	25.32	25.46	26.18	4.5
5	$[\text{Cd}(\text{tea})_2\text{C}_2\text{O}_4]$	23.25	24.15	26.55	4.2

metal(II) complexes, it is likely that this ligand is bound to the metal as a bidentate ligand like the ligands heen and dap in the oxalato bis-ligand complexes of these metals [8,9].

Activation energies for the thermal decomposition reactions in which one molecule of the ligand was lost, were calculated using three methods (Coats and Redfern, modified Horowitz and Metzger, and Swarin and Wim's method) and the linear plots are shown in Figs. 2 and 3. Values obtained from these methods are given in Table 3. The standard deviation for these values calculated by all the three methods is 1 kcal mole^{-1} . The values obtained from DSC data are slightly higher than those obtained from TG data. The precision of the values obtained from TG data may be attributed to the accuracy in the measurement of mass. Palermo and Chiu [12] and Madhusudanan et al. [13] have attributed the higher and equal values obtained from DSC and DTA data to their inherent errors which are comparable. The values of activation energy lie in the order $\text{Mn(II)} > \text{Zn(II)} > \text{Cd(II)} > \text{Ni(II)} > \text{Cu(II)}$. Except for cadmium(II), this order is similar to the one observed by Horowitz and Perros for decomposition of metal oxinates [14]. In the case of 'heen' complexes also, a similar order was followed [8] which can be explained on the basis of thermal stability due to stable electronic configurations (i.e. d^5 and d^{10} systems acquire more stability when compared to those systems having unfilled d orbitals). For the complexes of cadmium(II) and zinc(II), the order of the activation energy with respect to the amine as deduced from the present work and the previous two papers [8,9] is $\text{tea} > \text{dap} > \text{heen}$.

CONCLUSION

Oxalatobis-(triethanolamine) metal(II) complexes lose one molecule of the amine in the first step of thermal decomposition: this first step is found to be a first-order reaction. The values of activation energy for this reaction follow the order $\text{Mn(II)} > \text{Zn(II)} > \text{Cd(II)} > \text{Ni(II)} > \text{Cu(II)}$.

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