Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Musher, J. I. (1969). *Angew. Chem. Int. Ed. Engl.* **8**, 54–68; *Angew. Chem.* **81**, 68–83.

Paul, I. C., Martin, J. C. & Perozzi, E. F. (1972). *J. Am. Chem. Soc.* **94**, 5010–5017.

Pauling, L. (1960). *The Nature of The Chemical Bond*, 3rd ed. Cornell Univ. Press: Ithaca.

Perkins, C. W., Martin, J. C., Arduengo, A. J., Lau, W., Alegria, A. & Kochi, J. K. (1980). *J. Am. Chem. Soc.* **102**, 7753–7759.

Sakurai, T. & Kobayashi, K. (1979). *Rikagaku Kenkyusho Hokoku*, **55**, 69–74.

Sheldrick, G. M. (1986). *SHELXS86. Programs for the Solution of Crystal Structures.* Univ. of Göttingen, Germany.

Acta Cryst. (1994). **B50**, 157–160

Structure and Preliminary Electron Distribution of Copper Heptanoate from Room-Temperature X-ray Data

By Nour-Eddine Ghermani, Claude Lecomte*

Laboratoire de Minéralogie-Cristallographie et Physique Infrarouge, URA CNRS 809,
Université de Nancy I, *Faculté des Sciences, BP* 239, 54506 *Vandoeuvre-lès-Nancy CEDEX, France*

and Christophe Rapin, Pierre Steinmetz, Jean Steinmetz, Bernard Malaman

Laboratoire de Chimie Minérale, URA CNRS 158, *Université de Nancy* I, *Faculté des Sciences, BP* 239,
54506 *Vandoeuvre-lès-Nancy CEDEX, France*

(*Received* 3 *March* 1993; *accepted* 27 *September* 1993)

Abstract

Tetrakis(μ-heptanoato-κO:$\kappa O'$)dicopper [$Cu_2(C_7H_{13}O_2)_4$], $M_r = 643.4$, triclinic, $P\bar{1}$, $a = 5.170$ (1), $b = 8.518$, $c = 19.217$ (2) Å, $\alpha = 86.65$ (1), $\beta = 83.60$ (1), $\gamma = 75.46$ (1)°, $V = 813.78$ Å^3. The unit cell contains one dicopper dimer ($Z = 1$), $D_x = 1.314$ g cm^{-3}, $\mu = 1.350$ mm^{-1} for Mo $K\alpha$ radiation ($\lambda = 0.70928$ Å), $R(F) = 0.038$ for 4861 reflections. The copper–copper distance in the dimer is 2.578 Å and each copper is surrounded by five O atoms and one Cu atom in a pseudo-octahedral coordination polyhedron. The copper–copper distance between two dimers is 3.232 Å. The hydrocarbon chains are approximately along the c axis, explaining the high value of this parameter. A comparison is made with similar structures of copper alkanoates. Preliminary results of a charge-density study are also given.

Introduction

The crystal structure of copper heptanoate is of interest because thin coatings of this compound preserve copper metal or copper alloys from atmospheric corrosion (Rapin, Steinmetz, Steinmetz & Malaman, 1992). Crystal structures of similar compounds have been obtained: anhydrous copper butyrate, $Cu[CH_3(CH_2)_2COO]_2$ (Bird & Lomer, 1972), anhydrous copper(II) decanoate, $Cu[CH_3\text{-}(CH_2)_8COO]_2$, and copper octanoate, $Cu[CH_3\text{-}(CH_2)_6COO]_2$ (Lomer & Perera, 1974*a*,*b*). These authors reported the same space group ($P\bar{1}$), same stacking and same copper environment but the precision of the structural parameters was very low. Thus, we report the accurate crystal structure of copper heptanoate.

Experimental

The samples used in this study were obtained by the reaction of copper sulfate, $CuSO_4.5H_2O$, on sodium heptanoate. The blue–green precipitate obtained was filtered and washed with water to eliminate the excess sodium sulfate, then dried in vacuum. The crystallization was performed in xylene solution heated to 323 K. The crystals appeared after about 2 months of slow cooling from 323 K to room temperature.

These blue crystals have platelet or needle aggregate shapes which can be separated in xylene under the microscope. They are very brittle and show easy cleavage. The single crystal used for the X-ray investigation was a very thin platelet with the dimensions 0.57 × 0.28 × 0.03 mm. The X-ray diffraction experiment was carried out on an Enraf–Nonius CAD-4 four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.70928$ Å)

---

* Author to whom correspondence should be addressed.

Table 1. *Positional parameters with e.s.d.'s in parentheses*

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter, defined as:

$$(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	x	y	z	B (Å^2)
Cu	0.23550 (3)	0.48259 (2)	0.46665 (1)	2.195 (4)
C(1)	0.3274 (2)	0.5429 (1)	0.55846 (5)	2.60 (2)
O(2)	0.1222 (2)	0.7102 (1)	0.43791 (6)	3.12 (2)
O(3)	0.0808 (2)	0.4281 (1)	0.38567 (6)	3.30 (3)
O(4)	0.2825 (2)	0.2610 (1)	0.50283 (6)	3.17 (3)
C(1)	−0.1123 (3)	0.7908 (2)	0.45639 (8)	2.74 (3)
C(2)	−0.2051 (3)	0.9608 (2)	0.4262 (1)	3.27 (4)
C(3)	0.1616 (3)	0.5727 (2)	0.61259 (8)	2.41 (3)
C(4)	0.0644 (4)	0.6382 (3)	0.7412 (1)	4.09 (4)
C(5)	−0.4264 (3)	0.9681 (2)	0.3785 (1)	3.59 (4)
C(6)	0.2648 (3)	0.6107 (2)	0.67769 (9)	3.67 (4)
C(7)	−0.3249 (4)	0.8866 (3)	0.3097 (1)	4.37 (5)
C(8)	−0.5454 (4)	0.8770 (3)	0.2661 (1)	5.13 (5)
C(9)	0.1778 (5)	0.6812 (3)	0.8052 (1)	5.36 (6)
C(10)	−0.4494 (5)	0.8115 (3)	0.1944 (1)	6.73 (7)
C(11)	0.0215 (6)	0.7005 (4)	0.8698 (1)	7.68 (8)
C(12)	−0.6692 (7)	0.7831 (5)	0.1548 (2)	9.6 (1)
C(13)	0.0848 (8)	0.7478 (5)	0.9336 (1)	10.1 (1)
C(14)	−0.124 (1)	0.7740 (7)	0.9961 (2)	15.7 (2)

and ω–2θ scans [scan width $= (1.0 + 0.35\tan\theta)^\circ$] at room temperature. The unit-cell dimensions were refined with 25 reflections ($5 \leq \theta \leq 12^\circ$). Four standard reflections (022, 227, $0\bar{3}1$, $\bar{1}15$) were measured every 2 h and no significant decay was noted. The reflection profiles of 9586 *hkl* and $\overline{hkl}$ reflections were collected, $-9 \leq h \leq 9$, $-15 \leq k \leq 15$ and $0 \leq l \leq 34$, up to a resolution of $(\sin\theta/\lambda)_{\max} = 0.9$ Å^{-1}. To check the absorption correction, 1700 supplementary equivalent reflections with ψ ranging from 0 to 360° ($\Delta\psi = 10°$) were measured to account for the real optical path of the X-ray in the crystal for the same *hkl* reflection. The Nonius programs *MICROS* and *MICROR* were used to determine the indexation of the crystal faces [(010), $(0\bar{1}0)$, (001), $(00\bar{1})$]; the small faces were approximated by (623) and $(\bar{1}\bar{1},\bar{7},\bar{3})$, and the largest faces of the crystal are (001) and $(00\bar{1})$.

Structure determination and refinement

Profile analysis, Lorentz–polarization correction, scaling and averaging of the observed intensities were performed using the *DREAR* programs (Blessing, 1992), giving an internal agreement R factor of 0.0204 for 4861 unique reflections with $I > 3\sigma(I)$ without an absorption correction. Careful absorption corrections were then made on the data using *ABSORB* (DeTitta, 1985); sorting and averaging the data led to a better internal factor ($R = 0.0172$). The greatest absorption factor A is 0.717, which corresponds to a maximum intensity loss of 40% for the (001) reflections. The centrosymmetrical $P\bar{1}$ structure of the copper heptanoate was determined by direct methods using *MULTAN*82 (Main *et al.*, 1982). The structure refinement was carried out with *MOLLY* (Hansen & Coppens, 1978) using the atomic scattering factors for Cu, C, O and H from *International Tables for X-ray Crystallography* (1974, Vol. IV). Each reflection intensity was weighted by $w = 1/\sigma^2(|F|)$, where $\sigma(|F|)$ is the structure-factor standard deviation based on the statistical countings and instability factor p ($p = 0.01422$), $\sigma^2(|F|^2) = \sigma^2_{\rm count} + (p|F|^2)^2$. The H atoms were positioned by difference density Fourier maps. The hydrogen thermal factors were kept at 1.3 times the corresponding atom's thermal factor and refined during the last cycles. The final R factors for the structure determination were $R = 0.0378$ and $wR = 0.0326$, with a goodness-of-fit $G = 1.80$. Table 1 gives the atomic coordinates and equivalent temperature factors for the copper heptanoate molecule. Anisotropic thermal parameters, hydrogen coordinates and B values are given as supplementary material.*

Discussion

Molecular geometry

$Cu[CH_3(CH_2)_5COO]_2$ is a dimer in the solid state. Fig. 1 displays the *ORTEP* (Johnson, 1965) view of a dimer of copper heptanoate. Table 2 gives the interatomic distances and angles. Each Cu atom is coordinated to five O atoms and to the other Cu of the dimer, Cu′ ($-x$, $1-y$, $1-z$). The resulting coordination polyhedron is a distorted octahedron (Fig. 2), whose square base is formed by one O atom of each heptanoate anion of the dimer ($\langle$Cu—O$\rangle$ = 1.962 Å). The two other coordination sites are filled by Cu′ and O(1″) ($1-x$, $1-y$, $1-z$), with Cu—Cu′ = 2.578, Cu—O(1″) = 2.216 Å. The average O(1″)—Cu—O and O′—Cu—Cu′ angles are 95 and 85°, respectively. The O(1), O(3), C(3)... hydrocarbon chain is almost planar, runs perpendicular to both Cu, Cu′, O(2) and O(1), O(2), O(3), O(4) planes and is extended, making an angle of 15° with the c axis. The beginning of the other hydrocarbon chain [O(2), O(4), C(1), C(2)] belongs to the Cu, Cu′, O(2) plane and the other C atoms are rotated around the C(1)—C(2) axis to become parallel to the first hydrocarbon residue. The mean C—C distance for the chains is 1.51 Å and the mean C—C—C angle is 113.1°, except for C(1)—C(2)—C(5) which is 110.0° due to the chain bending (Fig. 1).

Stacking and arrangement of the molecules

The molecules are arranged as infinite zigzag lines (Cu—Cu′—Cu″) of Cu atoms; the Cu—Cu″ dis-

---

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71531 (34 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA0287]

tance for two neighbouring dimers is 3.232 Å, as shown in Fig. 3. The hydrocarbon chains lie on parallel planes slightly inclined with respect to the **ac** unit-cell plane. As reported by Bird & Lomer (1972), the distortion of the C(1), C(2)... chain reduces the molecular volume and then facilitates the packing in the crystal (see Fig. 4). In all the reported copper alkanoate structures, the hydrocarbon chains are also approximately in the *c*-axis direction. A comparison of the cell constants and packing shows that the parameters *a* and *b* are almost constant and *c* increases with respect to the number (*n*) of C atoms in the chain: if n_i and n_j are these numbers for two copper carboxylate structures *i* and *j*, the c_j parameter of the molecule *j* may be estimated as $c_j = c_i(n_j/n_i)$, as shown in Table 3; the first part of this table gives the cell parameters as a function of n_j and the second part estimates c_j from c_i using the formula above. The agreement between experimental and estimated *c* values is good when *n* is greater than 6.

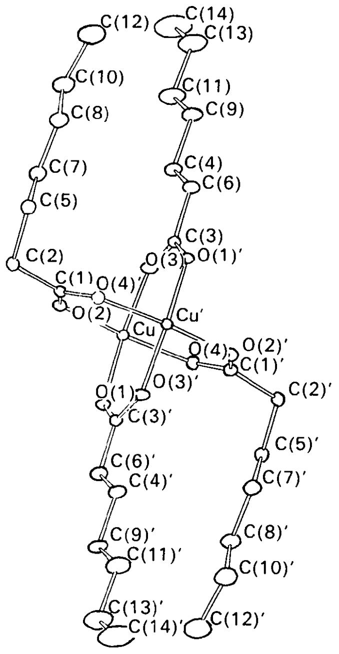

Fig. 1. *ORTEP* (Johnson, 1965) view of a dimer of copper heptanoate.

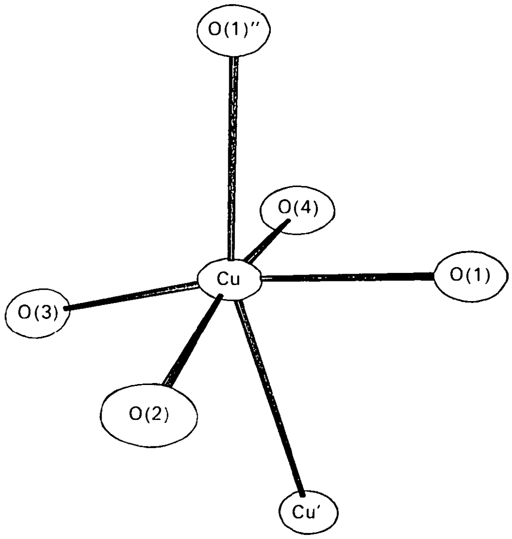

Fig. 2. Coordination polyhedron of a Cu atom.

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Cu···Cu′	2.5782 (2)	C(3)—C(6)	1.496 (2)
Cu—O(1)	2.005 (1)	C(4)—C(6)	1.500 (2)
Cu···O(1)″	2.2156 (9)	C(4)—C(9)	1.520 (3)
Cu—O(2)	1.946 (1)	C(4)···C(11)	2.525 (3)
Cu—O(3)	1.956 (1)	C(5)—C(7)	1.508 (3)
Cu—O(4)	1.939 (1)	C(5)···C(8)	2.526 (3)
O(1)···O(3)	2.221 (1)	C(6)···C(9)	2.521 (3)
O(1)···C(6)	2.363 (2)	C(7)—C(8)	1.509 (3)
O(2)···O(4)	2.231 (1)	C(7)···C(10)	2.534 (4)
O(2)···C(2)	2.384 (2)	C(8)—C(10)	1.500 (3)
O(3)···C(6)	2.369 (2)	C(8)···C(12)	2.527 (4)
O(4)···C(2)	2.355 (2)	C(9)—C(11)	1.512 (3)
C(1)—C(2)	1.510 (2)	C(9)···C(13)	2.530 (3)
C(1)···C(5)	2.491 (2)	C(10)—C(12)	1.511 (5)
C(2)—C(5)	1.531 (3)	C(11)—C(13)	1.511 (5)
C(2)···C(7)	2.542 (3)	C(11)···C(14)	2.507 (4)
C(3)···C(4)	2.533 (2)	C(13)—C(14)	1.510 (5)
O(2)—C(1)—O(4)′	124.9 (1)	C(2)—C(5)—C(7)	113.5 (1)
O(2)—C(1)—C(2)	118.7 (1)	C(3)—C(6)—C(4)	115.5 (2)
O(4)—C(1)—C(2)′	116.3 (1)	C(5)—C(7)—C(8)	113.7 (2)
C(1)—C(2)—C(5)	110.0 (1)	C(7)—C(8)—C(10)	114.7 (2)
O(1)—C(3)′—O(3)′	123.7 (1)	C(4)—C(9)—C(11)	112.8 (2)
C(1)—C(3)′—C(6)′	117.4 (1)	C(8)—C(10)—C(12)	114.1 (2)
O(3)—C(3)—C(6)	118.9 (1)	C(9)—C(11)—C(13)	113.7 (3)
C(6)—C(4)—C(9)	113.2 (2)	C(11)—C(13)—C(14)	112.2 (4)

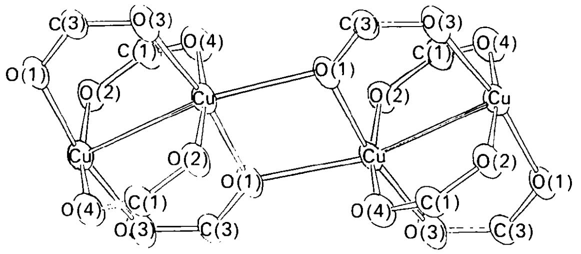

Fig. 3. Zigzag line of Cu atoms in the crystal structure.

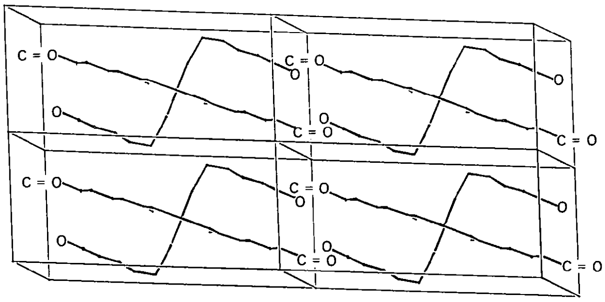

Fig. 4. Packing of copper heptanoate in the crystal.

Table 3. *Comparison of the cell parameters of similar structures and estimated c parameters*

(*a*) Similar structures

	$n = 4$(i)	7(ii)	8(iii)	10(iv)
a	9.00	8.51	8.80	7.94
b	5.16	5.17	5.20	5.28
c	11.74	19.22	22.06	28.13
α	94.70	96.40	95.10	94.60
β	95.20	93.40	92.40	97.10
γ	109.5	104.5	110.5	98.60

(*b*) Estimated *c* parameters

	$n_i = 4$	7	8	10
n_i				
4	—	20.55	23.48	29.35
7	10.98	—	21.96	27.46
8	11.03	19.30	—	27.58
10	11.25	19.69	22.50	—
c_i (exp)	11.74	19.22	22.06	28.13

References: (i) Bird & Lomer (1972), (ii) this study, (iii) Lomer & Perera (1974*a*), (iv) Lomer and Perera (1974*b*).

Preliminary results of electron-density study

Since the structure is centrosymmetric and the statistical indices are excellent in this medium resolution refinement [$R = 0.0378$, $wR = 0.0326$, $G = 1.80$ and $(\sin\theta/\lambda)_{\max} = 0.9$ Å^{-1}], we have been able to start a preliminary study of charge density from these room-temperature diffraction data. *MOLLY* (Hansen & Coppens, 1978) was used to calculate the charges of the atoms and the multipolar parameters of the copper metal in the following manner

$$\rho(\mathbf{r}) = \left[\sum_{j}^{\text{all atoms}} \rho_{j_c}(r) + P_{j\,\text{val}}\kappa_j'^3\rho_{j\,\text{val}}(\kappa' r)\right] + \left[\sum_{l}\kappa''^3 R_{nl}(\kappa'' r)\sum_{m} P_{lm\,\text{Cu}} Y_{lm}(\theta,\varphi)\right],$$

where ρ_c and ρ_{val} are spherically averaged core and valence densities, P_{val} is the valence population of the atoms and P_{lm} the multipole population of spherical harmonic functions Y_{lm} of the Cu atom. R_{nl} is a Slater-type radial function and κ' and κ'' are the contraction–expansion parameters. Each type of atom (Cu, C, O or H) was presumed to have the same net charge to reduce the number of parameters in the refinement. After the κ refinement, $R = 0.0375$, $wR = 0.0317$ and $g = 1.75$. The net charges of Cu, O, C and H are +1.04 (2), −0.405 (1), 0.060 (1) and 0.010 (1) e, respectively. We note that the pseudo-octahedron of five O atoms and one Cu atom around the Cu atom is almost neutral. Furthermore, the coordination of the copper suggests refinement of the population of the copper multipole also, respecting its pseudo-fourfold symmetry, *i.e.* the cubic hexadecapoles ($R = 0.0370$, $wR = 0.0310$ and $G = 1.74$). Fig. 5 shows the static density obtained around the Cu atom in the four O-atom plane. This map looks reasonable from a crystal field point of view, the $d_{x^2-y^2}$ orbitals are depopulated while the deformation density appears on the d_{xy} orbital. This result is promising and a low-temperature X-ray diffraction experiment is in progress.

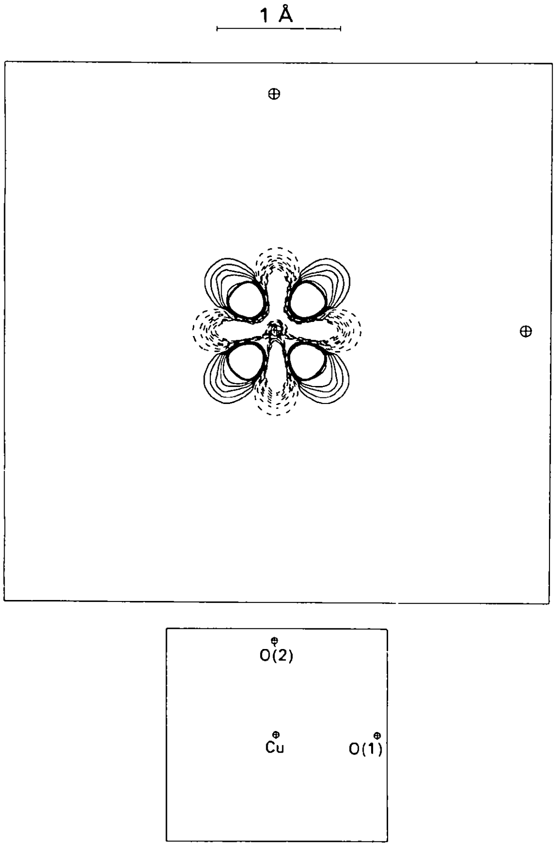

Fig. 5. Static deformation density of the Cu atom in the four O-atom plane (contours are 0.1 e Å^{-3}, negative contours are dashed).

The financial support of the CNRS and the University of Nancy I is gratefully acknowledged.

References

Bird, M. J. & Lomer, T. R. (1972). *Acta Cryst.* **B28**, 242–246.
Blessing, R. H. (1992). *J. Am. Chem. Soc.* **114**, 2371–2382.
DeTitta, G. (1985). *J. Appl. Cryst.* **18**, 75–79.
Hansen, N. K. & Coppens, P. (1978). *Acta Cryst.* **A34**, 909–921.
Lomer, T. R. & Perera, K. (1974*a*). *Acta Cryst.* **B30**, 2912–2913.
Lomer, T. R. & Perera, K. (1974*b*). *Acta Cryst.* **B30**, 2913–2915.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
Rapin, C., Steinmetz, P., Steinmetz, J. & Malaman, B. (1992). *Int. Conf. Adv. Corros. Protect.* 28 June–3 July, Manchester, England.