Thermochimica Acta, 149 (1989) 141–146
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

A STUDY OF THE THERMAL DECOMPOSITION OF AMORPHOUS BIMETALLIC CDTA COMPLEXES

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(Received 22 November 1988)

ABSTRACT

The study of the thermal behaviour of a family of bimetallic amorphous MM′(CDTA)·$n H_2O$ complexes has been performed using TG and DTA. The complexes decompose in three steps: dehydration, ligand pyrolysis and inorganic residue evoluation.

INTRODUCTION

A number of isostructural homo- and heterobimetallic complexes of general stoichiometry MM′(CDTA)·$6H_2O$ have previously been described [1,2]. Their crystal structure shows that the dimers are composed of a metallic ion surrounded by five water molecules in a "hydrated" sphere and bridged through the carboxylate group to another metallic ion surrounded by donor atoms of CDTA ligand in a "chelated" sphere. When the two metallic ions are different, there is an "occupational preference" for "chelated" or "hydrated" spheres. This behaviour is similar to that observed in MM′(EDTA)·$6H_2O$ complexes [3,4]. For the EDTA complexes, the differences in the crystalline and amorphous structures have been studied [5] and the thermal behaviour of the crystalline complexes has been reported [4].

A family of amorphous CDTA complexes with the general stoichiometry MM′(CDTA)·$n H_2O$ have been synthesized and characterized and a structural analogy has been established with an analogous crystalline compound of known crystalline structure [6].

In the present paper, the thermal behaviour of the homo- and heterometallic amorphous CDTA compounds ZnCu(CDTA)·$6H_2O$, CuCu (CDTA)·$4H_2O$, NiCu(CDTA)·$7H_2O$, CoCu(CDTA)·$7H_2O$, CoNi (CDTA)·$7.5H_2O$, CoCo(CDTA)·$8H_2O$ and NiNi(CDTA)·$8H_2O$ are described.

0040-6031/89/$03.50

EXPERIMENTAL

Samples

The first step in the synthesis of the amorphous complex was the preparation of the crystalline complexes as previously described [2,7–10]. The crystalline compounds were prepared by reaction between aqueous solutions of $Na_4(CDTA)$ and the corresponding nitrates in stoichiometric molar ratio dissolved in a minimum quantity of water. Following slow addition of acetone and refrigeration, crystals were formed. For synthesis of amorphous complexes from the crystalline ones, two methods were used. (1) The crystals were dissolved in a minimum of water, then excess acetone was added with stirring; a slimy solid was immediately obtained. This solid, separated by decantation and dried in air, has a pellet-like appearance. (2) Following addition of a minimum of water to the crystalline complexes, slow evaporation of the solution gave the amorphous solid.

Analysis

Metal contents were determined by atomic absorption using a Perkin–Elmer 300 spectrophotometer. The solid samples were previously heated with a HNO_3–H_2O_2 (7 : 3) mixture and the resulting products dissolved in the minimum volume of conc. H_2SO_4. C and N microanalyses were made using Coleman 33 and 29-B analysers respectively. Water contents were determined using a Setaram B70 simultaneous TG–DTA thermobalance. Crucibles containing approximately 60 mg of the samples were heated a 6 °C min^{-1} in air. Details are given in Table 1.

RESULTS AND DISCUSSION

Thermogravimetric (TG) and differential thermal analysis (DTA) curves for the isolated complexes are given in Fig. 1. The data provided by the thermal analysis of the amorphous complexes is summarized in Table 2.

All the complexes are stable below 60 °C. Above this temperature, in all cases, thermal decomposition occurs in three consecutive processes—dehydration, ligand pyrolysis and inorganic residue evolution.

The dehydration process is well defined and separated from the other two steps (ligand pyrolysis and inorganic residue evolution). This dehydration is an endothermic process. The ligand pyrolysis and inorganic residue evolution are exothermic and sometimes these steps are overlapping. This dehydration process is similar in all cases, starting at approximately 60 °C and, depending on the complex, finishing at 170–300 °C (see Table 2).

TABLE 1

Analysis data for MM′(CDTA)·nH$_2$O compounds

Compound MM′ [a]	%M		%M′		%C		%H		%N	
	calc.	found	calc.	found	calc.	found	calc.	found	calc.	found
CuCu			23.5	23.4	31.1	30.5	4.8	5.0	5.2	5.1
ZnCu	11.3	11.0	11.0	10.9	29.0	29.5	5.2	5.2	4.8	4.9
NiCu	9.9	9.8	10.8	10.5	28.5	28.0	5.5	5.4	4.7	4.7
CoCu	10.0	9.6	10.8	10.9	28.5	28.2	5.5	5.4	4.7	5.0
CoNi	9.9	9.7	9.9	9.6	28.3	28.3	5.6	5.7	4.7	4.6
CoCo			19.5	19.4	27.8	27.8	5.7	5.5	4.6	4.7
NiNi			19.4	19.4	27.8	27.8	5.7	5.7	4.6	4.4

[a] M = "hydrated" cation, M′ = "chelated" cation M′(CDTA)$^{2-}$.

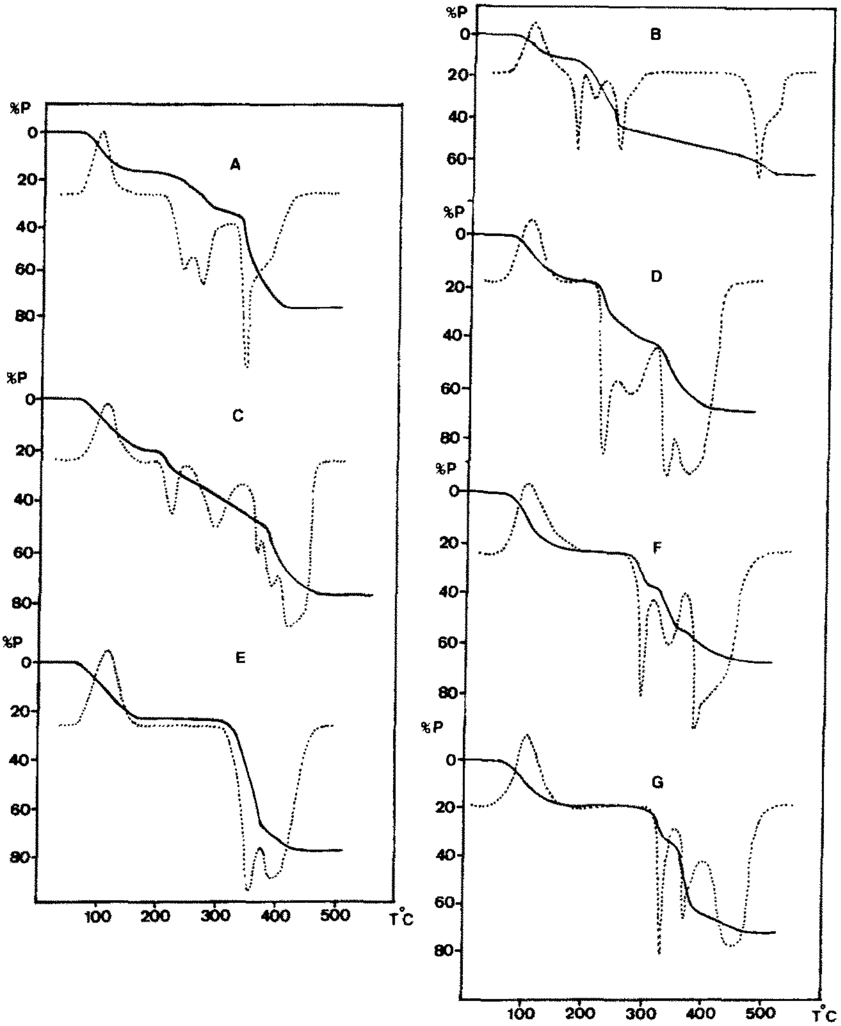

Fig. 1. TG and DTA thermal curves of ZnCu(CDTA)·6H_2O (A); CuCu(CDTA)·4H_2O (B); NiCu(CDTA)·7H_2O (C); CoCu(CDTA)·7H_2O (D); CoNi(CDTA)·7.5H_2O (E); CoCo(CDTA)·8H_2O (F); and NiNi(CDTA)·8H_2O (G).

The start of the ligand pyrolysis depends on the metallic ion (see Table 2). When the copper(II) ion is in the chelate position, a relatively low temperature (between 170 and 219 ° C) is found for the first decarboxylation process ($-CO_2(g)$). However when Ni(II) or Co(II) ions are in the chelate position, the temperature range for this process is 260–300 ° C.

The different behaviour of Cu(II) complexes can be attributed to two effects: the octahedral symmetry around the copper(II) is strongly distorted which could explain the thermal instability; and the ion complex $[Cu(CDTA)]^{2-}$ is the most stable in the $[M(CDTA)]^{2-}$ series, because the stronger Cu–CDTA interaction decreases the stability of the organic CDTA

TABLE 2

Thermal analysis data for MM′(CDTA)·$n$$H_2O$ compounds

Compound MM′ [a]			Dehydration	Ligand pyrolysis		Inorganic residue evolution
CuCu	TG [b]		13.24	16.16	15.96	21.02
	DTA [c]	s	62	170	220	254
		f	170	220	254	498
ZnCu	TG		17.47	15.0	–	44.20
	DTA	s	59	208	–	–
		f	208	320	–	411
NiCu	TG		21.79	28.94		24.29
	DTA	s	58	202		380
		f	202	370		467
CoCu	TG		19.89	13.35	–	36.14
	DTA	s	59	219	–	–
		f	219	248	–	426
CoNi	TG		23.67	–		51.75
	DTA	s	59	305		–
		f	240	–		430
CoCo	TG		23.50	14.73	15.08	14.73
	DTA	s	58	260	315	364
		f	252	315	364	467
NiNi	TG		23.15	13.55	–	35.70
	DTA	s	58	309	–	–
		f	309	360	–	483

[a] M = "hydrated" cation, M′ = "chelated" cation M′(CDTA)$^{2-}$.

[b] Percent weight loss.

[c] Temperature (°C): s = process start; f = process finish.

structure. The evidence provided by IR spectroscopy is significant: the values of the C–N stretching mode for $[Cu(CDTA)]^{2-}$ have lower energies than the C–N stretching mode of $[M(CDTA)]^{2-}$ complexes with M = Ni and Co (ν_{C-N} for MCu is 1095 cm^{-1}, for CoNi is 1110 cm^{-1}, for NiNi is 1115 cm^{-1} and for CoCo is 1120 cm^{-1}).

The total weight loss in the process corresponds well with formation of the monoxide as end products (except for the complexes containing cobalt(II) whose pyrolysis mainly yields Co_3O_4).

A general agreement with the results of the isostructural MM′(EDTA)·$6H_2O$ family, studied in air atmosphere [4], has been found.

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