

Thermal Decomposition of Copper (II) Dicalcium (II) Formate

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The unit cell obtained through X-ray single crystal analysis of the synthesized $\text{CuCa}_2(\text{HCOO})_6$ crystals corresponds to a supercell of the basic structure described by M. Sanchis *et al.* (*Inorg. Chem.* 31, 2915 (1992)). Thermal decomposition of this sample shows two stages up to 300°C; the first can be related to the superstructure, and the second corresponds to the breaking down of the remaining copper formate structural units and the simultaneous decomposition of the sample. © 1997 Academic Press

INTRODUCTION

Mixed copper formates may be considered among the best cuprate precursors for high T_c superconductors synthesis.

Sanchis *et al.* (1) obtained submicrometer CaCuO_2 and Ca_2CuO_3 particles from thermal decomposition of bimetallic formate precursors. We have already studied the thermal decomposition of $\text{CuSr}(\text{HCOO})_4$ and $\text{CuCa}(\text{HCOO})_4$ (2, 3). In the present work we study the different stages through which thermal decomposition of $\text{CuCa}_2(\text{HCOO})_6$ takes place and propose a decomposition mechanism which takes into account the intermediate reaction products and their crystal structures.

EXPERIMENTAL

Anhydrous copper dicalcium formate $\text{CuCa}_2(\text{HCOO})_6$, hereafter ACuCa_2F , has been obtained by dissolving CuO in a boiling 20% aqueous formic acid solution and adding CaCO_3 in stoichiometric proportion (4); single crystals were obtained by slow evaporation at ambient temperature. The Cu:Ca relationship was determined using a Jarrell Ash Model 82-529 atomic absorption spectrometer.

The crystals obtained were characterized by optical microscopy, by TGA in a Mettler TG 50 apparatus between 30 and 1000°C in air at heating rates of 1, 5, and 10°C/min, and by DSC on a Perkin-Elmer DSC-2 calorimeter between -30 and 250°C scanned at a heating rate of 10°C/min. X-ray powder diffraction patterns of as-grown and quen-

ched samples were taken on a Philips PW-3710 diffractometer ($\text{CuK}\alpha$ radiation).

RESULTS

Atomic absorption spectroscopy confirmed the 1:2 Cu:Ca ratio; the X-ray powder diffraction pattern is in good agreement with that calculated from single crystal studies (4); this crystal structure analysis involves a tridimensional array of copper and calcium ions bridged through formate bidentate groups; the formate bridge networks results in chains of edge-sharing pseudo-octahedra (Fig. 1) which are effectively isolated from each other by chains of calcium ions.

A supercell was detected when X-ray diffraction was performed on our single crystals. With the main reflections related to the basic cell (4), weak reflections were observed giving a supercell with the volume $V_{\text{super cell}} = 7 V_{\text{basic cell}}$. In Table 1 the relation between both cells is shown.

From TGA and DTG analysis up to 1000°C, we found that the decomposition of ACuCa_2F takes place, up to 300°C, through two well-differentiated stages; these two stages have always been observed, whatever the heating rate. At each stage and for different heating rates the resulting products were quenched and analyzed by X-ray powder diffraction. A step at 750°C is related to the reaction of CaCO_3 and CuO to give Ca_2CuO_3 .

A typical TGA tracing for a heating rate of 10°C/min is shown in Fig. 2, and the relevant temperatures and weight losses obtained at different temperatures are summarized in Table 2.

Thermogravimetric Analysis For All Heating Rates

(a) *First stage.* The first stage of the thermal decomposition of ACuCa_2F up to 200°C, with a weight loss from about 3 to 4% for different heating rates and a change in color from blue to reddish, can be related to the partial decomposition of the copper formate structural units contained in the unit cell. CO_2 and H_2O evolve; part of the

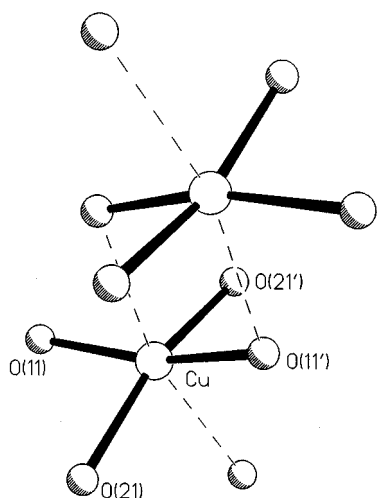


FIG. 1. Edge-sharing copper-oxygen pseudo-octahedra from dicalcium copper formate crystal structure (4).

copper separates as metallic copper (later oxidized to Cu_2O). These changes are reflected in a slight widening of the ACuCa_2F diffraction peaks. In samples quenched from 200°C , where the first stage of decomposition has been completed, X-ray diffraction patterns show ACuCa_2F as the main component with Cu and some Cu_2O .

(b) *Second stage.* The second stage of the thermal decomposition of ACuCa_2F takes place between 200 and 270°C and is accompanied by a weight loss of about 33%. In samples quenched from 260°C , where the second stage of decomposition has not been completed, X-ray diffraction

TABLE 1
Crystallographic Data for the Basic Cell and Supercell
for $\text{CuCa}_2(\text{HCOO})_6$

	Basic cell (4)	Supercell
FW	413.80	413.80
Crystallographic system	monoclinic	monoclinic
Space group	$C2/c$	$C2'$
a , Å	2.2296	2.7718
b , Å	0.8803	0.8799
c , Å	0.6377	3.5221
β deg.	101.00	90.52
V , Å^3	1.2286	8.5896
Z	4	28
Basic to supercell transformation		
$\bar{A} = -\bar{a} + 2\bar{c}$	$\bar{A}^* = 1/7(\bar{c}^* - 5\bar{a}^*)$	
$\bar{B} = -\bar{b}$	$\bar{B}^* = -\bar{b}^*$	
$\bar{C} = \bar{a} + 5\bar{c}$	$\bar{C}^* = 1/7(2\bar{a}^* + \bar{c}^*)$	

Note. A , B and C referred to the supercell and a , b , and c to the basic cell.

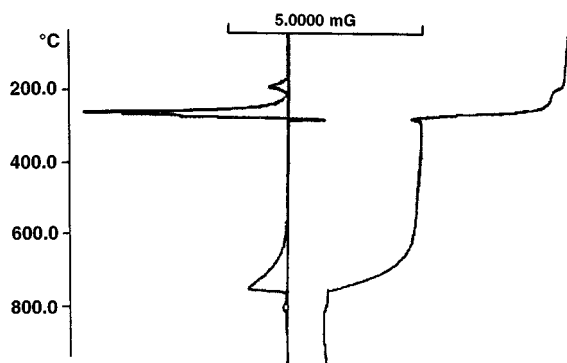


FIG. 2. DTG and TG tracings of ACuCa_2F ; heating rate $10^\circ\text{C}/\text{min}$.

patterns show the presence of Cu, Cu_2O , and CaCO_3 as the main crystalline components. CaO was not detected.

Similar results were obtained using single crystals and powder samples.

(c) On heating up to 1000°C , a weight loss of 21.3% takes place at 770°C ; X-ray diffraction patterns of quenched samples show only the presence of calcium cuprate, Ca_2CuO_3 .

Isothermal Heating

Isothermal heating at 160°C for 3 h showed that the phase obtained after a 3% weight loss is a stable one.

Differential Thermal Calorimetry

No phase transition was detected up to 180°C .

DISCUSSION AND CONCLUSIONS

The most interesting result obtained from heat treatment of ACuCa_2F is the appearance of a stable system comprising a deficient ACuCa_2F structure and metallic copper which appears when heating at about 200°C and which is

TABLE 2
Weight Losses during Thermal Decomposition of ACuCa_2F

T , $^\circ\text{C}$	Percentage weight loss	Calculated value
170–198	3.35	3.66 (Cu as Cu) ^a
260–270	32.70	31.5 (Cu as Cu_2O) ^b
277–304	+2.44	Cu + Cu_2O → CuO
500–770	21.26	21.27 (Ca as CaCO_3)

^aFrom four of the 28 copper formate structural units contained in the unit supercell.

^bFrom the all remaining formate ions.

accompanied by only about a 3% weight loss. It is not easy to correlate structural modifications of the basic structure with the weight loss observed at this stage since the loss of a single formic acid molecule per basic unit cell should give a weight loss of 10.87%.

The detection of a supercell opens a new possibility for the understanding of this behavior; in the unit cell of the observed superstructure there are 28 copper formate structural units, split into four sets of seven independent units. Decomposition of only one of these seven independent copper formate structural units should give a weight loss of 3.66% in good agreement with the experimental value observed in TGA. We propose that when one seventh of the total copper formate groups breaks down in the $ACuCa_2F$ superstructure, CO_2 and H_2O from one formic acid group evolve; this is followed by the separation of a copper atom in the copper oxygen chains, leaving a defective structure; the unit supercell contents of this defective structure should be $Ca_{56}Cu_{24}[V]_4(HCOO)_{160}[Vf]_8$, where $[V]$ means a copper vacancy and $[Vf]$ a formate ion vacancy. The defective

structure remains stable as seen in the isothermal and TG results.

The answer to the question of why only one seventh of the copper formate structural units leaves the structure can be considered only after a more careful examination of the superstructure is made: X-ray diffraction data are compatible with the presence of a modulation in all of the cation–oxygen bond distances calculated using a modified version (5) of refinement program REMOS (6) for modulated structures. The modulations of the Cu–O apical distances are given in Fig. 3a. Copper–oxygen distances for the two equatorial oxygen atoms bridging two copper atoms through a long apical bond and a short equatorial bond are given in Fig. 3b. These two distances are strongly correlated: oxygen atoms with the shortest apical distances show the longest equatorial bonds and vice versa.

Copper oxygen distances for the remaining two equatorial oxygen atoms bridging only one copper atom to a formate group are given in Fig. 3c. The modulation of the Cu–O distances in these two oxygen atoms is not identical:

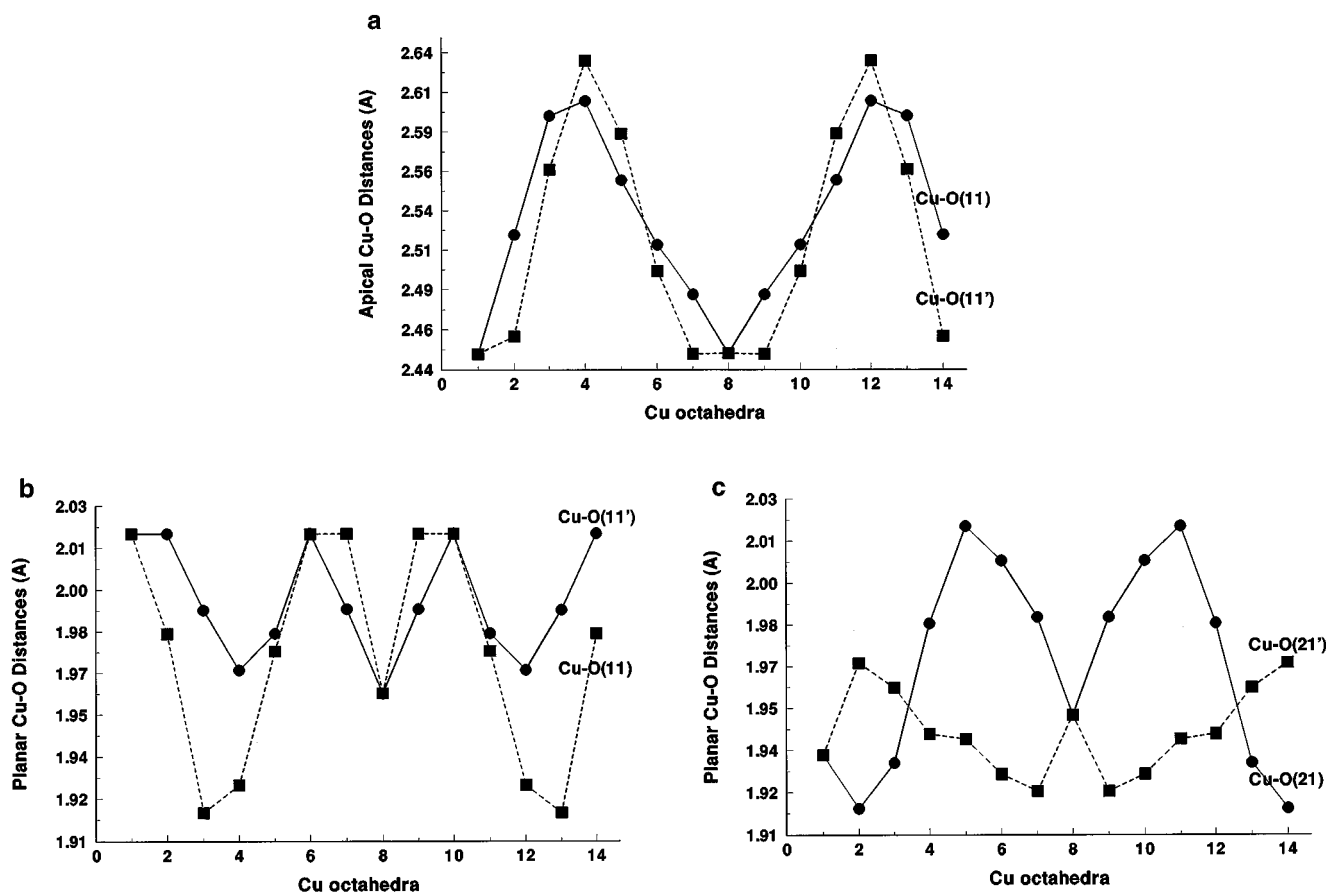
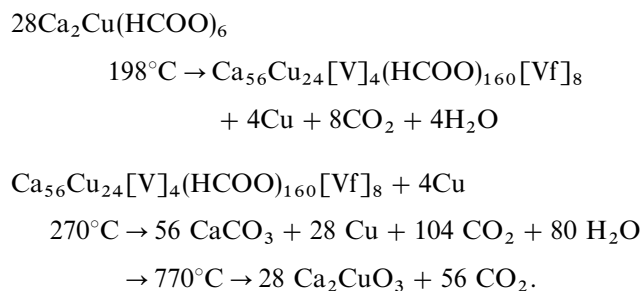


FIG. 3. Cu–O bond distances in the modulated structure. (a) Cu–O apical distances. (b) Cu–O–Formate equatorial distances. (c) Cu–O–Cu equatorial distances. Oxygen labelings are the same as those given in (4).

while for one of them fluctuations are small when compared to its average value, for the other, fluctuations are remarkably larger. We can tentatively correlate the first stage of decomposition to the modulation of this Cu–O bond in the equatorial plane; we propose that the decomposition process starts in the weakest (longest) Cu–O bond connecting a copper ion to a formate ion. As we can see in Fig. 3c there are two maxima, located on copper atoms labeled 5 and 11, for every 14 copper atoms in a copper–oxygen chain; this means that in the copper formate chains, at about 200°C, in two of every 14 copper formate units these copper–oxygen equatorial bonds have just reached the value up to which these structural units are stable. These are the driving forces leading to the destabilization of those particular copper formate structural units, which break down losing CO₂ and H₂O and leaving behind a defective, pentacoordinated copper atom in the copper–oxygen chain and probably modifying the neighboring copper–oxygen bond lengths. We propose that the first stage of the decomposition process is initiated at this copper formate structural unit leaving behind a “normal-defective,” nonmodulated structure. Higher energies are needed to break the remaining cation–oxygen bonds.

Taking into account all our experimental results and the behavior of the different formate groups as a function of temperature, the following decomposition path for ACuCa2F can be given:



These results agree with those obtained by (1), except for the presence of CaCO₃ and the absence of CaO in our second stage. This can be explained because of the different experimental conditions: while their results were obtained *in situ* using a high-temperature diffractometer, our diffractograms were obtained under ambient conditions (27°C, 50% humidity) working on quenched samples.

Comparison of the Thermal Behaviors of Anhydrous ACuCa2F and ACuCaF

Thermal decompositions of these alkaline earth copper formates are not identical. In both compounds thermal decomposition starts by the breaking down of some of the copper formate structural units: but while in ACuCaF half of these are lost in one stage, only one seventh of the copper formate structural units contained in the unit ACuCa2F supercell is lost in the first heating stage.

In ACuCa2F decomposition of the remaining Cu formate and Ca formate structural units occurs simultaneously at 210°C. On the other hand, for ACuCaF the decomposition path goes through the formation of $\beta\text{-Ca}(\text{HCOO})_2$ which never appears as a decomposition product of ACuCa2F. This difference can be related to the different crystal structures: ACuCaF and $\beta\text{-Ca}(\text{HCOO})_2$ both have two formate chelating ions in the calcium coordination polyhedra, while ACuCa2F has only one formate chelating unit.

Besides, in the last decomposition stage at about 800°C, different products are obtained for ACuCaF and ACuCa2F; for the first compound, the Ca:Cu = 1 ratio leads to a 50:50 mixture of CaCu₂O₃ and Ca₂CuO₃, while for the second compound the Ca:Cu = 2 ratio leads to the formation of Ca₂CuO₃ only.

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