Journal of Thermal Analysis and Calorimetry, Vol. 63 (2001) 105–116

THERMAL STUDIES ON SOLID COMPLEXES OF URACIL WITH SOME DIVALENT TRANSITION METAL IONS

H. Ölmez, O. Z. Yeşilel and H. Içbudak[*]

Department of Chemistry, Faculty of Arts and Sciences, Ondokuz Mayis University,
55139 Kurupelit, Samsun, Turkey

(Received September 3, 1999; in revised form August 25, 2000)

Abstract

The thermal behaviour of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pd(II) complexes of uracil was studied by TG, DTG and DTA in a dynamic nitrogen atmosphere. Two processes occur in the isolated uracil complexes: dehydration and pyrolytic decomposition. In the hydrated complexes, the first stage observed was the loss of water molecules, which was followed by decomposition of the uracil. The thermal dehydration of the complexes occurred in from one to three steps. The final decomposition products were found to be the respective metal oxides, except in the cases of the Co(II) and Pd(II) complexes, which produced metallic cobalt and palladium, respectively. The order of reaction and energy of activation for the dehydration stage were evaluated.

Keywords: divalent transition metals, kinetic analysis, thermal analysis, uracil complexes

Introduction

Various studies on the interactions of metal ions with nucleic acids have been reported in recent years [1–5]. The metal complexes of purines, pyrimidines and their nucleotides play a dominant role in many biochemical systems. However, the study of such large biological systems is very complex. This is due to the presence of a plethora of potential metal-binding sites in the nucleic acids and their constituents. Therefore, to promote an understanding of these important systems, wide-ranging studies on metal complexes with isolated nucleobases have been performed [7–12]. Some of the metal complexes of nucleic acids and their constituents are well known, which is very important because of the biological and clinical implications of these compounds [13]. The complexes of Co(III) and Cr(III) with nucleotides and their derivatives are useful for determining the points where enzymes are activated or inhibited [14]. The platinum group metal complexes with purines, pyrimidines and nucleic

---

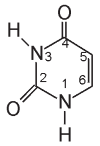
[*] Author for correspondence: E-mail: icbudak@omu.edu.tr

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

acids have been widely studied, and these complexes have been demonstrated to possess antitumour and antibacterial activity [15, 16]. It is well known that certain bioinorganic complexes containing transition metal ions such as Fe(II), Co(II), Cu(II), etc. play important roles in the human metabolism [17, 18].

A large number of metal complexes with uracil, is a pyrimidine base, are known, though few published data have appeared on the thermal properties of these complexes [19–22]. In the present work, we report in detail on the thermal behaviour and kinetic analysis of the uracil complexes of some transition metal ions.



Uracil (UH)

Experimental

Preparation of complexes

The metal-uracil complexes were prepared as described previously [23], and characterized by elemental analysis, infrared spectroscopy, atomic absorption spectrometry and magnetochemical measurements.

Instrumentation

A Rigaku TG 8110 thermal analyser combined with a TAS 100 thermogravimetric analyser was used to record simultaneous TG, DTG and DTA curves. The experiments were performed in a dynamic nitrogen atmosphere with a flow rate of 80 ml min^{-1}, at a heating rate of 10 K min^{-1} in the temperature range 20–1000°C, using platinum crucibles. The sample mass ranged from 5 to 10 mg. Highly sintered α-Al_2O_3 was used as a reference. The DTG sensitivity was 0.05 mg s^{-1}.

Kinetic analysis

The dehydration and decomposition of the complexes were subjected to detailed study. The energy of activation (E_a) and the order of reaction (n) were evaluated graphically by employing the Jeres modification [24] of the Freeman-Carrol method [25], via the relation

$$\frac{\Delta\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)}{\Delta\ln(1-\alpha)}=n-E_a\frac{\frac{\Delta(1/T)}{\Delta\ln(1-\alpha)}}{R} \qquad (1)$$

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 the order of reaction, respectively.

Table 1 Analytical data and colours of isolated complexes*

Compound	C/	H/	N/	M/	Yield/	Colour
	%					
$[Cd(CH_3COO)_2(UH)]\cdot H_2O$	26.62 (26.63)	2.48 (3.33)	7.15 (7.77)	32.12 (31.19)	84	colourless
$[FeCl_2(H_2O)(UH)_2]\cdot H_2O$	24.82 (24.82)	2.81 (3.10)	14.47 (14.48)	12.85 (14.44)	41	brown
$[Co_2(CH_3COO)_4(H_2O)(UH)_2]\cdot 2H_2O$	30.28 (30.39)	4.06 (4.11)	9.74 (8.86)	21.03 (19.21)	95	pink
$[NiCl_2(H_2O)_2(UH)]\cdot H_2O$	16.18 (16.24)	3.38 (3.38)	9.47 (9.90)	19.14 (19.84)	73	yellow
$[Cu(CH_3COO)_2(H_2O)(UH)]$	31.00 (30.84)	3.54 (3.85)	9.85 (8.99)	21.21 (20.38)	85	blue
$[Mn(CH_3COO)_2(UH)]$	34.10 (33.70)	3.25 (3.51)	10.66 (9.83)	20.98 (19.26)	86	pale-pink
$[Zn(CH_3COO)_2(UH)]$	32.09 (32.51)	3.48 (3.38)	9.54 (9.20)	19.44 (21.48)	88	colourless
$[Pd_2Cl_4(UH)_3]$	20.95 (20.86)	1.71 (1.74)	12.29 (12.16)	– –	41	brown

*Calculated values in parentheses

Table 2 Thermoanalytical results (TG, DTG and DTA) on isolated complexes*

Compound	Stage	Temp. range/°C	DTG_{max}/ °C	Mass loss/%	Total loss/%	Solid decomposition product	Colour
$[Cd(CH_3COO)_2(UH)]\cdot H_2O$	1	51–83	67	5.67 (4.99)	–	$[Cd(CH_3COO)_2(UH)]$	
	2–4	163–350	199, 215, 285	–	–	–	
	5	351–812	528	–	66.71 (64.40)	CdO	white
$[FeCl_2(H_2O)(UH)_2]\cdot H_2O$	1	38–71	59	4.99 (4.65)	–	$[FeCl_2(H_2O)(UH)_2]$	
	2	105–143	126	3.01 (2.33)	–	$[FeCl_2(H_2O)_{0.5}(UH)_2]$	
	3	143–198	174	2.76 (2.33)		$[FeCl_2(UH)_2]$	
	4	227–400	305	–	80.98 (79.42)	Fe_2O_3	brownish -red
$[Co_2(CH_3COO)_4(H_2O)(UH)_2]\cdot 2H_2O$	1	53–76	68	1.47 (1.42)	–	$[Co_2(CH_3COO)_4(H_2O)(UH)_2]\cdot 3/2H_2O$	
	2	76–121	100	4.23 (4.27)	–	$[Co_2(CH_3COO)_4(H_2O)(UH)_2]$	
	3	121–150	141	3.30 (2.85)	–	$[Co_2(CH_3COO)_4(UH)_2]$	
	4–6	201–337	239, 281, 321	–	–	–	

Table 2 Continued

Compound	Stage	Temp. range/°C	DTG_{max}/ °C	Mass loss/%	Total loss/%	Solid decomposition product	Colour
$[NiCl_2(H_2O)_2]\cdot H_2O$	1	42–74	61	6.62 (6.09)	–	$[NiCl_2(H_2O)_2(UH)]$	
	2	132–174	165	12.57 (12.17)	–	$[NiCl_2(H_2O)(UH)$	
	3	174–217	188	–	–	$[NiCl_2(UH)]$	
	4	245–324	305	–	76.66 (74.81)	–	
	5	467–641	572	–	–	NiO	greenish-black
$[Cu(CH_3COO)_2(H_2O)(UH)]$	1	85–140	113	6.00 (5.78)	–	$[Cu(CH_3COO)_2(UH)]$	
	2	247–292	260	–	–	–	
	3	400–600	–	–	–	–	
	4	849–911	883	–	74.66 (74.49)	CuO	brownish-black
$[Mn(CH_3COO)_2(UH)]$	1	201–251	220	–	–	–	
	2	252–390	303	–	–	–	
	3–4	450–820	–	–	72.46 (69.52)	MnO_2	brown
$[Zn(CH_3COO)_2(UH)]$	1–4	190–321	216, 230, 276, 297	–	–	–	
	5	490–604	560	–	–	–	
	6	700–934	811	–	73.70 (70.26)	ZnO	white
$[Pd_2Cl_4(UH)_3]$	1	217–330	293	–	–	–	
	2–3	390–766	485, 597	–	70.50 (68.20)	Pd	grey

The calculated values are given in parenthesis

Results and discussion

The results of chemical analysis are given in Table 1. The data are in agreement with the formulae proposed.

The thermal data on the complexes and the kinetic data associated with the dehydration processes are listed in Tables 2 and 3, respectively.

$[Cd(CH_3COO)_2(UH)]\cdot H_2O$

The first step in the decomposition corresponds to the dehydration of the complex (Fig. 1). The endotherm at 67°C corresponds to the dehydration, indicating that the water molecule is not coordinated to the metal ion. The thermal dehydration is of first order and the energy of activation is 17.5 kJ mol^{-1}. The anhydrous complex melts at 199°C (DTA). The third and fourth steps involve the endothermal decomposition of the uracil at 215 and 285°C (DTG), respectively. The final step involves the endothermal decomposition of the intermediates to form CdO.

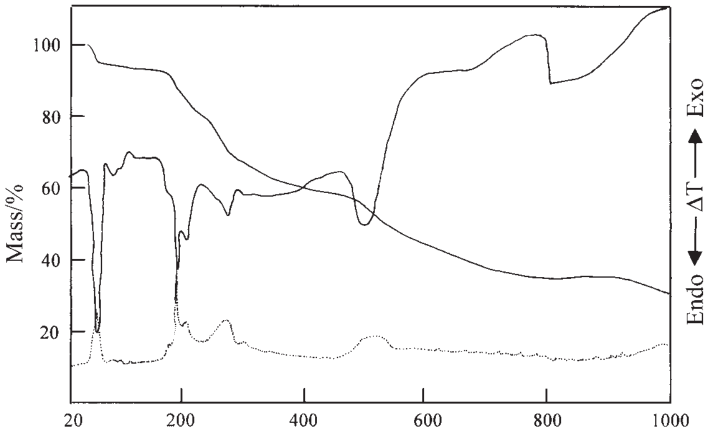


Fig. 1 DTA, TG and DTG curves of $[Cd(CH_3COO)_2(UH)]\cdot H_2O$

$[FeCl_2(H_2O)(UH)_2]\cdot H_2O$

Figure 2 depicts the thermal analysis curves of the complex. The elimination of one molecule of crystallization water occurs between 38 and 71°C (DTG). The thermal dehydration is of first order and the energy of activation is 17.5 kJ mol^{-1}. The second and third steps are endothermal and each step corresponds to the removal of 0.5 molecule of H_2O ligand. It was found that the second and third dehydration stages are of first order and the values of the energy of activation are 20.9 and 20.8 kJ mol^{-1}, re-

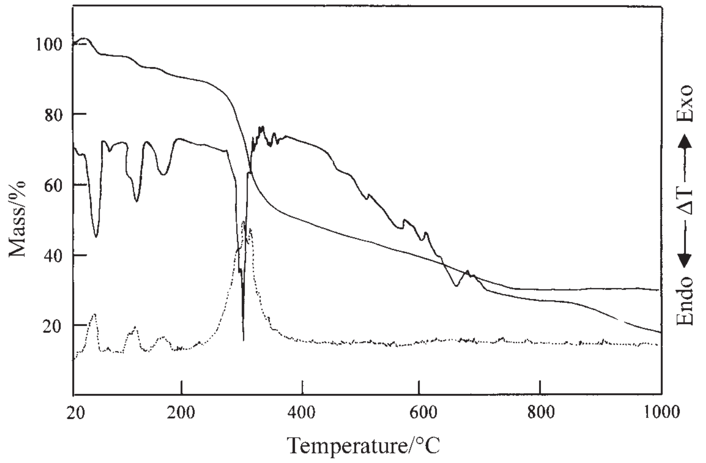


Fig. 2 DTA, TG and DTG curves of $[FeCl_2(H_2O)(UH)_2]\cdot H_2O$

spectively. The following step involves the endothermal decomposition of the uracil ligand. The final decomposition product is Fe_2O_3.

$[Co_2(CH_3COO)_4(H_2O)(UH)_2]\cdot 2H_2O$

The thermal analysis curves of the complex are shown in Fig. 3. The thermal dehydration of this complex occurs in three steps, giving endothermal effects at 68, 100 and 141°C (DTG), respectively. 0.5 molecules of crystallization water is removed in the first step of dehydration. The second step, in the temperature range 76–121°C, corresponds to the loss of 1.5 molecules of water. The third step, between 121 and

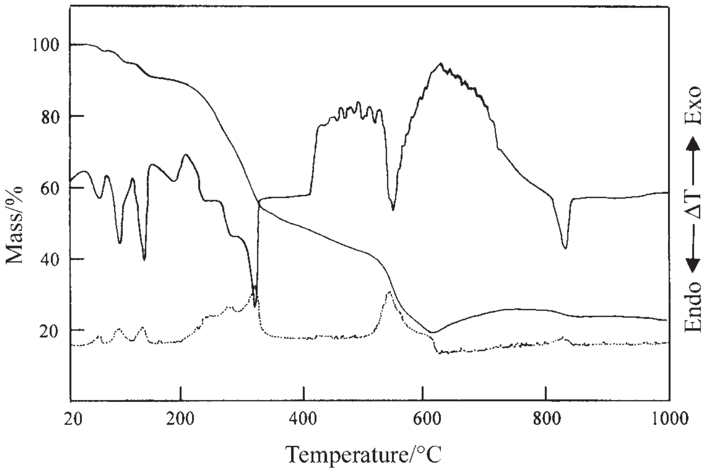


Fig. 3 DTA, TG and DTG curves of $[Co_2(CH_3COO)_4(H_2O)(UH)_2]\cdot 2H_2O$

Table 3 Kinetic data from Eq. (1) for the dehydration processes of the isolated compounds

Reaction	Group removed	E_a/ kJ mol^{-1}	n	r^*
$[Cd(CH_3COO)_2(UH)]\cdot H_2O_{(k)} \xrightarrow{51\pm 83°C} [Cd(CH_3COO)_2(UH)]_{(k)}+H_2O_{(g)}$	H_2O	17.5	1	0.99
$[FeCl_2(H_2O)(UH)_2]\cdot H_2O_{(k)} \xrightarrow{38\pm 71°C} [FeCl_2(H_2O)(UH)_2]_{(k)}+H_2O_{(g)}$	H_2O	17.5	1	0.99
$[FeCl_2(H_2O)(UH)_2]_{(k)} \xrightarrow{105-143°C} [FeCl_2(H_2O)_{0.5}(UH)_2]_{(k)}+1/2H_2O_{(g)}$	$1/2H_2O$	20.9	1	0.99
$[FeCl_2(H_2O)_{0.5}(UH)_2]_{(k)} \xrightarrow{143-198°C} [FeCl_2(UH)_2]_{(k)}+1/2H_2O_{(g)}$	$1/2H_2O$	20.8	1	0.99
$[Co_2(CH_3COO)_4(H_2O)(UH)_2]\cdot 2H_2O_{(k)} \xrightarrow{53-76°C} [Co_2(CH_3COO)_4(H_2O)(UH)_2]\cdot 3/2H_2O_{(k)}+1/2H_2O_{(g)}$	$1/2H_2O$	17.3	1	0.99
$[Co_2(CH_3COO)_4(H_2O)(UH)_2]\cdot 3/2H_2O_{(k)} \xrightarrow{76-121°C} [Co_2(CH_3COO)_4(H_2O)(UH)_2]_{(k)}+3/2H_2O_{(g)}$	$3/2H_2O$	19.1	0	0.99
$[Co_2(CH_3COO)_4(H_2O)(UH)_2]_{(k)} \xrightarrow{121-150°C} [Co_2(CH_3COO)_4(UH)_2]_{(k)}+H_2O_{(g)}$	H_2O	19.1	0	0.99
$[NiCl_2(H_2O)_2(UH)]\cdot H_2O_{(k)} \xrightarrow{42-74°C} [NiCl_2(H_2O)_2(UH)]_{(k)}+H_2O_{(g)}$	H_2O	17.7	1	0.99
$[NiCl_2(H_2O)_2(UH)]_{(k)} \xrightarrow{132-174°C} [NiCl_2(H_2O)(UH)]_{(k)}+H_2O_{(g)}$	H_2O	22.9	0	0.99
$[NiCl_2(H_2O)(UH)]_{(k)} \xrightarrow{174-217°C} [NiCl_2(UH)]_{(k)}+H_2O_{(g)}$	H_2O	22.9	0	0.99
$[Cu(CH_3COO)_4(H_2O)(UH)]_{(k)} \xrightarrow{85-140°C} [Cu(CH_3COO)_2(UH)]_{(k)}+H_2O_{(g)}$	H_2O	20.4	1	0.99

[*] Correlation coefficient of the linear plot

150°C, involves the endothermal loss of one molecule of H_2O ligand. After the dehydration steps, an endothermal peak was observed at 190°C (DTA); the origin of this is unknown. The following steps involve the endothermal decomposition of the intermediate formed, to give metallic Co as the final solid product.

$[NiCl_2(H_2O)_2(UH)]\cdot H_2O$

This complex decomposes in five steps (Fig. 4). The first step involves endothermal decomposition at 61°C (DTG), corresponding to loss of the crystallization water, as indicated by the TG mass loss. This reaction is of first order and the energy of activation is 17.7 kJ mol^{-1}. Such low-temperature dehydration confirms that this is the loss of crystallization water. The second step, at 165°C is endothermal and reveals the loss

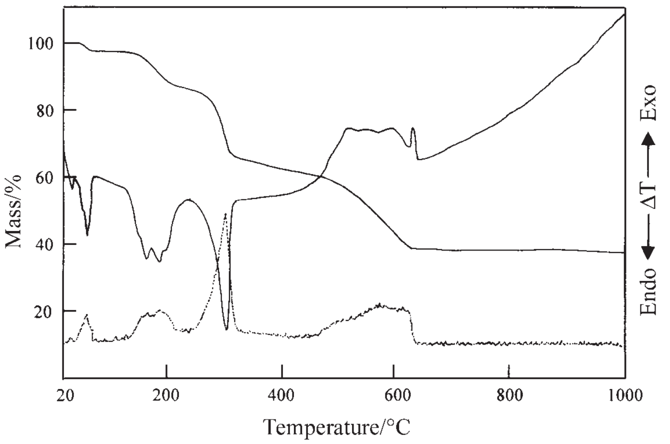


Fig. 4 DTA, TG and DTG curves of $[NiCl_2(H_2O)_2(UH)]\cdot H_2O$

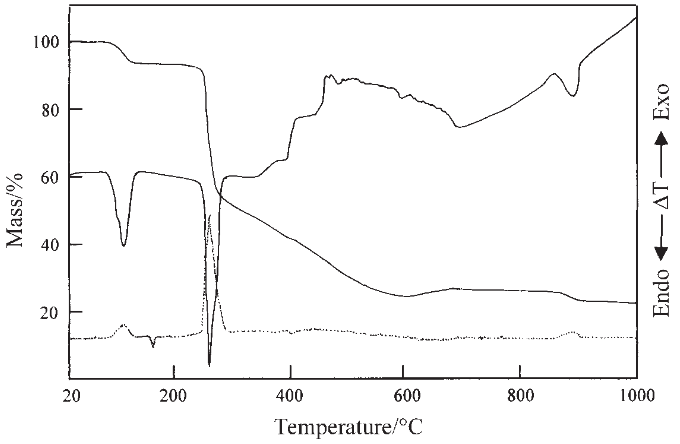


Fig. 5 DTA, TG and DTG curves of $[Cu(CH_3COO)_2(H_2O)(UH)]$

of one molecule of H_2O ligand. The following decomposition step, at 188°C, corresponds to the loss of the other H_2O ligand. Such high-temperature dehydration clearly involves the loss of water coordinated to the metal ion. The anhydrous complex then decomposes at 305°C (endo) and at 572°C (exo), to form NiO as the final product.

[Cu(CH$_3$COO)$_2$(H$_2$O)(UH)]

The first decomposition step for this complex gives an endothermal peak at 113°C (DTG) in the temperature range 85–140°C, and corresponds to the loss of one molecule of H_2O ligand (Fig. 5). This step is of first order and the energy of activation is 20.4 kJ mol^{-1}. Such high-temperature dehydration confirms the loss of coordinated water. The second step, at 260°C, is endothermal and relates to the decomposition of the uracil ligand. The subsequent decomposition step, completed at 600°C, produces CuO as the final solid product.

[Mn(CH$_3$COO)$_2$(UH)]

The complex begins to decompose with melting at 220°C (Fig. 6). The subsequent decomposition stages are due to the decomposition of the intermediate, and furnish MnO_2 as the final solid product at 800°C.

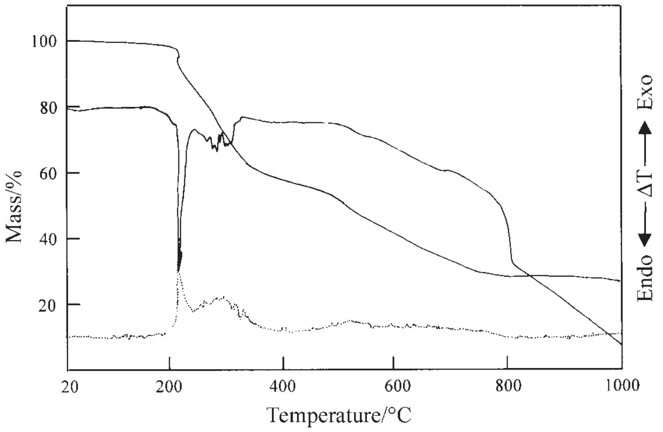


Fig. 6 DTA, TG and DTG curves of [Mn(CH_3COO)$_2$(UH)]

[Zn(CH$_3$COO)$_2$(UH)]

This anhydrous complex begins to decompose with melting at 216°C and undergoes decomposition in six steps (Fig. 7). The consecutive steps of endothermal decomposition at 216, 230, 276, 297, 560 and 817°C are related to the decomposition of uracil. The final product, formed at about 900°C, consists of ZnO.

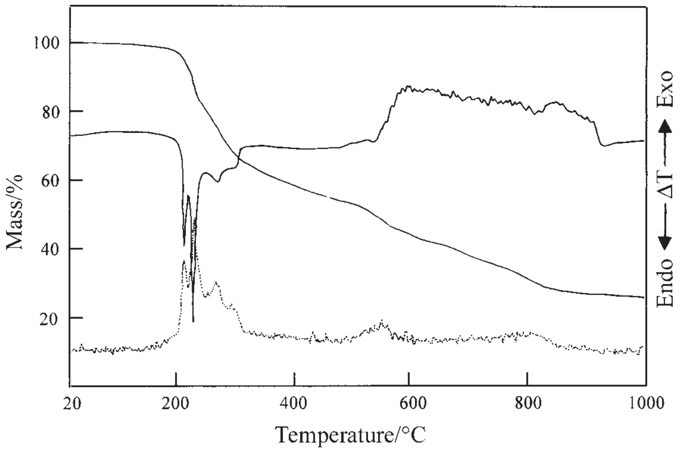


Fig. 7 DTA, TG and DTG curves of [Zn($CH_3COO)_2$(UH)]

[$Pd_2Cl_4(UH)_3$]

The decomposition of this anhydrous complex begins at 217 and ends at 766°C. The final product, formed at about 766°C, consists of Pd. The TG curve of the complex shows the consecutive decomposition (Fig. 8). This can be attributed to the polymeric structure of the complex [19, 20].

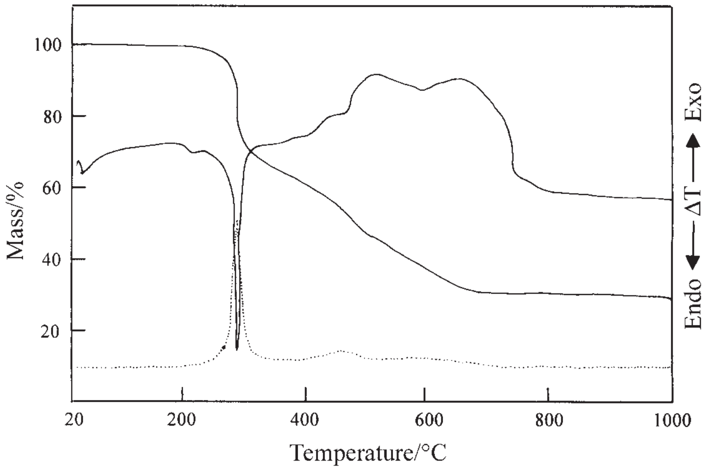


Fig. 8 DTA, TG and DTG curves of [$Pd_2Cl_4(UH)_3$]

Conclusions

The thermal decompositions of these compounds take place in two steps: dehydration and pyrolytic decomposition. The dehydration temperatures of the complexes lie in the range 38–234°C (Table 3). For the Cu(II) and Cd(II) complexes, the dehydration processes take place in a single stage. For the other complexes, the removal of water molecules takes place in several steps. The activation energies for the removal of crystallization and ligand water are 17.3–17.7 and 19.1–22.9 kJ $\mathrm{mol^{-1}}$, respectively. These high activation energies indicative of the removal of ligand water are consistent with the IR data [28]. All the complexes undergo thermal decomposition to form the corresponding metal oxides, except for the Co(II) and Pd(II) complexes, which decompose to form metallic cobalt and palladium as the final products.

References

1 J. A. Carrabine and M. Sundanalingam, Biochemistry, 10 (1971) 292.
2 A. S. Sarkar, P. Ghosh and R. K. Bandyopadhyat, Indian J. Chem., 27A (1988) 819.
3 M. Gupta and M. N. Srivastava, Polyhedron, 4 (1985) 475.
4 A. M. Bhandari, A. K. Solankiand and S. Wodhwa, J. Inorg. Nucl. Chem., 43 (1981) 2995.
5 S. Satyanarayana, M. S. Jyoti and C. A. Lincoln, Indian J. Chem., 22A (1983) 357.
6 F. Lianza, A. Albinati and B. Lippert, Inorg. Chim. Acta, 255 (1997) 313.
7 M. Goodgame and D. A. Jakubovic, Coord. Chem. Rev., 79 (1987) 97.
8 W. S. Sheldrick and D. Neumann, Inorg. Chim. Acta, 223 (1994) 131.
9 P. K. Santra, D. Das, T. K. Misra, R. Roy, C. Sinha and S. M. Peng, Polyhedron, 18 (1999) 1909.
10 M. Gupta and M. N. Srivestava, Syn. React. Inorg. Met. Org. Chem., 26 (1996) 305.
11 Y. Dohta, C. S. Browning, P. Rekonen, M. Kodako, T. Okada, K. Okamoto, R. Natale, C. Yip, D. H. Farrar and H. Okuno, Inorg. Chim. Acta, 263 (1997) 69.
12 O. Renn, B. Lippert and I. Mutikainen, Inorg. Chim. Acta, 218 (1994) 117.
13 E. Casassas, J. Inorg. Biochem., 39 (1990) 327.
14 J. J. Foil, A. Terron and D. Mulet, Inorg. Chim. Acta, 135 (1987) 197.
15 B. T. Khan and K. Annapoorna, Inorg. Chim. Acta, 171 (1990) 157.
16 M. Kodaka, H. Okuno and Y. Dohta, Reviews in Inorganic Chemistry, 19 (1999) 211.
17 E. Frieden, J. Chem. Educ., 62 (1985) 917.
18 B. T. Khan, A. Gaffuri, P. N. Rao and S. M. Zakeeruddin, Polyhedron, 6 (1987) 387.
19 M. N. Moreno-Carretero, J. M. Salas-Peregrin and A. Mata-Arjona, J. Thermal Anal., 29 (1984) 553.
20 F. Hueso-Urena and M. N. Moreno-Carretero, Thermochim. Acta, 182 (1991) 9.
21 F. Hueso-Urena, M. N. Moreno-Carretero, J. M. Salas-Peregrin and M. A. Romero-Molina, Thermochim. Acta, 177 (1991) 119.
22 F. Hueso-Urena, M. N. Moreno-Carretero and J. M. Salas-Peregrin, Thermochim. Acta, 170 (1990) 225.
23 M. Goodgame and K. W. Johns, J. Chem. Soc., Dalton Trans., 2 (1977) 1680.
24 A. Jeres, J. Thermal Anal., 26 (1983) 315.
25 E. S. Freeman and B. Carrol, J. Phys. Chem. Soc., (1953) 3192.
26 J. J. Foil and A. Jerron, Inorg. Chim. Acta, 125 (1986) 159.
27 B. Lippert, Inorg. Chem., 20 (1981) 4326.
28 O. Z. Yeşilel, Thesis, Ondokuz Mayis University, 1999.