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THERMAL DECOMPOSITION OF METAL COMPLEXES

VI. MIXED COMPLEXES OF COPPER(II) WITH BIDENTATE OR TRIDENTATE DICARBOXYLIC ACIDS AND HETEROCYCLIC DIIMINES OR TRIIMINES*

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ABSTRACT

A thermal decomposition study on a series of mixed complexes of cupric ion with dicarboxylic acids variously substituted (potentially bidentate or tridentate) and heterocyclic diimines or triimines was carried out. It is suggested that the decomposition mechanism is strongly influenced by the aromatic system of both ligands.

INTRODUCTION

The study of the correlation between the parameters obtainable from thermoanalytical techniques and the strength of the metal–ligand bond was the object of previous papers[1–4]. In this work some mixed complexes of the cupric ion with bidentate or tridentate dicarboxylic acids (aliphatic, aromatic or alicyclic) and heterocyclic diimines or triimines (see Table 1) were examined.

Since X-ray structural investigations pointed out the lack of isomorphism of these complexes, also of those for which it is reasonable to assume a similar structure, this work was directed to obtaine information on the mechanism of the reactions during thermal decomposition, with the purpose to find to which extent these processes are influenced by electronic effects due to substituents, structural differences and substrate capable of doing π-bonding. Our interest was also aimed at the study of how the "stronger" ligand influenced the thermal decomposition of these mixed complexes.

Thermal analysis on some cupric dicarboxylates was also carried out in order to compare two thermal patterns of cupric species containing a similar part, and considering the lack of information in the literature[5,6].

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TABLE 1

TEMPERATURES OF INITIAL DEHYDRATION (T_w) AND DECOMPOSITION OF ANHYDROUS OR DEHYDRATED SPECIES (T_d) OF MIXED COMPLEXES OF THE CUPRIC ION AT $\varnothing = 2\,^{\circ}\mathrm{C\ min^{-1}}$

MAL = malonic acid; Et-MAL = ethylmalonic acid; DBu-MAL = dibuthyl-malonic acid; Be-MAL = benzyl-malonic acid; CPRD = cyclopropan-1,1-dicarboxylic acid; CBUD = cyclobutan-1,1-dicarboxylic acid; CPED = cyclopentan-1,1-dicarboxylic acid; CHED = cyclohexan-1,1-dicarboxylic acid; OX = oxalic acid; MALE = maleic acid; PHT = phthalic acid; SUC = succinic acid; ITAC = itaconic acid; DIPIC = dipicolinic acid; IDA = iminodiacetic acid; ODA = oxydiacetic acid; THDA = thiodiacetic acid; ADB = aminodibenzoic acid; dip = 2,2′-dipyridyl; phen = 1,10-phenantroline; terpy = 2,2′,2″-terpyridyl; en = enthylendiamine.

Complex	T_w	T_d
Cu PHT·$2H_2O$	150	220
Cu CPRD·$2H_2O$	160	230
Cu MAL·$4H_2O$	70	192
Cu SUC·H_2O	60	244
Cu dip MAL·H_2O	80	196
Cu dip CPRD		220
Cu dip CBUD		202
Cu dip CHED		154
Cu dip OX		160
Cu dip PHT		144
Cu dip SUC		210
Cu dip MALE		140
Cu dip IDA		218
Cu dip DIPIC·$2H_2O$	110	215
Cu phen MAL		160
Cu phen CPRD		205
Cu phen CBUD		185
Cu phen CPED		170
Cy phen CHED		175
Cu phen OX		140
Cu phen PHT		180
Cu phen SUC		215
Cu phen MALE		190
Cu phen Et-MAL		180
Cu phen DBu-MAL·$2H_2O$	90	165
Cu phen Be-MAL		165
Cu phen ITAC·H_2O	90	150
Cu phen DIPIC		240
Cu phen IDA·$2H_2O$	100	190
Cu phen ODA		250
Cu phen THDA·$2H_2O$	140	190
Cu terpy MAL		180
Cu terpy CPRD·$2H_2O$	100	234
Cu terpy PHT·$2H_2O$	90	204
Cu terpy SUC·H_2O	95	180
Cu terpy IDA·$2H_2O$	100	196
Cu terpy ODA·H_2O	110	230
Cu terpy THDA		175
Cu en MAL·H_2O	90	179
Cu dip ADB		210

EXPERIMENTAL

The complexes reported in Table 1 were prepared following a procedure described elsewhere[7–9]. The simultaneous TG, DTG and DTA were performed with a Mettler vacuum thermoanalyzer in dynamic nitrogen atmosphere ($10\,l\,h^{-1}$). The heating rate and the experimental conditions were the same as previously described[1–4]. The "activation energy" E_a^* was determined by the methods knonw in the literature[10,11]. The simultaneous EGA was carried out with a Balzers mass-spectrometer type QMG 313; X-ray powder analysis was performed with Cu–K_α radiation (Ni filtered).

RESULTS AND DISCUSSION

Thermal behaviour of the cupric dicarboxylates

The TG and DTG curves are presented in Fig. 1. In dry nitrogen atmosphere, under reduced pressure or vacuum, the cupric dicarboxylates decomposed with an initial mass loss, in one step, corresponding to the dehydration stage:

$$CuPHT\cdot 2H_2O \rightarrow CuPHT\cdot 0.15H_2O + 1.85H_2O$$
$$CuMAL\cdot 4H_2O \rightarrow CuMAL\cdot 0.15H_2O + 3.85H_2O$$
$$CuSUC\cdot H_2O \rightarrow CuSUC\cdot 0.15H_2O + 0.85H_2O$$
$$CuCPRD\cdot 2H_2O \rightarrow CuCPRD\cdot 0.15H_2O + 1.85H_2O$$

As one can see the loss of water molecules was not complete, the remaining $0.15H_2O$ was eliminated in the following nearly horizontal step (see Fig. 1). After

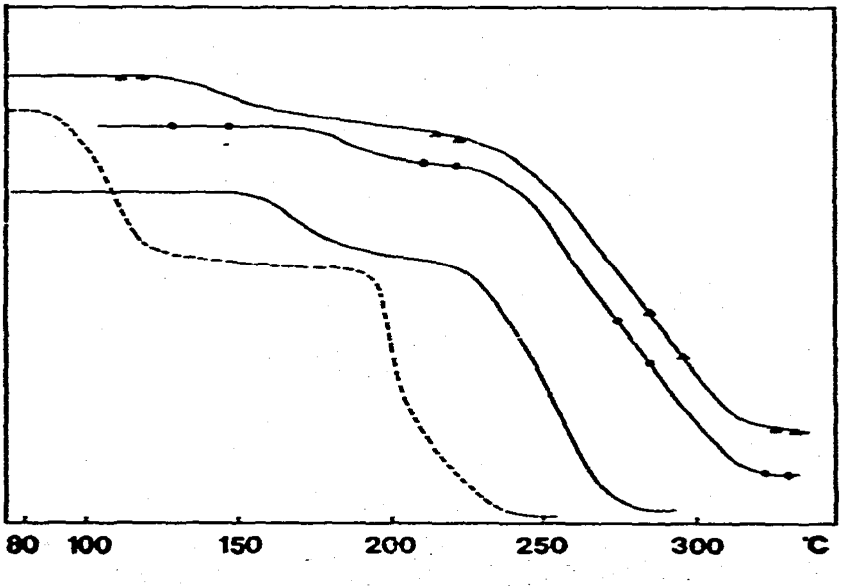


Fig. 1. TG curves at $\varnothing = 2\,°C\,min^{-1}$ of the following dicarboxylates: – – – – Cu MAL·$4H_2O$; ——— Cu PHT·$2H_2O$; —O—O— Cu CPRD·$2H_2O$; —Δ—Δ— Cu SUC·H_2O.

this step a rapid decomposition occurred, giving Cu_2O and CuO as residual products in nitrogen atmosphere and Cu under vacuum. For this particular decomposition mechanism it was not possible to prepare of the anhydrous species. These results are in agreement with those reported by various authors[5,6] in the study of the thermal behaviour of cupric hydrated dicarboxylates.

Thermal behaviour of the cupric mixed complexes

For the mixed complexes containing one or more water molecules, the initial mass loss, in one step, corresponded to the complete dehydration stage, unlike the behaviour of the dicarboxylates. At the end of this process the formation of stable anhydrous mixed complexes was obtained. The initial temperatures of the dehydration are reported in Table 1. In dry nitrogen atmosphere the anhydrous complexes of copper(II) with 2,2′-dipyridyl and bidentate dicarboxylic acids decomposed in two running steps that were not separable. An example of thermoanalytical curves for these complexes can be seen in Fig. 2. The first step corresponds to the removal of the dicarboxylate ligand and consequent probable formation of an unstable intermediate product CuO·2,2′-dipyridyl (this species was only assumed on the ground of the reaction stoichiometry). In the second step the 2,2′-dipyridyl is eliminated, leaving a CuO–Cu_2O mixture as residue.

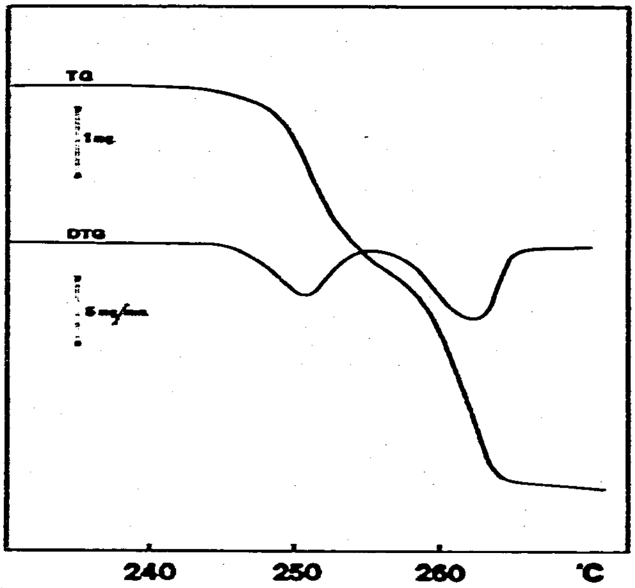


Fig. 2. TG and DTG curves of 9.0 mg of the mixed complex Cu dip CPRD at $\varnothing = 0.5$°C min^{-1}.

The anhydrous complexes of copper(II) with 2,2′-dipyridyl and tridentate dicarboxylic acids decomposed in one step with contemporary elimination of both ligands and formation of CuO and Cu_2O residual products.

The anhydrous or dehydrated complexes of copper(II) with 2,2′,2″-terpyridyl or 1,10-phenanthroline and bidentate or tridentate dicarboxylic acids decomposed, as in the case of the analogous complexes with 2,2′-dipyridyl and bidentate dicarboxylic acids, giving two non-separable steps, when heating rates from 0.5 to 2°C min^{-1} were used (Fig. 3). With heating rates of 4°C min^{-1} the complexes containing only the bidentate dicarboxylic acids decomposed in three non-separable steps. The first two correspond to the demolition of the dicarboxylic ligand and the third to the elimination of the heterocyclic diimine or triimine. An example of TG and DTG curves for these species is given in Fig. 4.

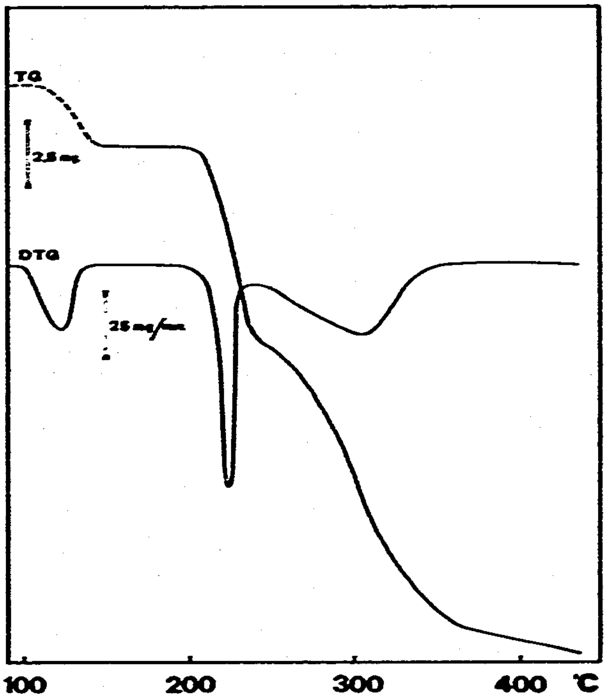
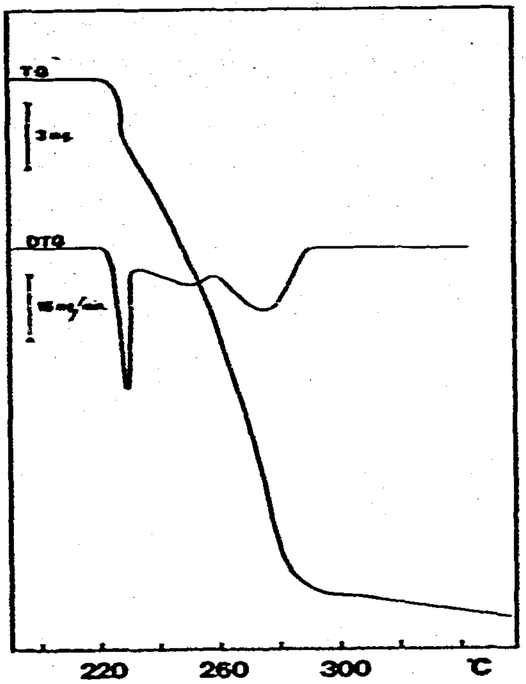


Fig. 3. TG and DTG curves of 31.0 mg of the mixed complex Cu phen IDA·$2H_2O$ at $\varnothing = 2$°C min^{-1}.

In an attempt to obtain further information about the decomposition mechanism and to prepare stable intermediate products, thermal analysis under reduced pressure and vacuum was also carried out. Under both conditions, all complexes decomposed in one step, forming a CuO–Cu_2O mixture, under reduced pressure, and Cu under vacuum, as residual products. An example is shown in Fig. 5.

The simultaneous EGA of decomposition products pointed out that the first step is due to the elimination of the dicarboxylate anion giving the CO_2 peaks together with the peaks of decomposition fragments. In the case of the CuMAL dip system the peak relative to the anhydride of the dicaboxylic acid was also found. From this fact and the reaction stoichiometry we think that the elimination of the dicarboxylate anion occurs as anhydride, that rapidly decomposes. The following elimination of the diimine or triimine occurs with demolition processes, shown also by the EGA peaks.



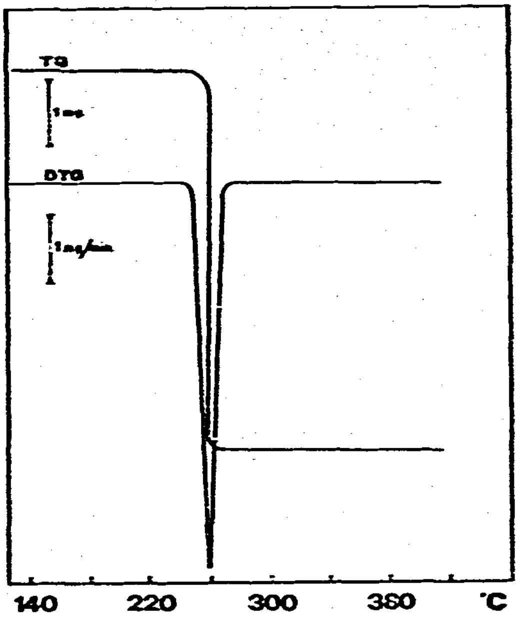


Fig. 4. TG and DTG curves of 31.4 mg of the mixed complex Cu terpy MAL at ⌀ = 4°C min^{-1}.

Fig. 5. TG and DTG curves of 6.8 mg of the mixed complex Cu dip CPRD at ⌀ = 2°C min^{-1} under reduced pressure (10^{-2} mm Hg).

From these considerations we can write the following general mechanism:

first step $CuR(COO)_2B \rightarrow CuOB + RC_2O_3$

$$\downarrow$$

$$CO_2 + \text{other fragments}$$

second step $CuOB \rightarrow Cu_2O + CuO + B$

$$\downarrow$$

$$CO_2 + \text{other fragments}$$

This mechanism is supported by the E_a^* values relative to the possible one; they are reported in Tables 2 and 3. High values of E_a^*, as in most of those relative to the first step, can be justified only by admitting more contemporary decomposition processes, namely the thermal decomposition is not a "single step" process, as shown by the curves, but under the curve envelope a "multi step" process lies. Moreover, the final residual products of CuO and Cu_2O can be explained taking account for ox-red reactions among the metal ion and the demolition products. One can see that this mechanism does not change by varying the dicarboxylate anion, the numbers of the chelate ring and the effective coordination number. This pattern may be attributable to the presence in the ternary species of molecules having an acceptor π-bonding system. This fact causes the formation of a very strong bond between the copper ion and the diimine or triimine by back-donation. In other words the π-bonding formation is responsable for the kind of decomposition mechanism found in thermal decomposition of these mixed complexes.

An important feature to note is the similarity of this decomposition mechanism in the solid state and the results of studies in solution on the metal ion-catalyzed decarboxylation, where the formation of special ternary complexes changes the rate

TABLE 2

E_a^* VALUES RELATIVE TO THE DECOMPOSITION STEPS OF THE ANHYDROUS OR DEHYDRATED MIXED COMPLEXES, USING HEATING RATES RANGING FROM 0.5°C min^{-1} TO 2°C min^{-1}

Complex	E_{a1}^*	E_{a2}^*
Cu dip MAL·H_2O	42	9
Cu dip CPRD	78	17
Cu dip CBUD	85	12
Cu dip CHED	92	21
Cu dip PHT	95	19
Cu dip SUC	96	11
Cu dip MALE	60	21
Cu dip IDA	85[a]	
Cu dip DIPIC·$2H_2O$	78[a]	
Cu phen MAL	35	16
Cu phen CPRD	73	15
Cu phen CBUD	80	16
Cu phen CPED	90	12
Cu phen CHED	85	17
Cu phen OX	n.v.	n.v.
Cu phen PHT	158	20
Cu phen SUC	162	15
Cu phen MALE	n.v.	17
Cu phen Et-MAL	130	7
Cu phen DBu-MAL·$2H_2O$	60	13
Cu phen Be-MAL	160	14
Cu phen ITAC·H_2O	122	13
Cu phen DIPIC	96	4
Cu phen IDA·$2H_2O$	74	8
Cu phen ODA	149	5
Cu phen THDA·$2H_2O$	15	8
Cu terpy MAL	145	17
Cu terpy CPRD·$2H_2O$	82	n.v.
Cu terpy PHT·$2H_2O$	159	8
Cu terpy SUC·H_2O	112	14
Cu terpy IDA·$2H_2O$	25	13
Cu terpy ODA·H_2O	113	8
Cu terpy THDA	77	14
Cu en MAL·H_2O	n.v.[a]	
Cu dip ADB	18	45

[a] Process in one step.

TABLE 3

E_a^* VALUES RELATIVE TO THE DECOMPOSITION STEPS OF SOME MIXED COMPLEXES USING A HEATING RATE OF 4°C min^{-1}

Complexes	E_{a1}^*	E_{a2}^*	E_{a3}^*
Cu phen MAL	9	11	19
Cu phen CPRD	53	20	17
Cu phen CBUD	n.v.	n.v.	19
Cu phen CPED	49	47	10
Cu phen CHED	60	21	17
Cu phen PHT	164	21	18
Cu phen SUC	64	120	7
Cu phen Et-MAL	128	7	7
Cu phen DBu-MAL·$2H_2O$	50	14	16
Cu phen Be-MAL	151	14	19
Cu phen ITAC·H_2O	80	39	11
Cu terpy MAL	96	57	18
Cu terpy CPRD·$2H_2O$	62	31	15
Cu terpy PHT·$2H_2O$	145	27	12
Cu terpy SUC·H_2O	80	35	9

of the last process. Moreover, the results of these kinetic studies showed that the catalytic activity in the decarboxylation was more effective, when the second ligand is an aromatic, namely when the metal ion formed effective π-bonds with this ligand. No enhancement was found to be in solution with aliphatic amine[12].

To point out the veracity of these conclusions we took the thermal behaviour of other two systems into account. The first was the CuenMAL (en is the abbreviation of ethylendiamine), where the aromatic substrate of the heterocyclic diimine was replaced by an aliphatic one. The second CudipADB (ADB is the abbreviation of aminodibenzoic acid), where the dicarboxylate anion, substituted with an aromatic one, could be competitive with the π-acceptor system of the neutral base.

In the first case the thermal decomposition occurred in one step, whereas in the second it is possible to observe an inversion in the order of the elimination of the ligands, the 2,2'-dipyridyl decomposed first.

These facts confirm the previous explanation of the decomposition mechanism supposed for these complexes. The π-bonding formation seems to be the factor controlling this thermal behaviour. In fact in the CuenMAL system the elimination of the dicarboxylate anion is not yet the first decomposition process but it occurs at the same time of the neutral base elimination. Moreover, in the CudipADB system, where the anion has conjugating capacities similar to or stronger than the diimine or triimine, the decomposition behaviour is inverted.

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