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Thermal properties of mixed-ligand bis(hydrazine) and bis(ethylenediamine) complexes of cobalt, nickel and copper saccharinates

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Abstract

The thermal decomposition of mixed-ligand complexes of cobalt, nickel and copper saccharinates with hydrazine and ethylenediamine were studied in static air atmosphere. The first decomposition stage usually corresponds to dehydration, dehydrazination or deethyleneamination. Kinetic analysis of data indicates that these stages follow a low energetic process. All complexes form metal saccharinates as intermediates and the final decomposition products are found to be the respective metal oxides.

Keywords: Hydrazine; Ethylenediamine; Metal saccharinates; Thermal analysis; Kinetic analysis

1. Introduction

Saccharin (sac) is extensively used as a non-caloric sweetening agent [1]. The saccharinate ion, $(C_7H_4NO_3S)^-$, is coordinated to metal ions through the N atom and acts as a monodentate ligand. Because of the interest shown in metal complexes containing ligands with pharmaceutical importance, a number of researchers synthesized and characterized the transition metal (II) saccharinates [2,3] and also their mixed-ligand complexes [3–6]. The thermal decomposition of the aqua complexes of the metal (II) saccharinates were studied by Magri et al. [7] and Içbudak et al. [8]. Recently, Yilmaz [9] has reported that the aqua complex of the Fe(II) saccharinate exhibited an intramolecular electron transfer in the solid state during its thermochemical decomposition. In this work, we studied the thermal behaviour of Co(II), Ni(II) and Cu(II) saccharinates with hydrazine (hyd) and ethylenediamine (en) ligands.

2. Experimental

2.1. Instrumentation

The TG, DTG and DTA curves were obtained using a Rigaku TG8110 thermal analyser combined with TAS 100 thermogravimetric analyser. 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 5 to 10 mg. Highly sintered α-alumina was used as a reference material.

2.2. Kinetic analysis

The first stage of decomposition of the complexes was chosen for the detailed kinetic analysis. The

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kinetic parameters such as energy of activation (E_a) and order of reaction (n) were evaluated graphically by employing Freeman–Carrol method [10] with Jeres modification [11].

2.3. Preparation of complexes

The complexes were prepared by the method reported earlier [5].

3. Results and discussion

Thermal data of the complexes are summarized in Table 1. Kinetic data associated with dehydration, dehydrazination and deethyleneamination are given in Table 2. All complexes except $[Cu_2(sac)_2(en)_2]$ do not have melting points and decompose at the temperatures given in Table 1.

3.1. Hydrazine complexes

3.1.1. $[Co(sac)_2(hyd)_2]$

This complex shows four distinct steps of decomposition (Fig. 1). The first step is the exothermic dehydrazination at 295°C to form Co(II) saccharinate. During the dehydrazination process, a colour change from pink to blue was observed. The energy of activation and order of dehydrazination was found to be 27 kJ mol^{-1} and zero, respectively. The following steps involve the exothermic decomposition of the saccharinate ligand in the temperature range 300–540°C to produce Co_3O_4. The endothermic peak at 909°C is related to the conversion of Co_3O_4 to CoO.

3.1.2. $[Ni(sac)_2(hyd)_2]$

The complex undergoes decomposition in three steps (Fig. 2). The first exothermic peak at 298°C corresponds to loss of two hydrazine molecules. The dehydrazination process causes a colour change from light blue to yellow. Kinetic analysis shows that this step is of zero order with an E_a of 40.3 kJ mol^{-1}. The subsequent decomposition stages are due to decomposition of $Ni(sac)_2$ to form NiO as the final solid product.

3.1.3. $[Cu_2(sac)_2(hyd)_2]$

Thermal decomposition of this complex begins at about 165°C and proceeds in four stages as shown in Fig. 3. The first step is due to exothermic loss of two hydrazine molecules at 197°C. The dehydrazination is of half-order and the energy of activation is 22.9 kJ mol^{-1}. In the subsequent stage, exothermic decomposition of $Cu_2(sac)_2$ occurs with oxidation and CuO forms as the end product.

Thermal reactivity of the copper complex differs from those of the Co(II) and Ni(II) complexes which show the same mode of decomposition. In the Co(II) and Ni(II) complexes, removal of hydrazine molecule

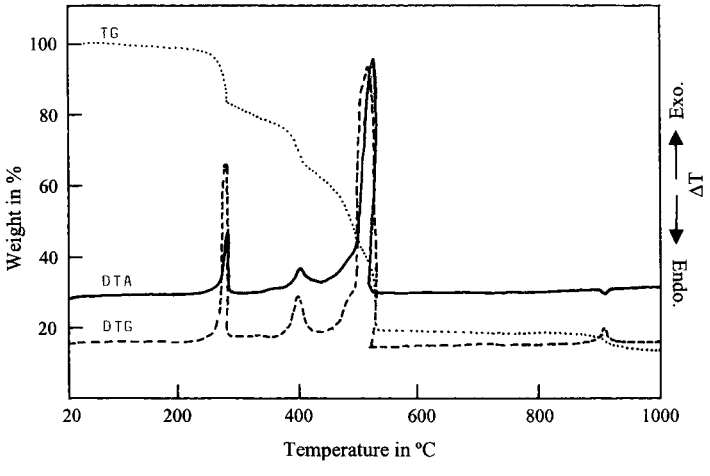

Fig. 1. DTA, TG and DTG curves of $[Co(sac)_2(hyd)_2]$.

Table 1
Thermoanalytical results (TG, DTG, DTA) for the metal complexes

Compound	Temperature range (°C)	DTG_{max}[a] (°C)	Removed group	Mass loss (%)		Total mass loss (%)		Solid decomposition product	Colour
				Found	Calculated	Found	Calculated		
[Co(sac)$_2$(hyd)$_2$] $C_{14}H_{16}N_6O_6S_2Co$									Pale pink
1	250–290	280(−)	2 hyd	14.68	13.14			[Co(sac)$_2$]	Blue
2	300–429	400(−)		19.16					
3	430–540	521(−)		42.44				Co_3O_4	
4	860–973	909(+)		6.78		83.06	83.51	CoO	Black
[Ni(sac)$_2$(hyd)$_2$] $C_{14}H_{16}N_6O_6S_2Ni$									Light blue
1	265–293	298(−)	2 hyd	15.80	13.15			[Ni(sac)$_2$]	Yellow
2	322–448	430(−)		35.50					
3	450–510	479(−)		30.90		82.20	84.65	NiO	Black–yellow
[Cu$_2$(sac)$_2$(hyd)$_2$] $C_{14}H_{16}N_6O_6S_2Cu_2$									Gray
1	167–212	197(−)	2 hyd	11.12	11.53			[Cu(sac)$_2$]	Yellow
2	215–282	237(+)		14.50					
3	334–430	416(−)		45.10					
4	660–725	678(+)		3.20		73.92	71.34	CuO	Black
[Co$_2$(sac)$_2$(OH)$_4$(en)$_2$]en·H$_2$O $C_{20}H_{38}N_8O_{11}S_2Co_2$									Red–pink
1	107–135	121(+)	2H$_2$O	4.80	4.81			[Co$_2$(sac)$_2$(O)(OH)$_2$(en)$_2$]en	Brown
2	189–213	204(−)	2 en	15.31	16.05				
3	214–360	295(−)		15.60					
4	355–469	409(−)		17.19					
5	470–516	500(−)		22.10				Co_3O_4	
6	860–940	910(+)		5.90		80.90	77.82	CoO	Black
[Ni(sac)$_2$(en)$_2$]en·2H$_2$O $C_{20}H_{36}N_8O_8S_2Ni$									Violet
1	83.5–139	125(+)	2H$_2$O	4.48	5.64			[Ni(sac)$_2$(en)$_2$]en	Pale violet
2	143–200	182(+)	en	8.61	9.39			[Ni(sac)$_2$(en)$_2$]	
3	298–425	317(−)		49.98					
4	425–566	506(−)		20.38					
5	681–774	720(+)		5.18		88.63	88.30	NiO	Black–yellow
[Cu(sac)$_2$(en)$_2$] $C_{18}H_{24}N_6O_6S_2Cu$									Dark blue
1	260–308	289(+)	1.5en	15.37	16.43			[Cu(sac)$_2$(en)$_{0.5}$][b]	
2	308–367	321(+)		13.67					
3	368–442	416(−)		30.18					
4	443–485	484(−)		24.07					
5	670–730	700(+)		2.79		86.08	85.48	CuO	Black

[a] (+)Endotherm; (−)exotherm.
[b] In the melted form.

Table 2
Kinetic data for the metal complexes

	Reaction	E_a (kJ mol^{-1})	n	r^a
$[Co(sac)_2(hyd)_2]$	(250–290°C)/(-2 hyd) $[Co(sac)_2]$	27.0	0	0.99
$[Ni(sac)_2(hyd)_2]$	(265–293°C)/(-2 hyd) $[Ni(sac)_2]$	40.3	0	0.98
$[Cu_2(sac)_2(hyd)_2]$	(167–212°C)/(-2 hyd) $[Cu_2(sac)_2]$	22.9	0.5	0.99
$[Co_2(sac)_2(OH)_4(en)_2]en{\cdot}H_2O$	(107–135°C)/(-2 H_2O) $[Co_2(sac)_2(O)(OH)_2(en)_2]en$	11.8	0.5	0.94
$[Ni(sac)_2(en){\cdot}2H_2O$	(83.5–139°C)/(-2 H_2O) $[Ni(sac)_2(en)_2]en$	16.1	0.5	0.95
$[Cu(sac)_2(en)_2]$	(260–308°C)/(-1.5 en) $[Cu(sac)_2(en)_{0.5}]$	28.9	0.5	0.99

[a] Correlation coefficient of the linear plot.

takes place in a single stage and is similar to that observed in the thermal decomposition of hydrazinate complexes [12]. However, the hydrazine molecule present in the copper complex are lost at a comparatively low temperature (Table 1). This may be associated with the different chemical structure of these complexes, since copper in the original complex exhibits an oxidation state of (I) [5].

3.2. Ethylenediamine complexes

3.2.1. $[Co_2(sac)_2(OH)_4(en)_2]en{\cdot}H_2O$

This complexes decomposes in six stages (Fig. 4). The first stage corresponds to dehydration process in the temperature range 107–135°C. The weight loss calculations (calculated 4.81%, experimental 4.80%) indicate the loss of two water molecules. In fact, the complex have a mole of crystallization water and the removal of the second water molecule is associated with the breaking of some of the OH bonds with the formation of a water molecule. This step is of zero order and energy of activation is 11.8 kJ mol^{-1}. The loss of ethyleneamine molecules is an exothermic process and takes place in the second stage of decomposition. The weight loss calculations (calculated 16.05%, found 15.31%) show that the two ethyleneamine molecules are removed in a single step. The other decomposition stages are related to decomposition of saccharinate ligand and other groups present in the complex, with both endothermic and exothermic effects, to form CoO at 910°C.

3.2.2. $[Ni(sac)_2(en)_2]en{\cdot}2H_2O$

The first decomposition stage corresponds the dehydration of complex in the temperature range 84–139°C. The thermal dehydration is of half-order and

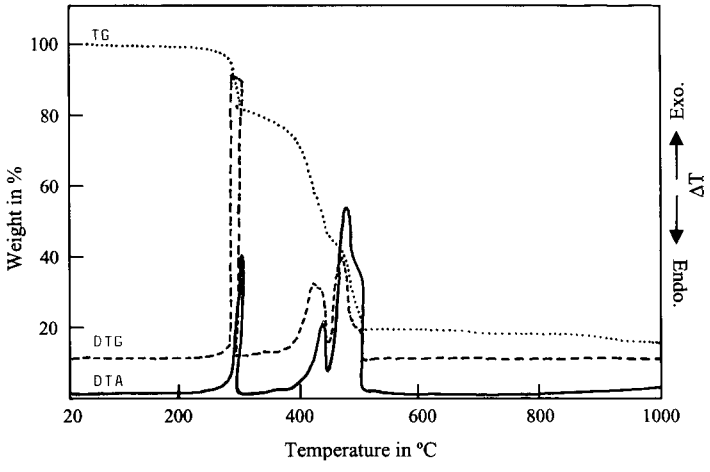

Fig. 2. DTA, TG and DTG curves of $[Ni(sac)_2(hyd)_2]$.

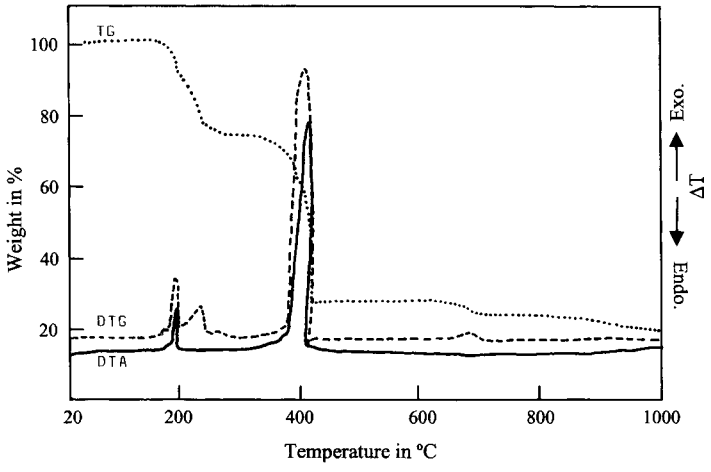

Fig. 3. DTA, TG and DTG curves of $[Cu_2(sac)_2(hyd)_2]$.

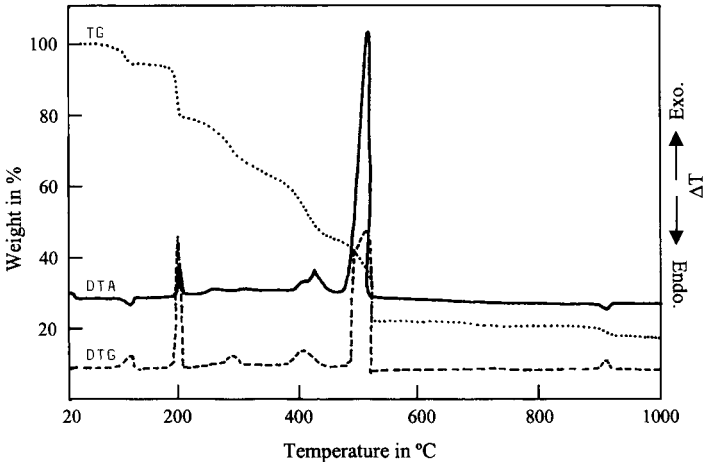

Fig. 4. DTA, TG and DTG curves of $[Co_2(sac)_2(OH)_4(en)_2]en{\cdot}H_2O$.

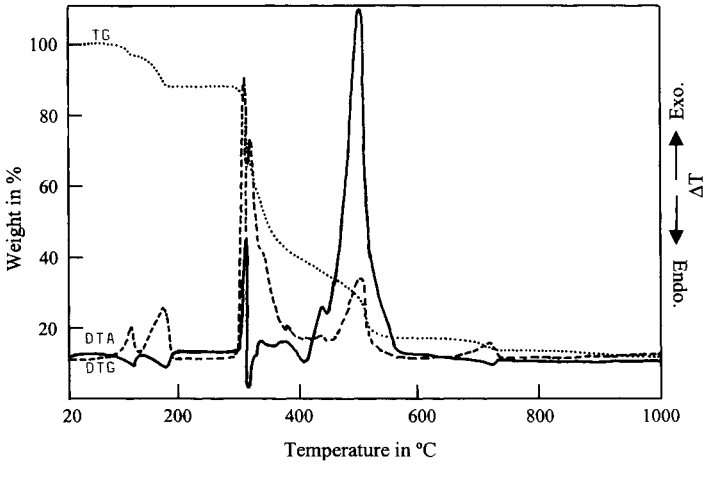

Fig. 5. DTA, TG and DTG curves of $[Ni(sac)_2(en)_2]en{\cdot}2H_2O$.

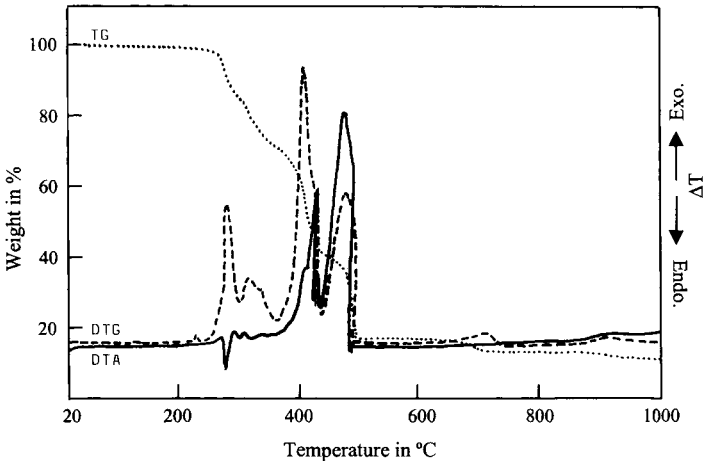

Fig. 6. DTA, TG and DTG curves of $[Cu(sac)_2(en)_2]$.

the energy of activation is 16.1 kJ mol^{-1}. In the second stage, removal of an ethyleneamine molecule present in the outer coordination sphere of the complex occurs at 182°C. The complex shows very complicated decomposition behaviour at temperatures higher than 300°C as given in Fig. 5. NiO is found to be the final decomposition product.

3.2.3. $[Cu(sac)_2(en)_2]$

This anhydrous complex is very stable up to 260°C and then begins to decompose with melting at 284°C. The complex undergoes deethyleneamination in the temperature range 260–330°C observed as two exotherm at 290°C and 321°C, respectively (Fig. 6). The energy of activation and order of reaction is 28.9 kJ mol^{-1} and 0.5, respectively. The violent exothermic decomposition of the Cu(II) saccharinate occurs after the removal of ethylenediamine molecules. The end product is found to be CuO.

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