

## THERMAL BEHAVIOUR OF TWO NEW SALTS OF MALONIC ACID: $\text{Cu}(\text{C}_3\text{H}_2\text{O}_4) \cdot 4\text{H}_2\text{O}$ AND $\text{Cu}(\text{NH}_4)_2(\text{C}_3\text{H}_2\text{O}_4)_2$

F. CHARBONNIER

*Laboratoire de Synthèse Minérale, U.E.R. de Chimie et Biochimie,  
Université Claude Bernard (Lyon I), 69621 Villeurbanne (France)*

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### ABSTRACT

Two new salts of malonic acid have been prepared: the copper(II) malonate tetrahydrate and the copper(II)-ammonium double malonate. Their study by thermal analysis (TG and DTA) leads to the following results:

$\text{Cu}(\text{C}_3\text{H}_2\text{O}_4) \cdot 4\text{H}_2\text{O}$ : the dehydration is rather complex and it is only under careful conditions that an intermediate hydrate  $\text{Cu}(\text{C}_3\text{H}_2\text{O}_4) \cdot 3\text{H}_2\text{O}$  could be traced. At about 170°C the dehydration is not ended (the salt holds yet about 0.15H<sub>2</sub>O) and the anhydrous salt occurs only at about 240°C. It decomposes immediately leading to residues the composition of which depends upon the surrounding atmosphere; the part played by the gas given off is discussed.

$\text{Cu}(\text{NH}_4)_2(\text{C}_3\text{H}_2\text{O}_4)_2$ : this salt melts and decomposes simultaneously at about 190°C. During the decomposition the copper nitride  $\text{Cu}_3\text{N}$  forms as intermediate compound (as well as copper metal). Concerning the final residues of the decomposition the results and the conclusions are the same as the ones of the previous case.

### INTRODUCTION

The bibliography states two hydrates of the copper(II) malonate: on the one hand the salt  $\text{Cu}(\text{C}_3\text{H}_2\text{O}_4) \cdot 3.75 \text{H}_2\text{O}$  prepared by Finkelstein<sup>1</sup>, on the other hand the trihydrate obtained by numerous authors<sup>2–9</sup>. But there is disagreement about the crystalline system of this trihydrate: for Haushofer<sup>2</sup> and Jaeger and Vandijk<sup>7</sup> it is orthorhombic while for Rajan<sup>9</sup> it is monoclinic.

The thermal behaviour of copper(II) malonate has been little studied; only investigations concerning the thermal dehydration have been made and the results are divergent. Thus Ploquin<sup>6</sup> who obtained the dihydrate and the monohydrate notices that it was not possible to prepare the anhydrous salt; on the other hand Asai, Kishito and Kubo<sup>8</sup> obtained this anhydrous salt drying the trihydrate in air atmosphere at 110°C during 12 h; Van My<sup>10</sup> has obtained the anhydrous salt drying under vacuo an unspecified hydrate.

Thereby it seemed interesting to investigate further the physico-chemical properties of the copper(II) hydrated malonate; but the method of preparation used

led to the hitherto unknown tetrahydrate instead of the oft-quoted trihydrate (the Finkelstein's salt with its 3.75 H<sub>2</sub>O was perhaps really a tetrahydrate).

No copper(II)ammonium double malonate is quoted in the bibliography. The one we have isolated does not possess water of crystallization.

## EXPERIMENTAL

### Materials preparation

The procedures used to prepare the compounds Cu(C<sub>3</sub>H<sub>2</sub>O<sub>4</sub>)·4H<sub>2</sub>O and Cu(NH<sub>4</sub>)<sub>2</sub>(C<sub>3</sub>H<sub>2</sub>O<sub>4</sub>)<sub>2</sub> were previously described<sup>1,1</sup>. They are succinctly quoted here.

The copper(II)malonate tetrahydrate is prepared by action of copper(II) hydroxide (obtained from Weiser, Milligan and Cook's procedure<sup>1,2</sup>, improved by Gauthier<sup>1,3</sup>) upon malonic acid (product of reagent grade). Well-crystallized blue crystals can be isolated from the saturated solution.

The double salt is obtained by crystallization from a solution containing stoichiometric quantities of copper(II) malonate and ammonium malonate. This solution provides tiny clear blue crystals. X-ray pattern proves that this double salt is a well-defined compound.

These compounds were analyzed for copper content by an electrolytic method<sup>1,4</sup>. Carbon, hydrogen and nitrogen contents are determined by the "C.N.R.S. Micro-analysis Laboratory" in Lyon.

Table 1 lists the analytical results.

TABLE 1  
RESULTS OF THE CHEMICAL ANALYSIS

	<i>Cu(C<sub>3</sub>H<sub>2</sub>O<sub>4</sub>)·4H<sub>2</sub>O</i>			<i>Cu(NH<sub>4</sub>)<sub>2</sub>(C<sub>3</sub>H<sub>2</sub>O<sub>4</sub>)<sub>2</sub></i>			
	<i>Cu</i> (%)	<i>C</i> (%)	<i>H</i> (%)	<i>Cu</i> (%)	<i>C</i> (%)	<i>H</i> (%)	<i>N</i> (%)
theor.	26.73	15.15	4.24	20.92	23.71	3.98	9.23
found	26.71	15.59	4.17	20.95	23.77	3.99	9.51

### Apparatus

*TG.* An Adamel-Chevenard thermobalance with graphical recording is used. A Pt-Pt Rh 10% thermocouple placed under the sample holder is employed. The mass of samples is 300 mg and the heating rate 2 or 5°C min<sup>-1</sup>. The controlled atmosphere consists of either dry air or dry deoxygenated nitrogen passing over the sample at 30 ml min<sup>-1</sup>.

*DTA.* A differential thermal microanalyser "Bureau de Liaison" (C. Mazières type) with hollow thermocouples and open crucibles is employed. The curves Δ*T*=*f*(*T*) are plotted on a Sefram recorder of the X-Y Luxytrace type after amplification of the differential temperature by an Amplispot AGT Sefram (10 μV cm<sup>-1</sup> that is 0.25°C cm<sup>-1</sup>).

After grinding in a mortar and pestle no more than 10 mg of sample are used in each run. The controlled atmosphere is as in the TG study. A heating rate of 2 or 5°C min<sup>-1</sup> is employed. No reference material is necessary.

*Radiocrystallographical analysis.* The X-ray patterns are obtained from powdered samples with filtered CuK $\alpha$  radiation. Apparatus and techniques employed for determining crystal lattices were previously described<sup>1,2</sup>.

## RESULTS AND DISCUSSION

A short communication presenting the major results of investigations about both these salts has been previously published<sup>1,2</sup>. In the present paper the results of the crystallographical study are briefly summarized while those concerning the thermal behaviour are presented in detail.

### *Crystallographical study*

The copper(II) malonate tetrahydrate crystallizes in the triclinic system while the copper(II) ammonium double malonate crystallizes in the monoclinic system. The unit cell parameters are in Table 2 (*Z* is the number of molecules per unit cell and *d* the density measured in CCl<sub>4</sub> with a pycnometer).

TABLE 2  
RESULTS OF THE CRYSTALLOGRAPHICAL STUDY AT 20°C

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\alpha$	$\beta$	$\gamma$	<i>Z</i>	<i>d</i> (g cm <sup>-3</sup> )
Cu(C <sub>3</sub> H <sub>2</sub> O <sub>3</sub> )·4H <sub>2</sub> O	7.630	10.327	5.285	103°14'	99°06'	108°54'	2	2.07
Cu(NH <sub>4</sub> ) <sub>2</sub> (C <sub>3</sub> H <sub>2</sub> O <sub>4</sub> ) <sub>2</sub>	9.118	13.789	9.403	90°	119°	90°	4	1.94

### *Thermal behaviour*

*Copper(II) malonate tetrahydrate TG results.* TG curves are presented in Fig. 1. In a dry air or dry nitrogen atmosphere the curves show an initial mass-loss AC with one or two inflection points (B and B'), a nearly horizontal plot CD (it is not a plateau), a second mass-loss DE and a terminal plateau EF. AC corresponds with the dehydration stage while DE reveals an abrupt and fast decomposition. With a slow heating rate (2°C min<sup>-1</sup>) inflection point B' does not appear. Table 3 indicates the mass-loss corresponding with the deaquation reactions at two heating rates.

Colour changes are observed: at the start the product is clear blue, at B dark blue, at C greenish blue and at D dark green.

The TG curve shows the formation of trihydrate as an intermediate (calculated loss: 7.58) when a slow heating rate is used. At C, the salt still holds about 0.15 H<sub>2</sub>O and this residual water eliminates slowly. At D the product seems to be the anhydrous salt which decomposes immediately.

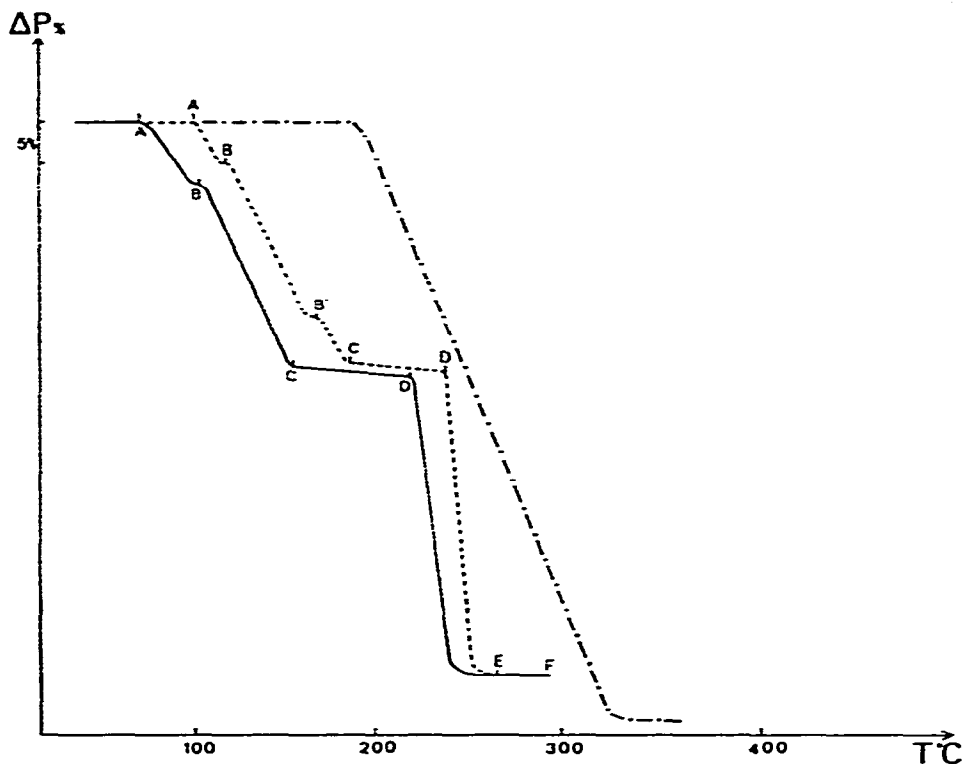


Fig. 1. TG curves. —,  $\text{Cu}(\text{C}_3\text{H}_2\text{O}_4) \cdot 4\text{H}_2\text{O}$  (dry air;  $2^\circ\text{C min}^{-1}$ ); ---,  $\text{Cu}(\text{C}_3\text{H}_2\text{O}_4) \cdot 4\text{H}_2\text{O}$  (dry air;  $5^\circ\text{C min}^{-1}$ ); - · - · -,  $\text{Cu}(\text{NH}_4)_2(\text{C}_3\text{H}_2\text{O}_4)_2$  (dry air;  $5^\circ\text{C min}^{-1}$ ).

TABLE 3

MASS-LOSSES OBSERVED DURING THE DEHYDRATION OF  $\text{Cu}(\text{C}_3\text{H}_2\text{O}_4) \cdot 4\text{H}_2\text{O}$   
(see Fig. 1)

Mass-loss calculated for  $1\text{H}_2\text{O}$  is 7.58 and for  $4\text{H}_2\text{O}$  30.32.

Heating rate ( $^\circ\text{C min}^{-1}$ )	Point			
	B	B'	C	D
5	5.6	18.5	29.5	30.1
2	7.5		29.9	30.2

The X-ray pattern of the trihydrate (different from that of the tetrahydrate) denotes a well-crystallized compound. On the other hand the patterns of the greenish blue and dark green products present no lines.

The trihydrate can be prepared from the dark green product set in a water vapour atmosphere. Its X-ray pattern is the same as the one of the compound obtained at B (with a heating rate of  $2^\circ\text{C min}^{-1}$ ).

The residual products after complete decomposition are CuO (air) and a mixture  $\text{Cu}_2\text{O} + \text{CuO}$  (nitrogen).

In vacuo the water eliminates in one step and the decomposition follows immediately after the deaquation (there is on the curve an inflection occurring at about 30% mass-loss). The anhydrous salt is not stable in the experimental conditions used. Only well-crystallized copper metal is obtained after complete decomposition.

Thus, in a nitrogen atmosphere, copper which is formed initially is oxidized by contact with the gas issued from the pyrolysis. The decomposition study of Cu(II) oxalate leads to the same results<sup>15</sup>.

*DTA results.* DTA curves are illustrated in Fig. 2.

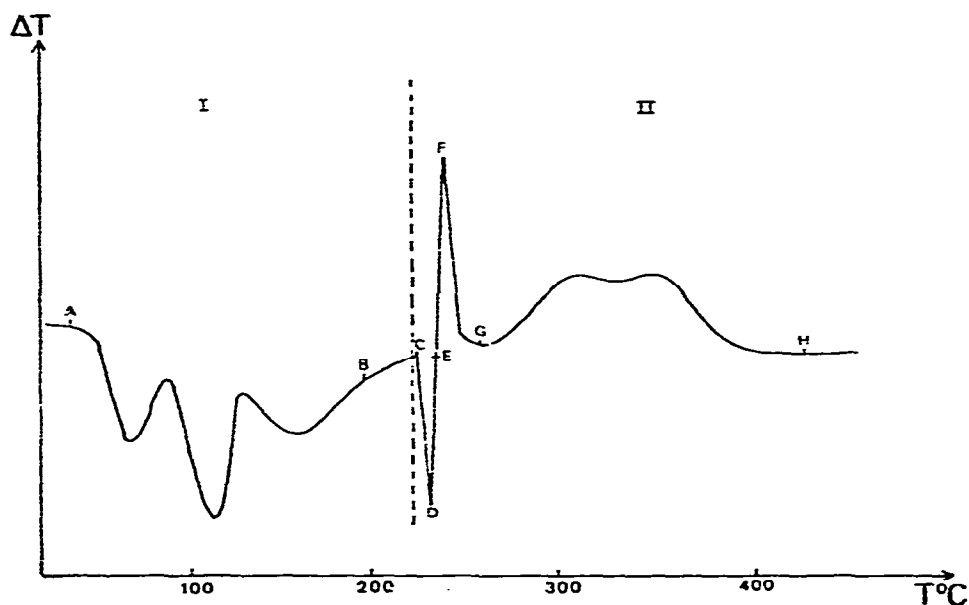


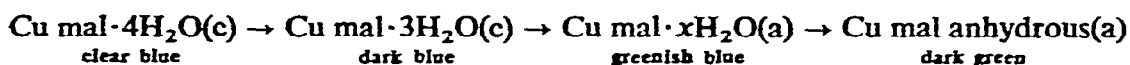
Fig. 2. DTA curve of  $\text{Cu}(\text{C}_3\text{H}_2\text{O}_4) \cdot 4\text{H}_2\text{O}$  (dry dynamic nitrogen atmosphere;  $5^\circ\text{C min}^{-1}$ ).

They may be divided in two portions (I and II) corresponding with the dehydration and decomposition reactions, respectively.

*Dehydration.* The loss of the water of crystallization results in some irreversible endotherms, the number of which depends upon the furnace heating rate and the sample mass. The influence of these factors on the dehydration of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  has been evidenced previously by Halmos et al.<sup>16</sup>.

For 8–10 mg samples the curves always show three peaks whatever the heating rate (increasing the heating rate increases their magnitude and their sharpness). When a sample mass of less than 3 mg is used, there are three peaks for a heating rate faster than  $5^\circ\text{C min}^{-1}$  and two peaks for a heating rate slower than  $2^\circ\text{C min}^{-1}$ . In all the cases the dark blue coloured product obtained after the first peak is well-crystallized and its X-ray pattern indicates that it is the trihydrate previously mentioned under

the TG study. But the compounds isolated, after the other two endotherms, present no lines in their patterns (they are greenish blue and dark green, respectively). The dehydration of the copper(II) malonate tetrahydrate by TG and DTA can be schematized as follows:



mal =  $\text{C}_3\text{H}_2\text{O}_4$

c = crystallized

$x \sim 0.15 \text{ H}_2\text{O}$

a = amorphous to X-ray

There is perhaps liquid water formation during dehydration and it would be interesting to investigate by electrical conductivity, whose merits have been proved by Wendlandt to detect quadruple points during the dehydration of numerous systems<sup>17</sup>.

*Decomposition.* The curve exhibits a narrow endotherm CDE immediately followed by a narrow exotherm EFG and finally a broad exotherm GH more marked under air than under nitrogen. Heating was stopped at some points (near E, at G and at H) and after cooling, air being excluded, the products obtained were analyzed by X-ray diffraction.

In E the compound (denoted X) obtained is brown. Its X-ray pattern (with numerous narrow lines) proves that it is well-crystallized and its infrared absorption spectrum exhibits the typical bands of the carboxylate group. The composition of X could not be determined.

In G, besides compound X there is also copper metal and cuprous oxide ( $\text{Cu}_2\text{O}$ ). In H the final residue is CuO (in air) and a mixture  $\text{Cu}_2\text{O} + \text{CuO}$  (under nitrogen atmosphere).

It seems that the narrow endotherm CDE is due to the formation of the undetermined compound X, the partial decomposition of which immediately occurs as the narrow exotherm EFG proves it. The broad peak GH is due to the decomposition of the remaining compound X and to the oxidation of the copper metal by the gas issued.

It is possible that compound X is the anhydrous salt which would have crystallized under the influence of the last traces of water. As its decomposition occurs immediately, it is hard to trace its formation by TG.

#### *Copper(II) ammonium double malonate*

A preliminary study shows that this compound melts and decomposes simultaneously at about  $190^\circ\text{C}$ ; but the evolving of ammonia gas begins before melting at about  $170^\circ\text{C}$ : in this case, the X-ray pattern of the product exhibits only the lines of the double salt.

*TG results.* The thermogravimetric curves, as presented in Fig. 1, have a simple shape whatever the experimental conditions. The plot at steady slope between the initial and final plateaus corresponds with the decomposition which happens at a steady rate; no intermediate product can be evidenced. During this decomposition

ammonia gas is evolved; the residual solid products are CuO in an air atmosphere,  $\text{Cu}_2\text{O} + \text{CuO}$  (in small amount for the last one) in nitrogen, and Cu in vacuo.

**DTA results.** The DTA curves are illustrated in Fig. 3. They show first a large endothermic peak AC followed by a small exotherm D before the return to the baseline, then a broad exothermic peak EI with some shoulders F, G and H. This broad

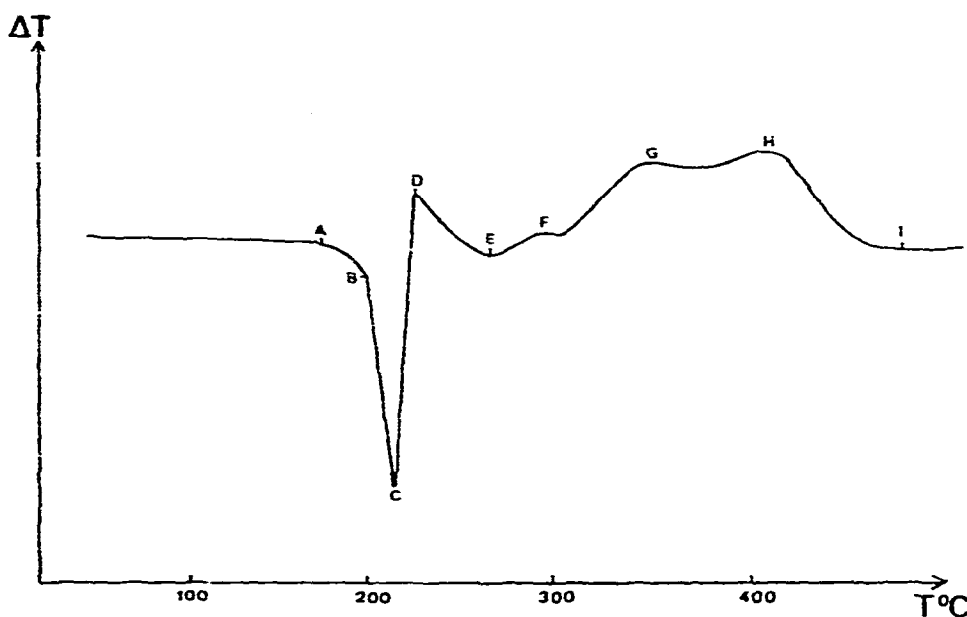


Fig. 3. DTA curve of  $\text{Cu}(\text{NH}_4)_2(\text{C}_3\text{H}_2\text{O}_4)_2$  (dry nitrogen dynamic atmosphere;  $5^\circ\text{C min}^{-1}$ ).

exotherm is bigger in air than in a nitrogen atmosphere. The shape of these curves indicates that intermediate products form during the decomposition. Heating was stopped at B, C, D, E, F and I points and after cooling, air being excluded, the products obtained are analyzed by X-ray diffraction. At B the ammonia is already being evolved but melting has not yet taken place (the product is clear blue). At C there is in the crucible a bright pellicle adhering rather firmly to the sides and a greenish blue powder at the bottom. At the other points there is only the pellicle.

Table 4 lists the results obtained from the X-ray study. The conclusions reached are as follows: the peaks AC and DE are due to the melting and decomposition of the double salt into the mixture  $\text{Cu} + \text{Cu}_3\text{N}$ ; at  $210^\circ\text{C}$  (point C) there is still a minute amount of non-decomposed salt, but at  $250^\circ\text{C}$  (E point) the decomposition is ended. The F shoulder at about  $300^\circ\text{C}$  must correspond with the exothermic dissociation of  $\text{Cu}_3\text{N}$  (this compound decomposes at  $300^\circ\text{C}$ <sup>18</sup> and its standard enthalpy of formation is positive<sup>19</sup>). At about  $325^\circ\text{C}$  the oxidation of copper metal begins by the gas of the decomposition ( $\text{CO}_2$ ), probably adsorbed on the surface. At  $500^\circ\text{C}$  copper metal has disappeared.

The formation of copper nitride  $\text{Cu}_3\text{N}$  is difficult to explain. On the one hand this compound can be formed by action of dry  $\text{NH}_3$  on  $\text{Cu}_2\text{O}$  both issued from the

TABLE 4

PRODUCTS FORMED DURING THE DECOMPOSITION OF  $\text{Cu}(\text{NH}_4)_2(\text{C}_3\text{H}_2\text{O}_4)_2$ , IDENTIFIED BY X-RAY DIFFRACTION (see Fig. 3)

vs = very strong; s = strong; rs = rather strong; w = weak.

Points	Lines of				
	double salt	copper metal	copper nitride, $\text{Cu}_3\text{N}$	copper oxide, $\text{Cu}_2\text{O}$	copper oxide, $\text{CuO}$
B	+(s)				
C	+(w)	+(vs)	+(rs)		
D		+(vs)	+(rs)		
E		+(vs)	+(rs)		
F		+(s)			
I				+(s)	+(w)

decomposition (ref. 20 states that this reaction is possible from  $250^\circ\text{C}$ ). This would explain why no cuprous oxide is present in the residues at C, D or E whereas this oxide appeared during the decomposition of the neutral copper malonate (see above). On the other hand it is possible that the double malonate decomposes giving only copper metal, a small amount of which would react with  $\text{NH}_3$  to give rise to  $\text{Cu}_3\text{N}$ . Terao<sup>21</sup> recently obtained  $\text{Cu}_3\text{N}$  by the action of dry  $\text{NH}_3$  upon thin layers (single crystalline or polycrystalline) of metal heated between 200 and  $450^\circ\text{C}$ .

#### CONCLUSION

This work makes a contribution to the study of metallic salts of malonic acid. A new hydrate of the copper(II) malonate has been isolated while the copper(II) ammonium malonate was prepared for the first time.

During the dehydration of the copper(II) malonate tetrahydrate, the trihydrate could be traced as an intermediate but the dihydrate and monohydrate previously obtained by Ploquin<sup>6</sup> have not been observed. At the end of the dehydration the last traces of water hardly eliminate and the anhydrous salt decomposes immediately. Concerning the double malonate, it is noteworthy that copper nitride  $\text{Cu}_3\text{N}$  is formed during the decomposition. In both cases the influence of the gas evolved on the composition of the final residues has been evidenced.

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