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Comparative studies on the thermal decomposition of $M[M(C_2O_4)_2] \cdot xH_2O$ ($x = 4$ for M = Mn(II), Co(II), Zn(II); $x = 5$ for M = Ni(II); $x = 6$ for M = Cd(II) and $x = 1$ for M = Sn(II))

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Abstract

The study reveals that the thermal decomposition of most of the complexes $M[M(C_2O_4)_2] \cdot xH_2O$ (where $x = 4$ for M = Mn, Co or Zn; $x = 5$ for M = Ni; $x = 6$ for M = Cd; and $x = 1$ for M = Sn) gives the anhydrous compound which on exposure to humid atmosphere is rehydrated to the original form. In air, the metal oxides were formed directly as a solid decomposition product and in nitrogen metal oxides were formed through the formation of an intermediate mixture of metal or metal oxide and metal oxalate. The evolved CO(g) exerted some additional effects in the decomposition of oxalates and the fused metal oxides had a profound effect on the decomposition of the intermediate metal oxalates. The kinetic parameters for the dehydration and decomposition steps varied according to the atmosphere and different values were obtained for the same step depending on the method applied. Variations were observed in the values calculated from thermogravimetric and differential scanning calorimetric curves.

INTRODUCTION

Although much of the work on oxalato complexes has been reviewed [1] and the thermal decomposition of these complexes has been studied extensively by Wendlandt and coworkers [2–5], relatively little is known about bimetallic complexes of the type $M_1[M_2(C_2O_4)_n] \cdot xH_2O$ (where M_1 and M_2 are the same metal). Recently we have synthesised [6–13] and characterised a series on oxalato complexes of Fe(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Sn(II) of the type $M_1[M_2(C_2O_4)_n] \cdot xH_2O$ and have reported their thermal decomposition in different media. As the

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molecular formulae of the complexes studied were similar, we considered it of interest to correlate the decomposition pattern, the intermediate and end products and the kinetic parameters of different pathways of the dehydration and decomposition (mainly in air and nitrogen) using thermogravimetry (TG), differential thermogravimetry (DTG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). We report here a comparative study of the thermal decomposition of bimetallic oxalato complexes. We also report the kinetic parameters of the decompositions.

EXPERIMENTAL

All experiments were carried out as described previously [6–13]. In the DSC, the kinetic parameters of the phase transformation process were evaluated by the method described by Wendlandt [14].

RESULTS AND DISCUSSION

The infrared (IR) spectra of the compounds showed [6–13] similar patterns in the wavenumber ranges 4000–600 cm^{-1} and 600–100 cm^{-1} and it was concluded that oxalato groups were coordinated to all the metal ions under study in a similar fashion. However, the water molecules were associated in different ways in different complexes. An interesting feature of the low-frequency IR spectra was that ν(M–M) for M = Mn, Co, Ni, Cu, Zn, Cd and Sn were observed [7–13] at 153, 180, 205, 198, 190, 130 and 210 cm^{-1}, respectively. All the spectral components were assigned to different transitions and, considering the diamagnetic nature of some of the compounds, the results of the elemental analysis and the extreme insolubility of the compounds, a binuclear metal(II) species with a strong metal–metal bond was visualized.

The complex multicomponent band observed [8,9] in the visible region of the solid compounds of Co(II) and Ni(II) indicate a severe distortion of the ideal geometry. The complexity of this band in the case of the Co(II) complex was attributed to the presence of both an octahedral and a tetrahedral environment around the two Co(II) atoms. Multicomponent bands in the Ni(II) complex centred around 20200 cm^{-1} indicate [9] both an octahedral and a square-planar geometry around the two nickel atoms, with severe distortion of octahedral environment. In the Cu(II) complex, $\delta \rightarrow \sigma$ and $\delta \rightarrow \pi$ or δ' transitions were observed [10] at 13260 and 15500 cm^{-1}, respectively. Like the Ni(II) complex, the low value of μ_{eff} for the copper complex is due to antiferromagnetic spin pairing between the two paramagnetic Cu(II) ions. The corresponding bands at 33100 and 188 cm^{-1} in the ultraviolet (UV) and IR spectra are associated with the Cu–Cu bond. From valence bond and molecular orbital arguments, the Cu–Cu covalent bond is probably of the δ type. A weak antiferromagnetic exchange interaction is thought to occur in the case of the Mn(II) complex [7]. M → L or L → M charge transfer bands at higher frequencies were observed for some of the complexes.

The results of the thermal studies show that the complexes are dehydrated in a single or successive well-defined stages. Except for the Cu(II) complex, all the complexes started to release water molecules in air medium in the following order of increasing temperature, Sn(II) < Ni(II) < Co(II) < Cd(II) < Zn(II) < Mn(II) (from initial-weight-loss temperature (t_i) values) and in nitrogen as Sn(II) < Ni(II) < Cd(II) < Co(II) < Zn(II) < Mn(II) (Tables 1 and 2). The dehydration of Co(II), Ni(II) and Zn(II) complexes in air took place in a series of successive stages and not all the water molecules were bonded in the same fashion. In the Mn(II) and Cd(II) complexes, all the water molecules were removed in a single well-defined stage, indicating that all the water molecules are bonded in the same way in these complexes. In the Cu(II) and Sn(II) complexes, the water molecules were removed during decomposition. In the Mn(II), Co(II) and Zn(II) complexes in nitrogen atmosphere all the water molecules were removed in a single step. The Cd(II) complexes first released three water molecules simultaneously between 59 and 126°C, the remaining three water molecules being released during decomposition.

The range of t_i values for the dehydration of complexes containing different metal ions was 35–117°C in air and 35–110°C in nitrogen. The linear relationship between t_i and $1/r$ (where r is the ionic radius), as shown in Fig. 1 for Sn(II), Cd(II) and Mn(II) in air, suggests [15] that there is a weak electrostatic interaction between the water molecules and the central metal ions. The data listed in Table 3 show that the initial-weight-loss temperature for the decomposition (t_d) increases in the order Sn(II) < Mn(II) < Co(II) < Cd(II) < Cu(II) < Ni(II) < Zn(II), which indicates that the thermal stability in air of the anhydrous compound increases in the same order. In nitrogen (Table 4), t_d increases in the order Sn(II) < Cd(II) < Mn(II) < Cu(II) < Co(II) < Ni(II) < Zn(II). The thermal stabilities of the anhydrous compounds are slightly higher in nitrogen than in air. CuO formed from the Cu(II) complex was reduced immediately to Cu by CO(g) (from TG in air). However, with DSC discrepancies were observed because the CO evolved during decomposition escaped [10] through the hole of the sample pan before reducing the CuO. Thus the results of TG and DSC in air medium show that the end products of the decomposition of the Cu(II) complex are metallic copper and CuO. The temperature at which corresponding metal oxides (end products) were formed from the other complexes increases in the order Co(II) < Cu(II) < Mn(II) < Cd(II) < Ni(II) < Zn(II). In nitrogen, the corresponding metal oxides (MnO, NiO, CuO, ZnO, CdO and SnO) were formed at approximately 416, 720, 483, 339, 400 and 429°C, respectively. Unstable intermediates comprising a mixture of

TABLE 1

Thermal data from the TG of the dehydration step of the complexes in air medium

Dehydration reaction	t_i [a] (°C)	DTA peak temperature (°C)	$1/r$ [b] (Å^{-1})	E^* [c] (kJ mol^{-1})
$Mn[Mn(C_2O_4)_2]\cdot 4H_2O \xrightarrow{117-147°C} Mn[Mn(C_2O_4)_2] + 4H_2O$	117	150	1.28	137
$Co[Co(C_2O_4)_2]\cdot 4H_2O \xrightarrow{60-120°C} Co[Co(C_2O_4)_2]\cdot 3H_2O + H_2O$ $\xrightarrow{206-251°C} Co[Co(C_2O_4)_2] + 3H_2O$	60	220	1.35	134
$Ni[Ni(C_2O_4)_2]\cdot 5H_2O \xrightarrow{50-172°C} Ni[Ni(C_2O_4)_2]\cdot 4H_2O + H_2O$ $\xrightarrow{172-248°C} Ni[Ni(C_2O_4)_2]\cdot H_2O + 3H_2O$ $\xrightarrow{\approx 330°C}$ Decomposed product $+ H_2O$	50	180, 270	1.37	51
$Cu[Cu(C_2O_4)_2]\cdot 2H_2O \xrightarrow{> 298°C}$ Decomposed product $+ 2H_2O$	-	-	1.39	-
$Zn[Zn(C_2O_4)_2]\cdot 4H_2O \xrightarrow{91-140°C} Zn[Zn(C_2O_4)_2]\cdot 3H_2O + H_2O$ $\xrightarrow{150-162°C} Zn[Zn(C_2O_4)_2]\cdot H_2O + 2H_2O$ $\xrightarrow{180°C} Zn[Zn(C_2O_4)_2] + H_2O$	91	183	1.39	55
$Cd[Cd(C_2O_4)_2]\cdot 6H_2O \xrightarrow{70-134°C} Cd[Cd(C_2O_4)_2] + 6H_2O$	70	110	1.04	27
$Sn[Sn(C_2O_4)_2]\cdot H_2O \xrightarrow{35-238°C} Sn[Sn(C_2O_4)_2] + H_2O$	35	-	0.91	-

[a] Initial-weight-loss temperature for dehydration.

[b] r = ionic radius.

[c] Activation energy.

TABLE 2

Thermal data from the TG of the dehydration step of the complexes in nitrogen medium

Dehydration reaction	t_i [a] (°C)	DTA peak temperature (°C)	$1/r$ [b] (Å^{-1})	E^* [c] (kJ mol^{-1})
$Mn[Mn(C_2O_4)_2]\cdot 4H_2O \xrightarrow{111-138°C} Mn[Mn(C_2O_4)_2] + 4H_2O$	111	133	1.28	67
$Co[Co(C_2O_4)_2]\cdot 4H_2O \xrightarrow{60-206°C} Co[Co(C_2O_4)_2] + 4H_2O$	60	218	1.35	93
$Ni[Ni(C_2O_4)_2]\cdot 5H_2O \xrightarrow{50-175°C} Ni[Ni(C_2O_4)_2]\cdot 4H_2O + H_2O$ $\xrightarrow{175-253°C} Ni[Ni(C_2O_4)_2]\cdot H_2O + 3H_2O$	50	180, 270	1.37	42
$Cu[Cu(C_2O_4)_2]\cdot 2H_2O \xrightarrow{\approx 292°C}$ Decomposed product $+ 2H_2O$	–	–	1.39	–
$Zn[Zn(C_2O_4)_2]\cdot 4H_2O \xrightarrow{92-181°C} Zn[Zn(C_2O_4)_2] + 4H_2O$	92	180	1.39	62
$Cd[Cd(C_2O_4)_2]\cdot 6H_2O \xrightarrow{59-126°C} Cd[Cd(C_2O_4)_2]\cdot 3H_2O + 3H_2O$ $\xrightarrow{\approx 355°C}$ Decomposed product $+ 3H_2O$	59	103	1.04	30
$Sn[Sn(C_2O_4)_2]\cdot H_2O \xrightarrow{35-429°C}$ Decomposed product $+ H_2O$	35	–	0.91	–

[a–c] See footnotes to Table 1.

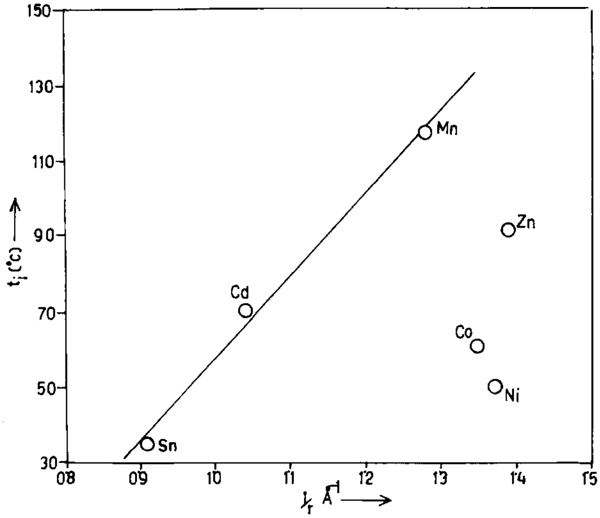

Fig. 1. Plot of t_i vs. $1/r$ at a heating rate of 10°C min^{-1} from TG in air medium.

metal oxides or metal and metal oxalates are suggested for some of the complexes. The intermediates decomposed immediately to subsequent products. However, the TG curves for some complexes do not indicate the formation of such intermediates, whereas in others some breaks in the TG or DTG curves are seen. This might be due to the heat produced which decomposed MC_2O_4 immediately, before the normal decomposition temperature had been reached. Fused metal oxides might also have an accelerating effect on the rapid decomposition of MC_2O_4. Some exothermic peaks

TABLE 3

Thermal data from the TG of the decomposition step of the complexes in air medium

Complex	t_d [a] (°C)	DTA peak temperature (°C)	Temperature for the formation of end product (°C)	Final product	$1/r$ [b] ($Å^{-1}$)	E^* [c] (kJ mol^{-1})
Mn(II)	246	297	314	Mn_2O_3	1.28	115
Co(II)	251	–	300	$Co_2O_3 + Co_3O_4$	1.35	110
Ni(II)	310	340	330 338	$NiO + NiC_2O_4$ NiO or $(NiO + Ni_2O_3)$	1.37	689
Cu(II)	298	–	310	Cu	1.39	504
Zn(II)	318	–	436	ZnO	1.39	230
Cd(II)	278	305	335	CdO	1.04	203
Sn(II)	238	–	310 387	$SnCO_3$ $SnCO_3 + SnO$	0.91	298

[a] Initial-weight-loss temperature for decomposition.

[b,c] See footnotes to Table 1.

TABLE 4

Thermal data from the TG of the decomposition step of the complexes in nitrogen medium

Complex	t_d [a] (°C)	Temperature for the formation of end product (°C)	Final product	$1/r$ [b] (Å^{-1})	E^* [c] (kJ mol^{-1})
Mn(II)	281	327 416	$MnO + MnC_2O_4$ MnO	1.28	34
Co(II)	300	394 420	$Co + CoC_2O_4$ $Co + CoO$	1.35	191
Ni(II)	311	358 410 720	$Ni[Ni(C_2O_4)_{1.5}]$ Ni or (Ni + NiO) NiO	1.37	96
Cu(II)	292	322 483	Cu + CuO CuO	1.39	348
Zn(II)	331	339	ZnO	1.39	287
Cd(II)	280	355 400	$CdO + CdC_2O_4$ Cd_xO_y	1.04	104 113
Sn(II)	238	429 > 429 ≈ 608	SnO $SnO_2 + Sn$ Sn	0.91	80

[a–c] See footnotes to Table 3.

TABLE 5

Thermal data from the DSC of the decomposition step of the complexes in air medium at a heating rate of 5°C min^{-1}

Complex	Exothermic peak temperature range (°C)	t_d [a] (°C)	Peak temperature (°C)	$\ln k_0$	$1/r$ [b] (Å^{-1})	E^* [c] (kJ mol^{-1})	ΔH (kJ mol^{-1})	Order of reaction
Mn(II)	255–350	255	303.1	40.84 ±2.89	1.28	220.33 ±13.44	34.77×10^4	1.57 ±0.11
Co(II)	275–307	275	297.4	13.04 ±5.76	1.35	86.47 ±0.5	36.89×10^4	0.28 ±0.01
Ni(II)	307–353	307	345.1	70.33 ±1.87	1.37	384.61 ±9.42	25.98×10^4	0.78 ±0.04
Cu(II)	260–297	260	285	61.59 ±3.97	1.39	308.52 ±18.14	13.83×10^4	0.89 ±0.09
	297–324	297	307	246.66 ±25.26		–	7.96×10^4	0.52 ±1.3
Zn(II)	347–412 (endothermic)	347	389.5	58.33 ±2.01	1.39	348.45 ±4.19	8.38×10^4	0.96 ±0.05
Cd(II)	–	–	–	–	1.04	–	–	–
Sn(II)	357–375	257	332.1	23.9 ±1.33	0.91	147.56 ±6.36	7.96×10^4	0.87 ±0.06

[a–c] See footnotes to Table 3.

TABLE 6

Thermal data from the DSC of the decomposition step of the complexes in air medium at 10°C min^{-1}

Complex	Exothermic peak temperature range (°C)	t_d [a] (°C)	Peak temperature (°C)	$\ln k_0$	$1/r$ [b] ($\mathrm{Å}^{-1}$)	E^* [c] (kJ mol^{-1})	ΔH (kJ mol^{-1})	Order of reaction
Mn(II)	260–380	260	325.7	32.44 ±2.67	1.28	184.72 ±12.86	36.87×10^4	1.39 ± 0.11
Co(II)	295–324	295	312.2	6.66 ±0.39	1.35	54.17 ±1.93	35.19×10^4	0.14 ± 0.01
Ni(II)	320–365	320	354.5	75.3 ±7	1.37	412.29 ±35.82	32.68×10^4	0.92 ± 0.13
Cu(II)	260–312	260	295.7	49.11 ±2.24	1.39	252.79 ±10.38	15.5×10^4	0.69 ± 0.06
	312–329	312	323.4	79.57 ±3.38	–	412.51 ±16.64	10.05×10^4	–
Zn(II)	360–425 (endothermic)	360	400.1	69.23 ±1.15	1.39	409.95 ±6.28	10.47×10^4	1.14 ± 0.03
Cd(II)	–	–	–	–	1.04	–	–	–
Sn(II)	270–395	270	358	18.38 ±1.33	0.91	122.56 ±6.56	82.5×10^4	0.66 ± 0.07

[a–c] See footnotes to Table 3.

can be seen on the DTA curves for few complexes (e.g. the Ni(II) complex) and these occurred without mass loss. These peaks are attributed to the interaction of or the solid–solid reaction of the products or to some oxidation of the product formed in the oxidising medium. This effect might also be due to some phase transformation or to some inhomogeneity in the fused sample.

The DSC curves recorded at heating rates of 5 and 10°C min^{-1} show the decomposition stages as sharp exothermic peaks. However, in the case of the Zn(II) complex an endothermic peak is observed for the decomposition. In the Cu(II) complex the decomposition is a two-stage process. All the kinetic parameters of the decomposition are listed in Tables 5 and 6. It can be concluded from the t_d values that the stability of the anhydrous complexes decreases in the order Sn(II) > Ni(II) > Co(II) > Mn(II); in the Cu(II) and Sn(II) complexes the water molecules were removed during decomposition. A plot of t_d vs. $1/r$ for a heating rate of 5°C min^{-1} is shown in Fig. 2. With the exception of the Sn(II) an Cu(II) complexes, t_d increased linearly with increasing $1/r$. In the case of the Sn(II) and Cu(II) complexes the plots deviated from linearity, probably due to the removal of water during decomposition. Thus two water molecules in the Cu(II) complex and a single water molecule in the Sn(II) complex might coordi-

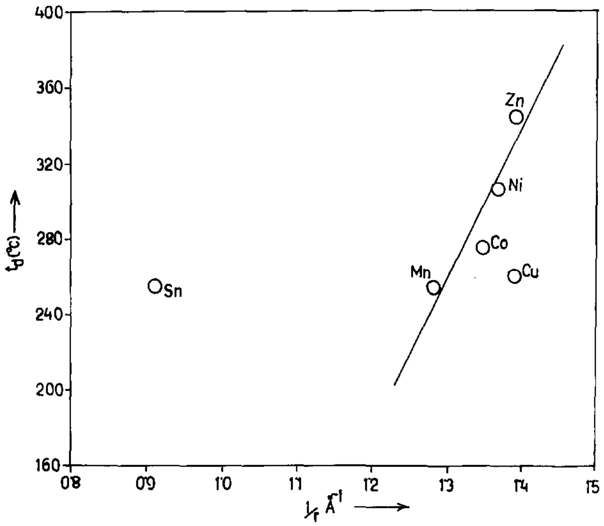

Fig. 2. Plot of t_d vs. $1/r$ at a heating rate of 5°C min^{-1} from DSC in air medium.

nate directly to the metal ion and the complexes can be formulated [15] as $Cu[Cu(H_2O)_2(C_2O_4)_2]$ and $Sn[Sn(H_2O)(C_2O_4)_2]$, like $K_2[Mn(H_2O)_2(C_2O_4)_2]$. A linear correlation was observed in the plot (Fig. 3) of the

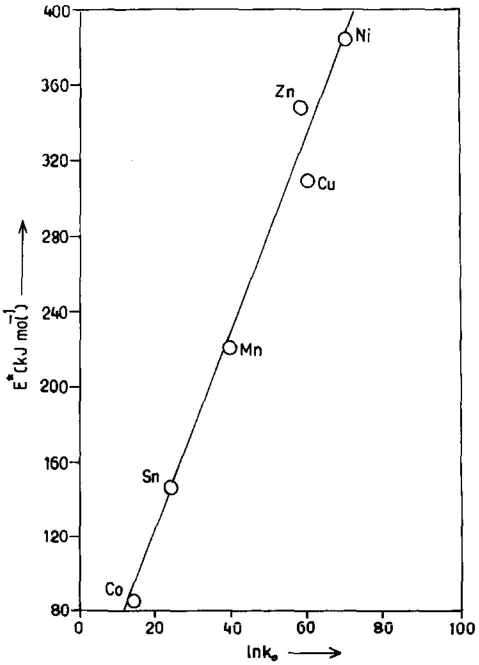

Fig. 3. Plot of E^* vs. ln k_0 for the decomposition step of the complexes from DSC in air medium at a heating rate of 5°C min^{-1}.

activation energy (E^*) vs. ln k_0 at a heating rate of 5°C min^{-1}: E^* increases with ln k_0 in the order Co(II) < Sn(II) < Mn(II) < Cu(II) < Zn(II) < Ni(II).

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