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THERMAL STUDIES ON SOLID COMPLEXES OF SACCHARIN WITH DIVALENT TRANSITION METAL IONS

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Abstract

The thermal decompositions of Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes of saccharin were studied in static air atmosphere. All of the complexes contain four molecules of coordination water and two molecules of crystallization water. The water molecules were removed in a single stage, except from the Zn(II) complex, which exhibited two endothermic effects. The dehydration process was usually accompanied by a sharp colour change. The anhydrous complexes exhibited a phase transition and the decomposition or combustion of saccharin occurred in the second and subsequent stages. The final decomposition products were identified by XRPD as the respective metal oxides. The kinetic parameters, such as the order of reaction and energy of activation for the dehydration stage, were evaluated and the thermal stabilities of the complexes are discussed.

Keywords: divalent transition metals, DTA, saccharin complexes, TG, XRPD

Introduction

Synthetic sweetening agents were developed to eliminate the caloric intake associated with carbohydrate sugars in the diet. Saccharin (Sac = $C_7H_5SO_3N$, o-sulfobenzoimide or 1,2-benzisothioazol-3(2H)-one-1,1-dioxide) was discovered in 1879 and is used extensively as a sweetening agent. The effects of Sac on the human metabolism have been investigated. It has been found that it is not metabolized and also has no food value. However, studies on mice indicated that Sac might produce urinary bladder carcinoma and, because of this effect, its use in soft drinks has been sharply curtailed over the past several years [1–3].

It is well known that bioinorganic complexes containing transition metal ions such as Fe(II), Co(II), Cu(II), etc. play important roles in the human metabolism [4]. Triphenylphosphine and triphenylarsine derivatives of zerovalent platinum

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and palladium complexes with Sac were reported by Roundhill [5] and Haider *et al.* synthesized the first row transition metal saccharinates [6]. However, there appear to be no published data on the thermal properties of these complexes. As a continuation of our investigations in this field, in the present work we report on the thermal behaviour and on a kinetic analysis of thermogravimetric data on Sac complexes of some of the first row divalent transition metal ions.

Experimental

Preparation of complexes

The metal-Sac complexes were prepared by the method reported earlier [6] and characterized by IR, UV-VIS spectroscopy, elemental analysis and magnetic susceptibility studies. Sac itself does not have a high solubility. The sodium or calcium salt is generally used in the preparation. The general reaction for the preparation of the metal complexes of Sac is:

$$MSO_4 + 2NaSac + 6\,H_2O \Rightarrow [M(Sac)_2(H_2O)_4]\cdot 2H_2O + Na_2SO_4$$

where M is Mn(II), Fe(II), Co(II), Ni(II), Cu(II) or Zn(II).

Instrumental

A Rigaku TG8110 thermal analyser combined with a TAS 100 thermogravimetric analyser were used to record simultaneous TG, DTG and DTA curves. The experiments were performed in static air atmosphere at a heating rate of 10 K min^{-1} in the temperature range 20–1000°C, using platinum crucibles. The sample sizes ranged in mass from 7 to 10 mg. Highly sintered α-Al_2O_3 was used as a reference. The DTG sensitivity was 0.05 mg s^{-1}.

In order to identify the solid decomposition products formed in the final stage of thermal decomposition, large amounts of metal(II) complexes of Sac were heated in a tube furnace at predetermined temperatures in static air atmosphere. The solid decomposition products formed in the final stages of thermal decomposition (usually at around 750°C) were identified by using a Siemens X-ray powder diffractometer (XRPD) with Ni-filtered CuK_α radiation.

Kinetic analysis

The first stage of decomposition (dehydration) of the complexes was chosen for detailed study. The kinetic parameters such as energy of activation (E_a) and order of reaction (n) were evaluated graphically by employing the Jeres modification [7] of the Freeman-Carrol method [8], applying the relation

$$[\Delta \ln(d\alpha / dt)] / \Delta \ln(1 - \alpha) = n - E_a [\Delta (1 / T) / \Delta \ln(1 - \alpha)] / R \qquad (1)$$

where T is the temperature in K, R is the gas constant, $\alpha = (m_{int}-m)/(m_{int}-m_{fnl})$, and E_a and n are the energy of activation and order of reaction, respectively.

Results and discussion

Thermal data on the complexes are given in Table 1, and kinetic data associated with the dehydration process in Table 2.

$[Mn(Sac)_2(H_2O)_4]\cdot 2H_2O$

This complex exhibits five steps of decomposition on TG and four peaks on DTG (Fig. 1). The first endothermic peak, in the temperature range 79–170°C (DTG), corresponds to the loss of the four water molecules coordinated to the Mn(II) and the two crystallization water molecules present in the complex. It was found that the loss of 6 water molecules is a first-order reaction and the value of the energy of activation for the dehydration process is 19.66 kJ mol^{-1}. After dehydration, the crystal structure of the complex is distorted, but on gradual heating the anhydrous complex undergoes a phase transition at 278°C, indicating a rearrangement of the species in the solid state. The second decomposition step, between 375 and 476°C, is endothermic, giving two DTA peaks at 338 and 453°C. The mass loss (exp. 24.19%; calcd. 24.29%) corresponds to the loss of two SO_2 molecules. The third and fourth steps are highly exothermic and related to the decomposition of the residual Sac left in the residue. In the final stage, the conversion of MnO_2 to the final product Mn_2O_3 occurs.

$[Fe(Sac)_2(H_2O)_4]\cdot 2H_2O$

Thermal analysis curves of this complex are shown in Fig. 2. The first step in the decomposition sequence corresponds to dehydration of the complex. The

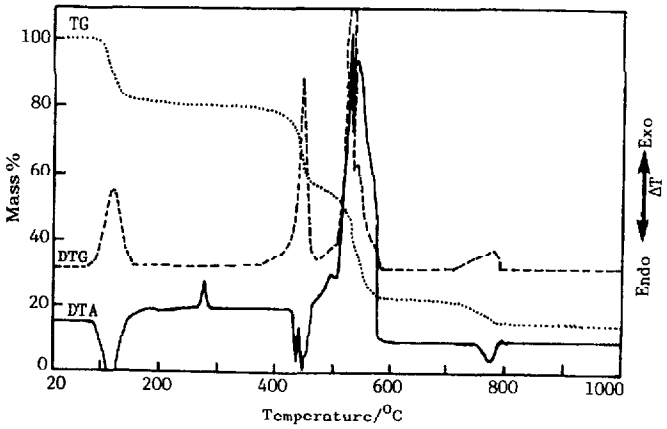

Fig. 1 DTA, TG and DTG curves of $[Mn(Sac)_2(H_2O)_4]\cdot 2H_2O$

Table 1 Thermoanalytical results (TG, DTG, DTA) on the divalent metal complexes of saccharin *

Stage	T_{range}/ °C	DTG_{max}/ °C	$T_{Phase\ trans.}$/ °C	Mass loss/ %	Total mass loss/ %	Solid decomp. product	Colour
$[Mn(Sac)_2(H_2O)_4]\cdot 2H_2O$							white
1	79–170 (endo)	118	278 (exo)	20.05 (20.50)		$[Mn(Sac)_2]$	white
2	375–476 (endo)	445		24.19		–	
3	476–585 (exo)	529		14.49			
4	530–585 (exo)	540		18.79			
5	670–802 (endo)	783		7.58	85.10 (85.02)	Mn_2O_3	black
$[Fe(Sac)_2(H_2O)_4]\cdot 2H_2O$							yellow
1	82–165 (endo)	123	–	19.10 (20.45)		$[Fe(Sac)_2]$	black
2	240–393 (exo)	373		33.78		–	–
3	394–747 (exo)	470		30.85	83.73 (85.10)	Fe_2O_3	brown-red
$[Co(Sac)_2(H_2O)_4]\cdot 2H_2O$							pink
1	85–205 (endo)	126	294(exo)	20.53 (20.34)		$[Co(Sac)_2]$	violet
2	369–465 (exo)	422		24.19		–	–
3	465–605 (exo)	541		34.39		–	–
4	664–820 (endo)	750		5.68		–	–
5	887–918 (endo)	909		1.28	86.07 (83.54)	Co_3O_4	black

Table 1 Continued

Stage	T_{range}/ °C	DTG_{max}/ °C	$T_{Phase\ trans.}$/ °C	Mass loss/ %	Total mass loss/ %	Solid decomp. product	Colour
$[Ni(Sac)_2(H_2O)_4]\cdot 2H_2O$							green
1	91–190 (endo)	134	332 (exo)	18.94 (20.35)		$[Ni(Sac)_2]$	yellow
2	362–451 (exo)	444		40.40			–
3	452–506 (exo)	471		16.11			–
4	510–750 (endo)	704		4.37	79.82 (81.60)	NiO	black
$[Cu(Sac)_2(H_2O)_4]\cdot 2H_2O$							blue
1	68–135 (endo)	103	292 (exo)	19.43 (20.17)		$[Cu(Sac)_2]$	dark-green
2	297–341 (exo)	324		21.67		–	–
3	341–443 (exo)	393		37.81		–	–
4	443–756 (endo)	712		6.27	85.18 (85.15)	CuO	black
$[Zn(Sac)_2(H_2O)_4]\cdot 2H_2O$							white
1	60–95 (endo)	93	227 (exo)	9.75 (10.05)		$[Cu(Sac)_2]$	white
2	95–126 (endo)	103		10.33 (10.05)		–	–
3	389–515 (endo)	461		32.18		–	–
4	515–655 (exo)	578		33.28	85.54 (84.86)	ZnO	white

* The calculated values are given in parentheses.

Table 2 Kinetic data from Eq. (1) for the first stage of decomposition of the metal-saccharin complexes

Reaction			E_a/kJ mol^{-1}	n	r*
$[Mn(Sac)_2(H_2O)_4]\cdot 2H_2O$	$\xrightarrow[-5H_2O]{}$	$[Mn(Sac)_2]$	19.66	1	0.999
$[Fe(Sac)_2(H_2O)_4]\cdot 2H_2O$	$\xrightarrow[-4H_2O]{}$	$[Fe(Sac)_2]$	17.68	0.5	0.998
$[Co(Sac)_2(H_2O)_4]\cdot 2H_2O$	$\xrightarrow[-4H_2O]{}$	$[Co(Sac)_2]$	18.65	0.5	0.999
$[Ni(Sac)_2(H_2O)_4]\cdot 2H_2O$	$\xrightarrow[-5H_2O]{}$	$[Ni(Sac)_2]$	18.73	0.5	0.993
$[Cu(Sac)_2(H_2O)_4]\cdot 2H_2O$	$\xrightarrow[-4H_2O]{}$	$[Cu(Sac)_2]$	18.42	0.5	0.998
$[Zn(Sac)_2(H_2O)_4]\cdot 2H_2O$	$\xrightarrow[-3H_2O]{}$	$[Zn(Sac_2(H_2O)_3]$	15.15	0.5	0.997
$[Zn(Sac)_2(H_2O)_3]$	$\xrightarrow[-3H_2O]{}$	$[Zn(Sac)_2]$	15.15	1	0.986

* Correlation cofficient of the linear plot

elimination of the water molecules occurs between 82 and 165°C. A sharp colour change from yellow to brown was noted on the removal of the water molecules. The dehydration reaction was found to be of half order and the energy of activation for thermal dehydration is 17.68 kJ mol^{-1}. This complex did not display a phase transition. In the second and third steps, the decomposition of Sac took place in the range 240–393°C and 394–747°C, respectively. Each step corresponds to removal of one Sac molecule, as supported by mass loss calculations. The final residue formed at 750°C was identified by XRPD as Fe_2O_3.

$[Co(Sac)_2(H_2O)_4]\cdot 2H_2O$

This complex decomposes in five stages (Fig. 3). The first step, between 85 and 205°C, involves endothermic dehydration of the complex. This step is of half

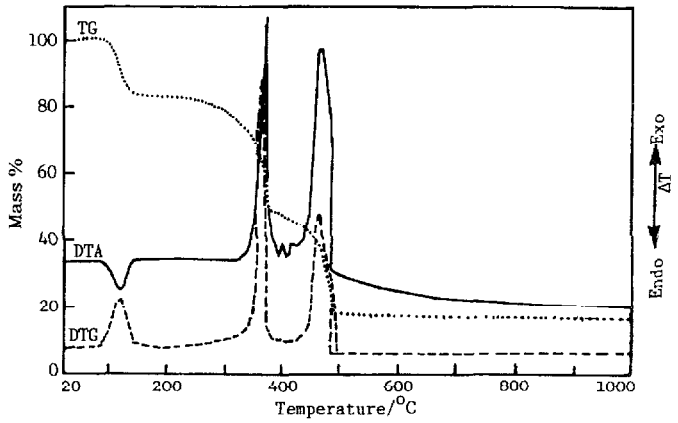

Fig. 2 DTA, TG and DTG curves of $[Fe(Sac)_2(H_2O)_4]\cdot 2H_2O$

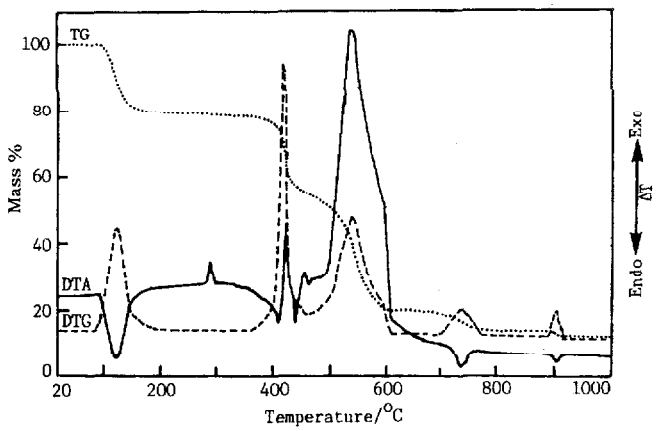

Fig. 3 DTA, TG and DTG curves of $[Co(Sac)_2(H_2O)_4]\cdot 2H_2O$

order and the energy of activation is 18.65 kJ mol^{-1}. The exothermic effect at 294°C corresponds to the solid-phase transition of the anhydrous complex $[Co(Sac)_2]$. The originally pale-pink colour of the complex changes to violet on dehydration. The second step starts at 369°C and finishes at 465°C. This endothermic process is due to the loss of two SO_2 molecules (mass loss: exp. 24.19%; calcd. 24.11%). In the third step, the intermediate formed by elimination of two SO_2 molecules decomposes to give CoO. The endothermic peak at 909°C is related to the conversion of CoO to Co_3O_4.

$[Ni(Sac)_2(H_2O)_4]\cdot 2H_2O$

Figure 4 illustrates the thermal analysis curves of the complex. Thermal dehydration begins at 91°C and ends at 190°C in a single stage. The dehydration is of half order and the energy of activation is 18.73 kJ mol^{-1}. A solid-state phase transition occurred at 332°C. A marked colour change from green to yellow was observed during dehydration. In the second and third stages, the organic part of the anhydrous complex undergoes violent exothermic decomposition. The end-product was found by XRPD analysis to be NiO.

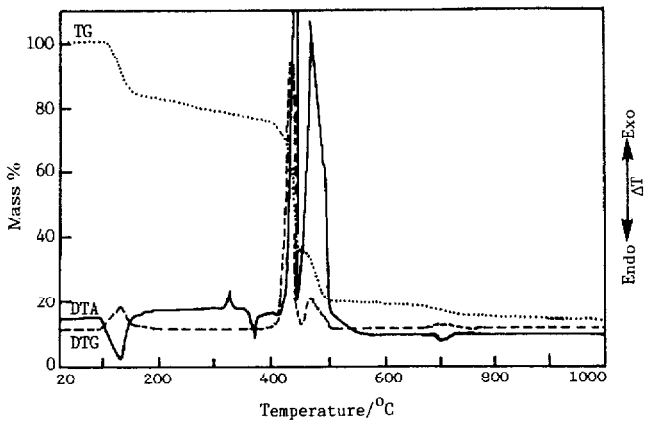

Fig. 4 DTA, TG and DTG curves of $[Ni(Sac)_2(H_2O)_4]\cdot 2H_2O$

$[Cu(Sac)_2(H_2O)_4]\cdot 2H_2O$

This complex exhibits four distinct decomposition steps, as shown in Fig. 5. The first step, in the temperature range 68–135°C, corresponds to loss of the water molecules. The thermal dehydration is of half order and the energy of activation of the thermal dehydration is 18.42 kJ mol^{-1}. On dehydration, a colour change from blue to dark-green was observed. The exothermic peak at 292°C relates to the solid-state phase transition. The second stage is exothermic and related to the loss of SO_2 molecules. In the third stage, the DTA curves reveal several simultaneous processes with a large exothermic effect due to the combustion of the intermediate formed. The final product formed at 750°C consists of CuO.

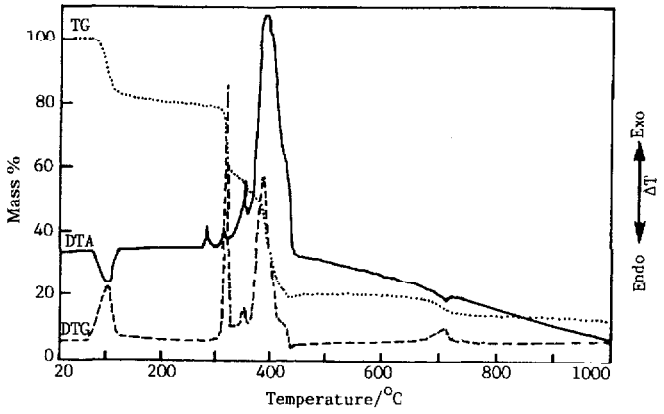

Fig. 5 DTA, TG and DTG curves of $[Cu(Sac)_2(H_2O)_4]\cdot 2H_2O$

$[Zn(Sac)_2(H_2O)_4]\cdot 2H_2O$

This complex exhibits a four-step thermal decomposition (Fig. 6). The thermal dehydration of this complex occurred in two steps, giving endothermic effects at 93 and 103°C. Three moles of water are removed in each stage of dehydration. This behaviour was not observed for the other complexes. It was found that the first and second dehydration stages are of half and first order, respectively, and the values of the energy of activation are 15.5 and 15.5 kJ mol^{-1}, respectively. A solid-state phase transition was observed at 227°C. The third (389–515°C) and fourth (515–655°C) steps correspond to the removal of two Sac molecules, as deduced from mass loss calculations (Table 1). The final product at 750°C was confirmed as ZnO.

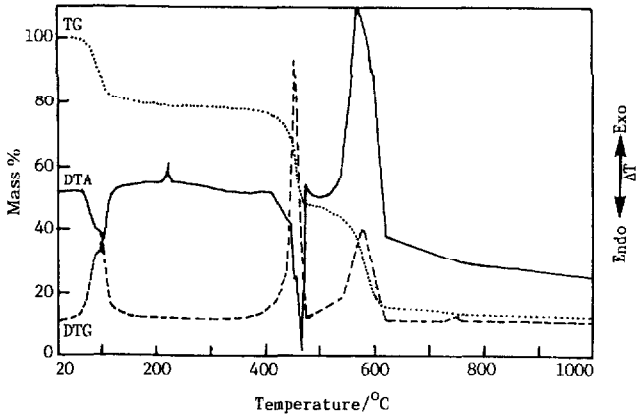

Fig. 6 DTA, TG and DTG curves of $[Zn(Sac)_2(H_2O)_4]\cdot 2H_2O$

The metal saccharinates studied contain six molecules of water and the first stage, from approximately 60 to 205°C, corresponds to dehydration. The experimental data on the mass loss of the dehydration step are consistent with the calculated data (Table 1). The water molecules present in the complexes can be divided into two groups. Four of them are directly bonded to the central metal ion as ligands, while the rest are present as crystallization water. However, the results of this work indicate that the metal-water bond strength is almost the same for all the water molecules and the metal-water bond seems to involve a simple ion-dipole interaction, so that the water molecules are removed in a single step. Only the zinc complex deviates from this behaviour. In general, the first stage of thermal dehydration can be written as

$$[M(C_7H_4SO_3N)_2(H_2O)_4]\cdot 2H_2O_{(s)} \rightarrow [M(C_7H_4SO_3N)_2]_{(s)} + 6H_2O_{(g)}$$

On loss of the four molecules coordination water, the originally octahedral complexes transform to a linear arrangement, in which the metal ions are in an incompletely coordinated environment. This destabilizes the anhydrous complexes and a phase transition occurs at higher temperature to rearrange the species in the solid state. Such a phase transition was not observed for the Fe(II) complex. Dehydration was usually accompanied by a colour change. It was noted that the colour change process was reversible for the Co(II) and Ni(II) complexes when they were left in air, whereas the anhydrous Fe(II) and Cu(II) complexes retained the same colour even when exposed to moist air or water.

The anhydrous Sac complexes show great thermal stability up to 240°C; and in the second and subsequent stages, the decomposition and combustion of Sac in the complexes occur. The nature of the intermediates formed in the second and later stages is not known, but they undergo violent decomposition to give the respective metal oxides as the final products. The oxidation of Mn(II), Fe(II) and Co(II) also occurred in these stages. The formation of metal oxides was confirmed by XRPD.

In order to discuss the thermal stability in the solid state, the initial temperatures of decomposition (dehydration) of the complexes were taken for comparative purposes. The thermal stabilities of the complexes follow the sequence: Ni(II)>Co(II)>Fe(II)>Mn(II)>Cu(II)>Zn(II). A plot of the initial decomposition temperatures of the complexes and the corresponding reciprocal ionic radii of the divalent metal ions against the atomic number exhibits some definite trends, as shown in Fig. 7. Since the studied complexes of Sac are of high-spin type, the high-spin state ionic radii were used in Fig. 7 [9]. The ionic radii of the divalent metal ions decrease from Mn(II) to Ni(II), while the initial temperatures of decomposition increase. The ionic radii for Cu(II) and Zn(II) increase and the thermal stabilities of these complexes decrease. It is evident that the thermal stabilities of the complexes increase as the ionic radii decrease. The thermal stabilities of the Mn(II), Fe(II), Co(II) and Ni(II) complexes in the solid state follow the

general trend found by Irving and Williams [10] for the stabilities of complexes in solution. The Cu(II) and Zn(II) complexes deviate from this general behaviour. Since the Irving-Williams series reflects electrostatic effects, these obser-

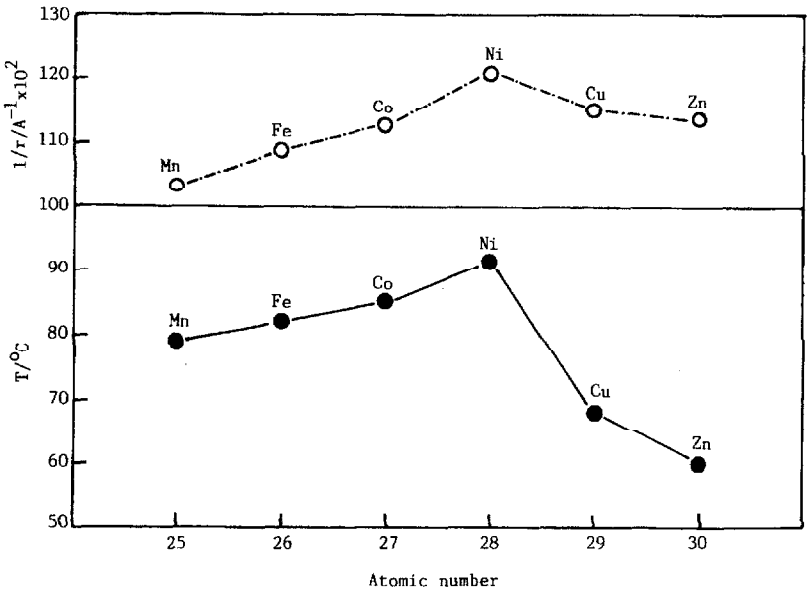

Fig. 7 Initial temperatures of dehydration of hydrated complexes and reciprocals of ionic radii of divalent metal ions *vs.* atomic number

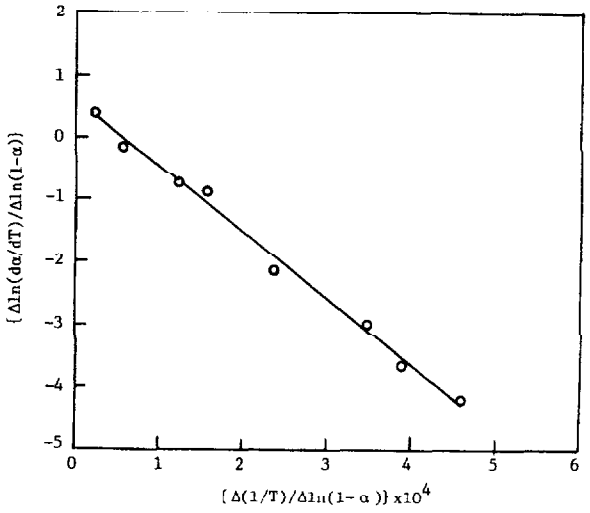

Fig. 8 Freeman-Carrol plot for thermal dehydration of $[Cu(Sac)_2(H_2O)_4]\cdot 2H_2O$

vations indicate that the water-metal interaction in these complexes is almost of ion-dipole type. A similar relationship was observed in the case of the double ammonium sulfate hexahydrate salts of the first row transition metals [11].

The kinetic parameters presented in Table 2 were determined by means of TG and DTG measurements. A typical curve of $[\Delta\ln(d\alpha/dt)/\Delta\ln(1-\alpha)]$ *vs.* $[\Delta(1/T)/\Delta\ln(1-\alpha)]$ for the Cu(II) complex is shown in Fig. 8. The slope of the plot gave the value of $-E_a/R$ and the order of the hydration reaction n was determined from the intercept. All the linear plots were evaluated by regression analysis and the corresponding correlation coefficients r were calculated (Table 2). The energies of activation reflecting the kinetic stabilities of the complexes are in the sequence: Mn(II)>Ni(II)>Co(II)>Cu(II)>Fe(II)>Zn(II). From Table 2, it can be concluded that the thermal dehydration of these complexes also follows a low energetic process. The activation energy values were comparable with these of double ammonium sulfate hexahydrates of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) [11].

References

1 Kirk-Othmer. Encyclopedia of Chemical Technology, 3rd ed., Vol. 2, Wiley, New York 1979, p. 448.
2 M. N. Hughes, 'Coordination Compounds in Biology' in Comprehensive Coordination Chemistry, G. Wilkinson, Ed., Pergamon, Oxford, Vol. 6, Chapter 62.1, 1987, p. 541.
3 Z. Szafran, R. M. Pike and M. N. Singh, 'Microscale Inorganic Chemistry', Wiley, New York 1991 p. 334.
4 E. Frieden, J. Chem. Educ., 62 (1985) 917.
5 D. M. Roundhill, Inorg. Chem., 9 (1970) 254.
6 S. Z. Haider, K. M. A. Malik and K. Ahmed, J. Inorg. Syn., 23 (1985) 47.
7 A. Jeres, J. Thermal Anal., 26 (1983) 315.
8 E. S. Freeman and B. Carrol, J. Phys. Chem., 62 (1985) 394.
9 R. D. Shannon, Acta Cryst., A32 (1976) 751.
10 H. Irving and R. J. P. Williams, J. Chem. Soc., (1953) 3192.
11 V. T. Yilmaz, H. İçbudak and H. Ölmez, Thermochim. Acta, 244 (1994) 85.