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Thermochimica Acta 348 (2000) 121–127
thermochimica acta
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Thermal decomposition of Hofmann-type complexes of di- and triethanolamine

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Received 29 June 1999; received in revised form 9 December 1999; accepted 15 December 1999

Abstract

Thermal behaviour of Hofmann-type complexes of di- and triethanolamine with cobalt, nickel, copper and cadmium was studied in dynamic nitrogen atmosphere by DTA, DTG and TG techniques. The first decomposition stage corresponds to dehydration. Kinetic analysis of dehydration data indicates that dehydration follows a low energetic process. Subsequently, release of di- or triethanolamine takes place to form bimetallic cyanides as intermediates and the final decomposition stage is the decomposition of cyanide to yield the respective metals. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Hofmann-type complexes; Diethanolamine; Triethanolamine; Thermal analysis; Kinetic analysis

1. Introduction

Hofmann-type complexes have the general formula $[M(L)_2Ni(CN)_4]$, where M is a transition metal such as Co, Ni, Cu or Cd, and L is an amine ligand such as ammonia, ethylenediamine or pyridine [1,2]. In these complexes, Ni is in a square-planar environment with the C atoms of four CN ligands, and M exhibits octahedral geometry with two L and N atoms of four CN ligands and, therefore, Hofmann-type complexes have a three-dimensional polymeric host structure for inclusion of small guest molecules such as benzene, thiophene and aniline [1,2]. The synthesis and structural properties of these complexes, mainly in connection with their inclusion ability, have been extensively studied [3–11]. Hofmann-type complexes were used as stationary phases in gas and liquid chromatography and effective separations of *n*-paraffins, aliphatic alcohols, aromatic hydrocarbons, aromatic amines, pyridine and its derivatives were achieved [12]. Thermal analysis was applied to determine the stability of the complexes and temperature ranges of liberation of ligands and included molecules [13–16]. Formation of new complexes by heating of the Hofmann-type complexes of ethylenediamine was also reported [14–16].

In a previous paper, we reported the preparation and spectroscopic properties of novel Hofmann-type host complexes of diethanolamine ($DEAH_2$) and triethanolamine ($TEAH_3$) with the formula $[M(L)Ni(CN)_4]$ (where M=Co(II), Ni(II), Cu(II) and Cd(II)) [17]. The aim of the present work is to investigate their thermal properties and the structural changes which occur on heating.

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PII: S0040-6031(00)00348-8

2. Experimental

2.1. Thermal measurements

Thermal behaviour of the complexes was measured on a Rigaku TG 8110 thermal analyser combined with TAS 100 thermogravimetric analyser. The experiments were carried out in dynamic nitrogen atmosphere with a flow rate of 80 ml min^{-1} in the temperature range 20–1000°C, using platinum crucibles. Sample sizes of 5–10 mg and a heating rate of 10°C min^{-1} were used. Sintered α-alumina was used as the reference material.

2.2. Kinetic analysis

The dehydration stage of the complexes was chosen for a detailed kinetic study. The kinetic parameters such as energy of activation (E_a) and order of reaction (n) were evaluated graphically by employing the Freeman–Carroll method [18] with Jeres modification [19].

2.3. Preparation of complexes

The Hofmann-type complexes with $DEAH_2$ and $TEAH_3$ were prepared by the method reported previously [17].

3. Results and discussion

Thermoanalytical data for the complexes are given in Table 1 and kinetic data associated with dehydration are listed in Table 2. Thermal analysis curves of Co(III) complexes of di- and triethanolamine are shown in Figs. 1 and 2, respectively.

3.1. Diethanolamine ($DEAH_2$) complexes

As reported earlier, the $[Co(DEAH)Ni(CN)_4]\cdot 2H_2O$ complex contains a $DEAH_2$ molecule in the anionic state as $DEAH^-$ and with cobalt in the (III) oxidation state [17]. This complex undergoes decomposition in three steps. The first endothermic peak at 59°C corresponds to dehydration, which results in a colour change from pink to violet. Kinetic analysis shows that this step is of first order with an E_a of 15.4 kJ mol^{-1}. In the second stage, endothermic decomposition of $DEAH^-$ takes place in the temperature range 215–400°C. The DTA curve indicates that the decomposition of the ligand is a complex process, consisting of at least three partial processes, with maxima at 267, 334 and 434°C. IR spectra of the residue obtained at 400°C and mass loss calculations (calculated 28.78%, experimental 27.97%) suggest the formation of $CoNi(CN)_4$. Formation of $MM'(CN)_4$ type of intermediates in the decomposition of Hofmann-type complexes was

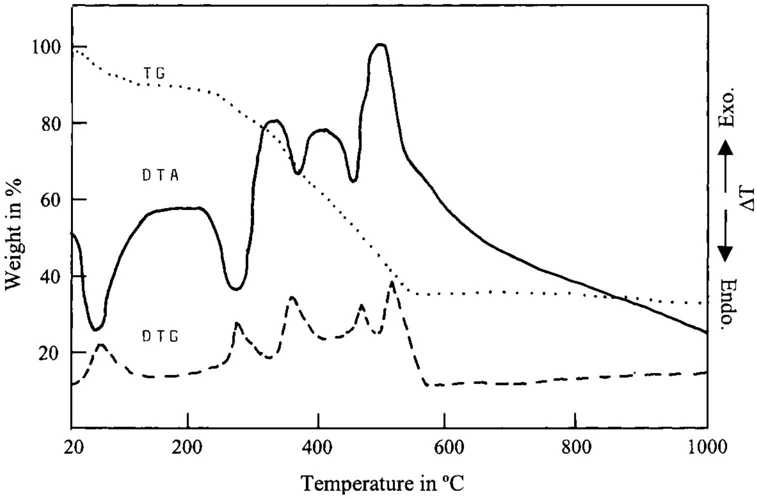

Fig. 1. Thermal analysis curves of Co(III)-DEAH complex.

Table 1
Thermoanalytical data (TG, DTG, DTA) for the Hofmann-type complexes of di- and triethanolamine

Complex	Stage	Temperature range (°C)	DTG_{max} (°C)	Removed group	Mass loan in %		Total mass loan in %		Solid decomp. product	Colour
					Found	Calcd.	Found	Calcd.		
$[Co(DEAH)Ni(CN)_4]\cdot 2H_2O$										pink-brown
$C_8H_{14}N_5O_4CoNi$										
	1	30–154	59(+)	$2H_2O$	10.45	9.95			$[Co(DEAH)Ni(CN)_4]$	violet
	2		267(+)							
	3	215–400	334(−)	DEAH	27.97	28.78			$CoNi(CN)_4$	
	4		434(+)							
	5	400–540	480(−)	4CN	28.42	28.75	66.84	67.48	Co–Ni	
$[Ni(DEAH_2)Ni(CN)_4]\cdot 2.5H_2O$										pale-blue
$C_8H_{16}N_5O_{4.5}NiNi$										
	1	25–120	63(+)	$2.5H_2O$	12.30	12.11			$[Ni(DEAH_2)Ni(CN)_4]$	pale-blue
	2	225–375	352(+)	$DEAH_2$	29.08	28.29			$NiNi(CN)_4$	
	3	375–555	518(−)	4CN	28.00	27.99	69.38	68.39	Ni–Ni	grey
$[Cu(DEAH_2)Ni(CN)_4]\cdot H_2O$										blue-green
$C_8H_{13}N_5O_3CuNi$										
	1	24–104	67(+)	H_2O	5.38	5.15			$[Cu(DEAH_2)Ni(CN)_4]$	pale blue-green
	2		166(−)		29.33	30.09			$CuNi(CN)_4$	
	3	122–361	241(+)	$DEAH_2$						
	4		325(+)							
	5		391(+)							
	6	370–665	590(−)	4CN	18.95	29.77				
	7	832–900	876(+)		3.00		56.66	65.01	Cu–Ni+carbon	dark grey
$[Cd(DEAH_2)Ni(CN)_4]\cdot 1.5H_2O$										
$C_8H_{14}N_5O_{3.5}CdNi$										
	1	25–121	56(+)	$1.5H_2O$	6.41	6.63			$[Cd(DEAH_2)Ni(CN)_4]$	white
	2		274(+)		25.38	25.81			$CdNi(CN)_4$	
	3	201–399	327(+)	$DEAH_2$						
	4		386(−)							
	5		450(+)							
	6	399–620	600(+)	4CN	24.65	25.54	56.44	57.98	Cd–Ni	grey
$[Co(TEAH_2)Ni(CN)_4]\cdot 2H_2O$										pale pink
$C_{10}H_{18}N_5O_5CoNi$										
	1	28–57	46(+)	H_2O	4.70	4.44			$[Co(TEAH_2)\text{-}Ni(CN)_4]$ $\cdot H_2O$	
	2	57–80	69(+)	$0.5H_2O$	2.17	2.22			$[Co(TEAH_2)\text{-}Ni(CN)_4]$ $\cdot 0.5H_2O$	
	3	80–100	88(+)	$0.5H_2O$	2.20	2.22			$[Co(TEAH_2)Ni(CN)_4]$	violet
	4	201–393	256(+)	$TEAH_2$	36.30	36.76			$CoNi(CN)_4$	
	5		360(+)							
	6	395–540	442(−)	4CN	24.67	25.63	70.04	71.86	Co–Ni	grey

Table 1 (*Continued*)

Complex	Stage	Temperature range (°C)	DTG_{max} (°C)	Removed group	Mass loan in %		Total mass loan in %		Solid decomp. product	Colour
					Found	Calcd.	Found	Calcd.		
$[Ni(TEAH_3)Ni(CN)_4]\cdot 1.5H_2O$ $C_{10}H_{18}N_5O_{4.5}NiNi$										pale blue
	1	24–100	44(+)	$1.5H_2O$	6.51	6.79			$[Ni(TEAH_3)Ni(CN)_4]$	pale blue
	2	239–362	352(+)	$TEAH_3$	38.23	37.52			$NiNi(CN)_4$	
	3	362–496	470(+)	4CN	26.01	26.16	71.30	70.39	Ni–Ni	grey
$[Cu\ (TEAH_3)Ni(CN)_4]\cdot 1.5H_2O$ $C_{10}H_{18}N_5O_{4.5}CuNi$										blue-green
	1	25–104	52(+)	$1.5H_2O$	6.37	6.71			$[Cu\ (TEAH_3)Ni(CN)_4]$	pale blue-green
	2	113–360	324(+)	$TEAH_3$	36.45	37.07			$CuNi(CN)_4$	
	3		331(+)							
	4	360–625	565(−)	4CN	23.70	25.85				
	5	834–885	862(+)		2.05		68.57	69.63	Cu–Ni	dark grey
$[Cd(TEAH_3)Ni(CN)_4]\cdot H_2O$ $C_{10}H_{17}N_5O_4CdNi$										white
	1	24–118	97	H_2O	4.12	4.07			$[Cd(TEAH_3)Ni(CN)_4]$	white
	2	281–370	314(+)	$TEAH_3$	34.22	33.73			$CdNi(CN)_4$	
	3		343(+)							
	4	380–661	625(+)	4CN	24.34	23.52	62.68	61.23	Cd–Ni	grey

Table 2
Kinetic data for the Hofmann-type complexes of di- and triethanolamine

Reaction	E_a (kJ mol^{-1})	n	r^a
$[Co(DEAH)Ni(CN)_4]\cdot 2H_2O_{(s)} \xrightarrow[-2H_2O]{30-154°C} [Co(DEAH)Ni(CN)_4]_{(s)}$	15.4	1.0	0.99
$[Ni(DEAH_2)Ni(CN)_4]\cdot 2.5H_2O_{(s)} \xrightarrow[-2.5H_2O]{25-120°C} [Ni(DEAH_2)Ni(CN)4]_{(s)}$	12.6	1.0	0.99
$[Cu(DEAH_2)Ni(CN)_4]\cdot H_2O_{(s)} \xrightarrow[-H_2O]{24-104°C} [Cu(DEAH_2)Ni(CN)_4]_{(s)}$	15.6	1.5	0.99
$[Cd(DEAH_2)Ni(CN)_4]\cdot 1.5H_2O_{(s)} \xrightarrow[-1.5H_2O]{25-121°C} [Cd(DEAH_2)Ni(CN)_4]_{(s)}$	14.6	1.0	0.99
$[Co(TEAH_2)Ni(CN)_4]\cdot 2H_2O_{(s)} \xrightarrow[-H_2O]{28-57°C} [Co(TEAH_2)Ni(CN)_4]\cdot H_2O_{(s)}$	14.3	0.5	0.99
$[Co(TEAH_2)Ni(CN)_4]\cdot H_2O_{(s)} \xrightarrow[-0.5H_2O]{57-80} [Co(TEAH_2)Ni(CN)_4]\cdot 0.5H_2O_{(s)}$	14.5	1.0	0.99
$[Co(TEAH_2)Ni(CN)_4]\cdot 0.5H_2O_{(s)} \xrightarrow[-0.5H_2O]{80-100} [Co(TEAH_2)Ni(CN)_4]_{(s)}$	15.1	1.5	0.98
$[Ni(TEAH_3)Ni(CN)_4]\cdot 1.5H_2O_{(s)} \xrightarrow[-1.5H_2O]{24-100°C} [Ni(TEAH_3)Ni(CN)_4]_{(s)}$	13.2	1.5	0.98
$[Cu(TEAH_3)Ni(CN)_4]\cdot 1.5H_2O_{(s)} \xrightarrow[-1.5H_2O]{16-104°C} [Cu(TEAH_3)Ni(CN)_4]_{(s)}$	12.1	1.5	0.97
$[Cd(TEAH_3)Ni(CN)_4]\cdot H_2O_{(s)} \xrightarrow[-H_2O]{24-118°C} [Cd(TEAH_3)Ni(CN)_4]_{(s)}$	14.9	0.5	0.99

[a] Correlation coefficient of the linear plot.

reported by others [14,15]. At temperatures above 400°C, exothermic decomposition of the cyano group begins and a stoichiometric mixture of metallic Co and Ni was found to be the final decomposition product.

Thermal decomposition of $[Ni(DEAH_2)Ni(CN)_4]\cdot 2.5H_2O$ takes place in three steps. In the first step, dehydration of the complex occurs in a single stage. The energy of activation and order of dehydration were found to be 12.6 kJ mol^{-1} and first order, respectively. The second and third stages are poorly distinguishable on the TG curve. In the temperature range 225–375°C, degradation of $DEAH_2$ proceeds and the last stage corresponds to decomposition of metal cyanides at 518°C to give only metallic nickel.

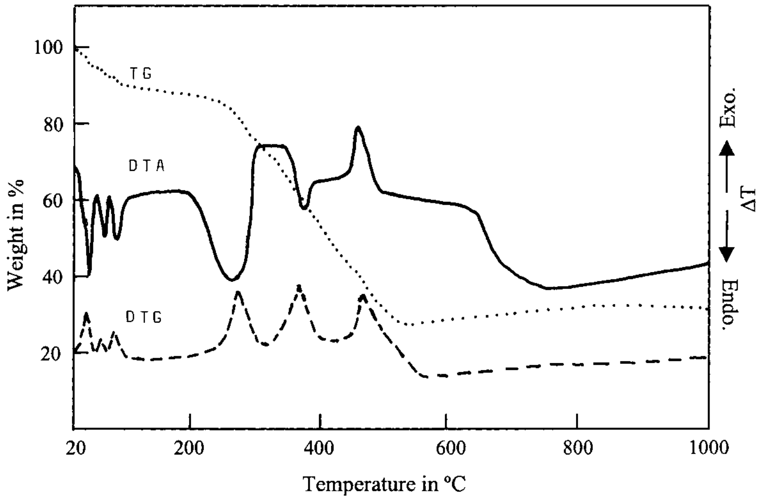

Fig. 2. Thermal analysis curves of Co(III)-$TEAH_2$ complex.

$[Cu(DEAH_2)Ni(CN)_4]\cdot H_2O$ loses water of crystallisation in the first stage of decomposition with a maximum at 67°C. The dehyration is of 1.5-order and the energy of activation is 15.6 kJ mol^{-1}. The subsequent stages above 120°C involve very complicated decomposition steps. At about 370°C, the TG indicates 29.33% mass loss, which corresponds to the formation of $CuNi(CN)_4$ (calculated 30.09%). The next mass loss step between 370 and 665°C is due to decomposition of the metal cyanide formed. An endothermic peak was observed at 876°C. The experimental total mass loss (56.66%) of the complex was found to be significantly lower than the calculated value (65.01%) and this difference was attributed the presence of carbon, formed as a residue in the decomposition of $CuNi(CN)_4$. Therefore, the final decomposition products were found to be a mixture of carbon and metallic Cu and Ni.

$[Cd(DEAH_2)Ni(CN)_4]\cdot 1.5H_2O$ loses water in a single step at 56°C. This step is of first order and the E_a value for the dehydration stage was found to be 14.6 kJ mol^{-1}. The anhydrous complex is stable up to 200°C and above this temperature decomposition of $DEAH_2$ proceeds with four maxima at 274, 327, 386 and 450°C. The last stage is the result of the decomposition of the cyano groups to yield Cd–Ni as the end product.

3.2. Triethanolamine ($TEAH_3$) complexes

Dehydration of $[Co(TEAH_2)Ni(CN)_4]\cdot 2H_2O$ takes place in three stages in the temperature range 30–100°C, with E_a values of 14.3, 14.5 and 15.1 kJ mol^{-1}, respectively. The anhydrous complex is stable up to 200°C. The second decomposition stage between 210 and 393°C is accompanied by a mass loss of 36.30% (calculated 36.76%) and is due to endothermic liberation of $TEAH_3$, and subsequent formation of $CoNi(CN)_4$. The final stage at 395–540°C corresponds to exothermic decomposition of cyano groups of the corresponding intermediate to form a mixture of metallic Co and Ni.

$[Ni(TEAH_3)Ni(CN)_4]\cdot 1.5H_2O$ exhibits three distinct decomposition stages. In the first stage, the dehydration of the complex occurs in the temperature range 24–100°C, with an E_a of 13.2 kJ mol^{-1}. In the second stage, removal of $TEAH_3$ takes place at 352°C. The final stage with a mass loss 26.16% (calculated 26.01%) is attributed to decomposition of $Ni(CN)_2$ to give metallic Ni.

$[Cu(TEAH_3)Ni(CN)_4]\cdot 1.5H_2O$ decomposes in five steps. The first step involves endothermic dehydration at 44°C. The dehydration process was of 1.5-order and the energy of activation was found to be 12.1 kJ mol^{-1}. The anhydrous complex undergoes a complicated endothermic decomposition between 110 and 360°C to yield $CuNi(CN)_4$. The step in the temperature range 360–625°C is related to the exothermic decomposition of the intermediate and an endothermic peak at 862°C with a mass loss of 2.05% results in formation of metallic Cu and Ni.

Thermal dehydration of $[Cd(TEAH_3)Ni(CN)_4]\cdot H_2O$ occurs at 88°C with an E_a of 14.9 kJ mol^{-1}. The anhydrous complex is stable up to 281°C and undergoes endothermic decomposition with two maxima at 314 and 343°C to give $CdNi(CN)_4$. In the temperature range 440–623°C, thermal decomposition of $CdNi(CN)_4$ takes place to produce a mixture of Cd and Ni.

Based on the thermal analysis data, the following generalised thermal decomposition process may be suggested for the Hofmann-type complexes of di- and triethanolamine:

$$[M(L)Ni(CN)_4]\cdot xH_2O_{(s)} \underset{-xH_2O_{(g)}}{\rightarrow} [M(L)Ni(CN)_4]_{(s)}$$

$$[M(L)Ni(CN)_4]_{(s)} \underset{-L_{(g)}}{\rightarrow} [MNi(CN)_4]_{(s)}$$

$$[MNi(CN)_4]_{(s)} \underset{-4CN_{(g)}}{\rightarrow} M_{(s)} + Ni_{(s)}$$

If the initial temperatures of decomposition of the individual unhydrated complexes are compared with each other, the following order of thermal stability is observed:

The $DEAH_2$ complexes:

$$\text{Ni–Ni}\ (225°C) > \text{Co–Ni}\ (215°C) > \text{Cd–Ni}\ (201°C) > \text{Cu–Ni}\ (122°C)$$

The$TEAH_3$ complexes:

$$\text{Cd–Ni}\ (281°C) > \text{Ni–Ni}\ (239°C) > \text{Co–Ni}\ (201°C) > \text{Cu–Ni}\ (113°C)$$

This order indicates that the Cu complexes exhibit much lower thermal stability than the others and the complexes of $DEAH_2$ and $TEAH_3$ show similar thermal stability when compared with the Hofmann-type complexes of ethylenediamine [15].

The activation energies of the first dehydration stage of the complexes range in between 12.0 and 15.5 kJ mol^{-1} (Table 2). The energies of activation reflecting the kinetic abilities of the complexes are in the sequence: Cu–Ni>Co–Ni>Cd–Ni>Ni–Ni for the $DEAH_2$ complexes and Cd–Ni>Co–Ni>Ni–Ni>Cu–Ni for the $TEAH_3$ complexes. From Table 2, it may be concluded that the thermal dehydration of these complexes follows a low energetic process. The energies of activation were comparable with these of double ammonium sulphate hexahydrates of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) [20].

Acknowledgements

We thank Ondokuz Mayıs University for the financial support given to the project.

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