*Acta Cryst.* (1972). B**28**, 242

# The Crystal and Molecular Structure of Anhydrous Copper Butyrate

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(*Received* 11 *March* 1971)

Anhydrous copper butyrate, $[CH_3(CH_2)_2COO]_2Cu$, is triclinic with $a=9{\cdot}004\pm0{\cdot}005$, $b=11{\cdot}736\pm0{\cdot}005$, $c=5{\cdot}162\pm0{\cdot}005$ Å, $\alpha=94{\cdot}7\pm0{\cdot}5$, $\beta=71{\cdot}3\pm0{\cdot}5$, and $\gamma=95{\cdot}2\pm0{\cdot}5°$. The space group is $P\bar{1}$ with each cell containing one dimer made up of two of the above formula units. Two of the hydrocarbon chains in each dimer are in the usual plane zigzag conformation but the other two are markedly deformed by rotations about single bonds. The small distance between copper atoms in a dimer is 2·565 Å which is similar to that in copper acetate monohydrate.

## Introduction

Divalent-metal salts of the higher fatty acids are often referred to as 'metal soaps' by analogy with the better known 'alkali' soaps which are the sodium and potassium salts of these acids. Many of the metal soaps have applications in industry: calcium soaps are used in the preparation of lubricating greases, aluminum soaps are used as waterproofing agents while iron and chromium soaps are used in colour printing and in dyeing. However, little is known of their crystal structures, although Iball (1947) has determined the unit cell and space group of copper butyrate monohydrate.

Copper butyrate, $[CH_3(CH_2)_2COO]_2Cu$, is a member of the homologous series, the copper alkanoates, which starts with copper formate, $(H.COO)_2Cu$, and copper acetate, $(CH_3.COO)_2Cu$, and includes the metal soaps copper palmitate, $[CH_3(CH_2)_{14}COO]_2Cu$, and copper stearate, $[CH_3(CH_2)_{16}COO]_2Cu$. A study of its crystal structure could thus indicate the possible structures of the higher soaps which are much more difficult to prepare in single-crystal form.

The magnetic properties of the copper alkanoates are interesting. The first compound to excite interest was copper acetate monohydrate. Lifschitz & Rosenbohm (1915) found that its molar susceptibility was anomalously low compared with that of other copper salts. Guha (1951) and Figgis & Martin (1956) have reported the temperature variation of susceptibility for copper acetate, both hydrated and anhydrous, and Martin & Waterman (1957) reported similar measurements for various higher members of the series. All these compounds show a paramagnetic susceptibility which has a maximum at about 270 °K and which falls steeply with decreasing temperature. Bleaney & Bowers (1952) suggested that these susceptibility results, together with their own paramagnetic resonance results, could be explained by a crystal structure containing isolated pairs of copper atoms which interacted through exchange forces, and had a singlet state lying only slightly lower in energy than a triplet state. At low temperatures the singlet state would thus be populated at the expense of the triplet state and the paramagnetic susceptibility would be low.

The crystal structure of copper acetate monohydrate was determined by van Niekerk & Schoening (1953) who found that the structure did indeed contain pairs of closely linked copper atoms and that the crystal was built up from dimers with the conformation shown diagramatically in Fig. 1. More recently Ablov, Simenov & Malinovskii (1967) have made a study of the crystal structures of anhydrous copper propionate, $\{Cu[CH_3(CH_2)COO]_2\}$, and anhydrous copper butyrate and have established the existence of similar dimers in these structures. They have not however reported the arrangement of the hydrocarbon chains in these structures.

## Experimental

Anhydrous copper butyrate was prepared by adding anhydrous copper carbonate in excess to an alcoholic solution of butyric acid. The reactants were agitated vigorously for some 15 minutes to ensure a maximum contact between the reactants. Carbon dioxide, copper butyrate and water were formed in the reaction which was judged to be completed when effervescence had ceased. The remaining excess of copper carbonate was removed by filtration leaving an alcoholic solution of copper butyrate. The filtered solution of the soap was allowed to evaporate slowly at room temperature and pressure. After about a week, crystals of anhydrous copper butyrate began to form.

When viewed between the crossed polars of a polarizing microscope the crystals appeared as birefringent, bright green oblong platelets. They were thin (~0·1 mm) and were very fragile showing a marked tendency to cleave into needle shapes along directions parallel to the long edges of the platelet. The plane of the platelet was subsequently found to be parallel to the (010) plane. The single crystals used for X-ray examination were platelets with the approximate dimensions 0·35 × 0·20 × 0·15 mm: zero layer Weissenberg photographs were taken with the crystal rotating about each of the three direct cell axes. The unit cell was found to be triclinic with $a=9{\cdot}004\pm0{\cdot}005$, $b=11{\cdot}736\pm0{\cdot}005$, $c=5{\cdot}162\pm0{\cdot}005$ Å, $\alpha=94{\cdot}7\pm0{\cdot}5$, $\beta=71{\cdot}3\pm0{\cdot}5$, $\gamma=95{\cdot}2\pm0{\cdot}5°$. Assuming two formula units per unit cell the calculated density was $1{\cdot}536\pm0{\cdot}005$ g.cm$^{-3}$, which agreed well with the value of $1{\cdot}52\pm0{\cdot}02$ g.cm$^{-3}$ observed by a flotation method using mixtures of carbon tetrachloride and liquid paraffin.

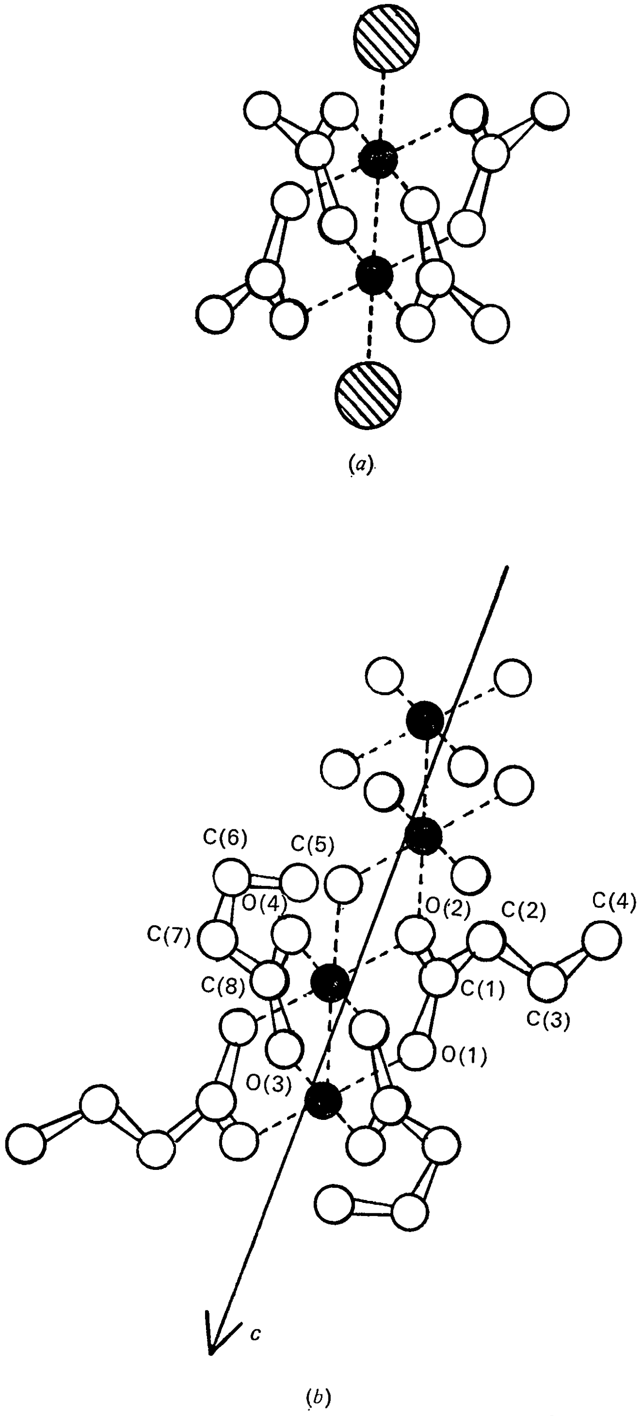

Fig. 1. Perspective diagrams of the arrangement of copper (full circles), carbon and oxygen atoms (open circles) and water molecules (hatched circles) in (*a*) a dimer of copper acetate monohydrate and (*b*) a dimer of anhydrous copper butyrate together with copper and oxygen atoms from a neighbouring dimer in the crystal structure.

The majority of the intensities were determined photometrically from integrated Weissenberg photographs about the *b* and *c* axes. Those that were too weak to be measured in this way were determined visually using the standard multiple film technique. In all, the intensities of 832 independent reflexions were determined. Lorentz, polarization and Tunell factors were corrected for by a computer program written by one of us (MJB) and absorption corrections were made by use of the *ABSCOR* program which is part of the *X-ray* 63 library of programs at the ATLAS laboratory, Chilton.

All the data were brought to a common scale by comparing the values of $|F_o|^2$ of reflexions which were observed in exposures about both the *b* and *c* axes.

### Determination of the structure

The structure was assumed to be centrosymmetrical: two-dimensional Patterson syntheses about the *a*, *b* and *c* axes allowed the copper atom positions to be fixed, and, assuming the copper and oxygen atom arrangement to be similar to that in copper acetate monohydrate, the oxygen atom positions could also be fixed from the two-dimensional Patterson syntheses. The Patterson syntheses also showed ridges of high density which could be interpreted as due to copper–carbon vectors for one of the two hydrocarbon chains in the asymmetric unit. These positions together with plausible positions for the carbon atoms of the other hydrocarbon chain were used to compute phases for use in the preparation of electron density projections along the *a* and *c* axes, from which improved coordinates for all the atoms were obtained.

These coordinates were refined initially for low-angle data ($h+k+l\leq6$), using equal weights and with a single scale factor and with a single overall isotropic temperature factor. The *R* value was reduced in 4 cycles from 0·41 to 0·17 and then increased to 0·19 when all the reflexion data were included.

The hydrogen atoms were then included in the structure factor calculations by assuming them to be arranged so that the coordination round each carbon atom was tetrahedral, and so that C–H bond lengths were 1·08 Å, and to have the same temperature factors as the carbon atoms to which they were bonded. After further cycles of refinement *R* was reduced to 0·16. In the next few cycles anisotropic temperature factors for the copper, oxygen and carbon atoms were refined together with their positional parameters and a single scale factor. Lists of observed and calculated structure factors were inspected for systematic variations of scale as functions of $(\sin\theta)/\lambda$ and of $|F|$ and for errors in the interlayer scaling. No systematic variations of scale of the types mentioned were observed but small corrections were required to the inter-layer scale factors. The largest of these was only about 6%. With the rescaled data a further three cycles of refinement of all the parameters except those of the hydrogen atoms decreased $R$ to its final value of 0·092. The parameters of the heavy atoms resulting from this last refinement are given in Table 1 together with their standard deviations, and the observed and calculated structure factors are given in Table 2.

Table 1. *Atom parameters: coordinates as fractions of the unit cell* ($\times 10^4$); *vibration components in* Å$^2$ ($\times 10^3$)

The standard deviations, given in brackets, are in units corresponding to the least significant digit in the parameters.

| | $x/a$ | $y/b$ | $z/c$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Cu | 227 (2) | − 534 (2) | −2347 (4) | 48 (1) | 39 (1) | 26 (1) | 9 (1) | −11 (1) | 7 (1) |
| O(1) | 451 (11) | − 981 (9) | 3239 (21) | 46 (6) | 24 (6) | 30 (5) | 22 (5) | −11 (5) | 2 (6) |
| O(2) | 794 (13) | −1833 (9) | 740 (19) | 72 (7) | 15 (5) | 25 (5) | 24 (6) | −24 (5) | − 3 (6) |
| O(3) | 1955 (12) | 1134 (9) | 858 (20) | 52 (6) | 41 (6) | 25 (5) | − 2 (6) | − 9 (5) | 8 (6) |
| O(4) | 2343 (11) | 173 (10) | −3164 (20) | 26 (5) | 53 (7) | 29 (5) | 5 (5) | 2 (4) | 3 (6) |
| C(1) | 852 (15) | −1800 (14) | 1660 (26) | 30 (6) | 27 (8) | 20 (6) | 10 (7) | − 1 (5) | −20 (9) |
| C(2) | 1373 (24) | −2792 (15) | 2656 (33) | 102 (15) | 30 (10) | 37 (9) | 27 (10) | −30 (10) | 14 (9) |
| C(3) | 1516 (36) | −3836 (17) | 976 (47) | 222 (31) | 23 (11) | 79 (16) | 50 (15) | −60 (19) | 10 (11) |
| C(4) | 2204 (32) | −4780 (19) | 2038 (48) | 134 (21) | 51 (14) | 81 (16) | 64 (15) | −17 (14) | − 4 (14) |
| C(5) | 4819 (24) | 1979 (20) | −5217 (38) | 77 (14) | 78 (15) | 40 (10) | −14 (12) | − 9 (9) | 33 (11) |
| C(6) | 3828 (31) | 3036 (20) | −4858 (53) | 124 (22) | 51 (14) | 101 (10) | 28 (15) | −26 (17) | 39 (14) |
| C(7) | 4436 (19) | 1381 (19) | −2460 (31) | 43 (9) | 87 (15) | 26 (8) | − 3 (10) | − 4 (7) | 25 (10) |
| C(8) | 2804 (18) | 825 (15) | −1525 (28) | 44 (8) | 44 (10) | 25 (7) | 11 (9) | −10 (7) | 14 (9) |

Table 2. *Calculated and observed structure factors*

Each ($hkl$) block is headed by its common $k$ and $l$ indices, and the three columns give the values of $h$, $10F_o$, and $10F_c$.

| h | 10Fo | 10Fc |
|---|---|---|
| (h,0,0) | | |
| 1 | 634 | 782 |
| 2 | 402 | 443 |
| 3 | 138 | 203 |
| 4 | 358 | 400 |
| 5 | 204 | 220 |
| 6 | 47 | 43 |
| (h,1,0) | | |
| 0 | 684 | 931 |
| 1 | 542 | 622 |
| 2 | 827 | 983 |
| 3 | 495 | 609 |
| 4 | 627 | 712 |
| 5 | 235 | 268 |
| 6 | 140 | 137 |
| (h,2,0) | | |
| 0 | 325 | 335 |
| 1 | 232 | 255 |
| 2 | 100 | 148 |
| 3 | 587 | 664 |
| 4 | 683 | 764 |
| 5 | 369 | 384 |
| 6 | 248 | 237 |
| 7 | 107 | 123 |
| 8 | 107 | 119 |
| 9 | 65 | 75 |
| (h,3,0) | | |
| 1 | 54 | 50 |
| 2 | 27 | 45 |
| 3 | 482 | 488 |
| 4 | 345 | 352 |
| 5 | 315 | 309 |
| 6 | 239 | 233 |
| 7 | 192 | 189 |
| 8 | 177 | 172 |
| 9 | 106 | 102 |
| (h,4,0) | | |
| 0 | 44 | -44 |
| 1 | 159 | -161 |
| 3 | 219 | 217 |
| 4 | 151 | 157 |
| 5 | 140 | 145 |
| 6 | 104 | 119 |
| 7 | 187 | 161 |
| 8 | 173 | 169 |
| 9 | 111 | 108 |
| (h,5,0) | | |
| 0 | 154 | -125 |
| 2 | 71 | 75 |
| 3 | 83 | 57 |
| 6 | 67 | 53 |
| 7 | 102 | 84 |
| 8 | 112 | 111 |
| 9 | 83 | 76 |
| (h,6,0) | | |
| 0 | 88 | -84 |
| 1 | 79 | -75 |
| (h,7,0) | | |
| 0 | 212 | -199 |
| 1 | 151 | -157 |
| 2 | 97 | -94 |
| 3 | 109 | -104 |
| 4 | 65 | -53 |
| (h,8,0) | | |
| 0 | 237 | -236 |
| 1 | 200 | -188 |
| 2 | 203 | -214 |
| 3 | 179 | -170 |
| 4 | 67 | -53 |
| (h,9,0) | | |
| 0 | 235 | -235 |
| 1 | 215 | -238 |
| 2 | 253 | -264 |
| 3 | 186 | -182 |
| (h,10,0) | | |
| 1 | 198 | -211 |
| 2 | 227 | -231 |
| 3 | 161 | -168 |
| 4 | 78 | -76 |
| (h,11,0) | | |
| 2 | 79 | -82 |
| 3 | 77 | -80 |
| 4 | 64 | -58 |
| (h,0,1) | | |
| 0 | 184 | 179 |
| 1 | 379 | 356 |
| 2 | 395 | -339 |
| 3 | 33 | -8 |
| 4 | 104 | 131 |
| 5 | 218 | 271 |
| 6 | 77 | 101 |
| 7 | 105 | 105 |
| 8 | 76 | 72 |
| 9 | 128 | 112 |
| 10 | 141 | 109 |
| 11 | 75 | 67 |
| (h,1,1) | | |
| 0 | 272 | 203 |
| 1 | 415 | 372 |
| 3 | 87 | 99 |
| 5 | 154 | 166 |
| 7 | 79 | 67 |
| (h,2,1) | | |
| 0 | 106 | -108 |
| 1 | 532 | -512 |
| 2 | 78 | 50 |
| 3 | 53 | 62 |
| 4 | 172 | 154 |
| 5 | 52 | 56 |
| (h,3,1) | | |
| 0 | 415 | -394 |
| 1 | 440 | -392 |
| 2 | 71 | -84 |
| 3 | 274 | -256 |
| 5 | 79 | -72 |
| 6 | 58 | 53 |
| (h,4,1) | | |
| 0 | 510 | -465 |
| 1 | 414 | -363 |
| 2 | 284 | -271 |
| 3 | 227 | -227 |
| 4 | 189 | -195 |
| 5 | 154 | -174 |
| (h,5,1) | | |
| 0 | 215 | -223 |
| 1 | 48 | -76 |
| 2 | 229 | -222 |
| 3 | 295 | -279 |
| 4 | 325 | -344 |
| 5 | 126 | -151 |
| (h,6,1) | | |
| 0 | 384 | -328 |
| 1 | 58 | -66 |
| 2 | 96 | -111 |
| 3 | 202 | -200 |
| 4 | 248 | -266 |
| 5 | 95 | -117 |
| 6 | 61 | -97 |
| (h,7,1) | | |
| 0 | 307 | -263 |
| 1 | 155 | -153 |
| 2 | 236 | -223 |
| 3 | 241 | -230 |
| 4 | 170 | -166 |
| (h,8,1) | | |
| 0 | 119 | -117 |
| 1 | 191 | -187 |
| 2 | 221 | -208 |
| 3 | 253 | -243 |
| 4 | 155 | -142 |
| (h,9,1) | | |
| 0 | 88 | -82 |
| 1 | 115 | -110 |
| 2 | 151 | -143 |
| 3 | 210 | -196 |
| 4 | 88 | -89 |
| 5(h,10,1) | | |
| 1 | 49 | -51 |
| 2 | 123 | -111 |
| 3 | 121 | -103 |
| (h,11,1) | | |
| 0 | 117 | 135 |
| 1 | 77 | 82 |
| 3 | 38 | -31 |
| (h,12,1) | | |
| 0 | 124 | 97 |
| 1 | 104 | 98 |
| 2 | 75 | 81 |
| (h,13,1) | | |
| 0 | 114 | 90 |
| 1 | 103 | 94 |
| 2 | 67 | 71 |
| (h,14,1) | | |
| 1 | 79 | 68 |
| 2 | 51 | 54 |
| (h,0,2) | | |
| 0 | 514 | -539 |
| 1 | 618 | -631 |
| 2 | 377 | -379 |
| 3 | 142 | -174 |
| 4 | 101 | -112 |
| 5 | 82 | -136 |
| 6 | 104 | -112 |
| 7 | 71 | -75 |
| (h,1,2) | | |
| 0 | 613 | -568 |
| 1 | 600 | -596 |
| 2 | 512 | -502 |
| 3 | 336 | -349 |
| 4 | 199 | -209 |
| 5 | 224 | -228 |
| 6 | 161 | -184 |
| 7 | 98 | -81 |
| (h,2,2) | | |
| 0 | 719 | -667 |
| 1 | 621 | -561 |
| 2 | 562 | -510 |
| 3 | 227 | -245 |
| 4 | 372 | -371 |
| 5 | 367 | -361 |
| 6 | 275 | -253 |
| 7 | 78 | -72 |
| 8 | 71 | 661 |
| 9 | 82 | -73 |
| (h,3,2) | | |
| 0 | 375 | -323 |
| 1 | 397 | -384 |
| 2 | 381 | -375 |
| 3 | 249 | -239 |
| 4 | 442 | -424 |
| 5 | 369 | -350 |
| 6 | 291 | -275 |
| 7 | 84 | -84 |
| 8 | 108 | -116 |
| 9 | 84 | -94 |
| (h,4,2) | | |
| 0 | 287 | -257 |
| 1 | 319 | -297 |
| 2 | 64 | -64 |
| 3 | 174 | -186 |
| 4 | 311 | -317 |
| 5 | 265 | -319 |
| 6 | 144 | -195 |
| (h,5,2) | | |
| 0 | 55 | 57 |
| 1 | 99 | -78 |
| 3 | 143 | -181 |
| 4 | 113 | -176 |
| 5 | 118 | -227 |
| (h,6,2) | | |
| 0 | 133 | 139 |
| 1 | 119 | 137 |
| 2 | 106 | 127 |
| 4 | 76 | -123 |
| 5 | 71 | -136 |
| (h,7,2) | | |
| 0 | 111 | 114 |
| 2 | 96 | 119 |
| 3 | 70 | 86 |
| (h,8,2) | | |
| 0 | 102 | 116 |
| 1 | 118 | 145 |
| 2 | 75 | 102 |
| 3 | 61 | 99 |
| (h,9,2) | | |
| 0 | 146 | 161 |
| 1 | 118 | 157 |
| 2 | 87 | 137 |
| 3 | 61 | 128 |
| (h,10,2) | | |
| 0 | 83 | 84 |
| 1 | 72 | 103 |
| 2 | 97 | 168 |
| 3 | 61 | 125 |
| (h,11,2) | | |
| 0 | 58 | 51 |
| 1 | 65 | 72 |
| (h,0,3) | | |
| 0 | 103 | -113 |
| 1 | 66 | -63 |
| 2 | 118 | -125 |
| 3 | 74 | -98 |
| 5 | 144 | -149 |
| 6 | 232 | -218 |
| 7 | 237 | -226 |
| 8 | 128 | -114 |
| 9 | 92 | -86 |
| 10 | 154 | -119 |
| 11 | 112 | -91 |
| (h,1,3) | | |
| 0 | 62 | -63 |
| 1 | 51 | -46 |
| 2 | 149 | -148 |
| 5 | 73 | -62 |
| 6 | 179 | -161 |
| 7 | 162 | -134 |
| 9 | 81 | -61 |
| 10 | 126 | -98 |
| (h,2,3) | | |
| 6 | 109 | -101 |
| 7 | 58 | -45 |
| 9 | 81 | -47 |
| 10 | 87 | -65 |
| (h,3,3) | | |
| 0 | 287 | 265 |
| 1 | 216 | 184 |
| 2 | 78 | 63 |
| 3 | 40 | 31 |
| 4 | 54 | 30 |
| 5 | 69 | -58 |
| 6 | 60 | -71 |
| 9 | 48 | -38 |
| (h,4,3) | | |
| 0 | 277 | 277 |
| 1 | 359 | 320 |
| 2 | 224 | 223 |
| 3 | 221 | 181 |
| 4 | 101 | 92 |
| (h,0,4) | | |
| 0 | 184 | 198 |
| 1 | 122 | 127 |
| 2 | 258 | 266 |
| 3 | 155 | 152 |
| 4 | 141 | 152 |
| 5 | 143 | 145 |
| 6 | 68 | 70 |
| (h,1,4) | | |
| 0 | 145 | 140 |
| 1 | 159 | 161 |
| 2 | 303 | 305 |
| 3 | 132 | 130 |
| 4 | 181 | 176 |
| 5 | 137 | 126 |
| 6 | 151 | 144 |
| (h,2,4) | | |
| 0 | 112 | 111 |
| 1 | 260 | 247 |
| 2 | 249 | 237 |
| 3 | 120 | 126 |
| 4 | 153 | 144 |
| 5 | 151 | 154 |
| 6 | 171 | 154 |
| 7 | 57 | 71 |
| 8 | 93 | 91 |
| 9 | 74 | 64 |
| (h,3,4) | | |
| 0 | 201 | 189 |
| 1 | 307 | 303 |
| 3 | 128 | 118 |
| 4 | 103 | 92 |
| 5 | 178 | 156 |
| 6 | 150 | 128 |
| 8 | 88 | 83 |
| 9 | 55 | 59 |
| (h,4,4) | | |
| 0 | 243 | 231 |
| 1 | 388 | 370 |
| 2 | 235 | 222 |
| 3 | 126 | 126 |
| 4 | 109 | 110 |
| 5 | 163 | 162 |
| (h,0,5) | | |
| 2 | 131 | 143 |
| 3 | 256 | 275 |
| 4 | 173 | 178 |
| 5 | 173 | 168 |
| 6 | 155 | 153 |
| 7 | 160 | 151 |
| 8 | 76 | 78 |
| 9 | 62 | 60 |
| (h,1,5) | | |
| 0 | 74 | -80 |
| 2 | 66 | 72 |
| 3 | 124 | 119 |
| 5 | 139 | 123 |
| 6 | 187 | 160 |
| 7 | 211 | 179 |
| 8 | 102 | 86 |
| 9 | 89 | 74 |
| (h,2,5) | | |
| 0 | 90 | -98 |
| 1 | 76 | -76 |
| 2 | 43 | 43 |
| 6 | 103 | 96 |
| 7 | 136 | 122 |
| 8 | 87 | 75 |
| 9 | 92 | 77 |
| (h,3,5) | | |
| 0 | 108 | -104 |
| 1 | 104 | -82 |
| 3 | 104 | -94 |
| 4 | 61 | -69 |
| 6 | 57 | 46 |
| (h,4,5) | | |
| 3 | 133 | -113 |
| (h,0,6) | | |
| 0 | 72 | -83 |
| 1 | 75 | -85 |
| 2 | 39 | -56 |
| (h,1,6) | | |
| 0 | 80 | -95 |
| 1 | 111 | 115 |
| 2 | 102 | -96 |
| 3 | 60 | -49 |
| 4 | 57 | -56 |
| 5 | 55 | -54 |
| (h,2,6) | | |
| 0 | 70 | -83 |
| 1 | 90 | -107 |
| 2 | 99 | -105 |
| 3 | 88 | -86 |
| 4 | 112 | -110 |
| 5 | 80 | -76 |
| 6 | 38 | -39 |
| (h,3,6) | | |
| 0 | 75 | -77 |
| 1 | 88 | -98 |
| 2 | 93 | -93 |
| 3 | 75 | -91 |
| 4 | 113 | -109 |
| 5 | 73 | -75 |
| 6 | 74 | 64 |
| (-h,1,0) | | |
| 1 | 455 | 523 |
| 2 | 54 | -17 |
| 3 | 101 | 120 |
| 4 | 151 | 156 |
| 5 | 141 | 133 |
| (-h,2,0) | | |
| 1 | 607 | 654 |
| 2 | 141 | -116 |
| 3 | 77 | -60 |
| 5 | 112 | 123 |
| 6 | 65 | -80 |
| 10 | 44 | -44 |
| (-h,3,0) | | |
| 1 | 257 | 260 |
| 2 | 65 | -65 |
| 4 | 77 | -85 |
| 6 | 97 | -94 |
| 7 | 63 | -65 |
| 9 | 82 | -77 |
| 10 | 75 | -78 |
| (-h,4,0) | | |
| 1 | 219 | 204 |
| 2 | 135 | -109 |
| 3 | 104 | -104 |
| 6 | 125 | -130 |
| 7 | 195 | -203 |
| 9 | 101 | -93 |
| (-h,5,0) | | |
| 1 | 79 | -67 |
| 3 | 265 | -239 |
| 5 | 261 | -254 |
| 6 | 217 | -227 |
| 7 | 245 | -230 |
| 8 | 106 | -99 |
| (-h,0,1) | | |
| 1 | 361 | 334 |
| 2 | 31 | 44 |
| 3 | 73 | -67 |
| 4 | 141 | -149 |
| 5 | 221 | -223 |
| 6 | 86 | -102 |
| 7 | 82 | -79 |
| 8 | 124 | -116 |
| 9 | 94 | -91 |
| 10 | 46 | -49 |
| (-h,1,1) | | |
| 1 | 411 | -398 |
| 2 | 151 | -167 |
| 3 | 226 | -233 |
| 4 | 234 | -254 |
| 7 | 56 | -49 |
| 8 | 91 | -91 |
| 10 | 51 | -53 |
| (-h,2,1) | | |
| 1 | 447 | -456 |
| 2 | 232 | -262 |
| 3 | 231 | -254 |
| 7 | 57 | -40 |
| 8 | 73 | -72 |
| (-h,3,1) | | |
| 1 | 514 | -517 |
| 2 | 316 | -325 |
| 3 | 89 | -113 |
| 7 | 46 | -41 |
| 8 | 62 | -57 |
| 9 | 86 | -90 |
| (-h,4,1) | | |
| 1 | 329 | -305 |
| (-h,5,1) | | |
| 3 | 71 | -113 |
| (-h,6,1) | | |
| 1 | 364 | -314 |
| 2 | 441 | -393 |
| 3 | 237 | -242 |
| (-h,7,1) | | |
| 1 | 379 | -356 |
| 2 | 249 | -257 |
| 3 | 221 | -212 |
| (-h,8,1) | | |
| 1 | 243 | -212 |
| 2 | 131 | -129 |
| 3 | 182 | -160 |
| (-h,9,1) | | |
| 1 | 164 | -123 |
| 2 | 86 | -81 |
| (-h,10,1) | | |
| 1 | 73 | 88 |
| 2 | 141 | 162 |
| 3 | 180 | 162 |
| (-h,11,1) | | |
| 1 | 113 | 117 |
| 2 | 115 | 118 |
| (-h,12,1) | | |
| 1 | 105 | 84 |
| 2 | 126 | 106 |
| (-h,13,1) | | |
| 1 | 81 | 65 |
| (-h,0,2) | | |
| 1 | 347 | -362 |
| 2 | 277 | -253 |
| 3 | 413 | -403 |
| 4 | 388 | -384 |
| 5 | 190 | -196 |
| 7 | 113 | -117 |
| 8 | 79 | -89 |
| 9 | 51 | -57 |
| (-h,1,2) | | |
| 1 | 402 | -385 |
| 2 | 313 | -304 |
| 3 | 355 | -341 |
| 4 | 291 | -299 |
| 5 | 201 | -203 |
| 7 | 54 | -55 |
| 8 | 52 | -55 |
| (-h,2,2) | | |
| 1 | 391 | -346 |
| 2 | 108 | -114 |
| 3 | 195 | -206 |
| 4 | 221 | -226 |
| 5 | 113 | -136 |
| 7 | 55 | 44 |
| (-h,3,2) | | |
| 1 | 322 | -298 |
| 2 | 116 | -105 |
| 3 | 32 | -40 |
| 4 | 50 | -49 |
| 6 | 54 | 57 |
| 7 | 84 | 88 |
| (-h,4,2) | | |
| 1 | 185 | -148 |
| 3 | 144 | 149 |
| (-h,5,2) | | |
| 1 | 129 | 105 |
| 2 | 129 | 136 |
| 3 | 110 | 126 |
| 4 | 149 | 151 |
| 5 | 102 | 116 |
| 6 | 104 | 97 |
| 7 | 110 | 101 |
| (-h,6,2) | | |
| 1 | 121 | 119 |
| 2 | 143 | 134 |
| 5 | 115 | 151 |
| (-h,7,2) | | |
| 1 | 201 | 201 |
| 2 | 155 | 127 |
| 3 | 114 | 165 |
| 5 | 113 | 165 |
| (-h,8,2) | | |
| 1 | 271 | 257 |
| 2 | 239 | 222 |
| (-h,9,2) | | |
| 1 | 189 | 189 |
| 2 | 189 | 171 |
| (-h,10,2) | | |
| 1 | 103 | 88 |
| 2 | 148 | 155 |
| (-h,0,3) | | |
| 5 | 109 | 124 |
| (-h,1,3) | | |
| 1 | 103 | 94 |
| 3 | 116 | 108 |
| 4 | 97 | 83 |
| 5 | 141 | 145 |
| 6 | 97 | 90 |
| 7 | 55 | 41 |
| (-h,2,3) | | |
| 1 | 146 | 133 |
| 2 | 228 | 206 |
| 3 | 231 | 217 |
| 4 | 159 | 152 |
| 5 | 82 | 80 |
| 6 | 90 | 85 |
| (-h,3,3) | | |
| 1 | 250 | 236 |
| 2 | 214 | 206 |
| 3 | 146 | 132 |
| 4 | 159 | 156 |
| 5 | 59 | 69 |
| 6 | 86 | 77 |
| 7 | 32 | 26 |
| (-h,4,3) | | |
| 1 | 111 | 99 |
| 2 | 117 | 115 |
| 3 | 141 | 127 |
| 4 | 162 | 159 |
| (-h,5,3) | | |
| 3 | 110 | 100 |
| 4 | 126 | 129 |
| 5 | 118 | 126 |
| (-h,0,4) | | |
| 1 | 115 | 122 |
| 2 | 204 | 211 |
| 3 | 108 | 122 |
| 4 | 97 | 110 |
| 5 | 77 | 77 |
| 6 | 79 | 84 |
| (-h,1,4) | | |
| 1 | 125 | 130 |
| 2 | 196 | 201 |
| 3 | 173 | 184 |
| 4 | 125 | 127 |
| 5 | 107 | 109 |
| 6 | 61 | 77 |
| (-h,2,4) | | |
| 1 | 145 | 138 |
| 2 | 206 | 198 |
| 3 | 245 | 258 |
| 4 | 130 | 138 |
| 5 | 83 | 87 |
| (-h,3,4) | | |
| 1 | 207 | 203 |
| 2 | 180 | 181 |
| 3 | 184 | 199 |
| 4 | 41 | 55 |
| (-h,1,5) | | |
| 3 | 58 | -61 |
| (-h,2,5) | | |
| 1 | 102 | -95 |
| 2 | 22 | -32 |
| (-h,3,5) | | |
| 1 | 87 | -80 |
| 2 | 35 | -13 |
| 3 | 44 | -29 |
| (h,-1,1) | | |
| 0 | 143 | -83 |
| 1 | 392 | 389 |
| 2 | 169 | 178 |
| 3 | 61 | -18 |
| 4 | 82 | 117 |
| 5 | 296 | 343 |
| 6 | 212 | 239 |
| 7 | 133 | 143 |
| 8 | 148 | 140 |
| 9 | 126 | 115 |
| 10 | 158 | 130 |
| 11 | 66 | 63 |
| (h,-2,1) | | |
| 0 | 321 | 298 |
| 1 | 530 | 538 |
| 2 | 268 | 294 |
| 3 | 29 | 64 |
| 4 | 133 | 179 |
| 5 | 292 | 347 |
| 6 | 366 | 391 |
| 8 | 200 | 193 |
| 9 | 108 | 104 |
| (h,-3,1) | | |
| 0 | 28 | 14 |
| 1 | 614 | 583 |
| 2 | 472 | 524 |
| 3 | 65 | 137 |
| 4 | 278 | 336 |
| 5 | 362 | 416 |
| 6 | 420 | 483 |
| 7 | 196 | 213 |
| 8 | 113 | 118 |
| 9 | 64 | 70 |
| 10 | 39 | 47 |
| (h,-4,1) | | |
| 1 | 502 | 493 |
| 2 | 861 | 847 |
| 3 | 503 | 503 |
| 4 | 370 | 424 |
| 5 | 333 | 374 |
| 6 | 245 | 269 |
| 7 | 131 | 143 |
| (h,-5,1) | | |
| 0 | 380 | 349 |
| 1 | 691 | 610 |
| 2 | 850 | 814 |
| 3 | 511 | 488 |
| 5 | 153 | 183 |
| 6 | 135 | 146 |
| (h,-6,1) | | |
| 0 | 393 | 343 |
| 1 | 366 | 343 |
| 2 | 365 | 347 |
| 3 | 313 | 287 |
| (h,-7,1) | | |
| 0 | 167 | 163 |
| 1 | 91 | 94 |
| 2 | 250 | 218 |
| (h,-8,1) | | |
| 0 | 90 | 96 |
| 1 | 167 | -112 |
| (h,-1,2) | | |
| 0 | 387 | -392 |
| 1 | 115 | -147 |
| 2 | 288 | -266 |
| 3 | 151 | -167 |
| 4 | 90 | -96 |
| 5 | 62 | -71 |
| (h,-2,2) | | |
| 0 | 299 | -270 |
| 1 | 102 | -120 |
| 2 | 120 | -112 |
| 3 | 195 | -191 |
| 4 | 71 | -70 |
| 5 | 42 | 30 |
| 6 | 123 | 125 |
| 7 | 107 | 113 |
| 8 | 49 | 59 |
| 9 | 56 | 51 |
| 11 | 55 | 53 |
| (h,-3,2) | | |
| 0 | 124 | -143 |
| 1 | 204 | -198 |
| 2 | 117 | 100 |
| 3 | 28 | 24 |
| 4 | 106 | 91 |
| 5 | 212 | 208 |
| 6 | 190 | 194 |
| 7 | 131 | 133 |
| 8 | 46 | 63 |
| 9 | 52 | 62 |
| 10 | 46 | 49 |
| 11 | 61 | 64 |
| (h,-4,2) | | |
| 2 | 507 | 417 |
| 3 | 376 | 367 |
| 5 | 60 | 65 |
| 6 | 184 | 186 |
| 7 | 163 | 176 |
| 8 | 98 | 110 |
| (h,-5,2) | | |
| 0 | 220 | 183 |
| 1 | 215 | 195 |
| 2 | 368 | 336 |
| 3 | 237 | 235 |
| 4 | 141 | 138 |
| 5 | 107 | 106 |
| 6 | 212 | 203 |
| 7 | 211 | 210 |
| 8 | 107 | 99 |
| (h,-6,2) | | |
| 0 | 115 | 134 |
| 2 | 293 | 258 |
| 3 | 469 | 425 |
| 4 | 240 | 204 |
| 5 | 119 | 118 |
| 6 | 119 | 93 |
| 7 | 161 | 192 |
| 8 | 128 | 110 |
| (h,-7,2) | | |
| 0 | 150 | 158 |
| 1 | 183 | 175 |
| 2 | 174 | 145 |
| 3 | 387 | 362 |
| 4 | 156 | 134 |
| 5 | 126 | 103 |
| 6 | 132 | 105 |
| 7 | 102 | 129 |
| 8 | 109 | 110 |
| (h,-8,2) | | |
| 0 | 163 | 141 |
| 1 | 104 | 110 |
| 3 | 203 | 265 |
| 4 | 296 | 264 |
| 5 | 92 | 56 |
| 6 | 107 | 90 |
| 7 | 125 | 124 |
| 8 | 119 | 130 |
| (h,-9,2) | | |
| 0 | 206 | 195 |
| 1 | 129 | 109 |
| 2 | 170 | 158 |
| 5 | 107 | 107 |
| 6 | 106 | 110 |
| 8 | 84 | 85 |
| (h,-10,2) | | |
| 5 | 123 | 148 |
| (h,-1,3) | | |
| 0 | 70 | 56 |
| 1 | 211 | -219 |
| 2 | 189 | -189 |
| 3 | 318 | -324 |
| 4 | 151 | -147 |
| 5 | 234 | -235 |
| 6 | 288 | -293 |
| 7 | 281 | -293 |
| 8 | 173 | -173 |
| 9 | 103 | -99 |
| 10 | 119 | -107 |
| 11 | 92 | -79 |
| (h,-2,3) | | |
| 1 | 363 | -375 |
| 2 | 345 | -356 |
| 3 | 453 | -468 |
| 4 | 320 | -343 |
| 5 | 256 | -272 |
| 6 | 262 | -275 |
| 7 | 274 | -285 |
| 8 | 191 | -191 |
| 9 | 84 | -76 |
| 10 | 64 | -60 |
| (h,-3,3) | | |
| 0 | 166 | -200 |
| 1 | 359 | -382 |
| 2 | 475 | -495 |
| 3 | 410 | -427 |
| 4 | 331 | -361 |
| 5 | 260 | -271 |
| 6 | 254 | -260 |
| 7 | 200 | -191 |
| 8 | 134 | -129 |
| (h,-4,3) | | |
| 0 | 298 | -321 |
| 1 | 272 | -282 |
| 2 | 428 | -415 |
| 3 | 364 | -379 |
| 4 | 405 | -421 |
| 5 | 205 | -195 |
| 6 | 129 | -123 |
| (h,-5,3) | | |
| 3 | 184 | -194 |
| 4 | 155 | -170 |
| (h,-1,4) | | |
| 1 | 146 | 145 |
| 2 | 145 | 149 |
| 3 | 159 | 167 |
| 6 | 49 | -57 |
| 7 | 81 | -90 |
| 8 | 124 | -120 |
| (h,-2,4) | | |
| 1 | 121 | 145 |
| 4 | 106 | -123 |
| 6 | 100 | -114 |
| 7 | 109 | -115 |
| 8 | 134 | -128 |
| (h,-3,4) | | |
| 2 | 114 | -132 |
| 3 | 120 | -134 |
| 4 | 181 | -203 |
| 5 | 112 | -118 |
| 6 | 86 | -77 |
| 7 | 86 | -79 |
| 8 | 64 | -73 |
| 9 | 47 | -51 |
| (h,-4,4) | | |
| 2 | 176 | -192 |
| 3 | 221 | -235 |
| 4 | 162 | -172 |
| 9 | 111 | -108 |
| 3 | 112 | -137 |
| 7 | 125 | -114 |
| 8 | 142 | -137 |
| 9 | 136 | -132 |
| (h,-1,5) | | |
| 3 | 294 | 308 |
| 4 | 199 | 200 |
| 5 | 115 | 114 |
| 6 | 124 | 123 |
| 7 | 121 | 118 |
| 8 | 94 | 89 |
| 9 | 54 | 52 |
| (h,-2,5) | | |
| 3 | 216 | 224 |
| 4 | 188 | 189 |
| 5 | 95 | 96 |
| 6 | 117 | 124 |
| 7 | 106 | 102 |
| 8 | 107 | 97 |
| (h,-3,5) | | |
| 3 | 144 | 166 |
| 4 | 153 | 178 |
| 5 | 77 | 94 |
| 6 | 121 | 128 |
| 7 | 104 | 104 |
| 8 | 72 | 66 |
| (h,-4,5) | | |
| 0 | 147 | 153 |
| 1 | 123 | 140 |
| 3 | 102 | 115 |
| 4 | 154 | 171 |
| 5 | 117 | 119 |
| (h,-5,5) | | |
| 3 | 113 | 116 |
| (-h,-1,1) | | |
| 1 | 151 | -100 |
| 3 | 307 | 288 |
| (-h,-2,1) | | |
| 1 | 195 | -151 |
| 3 | 161 | 140 |
| (-h,-3,1) | | |
| 2 | 223 | 247 |
| 3 | 227 | 208 |
| (-h,-4,1) | | |
| 1 | 185 | 191 |
| 2 | 244 | 224 |
| 3 | 325 | 293 |
| (-h,-5,1) | | |
| 1 | 315 | 299 |
| 2 | 441 | 402 |
| 3 | 342 | 331 |
| (-h,-6,1) | | |
| 1 | 485 | 441 |
| 2 | 573 | 509 |
| 3 | 309 | 265 |
| 4 | 140 | 152 |
| (-h,-7,1) | | |
| 1 | 340 | 333 |
| 2 | 456 | 399 |
| 3 | 253 | 227 |
| 4 | 223 | 201 |
| 5 | 103 | 105 |
| 6 | 116 | 144 |
| 7 | 99 | 95 |
| (-h,-8,1) | | |
| 1 | 110 | 156 |
| 3 | 119 | 132 |
| 4 | 149 | 158 |
| 5 | 113 | 113 |
| 6 | 105 | 150 |
| (-h,-1,2) | | |
| 1 | 307 | -321 |
| 2 | 391 | -372 |
| 3 | 474 | -423 |
| 4 | 388 | -347 |
| 5 | 156 | -139 |
| 6 | 121 | -83 |
| 7 | 142 | -136 |
| 8 | 108 | -105 |
| (-h,-2,2) | | |
| 2 | 321 | -294 |
| 3 | 367 | -329 |
| 4 | 391 | -346 |
| 5 | 112 | -105 |
| 6 | 116 | -126 |
| 7 | 141 | -130 |
| 8 | 105 | -115 |
| (-h,-3,2) | | |
| 1 | 85 | -111 |
| 2 | 190 | -173 |
| 3 | 180 | -156 |
| 4 | 226 | -211 |
| 6 | 133 | -160 |
| 7 | 123 | -126 |
| 8 | 119 | -110 |
| (-h,-4,2) | | |
| 1 | 142 | -132 |
| 3 | 180 | -175 |
| 6 | 132 | -110 |
| 7 | 118 | -107 |
| 8 | 91 | -87 |
| (-h,-5,2) | | |
| 1 | 121 | 112 |
| 2 | 134 | 118 |
| 3 | 114 | -106 |
| 7 | 107 | -78 |
| (-h,-6,2) | | |
| 1 | 299 | 280 |
| 2 | 186 | 186 |
| (-h,-7,2) | | |
| 1 | 272 | 246 |
| 2 | 153 | 142 |
| 3 | 138 | 123 |
| (-h,-8,2) | | |
| 1 | 298 | 282 |
| 2 | 124 | 110 |
| 3 | 116 | 92 |
| (-h,-9,2) | | |
| 1 | 210 | 185 |

## Discussion of results

The atomic positions given in the previous section show that the crystal contains dimers: one of these is shown in Fig. 1 where it may be compared with the copper acetate monohydrate dimer.

The similarity of the arrangement of the copper and oxygen atoms is striking. Each copper atom is in a state of sixfold coordination which is completed in the acetate structure by a molecule of water of crystallization, and in the anhydrous butyrate structure by an oxygen atom from a neighbouring dimer. The copper–copper and the copper–oxygen separations are listed in Table 3: they are not significantly different from the corresponding lengths in the acetate dimer.

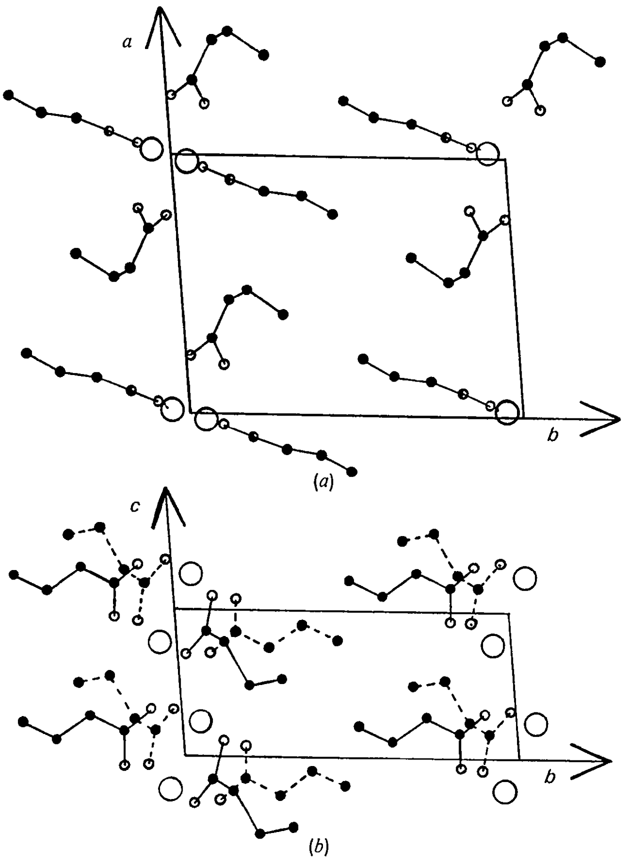

Fig. 2. Projections of the structure of anhydrous copper butyrate (*a*) along the *c* axis, and (*b*) along the *a* axis. Small full circles are carbon atoms and small open circles are oxygen atoms.

In the copper acetate monohydrate dimer the acetate groups are arranged with two in each of two planes which are very nearly perpendicular to each other. In the butyrate structure this arrangement of the acid groups is not exactly maintained, presumably because the relatively long hydrocarbon chains in the butyrate group if extended in directions at right angles to each other, could not pack neatly together. This packing difficulty is avoided by the distortion of two of the four chains from the more usual plane zigzag structure of hydrocarbon chains in crystals.

The distortion may be visualized as resulting from the plane zigzag structure by a rotation of approximately 55° about the bond between C(8) and C(7) in Fig. 1, followed by a rotation of approximately 120° about the bond between C(7) and C(6), *i.e.* simply a change from a *trans* to a *gauche* configuration. The first of these rotations occurs about the bond joining the carboxyl group to the first $CH_2$ group in the chain. Molecular models show that there is little or no steric hindrance to rotations about such a bond and similar rotations have been observed by Lewis & Lomer (1969) in potassium caprate and by Lomer (1963) in lauric acid. The plane of the undistorted hydrocarbon chain in the butyrate structure is rotated about the corresponding bond by 13° relative to its carboxyl group. The only other examples known to us of bending of hydrocarbon chains in solids by rotation about bonds between $CH_2$ groups occur in the structure of the cyclic paraffin cyclotetratriacontane, $[CH_2]_{34}$ reported by Kay & Newman (1968) and in the structure of the *B* form of stearic acid reported by von Sydow (1955). The bond lengths and angles in the hydrocarbon chains in copper butyrate are given in Table 3. The mean C–C bond length is $1{\cdot}510 \pm 0{\cdot}018$ Å and the mean C–C–C bond angle is $113{\cdot}7 \pm 1{\cdot}2°$.

The crystal structure consists of chains of dimers, running parallel to the *c* axis of the crystal, in which

Table 3. *Bond lengths and angles*

Atoms in the asymmetric unit are numbered as in Fig. 1(*b*). Atoms in the centrosymmetrically related unit are primed, and atom in neighbouring dimer is double primed.

| | | | | | |
|---|---|---|---|---|---|
| Cu —Cu | 2·565 Å | C(1)–O(1) | 1·210 Å | O(1)–C(1)–O(2) | 121·8° |
| Cu —O(1) | 2·064 | C(1)–O(2) | 1·254 | O(1)–C(1)–C(2) | 118·3 |
| Cu —O(2′) | 1·973 | C(1)–C(2) | 1·483 | O(2)–C(1)–C(2) | 119·9 |
| Cu —O(3) | 1·954 | C(2)–C(3) | 1·433 | C(1)–C(2)–C(3) | 117·2 |
| Cu —O(4′) | 1·936 | C(3)–C(4) | 1·534 | C(2)–C(3)–C(4) | 113·4 |
| O(1)–O(2) | 2·152 | C(8)–O(4) | 1·238 | O(3)–C(8)–O(4) | 124·8 |
| O(3)–O(4) | 2·221 | C(8)–O(3) | 1·269 | O(3)–C(8)–C(7) | 116·3 |
| O(2)–O(4) | 2·796 | C(8)–C(7) | 1·497 | O(4)–C(8)–C(7) | 118·6 |
| O(1)–O(3) | 2·885 | C(7)–C(6) | 1·563 | C(8)–C(7)–C(6) | 113·2 |
| O(1)–O(4′) | 2·782 | C(6)–C(5) | 1·559 | C(7)–C(6)–C(5) | 111·1 |
| O(2)–O(3′) | 2·969 | | | | |
| Cu —O(2″) | 2·245 | | | | |

every copper atom is coordinated with four oxygen atoms and one copper atom from its own dimer and by a single oxygen atom from a neighbouring dimer. The arrangement is indicated in Fig. 1, while Fig. 2 shows diagrams of the structure in projections from which the side-by-side packing of these chains of dimers may be visualized.

The components of the vibration tensor, reported in Table 1, are defined by $\overline{U_l^2}=\sum_i\sum_j U_{ij}l_il_j$ where $\overline{U_l^2}$ is the mean-square displacement of the atom in the direction defined by the unit vector $\mathbf{l}$ which has components $l_1$, $l_2$ and $l_3$ referred to reciprocal cell axes.

The principal values and axes of the vibration tensor were calculated for each atom from the $U_{ij}$ values in Table 1.

The only atoms showing marked anisotropy of their thermal motions are C(3), C(4), and C(5), which lie near the ends of the hydrocarbon chains. As usual in these cases the direction of maximum displacement is perpendicular to the chain.

The similarity of the structures of copper butyrate and copper acetate, together with the similarity of the magnetic properties of these compounds to those of the higher copper soaps, suggests that the higher copper soaps will prove to have structures based on the same copper ion environment, and that distortions of the acid groups will occur in such a way as to allow the long hydrocarbon chains to pack together in one or other of the known packing arrangements for such chains.

We are indebted to I.C.I. Ltd. for the loan of the integrating Weissenberg camera used in this work and to the Royal Society for the provision of a microdensitometer. One of us (MJB) acknowledges with gratitude the S.R.C. studentship during the tenure of which this work was done.

### References

ABLOV, A. V., SIMENOV, YU. A. & MALINOVSKII, T. I., (1967). *Sov. Phys. Doklady*, **11**, 1029.

BLEANEY, B. & BOWERS, K. D. (1952). *Proc. Roy. Soc.* A**214**, 451.

FIGGIS, B. N. & MARTIN, R. L. (1956). *J. Chem. Soc.* p. 3837.

GUHA, B. C. (1951). *Proc. Roy. Soc.* A**206**, 353.

IBALL, J. (1947). *Nature, Lond.* **159**, 95.

KAY, H. F. & NEWMAN, B. A. (1968). *Acta Cryst.* B**24**, 615.

LEWIS, E. L. V. & LOMER, T. R. (1969). *Acta Cryst.* B**25**, 702.

LIFSCHITZ, J. & ROSENBOHM, E. (1915). *Z. Electrochem.* **21**, 499.

LOMER, T. R. (1963). *Acta Cryst.* **16**, 984.

MARTIN, R. L. & WATERMAN, H. (1957). *J. Chem. Soc.* p. 2545.

NIEKERK, J. N. VAN & SCHOENING, F. R. L. (1953). *Acta Cryst.* **6**, 227.

SYDOW, E. VON (1955). *Acta Cryst.* **8**, 557.

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*Acta Cryst.* (1972). B**28**, 246

# The Crystal Structure of a Sulfone, 4,5-Dihydrothiepin 1,1-Dioxide

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(*Received* 14 *January* 1971)

4,5-Dihydrothiepin 1,1-dioxide, $C_6H_8SO_2$, crystallizes in the monoclinic space group $P2_1/n$ with cell dimensions of $a=11{\cdot}415$, $b=6{\cdot}476$, $c=9{\cdot}597$ Å, $\beta=108{\cdot}02°$, and with $Z=4$. Three-dimensional X-ray intensity data were collected with Mo radiation using a Picker diffractometer. The structure was solved with direct methods. Full-matrix least-squares refinement, using anisotropic temperature factors for C, O, and S and isotropic terms for H, gave an $R$ of 0·049 (weighted $R=0{\cdot}039$). The conformation of the 7-membered ring is not symmetrical. Although the C–S lengths are typical of many of the values reported for aromatic sulfones, the C=C distances are smaller than the usual 1·34 Å ethylenic value. A possible rationale for this shortening is given.

## Introduction

A number of examples of the $Csp^2$–$SO_2$ distance in phenyl sulfones and vinyl sulfones can be found in the crystallographic literature. There are, however, no reported* examples of this length in 'simple' vinyl sulfones, molecules in which the C–S bonds should be free

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* We make this statement with some hesitation, knowing well that a simple sulfone or two may have escaped our literature searches.