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$Ba_2Cu(HCOO)_6$, Thermal Behavior and Crystal Structure of the Room Temperature Phase

D. Vega, G. Polla, A. G. Leyva, H. Lanza, P. K. de Perazzo, R. Baggio, and M. A. R. de Benyacar

Departamento de Fisica, CNEA, Avenida del Libertador 8250, 1429 Capital Federal, Argentina

J. Ellena

Departamento de Fisica, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, La Plata, Argentina

and

H. Tolentino and M. do Carmo Martins Alves

Laboratorio Nacional Luz Sincrotron, Campinas, Sao Paulo, Brazil

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$Ba_2Cu(HCOO)_6$ grown at room temperature crystallizes in space group $P2_1$; $a=11.092$ Å, $b=7.079$ Å, $c=17.391$ Å, $\beta=91.64°$; $V=1365$ Å^3, $Z=4$, $D_c=2.96$ g/cm^3. On heating, the following changes are observed: (1) a reversible, hysteretic, first-order phase transition at about 40–90°C; (2) partial decomposition at 190°C; and (3) an irreversible change at 230°C related to decomposition. We have assigned to a new γ-$Ba(HCOO)_2$ metastable phase one of the main components found when $Ba_2Cu(HCOO)_6$ samples are quenched from 190°C. A room temperature model structure of $Ba_2Cu(HCOO)_6$ is given. The copper atoms are surrounded by seven oxygen atoms, five of them defining an almost perfect square pyramid, and the remaining two, opposite to the apex, at hemicoordination distances of ca. 2.85 Å. The barium atoms display irregular, ninefold coordination polyhedra. © 1999 Academic Press

Key Words: **$Ba_2Cu(HCOO)_6$; crystal structure; thermal behavior.**

INTRODUCTION

Mixed carboxylates have been the subject of interest for different authors (1–4) in reference to their ability to yield (through their thermal decomposition) basic metal cuprate precursors, as an important step in the synthetic route toward new materials of basic or technological interest, as high T_c superconductors and magnetoresistant materials. In this line of thought, a systematic thermal behavior study of copper-containing alkaline earth coordination formates has been carried out for years in our laboratory (5–9); it has been found that the decomposition response of these compounds depends heavily on the diversity of coordination structures displayed by the cations; viz. the copper formate structural units can be found forming either chains of edge sharing $[CuO_6]$ octahedra (as in $CaCu(HCOO)_4$ and $Ca_2Cu(HCOO)_6$ (10) and $CuSr(HCOO)_4$ (5, 6)) or dimeric entities through two edge sharing octahedra (as in α-$Cu(HCOO)_2$ (11)). Besides, a large diversity of coordination polyhedra for the alkaline earth ions have been found in many cases such as Sr and Ca in their corresponding 1:1 copper formates with octahedral enviroment (5, 10) and of seven coordination polyhedra as in $Ca_2Cu(HCOO)_6$ (10).

However, and in spite of the rather thorough knowledge regarding many of the complexes of the type, a related search on the title compound $Ba_2Cu(HCOO)_6$ did not provide much information: no structural data of the complex had ever been reported, presumably due to the fact that the crystals invariably grow as microtwins, thus preventing the use of conventional structural resolution techniques, and only early works on its thermal characterization (12, 13), with partial information, could be traced.

It was accordingly decided to proceed to a full thermal and structural characterization of the complex, which is the one herein reported. The former part of the study has been performed from room temperature up to 300°C, with identification of the decomposition products through X-ray diffraction (XRD) methods using quenched powder samples at the different stages observed in thermal gravimetric analysis (TGA). A previously unreported metastable phase of $Ba(HCOO)_2$ has been found and characterized. Finally, the crystal structure of the title compound, in its room temperature stable phase, has been determined and refined through the combined use of single crystal analysis performed on

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twinned specimens, Rietveld refinement on powder samples, and extended X-ray absorption fine structure (EXAFS).

EXPERIMENTAL

Crystals of $Ba_2Cu(HCOO)_6$ (hereafter CUBA) were grown starting from $BaCO_3$ and CuO in a 20% aqueous formic acid solution at room temperature. Irrespective of the growth conditions, the specimens obtained were invariably twinned, both at an obvious macroscopic level which was clearly detectable by optical inspection in cross polars and at a second, much subtler one, only suggested by the elusive interference figure of otherwise excellent crystals.

The material obtained was characterized by TGA in a Mettler TG 50 apparatus, between 30 and 300°C in air, at a heating rate of 10°C/min, and by differential scanning calorimetry (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 samples quenched from different temperatures were taken, at room conditions, on a Philips PW-3710 diffractometer (Cu$K\alpha$ radiation).

Even though macrotwinning could be somehow avoided through a careful selection of the specimens under a polarizing microscope, it was impossible to get rid of the microtwins, as the whole lot seemed to be similarly affected. In the hope that a conventional single crystal experiment could be of any value, two independent data sets were gathered out of two microtwined "single crystals" of similar dimensions (roughly $0.30 \times 0.30 \times 0.25\ \mathrm{mm}^3$) and collected with a CAD4 Enraf Nonius diffractometer using graphite monochromatized Mo$K\alpha$ radiation. The cell parameters were readily (and consistently) determined, and data collection produced two almost identical data sets up to $\theta = 29.96°$. The only obvious hint about twinning was perhaps the unusually large number of reflections with a rather asymmetric background.

The heavy atom positions were deduced from direct methods and the other atoms were located from subsequent difference Fourier synthesis. The process ended up with a structure with $Z = 4$ which displayed a strong pseudocentrosymmetric character, thus suggesting $P2_1/n$ as the correct space group. However, the large number of violations of the required systematic extinctions ($N = 99$ $[I > 3\sigma]$, mean $I/\sigma(I) = 6$), as well as the strong indication from the final R indices obtained ($R = 0.0529$ in $P2_1$, 0.102 in $P2_1/n$), were considered definitive arguments in favor of the non centrosymmetric space group. Anisotropic refinement on any of the space groups tried required soft restraints on the diagonal elements of the displacement ellipsoids of carbon and oxygen atoms in order to prevent some of them from running negative definite. This was one of the side effects of the systematic errors present; the other was the rather large $\Delta\rho$ values observed ($+2.80/-2.95\ \mathrm{e/\AA^3}$), mainly around barium atoms. In spite of these drawbacks, the resulting model appeared very sound, and a weighted refinement with SHELX97 converged to a conventional R factor of 5.29%. Unfortunately, and in spite of our efforts in that sense, we were not able to visualize any eventual twin law which could help in applying the capabilities of twin refinement in SHELX97.

The formally questionable validity of the "single crystal" methods employed prompted us to look for independent ways to cross-check the otherwise seemingly reasonable results thus obtained. This was done through two independent procedures. The first one was a symplified Rietveld refinement using rigid, idealized formate units and performed on powder X-ray data gathered with the Philips PW-3710 diffractometer (Cu$K\alpha$ radiation), a method which in principle should not be biased by the twinned character of the sample employed. Even though the uncertainties in the parameters were rather large, the refinement confirmed the general aspects of the model found, save perhaps for the fact that it could not confidently discriminate between the two space groups under discussion. The second attempt was through an EXAFS experiment, at the LNLS laboratory, in order to probe the copper atom neighborhood, and which results were in excellent agreement with those obtained from the "single crystal" technique.

RESULTS

Thermal Behavior

Before decomposition starts, crystals of CUBA undergo a reversible, strongly hysteretic first-order phase transition at about 40–90°C with a very small transformation energy, as detected by DSC. If the sample is cooled down to -30°C immediately after the transition to the high temperature form has taken place, no transition to the low temperature form can be detected; this is true even if the heating–cooling–heating cycle is repeated. Only after the sample is kept for several hours at ambient temperature can the transformation to the high temperature phase be observed again. The transition temperature is strongly dependent on the specimen, and the process is tentatively considered to be defect controlled.

From TGA and DTG analysis up to 300°C, it was found that the decomposition of CUBA takes place in two well-differentiated stages; Fig. 1 shows typical TGA and DTG tracings. The first one, at about 190°C, is accompanied by a weight loss of 15.3% due to the decomposition of the copper formate structural units (calculated weight loss 14.79%); as a consequence of their breaking down, CO_2 and H_2O evolve and most of the copper separates as metallic copper and Cu_2O. These changes are reflected in a change in the crystal color: the blue crystals become reddish. The resulting powder was quenched and analyzed using XRD methods. It was possible to ascertain the presence of Cu_2O

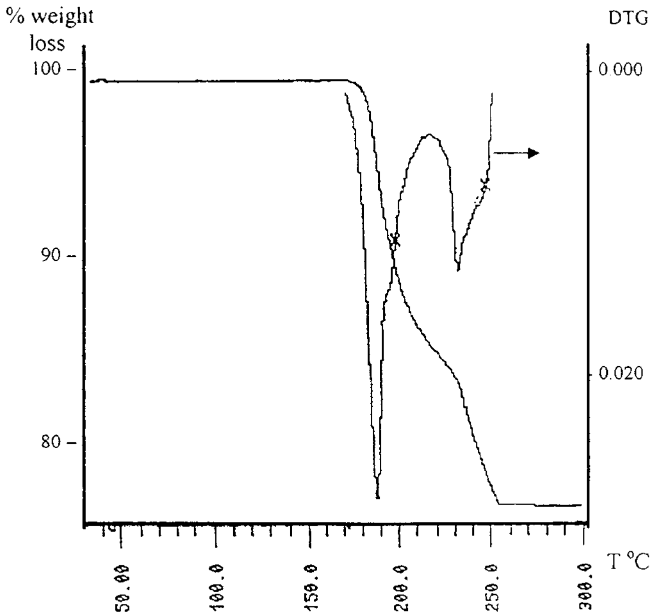

FIG. 1. DTG and TGA tracings of $Ba_2Cu(HCOO)_6$.

TABLE 1
X-ray Powder Diffraction Data of a New High Temperature Form of Barium Formate, Orthorhombic $a = 15.504(5)$ Å, $b = 12.784(4)$ Å, $c = 5.344(6)$ Å

Relative intensity	*d*, observed	*d*, calculated	*h k l*
20	9.93	9.86	1 1 0
47	7.76	7.75	2 0 0
22	4.93	4.93	2 2 0/0 1 1
73	4.10	4.10	0 2 1
100	3.29	3.286	3 3 0
13	3.19	3.196	0 4 0
25	2.526	2.527	4 3 1/2 0 2
24	2.225	2.225	5 4 0/3 2 2
38	2.182	2.183	7 1 0
22	2.130	2.129	0 6 0

and pure $Ba(HCOO)_2$ as most of the peaks given in the ICDD (14) card 15-0905 are present. However, the existence of ten extra peaks which could not be matched by any diffractogram contained in the ICDD data base suggested the presence of an unknown barium-containing organic compound.

After keeping the quenched sample at ambient temperature for some days, we found that the only barium-containing phase detected coincides with the ambient temperature stable phase of pure barium formate (ICDD card 39–0701); we shall call this phase α-$Ba(HCOO)_2$ following Baraldi's suggestion (15) for the pure metal carboxylates stable phases. So, it was found that the ICDD card 15-0905 barium formate, which we shall call β-$Ba(HCOO)_2$, transforms under ambient conditions into the α-$Ba(HCOO)_2$ phase. This transition was also detected by Baraldi (15) (transition temperature 255°C), using IR spectroscopy. We could not detect this transition using DSC even when using high sensitivity conditions, the change in enthalpy involved being probably very small; besides, there are very small differences between the X-ray diffraction patterns of the α and β phases of anhydrous barium formate.

The ten extra peaks (Table 1) which could not be matched with any of the known forms of $Ba(HCOO)_2$ just described, were used as input values to the TREOR code (16), which produced a most probable orthorhombic unit cell of parameters $a = 15.504(5)$ Å, $b = 12.784(4)$ Å, $c = 5.344(6)$ Å, with a rather good figure of merit (17) ($M(10) = 23$, $F(10) = 16$)). Unfortunately, the quality of the X-ray diffraction patterns obtained, as well as the fact that they are not single phase patterns, because of the presence of decomposition products Cu, Cu_2O, and β-$Ba(HCOO)_2$, precluded any *ab initio* solving strategy for its crystal structure.

These results show that decomposition of CUBA yields at 190°C a new, high temperature $Ba(HCOO)_2$ phase, metastable at ambient temperature, which we shall call the γ phase. Trials to obtain this γ-$Ba(HCOO)_2$ phase in a pure form have been, so far, fruitless.

The second stage of the thermal decomposition of CUBA takes place between 220 and 250°C and it is accompanied by a weight loss of 8.4%. X-ray diffraction powder methods showed that the resulting quenched samples contained $BaCO_3$, C particles, Cu, and Cu_2O while CO_2 and H_2O evolved. BaO was not detected.

It is interesting to note that although the main component of the sample quenched from about 200°C is $Ba(HCOO)_2$, its decomposition temperature as estimated from our own experiments differs substantially from the one reported in the literature for the pure barium formate (300°C) (15). This is due to the presence of copper in the former samples, which seems to act as a catalyst for the decomposition of the alkaline-earth formates (8).

The total weight loss up to 300°C is 24.1%, in good agreement with the loss of six formate groups per $Ba_2Cu(HCOO)_6$ molecule (calculated weight loss 24.7%). The final decomposition products are in agreement with those obtained in (12).

Crystal Structure Determination

Crystal data for CUBA obtained at room temperature are listed in Table 2. Selected bond distances and angles are presented in Table 3. The unit cell contents are shown in Fig. 2. The Rietveld refinement is shown in Fig. 3.

Coordination distances to the copper atoms are similar to those found in other mixed copper-alkaline earth oxides

(18), and their coordination geometry is strictly describable as a square pyramid, with the cation lying on the basal least squares plane (range of basal Cu–O distances 1.88 to 2.01(1) Å) and the apical site deviating ca. 16° from the base normal (range of apical Cu–O 2.40–2.44(1) Å). However, the copper interaction picture is somewhat more complicated as, opposite to the pyramid apex, and somehow fulfilling the role of a shared second apex of an eventual square bipyramid, there are two other oxygen atoms belonging to two chelating formates, which stand at 2.75–2.95 Å from the copper. Though this is too long a distance to be strictly considered a bonding contact, it is also too short for us to assume that no interaction whatsoever is present. It is possible to find in the CSD (19) a few, very similar cases of "double hemicoordination" to a pentacordinated copper center, at distances ranging from 2.75 to 2.95 Å, and where the "hemicoordinated" pair corresponds also to chelating carboxylates (CSD codes HICJEI, TEPTOX, MXPOCU, FORXAL, CUNPYO, CUNNME, CUHIPT). Finally, it must be stressed that the sevenfold Cu coordination found for CUBA (Fig. 4) is completely different from those reported in all previously studied copper and mixed copper-alkaline earth anhydrous formates.

Although both X-ray methods employed agreed on the fairness of the model found, we decided to check the results on the copper environment via an EXAFS experiment where the copper absorption spectrum was fitted with the contributions of different neighboring shells first (ca. 1.93 Å), second (ca. 2.00 Å), third (ca. 2.31 Å) and finally the fourth (ca. 2.86 Å). Even though the two nearest neighbor contributions accounted fairly well for many of the details of the EXAFS absorption curve, only the inclusion all four coordination shells improved the fitting (Fig. 5).

The two sets of independent barium cations display irregularly structured nine-coordination polyhedra (Ba–O: 2.68(1) Å to 3.03(1) Å) similar to that found in Ba(HCOO)$_2$ (20). The BaO$_9$ polyhedra share a face with each other and are in turn coordinated to the same copper ion. The resulting structural units interact with their neighboring equivalents through the sharing of two edges thus defining some kind of corrugated ribbons extending along the *c* crystallographic axis. The lateral interaction of the later determines in turn the building up of corrugated layers parallel to (100). Finally, corner sharing between polyhedra in neighboring layers determines a tridimensional network.

TABLE 3
Selected Bond Lengths for CUBA

Bal–O51	2.734(13)	Bal–O12^{a}	2.747(11)
Bal–O62^{b}	2.75(2)	Bal–O22^{b}	2.777(13)
Bal–O41^{c}	2.79(2)	Bal–O51A^{c}	2.806(13)
Bal–O42	2.812(13)	Bal–O52A^{d}	2.96(2)
Ba1–O21	3.032(13)	Ba1–Ba2	4.4472(14)
Ba2–061A^{e}	2.702(10)	Ba2–O32^{c}	2.70(2)
Ba2–O52A^{f}	2.76(2)	Ba2–O12^{a}	2.800(11)
Ba2–O61	2.81(2)	Ba2–O62	2.90(2)
Ba2–O31	2.909(14)	Ba2–O22^{b}	2.918(12)
Ba2–O21	2.978(13)	Cul–O11	1.877(13)
Cul–O31	1.956(13)	Cul–O21	1.978(12)
Cul–O42	2.012(12)	Cul–O12^{a}	2.405(14)
BalA–O41A^{g}	2.685(13)	BalA–O62A^{h}	2.709(14)
Ba1A–O51A	2.716(11)	BalA–O51^{i}	2.80(2)
Ba1A–O12A^{j}	2.816(13)	BalA–O42A	2.832(14)
Ba1A–O22A^{h}	2.848(11)	BalA–O52^{i}	2.981(14)
Ba1A–O21A	3.01(2)	Ba2A–O61^{k}	2.72(2)
Ba2A–O32A^{a}	2.73(2)	Ba2A–O52^{l}	2.741(12)
Ba2A–O22A^{h}	2.812(11)	Ba2A–O12A^{j}	2.862(12)
Ba2A–O61A	2.877(12)	Ba2A–O31A	2.889(14)
Ba2A–O21A	2.941(14)	Ba2A–O62A	2.96(2)
Cu1A–O42A	1.882(13)	Cu1A–O11A	1.97(2)
Cu1A–O31A	1.974(13)	Cu1A–O21A	1.989(14)
Cu1A–O12A^{j}	2.44(2)		
Ba2–Cu1	3.699(3)	Ba1–Cu1	3.721(2)
Ba2A–Cu1A	3.660(3)	Ba1A–Cu1A	3.692(3)
Ba1A–Ba2A	4.454(2)	Bal–Ba2	4.447(2)
Cu1A–Cu1A^{j}	5.370(3)	Cu1–Cu1^{m}	5.334(3)

Note. Symmetry transformations used to generate equivalent atoms are indicated in footnotes.

[a] $-x+2,\ y+1/2,\ -z+1.$

[b] $-x+1,\ y+1/2,\ -z+1.$

[c] $x,\ y+1,\ z.$

[d] $x+1,\ y,\ z+1.$

[e] $x+1,\ y,\ z.$

[f] $-x,\ y+1/2,\ -z.$

[g] $x,\ y-1,\ z.$

[h] $-x,\ y-1/2,\ -z.$

[i] $x-1,\ y,\ z-1.$

[j] $x-1,\ y-1/2,\ -z.$

[k] $x-1,\ y,\ z.$

[l] $-x+1,\ y-1/2,\ -z+1.$

[m] $-x+2,\ y+1/2,\ -z+1.$

TABLE 2
Crystallographic Data for CUBA

$C_6H_6Ba_2CuO_{12}$	fw: 608.32
System: monoclinic	space group: $P\ 2(1)$ (no. 4)
$a = 11.092(2)$ Å	crystal size: $0.25 \times 0.25 \times 0.12$
$b = 7.079(1)$ Å	crystal shape, color: prisms, blue
$c = 17.391(3)$ Å	F000 = 1116
$\beta = 91.64(3)$	$\mu = 7.31$
$V = 1365.0(4)$	θ range = 1.17 to 30.01
$z = 4$	$-15 \leq h \leq 15$
$d_{\text{calc}} = 2.96$	$-1 \leq 1 \leq 9$
Unique refl. (R_{int}): 4881(0.054)	$0 \leq 1 \leq 24$
Absorption correction: Psi-scan	R1,^{a} w$R2$ [$F^2 > 2s(F^2)$]^{b}: 0.053, 0.151
Max., min transm.: 0.12, 0.05	$R1^{a}$, $wR2$ [all data]^{b}: 0.065, 0.166
Max, min $\Delta\rho$: 2.80, -2.95 eÅ^{-3}	

[a] $R1$: $\sum||Fo|-|Fc||/\sum|Fo|$.

[b] w$R2$: $[\sum[w(Fo^2-Fc^2)^2]/\sum[w(Fo^2)^2]]^{1/2}$.

The shortest intercalation distances present in the structure are: Cu ··· Ba, 3.699(3)–3.721(2) Å, Ba ··· Ba,

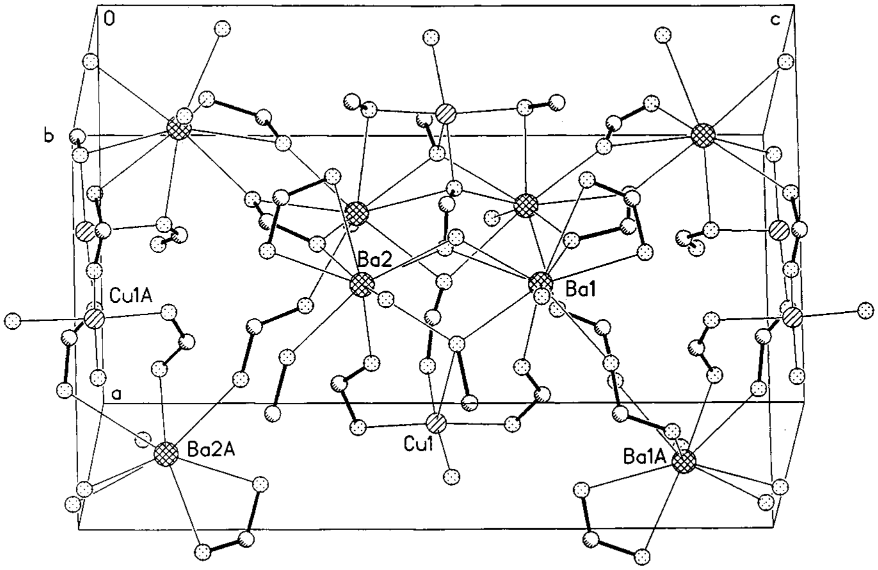

FIG. 2. $Ba_2Cu(HCOO)_6$, perspective view of the unit cell atomic structure.

4.447–4.454(2) Å. In both cases they correspond to typical values for the corresponding pairs linked by a double oxygen bridge. Mean values for similar enviroments searched for in the CCDC database are: Cu ··· Ba, 3.54(12) Å for 20 pairs in 6 structures; Ba ··· Ba, 4.06(27) Å for 193 pairs in 42 structures.

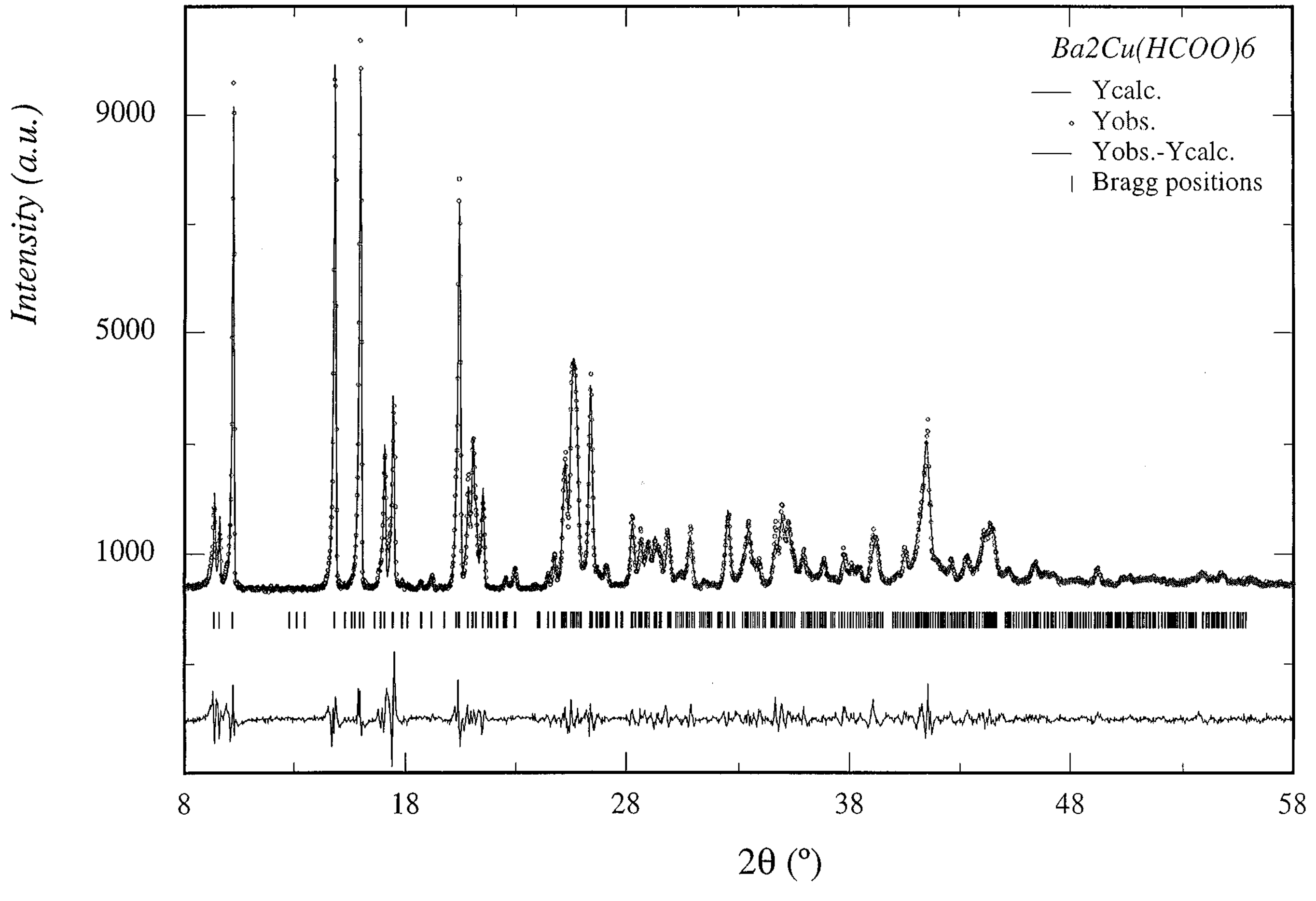

FIG. 3. Rietveld refinement in which $R_p = 10.6$ and $R_{wp} = 13.8$.

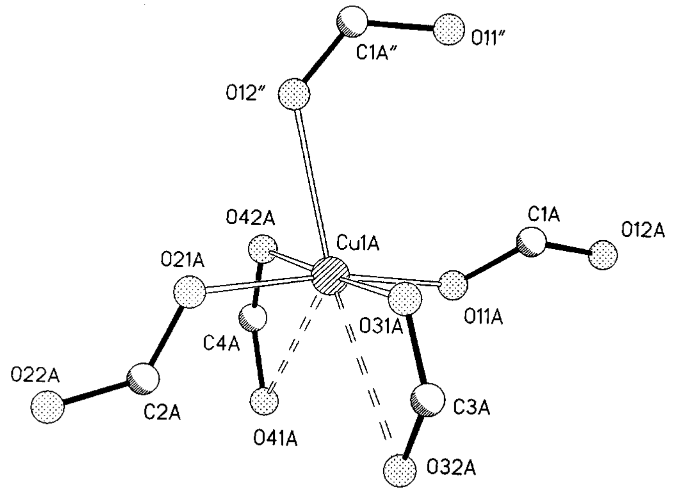

FIG. 4. Sevenfold coordination for the copper atoms in $Ba_2Cu(HCOO)_6$.

DISCUSSION

The thermal behavior of CUBA is a fairly complex one, involving phase transitions and partial decomposition, leading to the formation of a new barium formate phase (γ phase) metastable at room temperature, before the final decomposition takes place yielding $BaCO_3$, Cu_2O, and C as final decomposition products. There is also a reversible, highly hysteretic first-order phase transition at about 40–90°C, which we believe is related to the rearrangement of ions without breaking any nearest-neighbor bonds.

The copper formate structural units usually present a much lower stability compared to their alkaline-earth homologues, and this is reflected in the lower temperature at which they break up. In related mixed formates this is achieved leaving behind either a defective, ill-crystallized material ($Ca_2Cu(HCOO)_6$ (9)) or inducing the collapse of the whole structure ($SrCu(HCOO)_4$ (6)). In CUBA, however, and probably because the copper-formate structural units are arranged in tunnels and connected in pairs through a bridging formic acid ion, the barium formate layers are able to rearrange themselves so as to give a well-crystallized new barium formate phase which, after some days, transforms into the α form, which is stable at room temperature.

Continuous heating of the intermediate high temperature β and γ barium formate phases, which coexist in the quenched samples, ends up in the decomposition of the sample, to give barium carbonate, carbon particles, CO_2, and H_2O, in good agreement with previous results obtained on studying the isothermal behavior of the compound at 240 and 360°C (13, 21).

With reference to the thermal behavior of pure $Ba(HCOO)_2$, we observed from X-ray diffraction analysis of quenched samples the β–α phase transition already detected by Baraldi (15) using IR spectroscopy.

As a future line of research, we are planning a thorough study of the γ–α and γ–β $Ba(HCOO)_2$ phase transitions.

CONCLUSIONS

Two structural results are worth noting, the unusual (sevenfold) coordination displayed by the copper atoms and

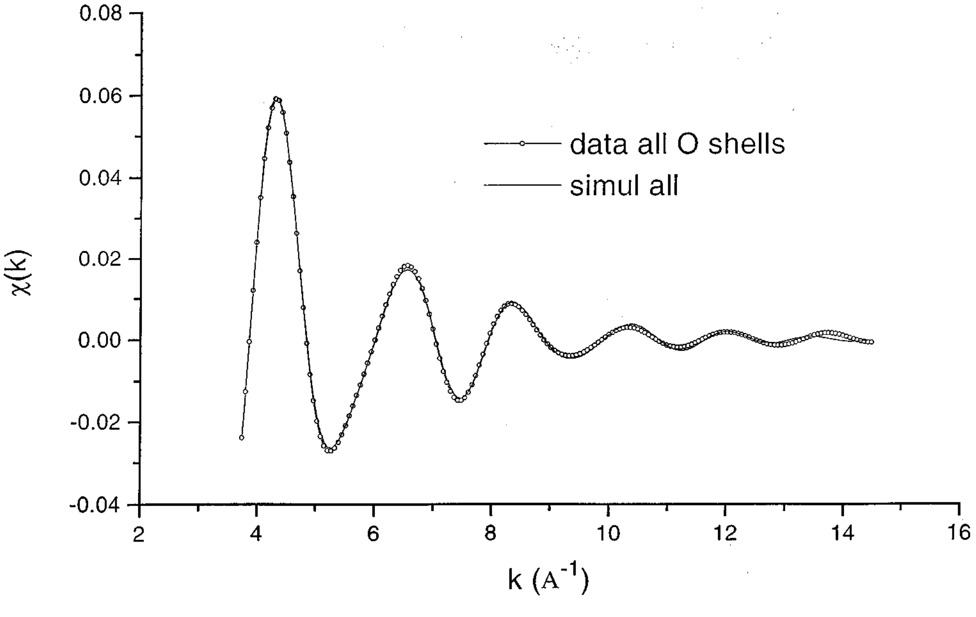

FIG. 5. Comparison between EXAFS experimental data and simulation taking into account four coordination shells.

the corrugated sheets made up of barium formate ions, which include in their channels pairs of copper–oxygen units bridged by a formate ion. Both features are quite characteristic of CUBA and are found neither in the mono- (or di-) calcium copper formates nor in the mono-strontium copper formate.

It is suggested that the structural corrugated barium formate sheets in CUBA provide unique nucleation sites for the growth of a new high temperature $Ba(HCOO)_2$ phase, which we have called γ-$Ba(HCOO)_2$ and which we could not obtain by heating the stable, low temperature α-phase.

Regarding the thermal behavior, a first-order phase transition was detected. Besides, the appearence of anhydrous barium formate before final decomposition differentiates CUBA from its dicalcium homologues. These different behaviors can be attributed to the very different crystal structures of both mixed carboxylates.

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