

Crystal Structure and Thermal Decomposition of Copper(II) Strontium(II) Formate

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The crystal structure of anhydrous copper strontium formate ($P2/c$, $Z = 4$, $a = 7.3296(12)$ Å, $b = 8.6402(9)$ Å, $c = 6.6690(8)$ Å, $\beta = 97.22(1)^\circ$) has been solved from conventional X-ray diffractometric data at room temperature. The presence of different stages in its thermal decomposition process has been established by means of DSC, TGA, and X-ray diffraction. At temperatures up to 185°C, partial decomposition takes place, yielding CuO, Cu₂O, and the α and β -phases of anhydrous strontium formate. Between 185 and 270°C, decomposition of these phases occurs, and comparison with the thermal behavior of the pure phases reveals the influence of copper oxides in the decomposition process. © 1995 Academic Press, Inc.

INTRODUCTION

Copper strontium formate has been synthesized and used as the precursor for binary oxides, which were tried as reactants to obtain high T_c superconductors. For example, to prepare superconductors of the Bi family, methods starting from complex mixed oxides have been used (2–4); we obtained ceramic samples of Bi₂Sr₂Ca₁Cu₂O_y (the $T_c = 80$ K phase) of good quality using a new method of synthesis starting from the pure binary oxides Ca₂CuO₃, Sr₂CuO₃, and Bi₂CuO₄ (5), which were prepared through the thermal decomposition of the corresponding copper–strontium and copper–calcium formates. No structural information on these formates could be found in the literature.

The only previous work on these double formates is related to the topotactic transformation during the dehydration of CuSr₂(HCOO)₆ · 8H₂O yielding CuSr(HCOO)₄ (hereafter denoted ACSF) plus Sr(HCOO)₂ (hereafter denoted ASF) (1). The thermal behavior of ASF, as well as that of the simple calcium and copper formates, has already been studied, and different polymorphic phases were detected (6–8).

The aims of this work are: (i) to determine the crystal structure of anhydrous copper strontium formate, (ii) to study the different stages through which thermal decomposition of this formate takes place, and (iii) to propose a decomposition mechanism which takes into account the intermediate reaction products and their crystal structures.

EXPERIMENTAL

Good single crystals of ACSF are obtained when CuO is dissolved in a boiling 20% aqueous formic acid solution and SrCO₃ is added in stoichiometric proportion; the resulting solution is kept at 60°C until crystallization of the anhydrous double formate occurs.

The material obtained was blue and homogeneous, and its X-ray diffraction powder pattern was identical to that already reported for ACSF (1). Well-developed single crystals of ACSF belonging to space group $P2/c$ appear in the form of monoclinic (010) platelets, showing a perfect cleavage on (101).

A small and optically clear single crystal was used for X-ray diffractometer data. The structure was solved using the heavy atom method to locate the copper and strontium atoms. Successive Fourier difference maps gave the coordinates of nonhydrogen atoms. Complex ionic scattering factors were obtained from (9). The refinement was made using full-matrix least-squares with anisotropic thermal parameters for the nonhydrogen atoms including the anomalous dispersion term for Cu and Sr and using non-zero reflections.

In addition, crystals obtained were characterized by optical microscopy, by TGA in a Mettler TG 50 apparatus, between 30 and 1000°C in air, at a heating rate of 10°C/min, and by DSC on a Perkin–Elmer DSC-2 calorimeter between –30 and 250°C scanned at the same heating rate; X-ray diffraction powder patterns were taken on a Philips PW-3710 diffractometer (CuK α radiation).

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RESULTS

1. Crystal Structure Determination

Crystallographic and other experimental data obtained at room temperature are listed in Table 1. Atomic coordinates, interatomic distances, and anisotropic thermal parameters for nonhydrogen atoms are given in Table 2.

A unit cell of ACSF atomic structure is shown in Fig. 1; the copper atom is required to be on one of the two crystallographically independent twofold axes and is surrounded by six oxygen atoms belonging to six different formate ions, each contributing one oxygen atom to the copper coordination polyhedron (c.p.). This is a typical Jahn–Teller deformed octahedron with four short equatorial (1.947 and 1.966 Å) and two long axial (2.613 Å) bonds. The resulting bipyramid has the base stretched out of the ideal square plane, owing to strong interaction with the Sr atom. These bipyramids share two opposite, parallel edges with neighboring c.p., forming chains parallel to the *c* direction.

The Sr atom is also required to be on the other independent twofold axis of the *P2/c* space group and is coordinated to eight nearest neighbors, thus generating the symmetric c.p. shown in Fig. 2a. Two pairs [O(1) and O(2)]

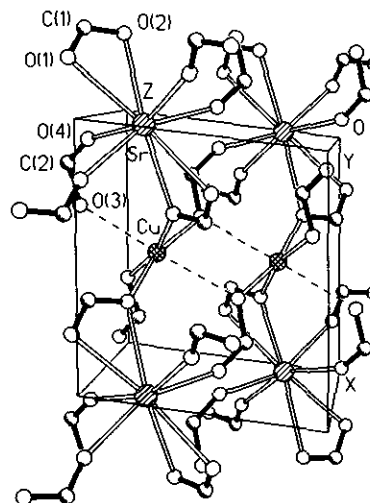


FIG. 1. Structure of $\text{CuSr}(\text{HCOO})_4$.

TABLE 1
Crystal Data

Empirical formula	$\text{CuSr}(\text{HCOO})_4$
Formula weight	331.24
Temperature	293 K
Wavelength	0.70930 Å
Crystal system	Monoclinic
Space group	<i>P2/c</i>
Unit cell dimensions	$a = 7.3296$ (12) Å $b = 8.6402$ (9) Å $c = 6.6690$ (8) Å $\beta = 97.22$ (1)°
Cell volume	418.99 (10) Å ³
<i>z</i>	4
X-ray density	2.625 mg/m ³
Absorption coefficient	8.921 mm ⁻¹
<i>F</i> (000)	318
θ range for data collection	2.35° to 29.91°
Index ranges	$0 < h < 10$, $0 < k < 12$, $-9 < l < 9$
Reflections collected	1256
Independent reflections	1166 ($R_{\text{int}} = 0.0437$)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1166/0/66
Goodness of fit on F^2	1.046
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.035$ $wR_2 = 0.094$
<i>R</i> indices (all data)	$R_1 = 0.043$ $wR_2 = 0.098$
Extinction coefficient	0.053 (5)
Largest diff peak hole	1.118 and -0.711 e/Å ³
Structure solution	SHELXS – 86 (Sheldrick, 1990) (12)
Structure refinement	SHELXL – 93 (Sheldrick, 1993) (13)

and [O(1'') and O(2'')] belong to two different chelating formate groups; both pairs are symmetry related. The remaining four oxygen atoms, also symmetry related, belong to four different nonchelating formate ions. Although the acidic character is shared between both oxygen atoms, C–O distances vary between 1.265 Å (for C(2)–O(4) where the oxygen atom is coordinated to two copper atoms) and 1.225 Å (for C(2)–O(3), where the oxygen atom is coordinated to only one strontium atom), so formate C(2) groups show a rather unusual asymmetrical disposition of the two C–O bonds (incomplete resonance): the shorter C–O bond is coordinated to one Sr cation and the longer to two Cu cations. On the other hand, all other oxygen atoms are coordinated either to two strontium atoms [O(2)] or to one strontium and one copper atom [O(1)], with similar C(1)–O(2) (1.233 Å) and C(1)–O(1) (1.247 Å) distances, showing that the two C–O bonds are disposed more symmetrically than in most formate structures.

2. Thermal Decomposition

From TGA and DTG analysis, we observe that the decomposition of ACSF takes place through well-differentiated stages; at each stage the resulting quenched products were analyzed by X-ray powder diffraction methods.

TGA recordings are drawn in Fig. 3 and several stages may be noted; the relevant temperatures, weight losses, and compositions of the quenched samples obtained at different temperatures are summarized in Table 3.

a. First stage. The first stage of the thermal decomposition of ACSF up to 185°C with a weight loss of 18% is closely related to the decomposition of copper formate. As a consequence of the breaking of the copper formate structural units, CO₂ and H₂O evolve, leaving the two copper oxides Cu₂O and CuO; the strontium–formate

TABLE 2
Atomic Coordinates, Interatomic Distances, and Anisotropic Thermal Parameters

Atom	Atomic Coordinates			z/c
	x/a	y/b		
Cu	0.5000	0.40495(8)		0.2500
Sr	0.0000	0.13505(6)		0.2500
O(1)	0.3214(4)	0.2440(3)		0.1516(4)
O(2)	0.2100(4)	0.0488(4)		-0.0349(5)
O(3)	0.0913(5)	0.3166(5)		0.5225(5)
O(4)	0.3580(4)	0.5617(4)		0.0887(4)
C(1)	0.2159(6)	0.1506(5)		0.0097(7)
H(1)	0.4255(6)	0.1590(5)		-0.0704(7)
C(2)	0.2000(6)	0.6005(5)		0.1280(6)
H(2)	0.1635(6)	0.5626(5)		0.2523(6)

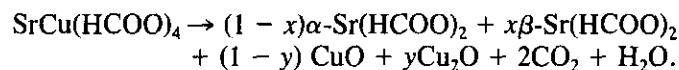
Atom	Anisotropic thermal parameters					
	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu	0.0130(3)	0.0120(3)	0.0234(4)	0.000	-0.0034(3)	0.000
Sr	0.0128(3)	0.0141(3)	0.0087(2)	0.000	0.00343(15)	0.000
O(1)	0.0145(12)	0.0200(14)	0.0214(14)	-0.0053(11)	0.0036(10)	-0.0043(10)
O(2)	0.0243(15)	0.023(2)	0.0248(15)	-0.0099(13)	0.0060(12)	-0.0059(12)
O(3)	0.028(2)	0.046(2)	0.029(2)	0.021(2)	0.0091(13)	0.017(2)
O(4)	0.0161(13)	0.0215(14)	0.0211(14)	0.0080(12)	0.0046(10)	0.0040(11)
C(1)	0.021(2)	0.023(2)	0.023(2)	-0.005(2)	0.0110(15)	-0.002(2)
C(2)	0.018(2)	0.030(2)	0.014(2)	0.0094(15)	0.0083(15)	0.006(2)

Interatomic distances (Å)						
Cu-O(4)	1.947(3)	C(1)-O(1)	1.247(5)	O(1)-C(1)-O(2)	124.1(4)	
Cu-O(1)	1.966(3)	C(1)-O(2)	1.233(5)			
Cu-O(1)	2.613(3)	C(2)-O(3)	1.225(5)	O(3)-C(2)-O(4)	125.6(4)	
		C(2)-O(4)	1.265(5)			

structural units rearrange to yield β - and α -ASF, as detected by the X-ray diffraction of quenched samples.

The calculated value for the weight loss for the proposed decomposition mechanism, considering that all Cu is present as CuO, is 17.5%. The difference between this value and the experimental one is attributed to the presence of Cu₂O.

The stoichiometry of the first stage of ACSF decomposition in air is



These results were compared with those obtained while heating ACSF on the heating stage of an X-ray powder diffractometer. In both cases we detected the simultaneous appearance of the α and β -phases of ASF and the presence of cupric and cuprous oxides; no copper formates were ever detected.

Comel and Mentzen (6) showed that the β phase can be only obtained from the δ phase, but not from the α phase; so the presence of the α and β phases of ASF in both heating products induced us to check the thermal

behavior and the stability at room temperature of pure ASF and to compare them with the thermal behavior of ACSF.

Single crystals of α -ASF, obtained by slow evaporation at 60°C of an aqueous 20% formic acid solution, were subjected to several consecutive thermal cycles on the DSC equipment. On heating, during the first cycle, and α - δ phase transition at 235°C was the only one observed; on cooling to -30°C, no thermal effect was detected. In the course of a second cycle performed immediately after the first one, no thermal effects were observed either on heating or on cooling. After keeping the sample in the

TABLE 3
Weight Loss and Thermal Decomposition Products of ACSF

T (°C)	% Weight loss	Quenching T (°C)	Detected products of quenched samples
150-200	18	185	α ASF + β ASF + CuO + Cu ₂ O
200-270	10	300	SrCO ₃ + CuO
700-1000	10.5	1000	Sr ₂ CuO ₃

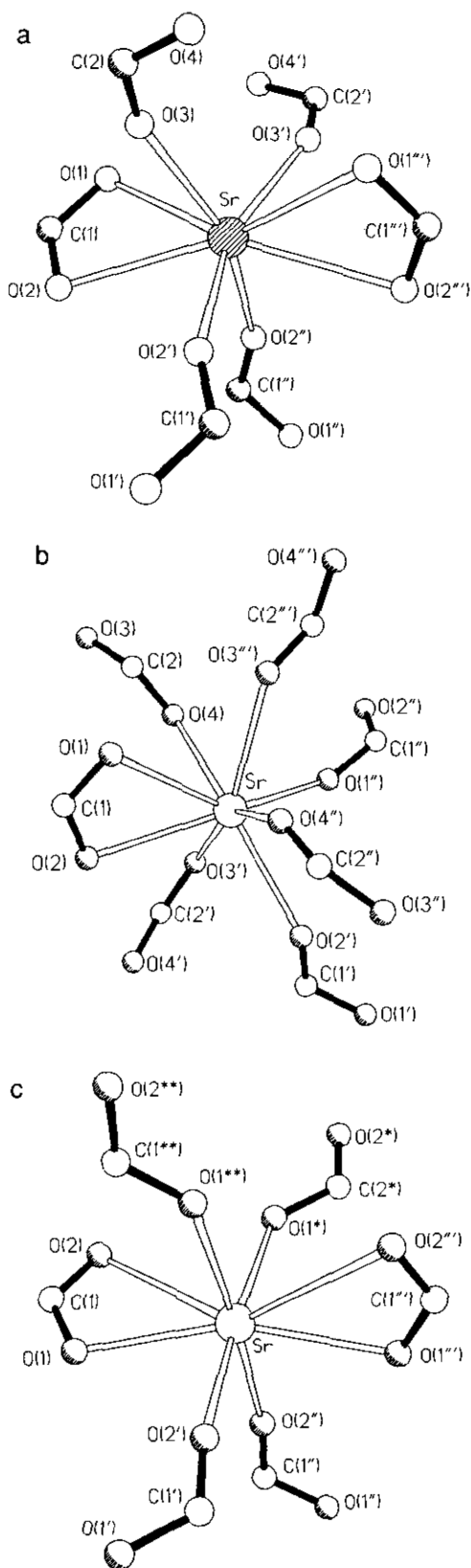


FIG. 2. Sr ion environments: (a) in $\text{CuSr}(\text{HCOO})_4$, (b) in $\alpha\text{-Sr}(\text{HCOO})_2$ as obtained from (10), and (c) in $\beta\text{-Sr}(\text{HCOO})_2$ as obtained from (11).

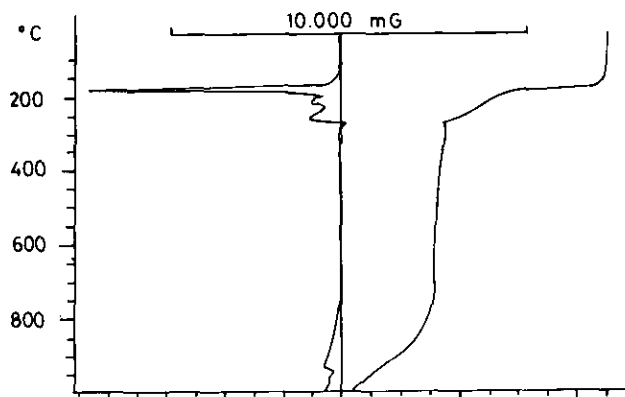


FIG. 3. DTG and TG tracing of ACSF.

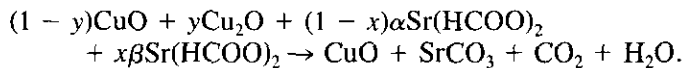
sample holder of the DSC at room temperature for periods longer than 4 hr, a third thermal cycle was performed; only after this time had elapsed is the phase transition at 235°C, on heating, recovered.

This behavior was confirmed on a heating stage under an 80× stereoptical microscope keeping the single crystal under silicon oil to avoid contact with ambient humidity.

Under our experimental conditions, the presence of extraneous water vapor seems not to be necessary for recovering the α phase. These results are different from those obtained by Comel and Mentzen (6, 7), who, working with α -ASF obtained by the dehydration of $\text{Sr}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$, found that, after going through the α - δ transition, the α phase is not recovered in a dry atmosphere.

In agreement with their findings, we never observed the α - β transition.

b. Second stage. TGA tracings (Fig. 3) show that between 200 and 300°C two peaks appear (at 214 and 259°C), which we have assigned to decomposition of the α and β phases of ASF. These processes are accompanied by a 10% weight loss on samples quenched at 300°C or between 14 and 17% (calculated value: 16.9%) in samples where the decomposition is completed according to the following reaction, as concluded from X-ray diffraction data:



It is worth noting that pure ASF decomposes at temperatures higher than 360°C. A possible cause for this discrepancy in decomposition temperature could be the presence of copper oxides together with ASF. This hypothesis was confirmed through several experiments which were carried out mixing α -ASF with CuO , Cu_2O and Al_2O_3 (cation molar ratio = 1:1); in each case, TGA tracings showed only one peak (Fig. 4), and decomposition temperatures,

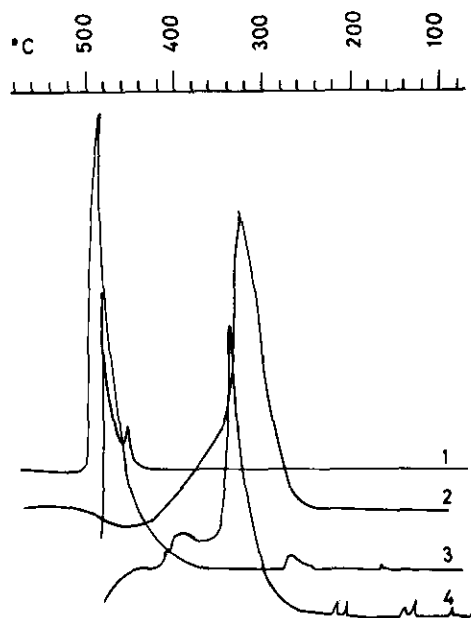


FIG. 4. DTG tracings of ASF:metal oxides (1:1) (1) Pure ASF, (2) ASF + (0.5 CuO + 0.5 Cu₂O), (3) ASF + Al₂O₃, and (4) ASF + Bi₂O₃.

which were found to be dependent on the added oxide, are summarized in Table 4.

As we can see, results are different for samples containing Al₂O₃, which only slightly changes the decomposition temperature of ASF, and for samples containing both pure CuO and Cu₂O and their 50% mixture; in all these cases decomposition temperatures are always depressed, depending slightly on the oxidation state of the copper cation. This implies a catalytic role of the copper compounds during the reaction.

To check the influence of other oxide-containing cations that can have different oxidation states, we prepared mixtures with Bi₂O₃ (cation molar ratio: 1:1); again the decomposition temperature is noticeably depressed (Table 4).

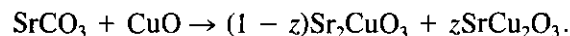
TABLE 4
Influence of Different Oxides on the
Decomposition Temperature of ASF

ASF: added oxide (1:1)	Decomposition temperature (°C)
—	493
CuO	324
CuO-Cu ₂ O	319
Cu ₂ O	300
Al ₂ O ₃	472
Bi ₂ O ₃	326

DSC analysis of all these mixtures showed that the α - δ transition temperature of ASF does not change, whereas the decomposition temperature of ASF is altered.

As our samples of ACSF were always kept at temperatures lower than that of the ASF α - δ transition (235°C), we believe that the β phase is formed simultaneously with the alpha phase during thermal decomposition. Besides, no phase transition was observed on single crystals of ACSF below the decomposition temperature either by differential scanning calorimetry or by optical microscopy on a heating stage. From these results, we can further justify our previous assignment of the 230 and 250°C peaks in Fig. 3 to the decomposition of the α and β phases of ASF; although the presence of copper oxides has a strong influence in the decomposition processes, the oxides have no influence at lower temperatures where the α - δ phase transition takes place.

C. Third stage. Heating to 1000°C, a weight loss of 10.5% takes place at 927°C on quenched samples (Fig. 3) according to the reaction



By X-ray diffraction, we detected the presence of Sr₂CuO₃ as the main final product.

CONCLUSIONS: PROPOSED PATH FOR THE DECOMPOSITION PROCESS

The knowledge of the alkaline-earth and copper atom c.p. and the different types of formate groups present in the atomic structure is important for understanding the reaction pathway leading to the high T_c superconductors when using different formates as starting materials.

From crystal structure considerations and X-ray pow-

TABLE 5
Sr-O Distances (Å)

CuSr(HCOO) ₄	α Sr(HCOO) ₂ ^a	β Sr(HCOO) ₂ ^b
2.696(3) ^c (×2)	2.702 ^c	2.944 ^c (×2)
2.693(3) ^c (×2)	2.659 ^c	2.484 ^c (×2)
2.529(3) (×2)	2.669	2.364 (×2)
2.430(3) (×2)	2.633	2.311 (×2)
	2.599	
	2.594	
	2.541	
	2.504	

^a As obtained by M. M. and T. W. (11).

^b As obtained by T. W. and M. M. (10).

^c Distances to oxygen atoms from the chelating formate group.

der diffraction, DSC, and DTA data, a possible decomposition path accounting for the presence of the products found during thermal decomposition of ACSF may be outlined. The first stage in the decomposition yields cupric and cuprous oxides, showing that Cu formate structural units are the first to be broken; the appearance of the α and β phases of ASF shows that there are no drastic changes in the strontium surroundings (Figs. 2a, 2b, and 2c). We can conclude that during the decomposition of ACSF some strontium atoms keep their two chelating formate groups yielding the ASF β phase, although Sr–O distances change. The presence of the α phase can be explained as a consequence of the breaking of one of the chelating Sr–O bonds in ACSF, thus changing the strontium atom surroundings to those of the α phase, keeping Sr–O distances almost unchanged (Table 5).

In addition, we can conclude that in the second stage of the decomposition process copper oxides act as catalysts for the decomposition of both phases of ASF.

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