

## Dinuclear Copper(II) Acetate Monohydrate: a Redetermination of the Structure by Neutron-Diffraction Analysis\*†

BY GEORGE M. BROWN AND R. CHIDAMBARAM‡

Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, U.S.A.

(Received 30 October 1972; accepted 30 May 1973)

The crystal structure of dinuclear Cu(II) acetate monohydrate,  $\text{Cu}_2(\text{O}_2\text{CCH}_3)_4 \cdot 2\text{H}_2\text{O}$  [van Niekerk, J. N. & Schoening, F. R. L. (1953). *Acta Cryst.* 6, 501–504], was refined by the full-matrix least-squares method using three-dimensional neutron data and revised cell parameters [ $a = 13.167$  (4),  $b = 8.563$  (2),  $c = 13.862$  (7) Å,  $\beta = 117.019$  (2)° ( $\lambda_{\text{Cu K}\alpha_1} = 1.54051$  Å),  $C2/c$ ,  $Z = 4$ ]. A reasonable description of the methyl groups, which are in large-amplitude torsional oscillation, was obtained by use of a special model (see the preceding paper).  $R(F) = 0.051$  and  $R(F^2) = 0.072$  for  $F^2 > \sigma$ , excluding the very weak reflections and reflections mildly affected by extinction. The intramolecular Cu–Cu vector is 2.6143 (17) Å long and oriented almost exactly as reported from measurements of magnetic anisotropy and electron spin resonance. The water oxygen atom is trigonally coordinated; its Cu–O distance is 2.1613 (17) Å. Average lengths of other bonds, with r.m.s. deviations in brackets and maximum individual e.s.d.'s in parentheses, are: Cu–O, 1.9689[223](17); C–O, 1.2596[20](19); C–C, 1.5013[11](16); C–H, 1.093[12](6); O–H, 0.955 [4] (3) Å. The H–O–H angle is 106.6 (3)°. Two hydrogen bonds link the water molecule to two acetate oxygen atoms. The Cu–O bonds to these two oxygen atoms are 0.04 to 0.05 Å longer than those to the other two acetate oxygen atoms.

### Introduction

A number of complexes of bivalent copper have been found to have subnormal magnetic moments (see review by Kato, Jonassen & Fanning, 1964). The reduction in magnetic moment can be attributed either to direct antiferromagnetic exchange interaction between neighboring copper atoms or to a 'super-exchange interaction' operating through the bridging ligands between copper atoms. The magnetic behavior of copper(II) acetate monohydrate is typical of a large number of these complexes. The magnetic moment at room temperature is about 1.4 Bohr magnetons, less than the normal value of about 1.9 or the theoretical spin-only value of 1.73. The magnetic susceptibility is at a maximum near 270°K and decreases rapidly as the temperature is lowered below that value. The electron spin resonance is also anomalous.

Considerable support for a mechanism of direct magnetic exchange in copper(II) acetate monohydrate was provided by the X-ray crystal-structure analysis of van Niekerk & Schoening (1953), which indicated a Cu–Cu nearest-neighbor distance of 2.64 Å, slightly greater than the interatomic distance of 2.556 Å in metallic copper at 20°C (*International Tables for X-ray Crystallography*, 1962, p. 278). The two copper atoms are held together in a centrosymmetric dimeric unit by

four acetate bridges, and each atom also has a water molecule coordinated to it. § Other complexes of copper(II) classified by Kato *et al.* as exhibiting direct copper-to-copper interactions are in general thought to have similar structures with four three-atom bridges between nearest-neighbor copper atoms. For a few of these complexes besides  $\text{Cu}_2(\text{O}_2\text{CCH}_3)_4 \cdot 2\text{H}_2\text{O}$  dinuclear bridge structures have been proved by X-ray analysis; namely, for both orthorhombic monopyridine Cu(II) acetate (Hanic, Štempelová & Hanicová, 1964) and monoclinic monopyridine Cu(II) acetate (Barclay & Kennard, 1961), for Cu(II) succinate dihydrate (O'Connor & Maslen, 1966), and for the two ions  $[\text{Cu}(\text{O}_2\text{CH})_2(\text{NCS})_2]_2^-$  and  $[\text{Cu}(\text{O}_2\text{CCH}_3)_2(\text{NCS})_2]_2^-$  (Goodgame, Hill, Marsham, Skapski, Smart & Troughton, 1969). The compounds chromium(II) acetate monohydrate (van Niekerk, Schoening & de Wet, 1953; Cotton, DeBoer, LaPrade, Pipal & Ucko, 1971) and rhodium(II) acetate monohydrate (Cotton *et al.* 1971) are isostructural with Cu(II) acetate monohydrate and also have dinuclear bridged structures.

The question of the mechanism for direct interaction between the adjacent copper atoms in such complexes as Cu(II) acetate monohydrate is not yet settled, though it has been the subject of many discussions in the literature (for leading references see: Kato *et al.*, 1964; Baird, 1968; Oldham, 1968; Goodgame *et al.*, 1969; Gregson, Martin & Mitra, 1971). Both  $\delta$  interactions involving  $d_{x^2-y^2}$  orbitals and  $\sigma$  interactions involving  $d_{z^2}$  orbitals have been proposed and explored theoretically without settling the matter. It is, in fact, an open

\* Research sponsored in part by the U.S. Atomic Energy Commission under contract with Union Carbide Corporation and in part by the U.S. Agency for International Development.

† A brief report of this work was given by Chidambaram & Brown (1972).

‡ Permanent address: Nuclear Physics Division, Bhabha Atomic Research Centre, Trombay, Bombay 85, India.

§ An appropriate systematic name is tetra- $\mu$ -acetato-bis-{aquaocopper(II)}.

question still as to whether the interaction does not occur wholly or in part through super-exchange.

In view of the sustained interest in the nature of the magnetic interaction in the dinuclear complex  $\text{Cu}_2(\text{O}_2\text{CCH}_3)_4 \cdot 2\text{H}_2\text{O}$  and in similar complexes, we have redetermined the structure of the complex by the neutron-diffraction method with the aim of obtaining more accurate structure parameters than those of van Niekerk & Schoening (1953). The choice of the neutron-diffraction method for this study allowed us also to determine precisely the pattern of hydrogen bonding and the geometry of the water molecule. Attempts to account properly in least-squares refinement for large-amplitude torsional motions of the methyl groups about their C-C axes and to minimize the attendant effects on the apparent C-H distances led us to develop and apply the model for torsional oscillation which is the subject of the accompanying paper (Chidambaram & Brown, 1973).

### Experimental

An apparently suitable crystal† was systematically examined by taking a number of orientation precession photographs with the X-ray beam bathing different volume elements, and a portion of the crystal which was found to be misoriented was carefully removed. The remaining portion was ground to the form of an almost regular parallelepiped bounded by the faces of the forms  $\{001\}$  and  $\{110\}$ , with edges about 2.5 mm long. The weight of the specimen was 35.8 mg.

The specimen was sealed inside a thin-walled quartz tube and mounted on the Oak Ridge automatic neutron diffractometer (Busing, Smith, Peterson & Levy, 1964) with the reciprocal axis  $c^*$  along the spindle axis. A total of 2762 intensity observations were made in the range  $2\theta \leq 111^\circ$  (the limit of the instrument) at a neutron wavelength of  $1.078 \text{ \AA}$  ( $\lambda^{-1} \sin \theta \leq 0.754 \text{ \AA}^{-1}$ ). The number of symmetrically nonequivalent reflections was 2491. The  $R$  value between  $86 \text{ } 0k1F_o^2$  values and their equivalent  $0k1F_o^2$  values was 0.089. The preliminary data processing followed the same procedures used in other neutron-diffraction studies reported from this laboratory (Brown & Levy, 1964; Brown & Chidambaram, 1969; Worsham & Busing, 1969). The few negative values of  $F_o^2$  (resulting from statistical fluctuations and instrument errors) were replaced by zero values.

For calculation of corrections for absorption by the method of Busing & Levy (1957), the coordinates of the 8 corners of the crystal were measured with a tool-maker's microscope, and the equations of the 6 face planes were calculated. The value  $1.93 \text{ cm}^{-1}$  for the linear absorption coefficient  $\mu$  was established by determining the transmission factor  $\exp(-\mu d)$  through a crystal of known thickness  $d$ , using the diffractometer

counter at zero  $2\theta$  and a fine beam of neutrons defined by a pinhole in a piece of boron carbide. The correction factors applied to the  $F_o^2$ 's were in the range 1.39 to 1.68.

An empirical correction term  $(0.03F_o^2)^2$  was added to the statistical variance  $\sigma_s^2(F_o^2)$  of each observation  $F_o^2$  to obtain the variance  $\sigma^2(F_o^2)$ , the reciprocal of which was taken as the weight of the observation in least-squares refinement. The extra term makes allowance for instability in the instrument, deficiencies of the structure model, and so forth (Peterson & Levy, 1957). The  $F_o^2$  values for 1943 of the 2491 independent reflections were greater than their corrected  $\sigma(F_o^2)$  values.

The unit-cell parameters were redetermined from  $2\theta$  observations in the range  $135$  to  $158^\circ$  for 12 resolved  $\text{Cu } K\alpha_1$  reflections from a small crystal mounted on the Oak Ridge computer-controlled X-ray diffractometer (Busing, Ellison, Levy, King & Roseberry, 1968). Unit weights were used in this least-squares determination. The new cell parameters and their standard errors appear in Table 1, with the parameters reported by van Niekerk & Schoening (1953); these new parameters were used in calculations of bond lengths, valence angles, and so forth.

Table 1. Unit-cell parameters of *Cu(II) acetate monohydrate* (space group  $C2/c$ )

	This work	van Niekerk & Schoening
$a$	13.167 (4) Å	13.15 Å
$b$	8.563 (2)	8.52
$c$	13.862 (7)	13.90
$\beta$	117.019 (2)°	117.0°
$\lambda$	1.54051 Å	
Temperature	$23 \pm 1^\circ\text{C}$	

The reflections which were observed in both our neutron and our X-ray experiments were those which satisfy the following conditions:  $hkl$ 's,  $h+k=2n$ ;  $h0l$ 's  $l=2n$ , ( $h=2n$ );  $0k0$ 's, ( $k=2n$ ). These conditions, the same as those reported by van Niekerk & Schoening, are characteristic of space groups  $C2$  and  $C2/c$  (*International Tables for X-ray Crystallography*, 1952, pp. 89 and 101).

### Structure refinement

By standard Fourier refinement procedures starting with the coordinates of the copper, oxygen, and carbon atoms as given by van Niekerk and Schoening for their rough structure of  $C2/c$  symmetry, the eight hydrogen atoms of the dinuclear asymmetric unit were located. In subsequent refinement by the full-matrix least-squares method, the quantity  $\sum w(F_o^2 - S^2F_c^2)^2$  was minimized by adjustment of the following 166 parameters: the overall scale factor  $S$  on the  $F_c$ 's; three positional parameters and six anisotropic thermal parameters‡

† From a batch of crystals grown by Dr S. Srikanta of the Bhabha Atomic Research Centre by slow evaporation of a saturated aqueous solution.

‡ The temperature factor was of the familiar form  $\exp(-h^2\beta_{11} - k^2\beta_{22} - l^2\beta_{33} - 2hk\beta_{12} - 2hl\beta_{13} - 2kl\beta_{23})$ .

$B_{ij}$  for each of the 18 atoms of the asymmetric unit; the neutron scattering lengths of copper, oxygen, and hydrogen.† At convergence the conventional measures of goodness of fit were as given in Table 2.

Table 2. *Measures of goodness of fit\* in least-squares refinement*

The first entry for each quantity includes contributions from all data not weighted zero; the second entry (in parentheses) does not include data for which  $F_o^2 \leq \sigma(F_o^2)$ .

	Standard l.s. refinement	Torsional- oscillator refinement	Three- cumulant refinement
$R(F)$	0.095 (0.066)	0.091 (0.061)	0.096 (0.063)
$R(F^2)$	0.0895 (0.0818)	0.080 (0.072)	0.067 (0.060)
$R_w(F^2)$	0.100 (0.097)	0.092 (0.088)	0.083 (0.079)
$\sigma_1$	1.171 (1.287)	1.072 (1.170)	1.030 (1.138)

\* These are the familiar measures used regularly by crystallographers. For explicit definitions, see Brown & Chidambaram (1969), among others.

At this stage of refinement, the usual termination stage, the coordinate standard errors calculated from the least-squares covariance matrix were about 0.0010 Å for the copper atom, 0.0010 to 0.0021 Å for the carbon and oxygen atoms, 0.004 Å for the hydrogen atoms

† Since the overall scale factor was being adjusted, it was not possible to adjust all of the four different scattering lengths; therefore, the scattering length of carbon was held fixed. Adjustment of the three scattering lengths provides independent estimates of the ratios of the scattering lengths of the four atoms for comparison with tabulated values from other experimental sources. In this laboratory we have routinely made such adjustments in least-squares refinements, and we have sometimes found strong indications for revision of tabulated values (see for example: Brown & Walker, 1966; El Saffar & Brown, 1970, and references therein) which have been verified by other work and have now been made in the tabulation of the Neutron Diffraction Commission (1969). When the present work began, there was reason to suspect (Peterson, 1962) that the scattering length  $0.79 \times 10^{-12}$  cm given for copper in Bacon's (1962) table was somewhat high.

of the water molecule, and 0.005 to 0.012 Å for the hydrogen atoms of the methyl groups. All of the calculated bond lengths and angles not involving the methyl hydrogen atoms were chemically sensible. However, the apparent C–H bond lengths were unsatisfactory; they varied from 1.024 to 1.050 Å and averaged 1.037 Å instead of the expected value of about 1.11 Å (see Table 3). The H–C(2)–H angles were apparently somewhat distorted from the symmetrical pattern expected for an isolated methyl group; they were calculated as 110, 110, 102°. The three C–C(2)–H angles were 109, 112, and 114°.

The aberrant values of the C–H bond lengths were clearly consequences of large-amplitude torsional oscillations of the methyl groups about their respective carbon–carbon axes. Analysis of the anisotropic thermal parameters of the methyl hydrogen atoms showed that for each hydrogen the largest principal-axis root-mean-square vibrational displacement was near 0.5 Å (Table 4) and that the axis of largest amplitude was nearly parallel to the tangent to the arc that would be described by the hydrogen atom in torsional oscillation about the C–C axis of its acetate group. The vibrational motion is shown pictorially by the ellipsoid drawing of Fig. 1. That apparently short C–H bond lengths should result from such large-amplitude torsional oscillations follows from the discussions of Cruickshank (1956) and of Busing & Levy (1964) on the effects of thermal motion on bond lengths as calculated from atomic coordinates determined by crystal-structure analysis. The angular distortions in the methyl groups were thought to be related to the excessive smearing out of the scattering densities of the methyl hydrogen atoms, which would be expected to increase the difficulty of determining accurately the atomic positions.

'Corrected' values (see Table 3) of the C–H bond lengths calculated according to the 'riding' model of Busing & Levy (1964) were hardly to be preferred over the uncorrected values; the spread of the C–H bond lengths was not narrowed and the average value of 1.144 Å was too high. The model explained in the accompanying paper (Chidambaram & Brown, 1973) for an atom in torsional oscillation was developed in an at-

Table 3. *C–H bond lengths in copper acetate monohydrate*

	From normal least-squares refinement			From special refinements	
	Raw	Riding model	Seg. body analysis	Torsional oscillator	Three-cumulant*
H(3)	1.024 (5)	1.120	1.114	1.078 (5)	1.011
H(4)	1.032 (6)	1.137	1.124	1.084 (6)	1.095
H(5)	1.050 (7)	1.178	1.160	1.118 (6)	1.099
H(6)	1.050 (5)	1.128	1.132	1.093 (5)	1.104
H(7)	1.043 (6)	1.132	1.135	1.093 (5)	1.081
H(8)	1.020 (6)	1.168	1.145	1.095 (5)	1.034
Ave.	1.037 [12]	1.144 [21]	1.135 [15]	1.093 [12]	1.071 [38]

\* These are intermode distances (see text).

Table 4. *R.m.s. vibrational amplitudes of methyl hydrogen atoms in copper acetate monohydrate*

Numbers in brackets give r.m.s. deviations from averages.

	Standard refinement		Segmented body analysis (°)	Torsional oscillator refinement (°)
	(Å)	(°)		
H(3)	0.50 (1)	24		24.9 (7)
H(4)	0.50 (1)	24		21.9 (6)
H(5)	0.52 (1)	25		27.0 (8)
Ave.	0.51	24	23.2	24.6 [2.1]
H(6)	0.43 (1)	21		19.2 (5)
H(7)	0.46 (1)	23		23.2 (5)
H(8)	0.56 (1)	27		28.3 (8)
Ave.	0.48	24	22.5	23.6 [3.7]

tempt to describe properly the motion of the methyl hydrogen atoms and to obtain physically sensible C-H distances.

In the expression for the contribution  $F_H(\mathbf{h})$  of a single methyl hydrogen atom to a structure factor  $F(\mathbf{h})$  according to the new model, the four adjustable parameters  $\delta^2$ ,  $U_{11}$ ,  $U_{22}$ , and  $U_{12}$  replace, in effect, the six adjustable parameters of the usual model for anisotropic motion. In addition, however, an anisotropic temperature factor of the usual form is involved to take care of that part of the motion of the hydrogen atom which may be assumed to result from motion of the whole acetate group to which the given hydrogen belongs. The six parameters  $\beta_{ij}^R$  of this temperature factor are evaluated in a preliminary calculation and not adjusted thereafter.

For copper acetate monohydrate the evaluation of these last six parameters for each methyl hydrogen atom from the anisotropic thermal parameters of the standard least-squares refinement already described was possible only through use of the segmented-body program, *ORSBA*, of our colleague C. K. Johnson (1970*b*). It was clear from inspection of Fig. 1. and of the calculated atomic principal-axis displacements that the whole dinuclear complex unit is not rigid and that

the acetate groups are the only portion of it which approach rigidity. The problem was to perform a rigid-body analysis for each acetate  $\text{CCO}_2$  group and then to compute the six  $\beta_{ij}^R$  terms of each hydrogen atom which correspond to the parameters established for the rigid-body motion. However, as is implied by Schomaker & Trueblood (1968) and stated explicitly by Johnson (1970*c*), a singularity occurs in the solution of the normal equations in the least-squares rigid-body analysis when only four atoms in a plane arrangement define the rigid body. By use of the program *ORSBA*, the  $U_{ij}$ 's\* corresponding to the  $\beta_{ij}^R$ 's of the methyl hydrogen atoms from the standard least-squares refinement of the crystal structure were included as observations for a segmented-body analysis. Each of the two acetate groups was treated as two rigid segments,  $\text{O}_2\text{C}$  and  $\text{CH}_3$ , in relative motion about the C-C axis. The use of the  $U_{ij}$ 's of the hydrogen atoms removed the singularity and yielded a description of the rigid motion of each group. The standard deviation of an observation of unit weight (which in this case was just the root-mean-square  $\Delta U_{ij}$  corrected according to the number of degrees of freedom) was  $0.0014 \text{ \AA}^2$  for acetate group 1, which includes atoms O(1), O(2), C(1), and C(2), and  $0.0028 \text{ \AA}^2$  for acetate group 2, which includes O(3), O(4), C(3), and C(4). The desired  $\beta_{ij}^R$ 's for the methyl hydrogen atoms were computed with the program *ORSBA* from the two sets of parameters for segmented-body motions of the two acetate groups.

The calculation with *ORSBA* also yielded, as one of the parameters of motion of the segmented-body, the root-mean-square amplitude of torsional oscillation about the C-C bond of each acetate group (see Table 4). It also provided corrected values for the bond lengths and angles in the acetate groups, the corrections being calculated as combinations of the effects of

\* The  $U_{ij}$ 's which are the observational data for the rigid-body least-squares analysis are the components of the tensors of mean-square vibrational displacement referred to a Cartesian coordinate system. Unit weight was used for each observation.

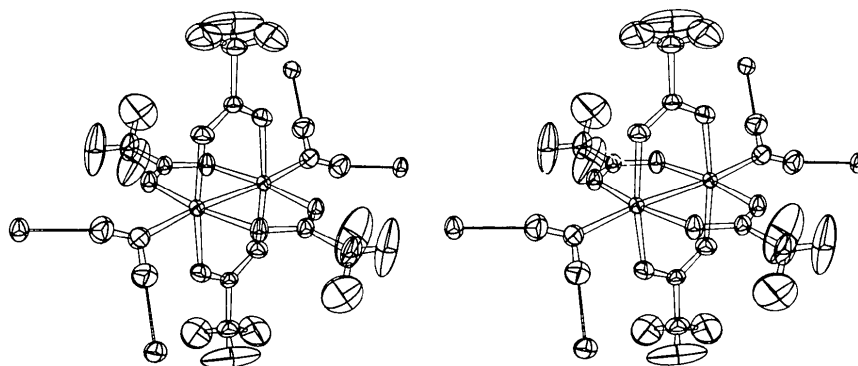


Fig. 1. Stereoscopic view of the dinuclear unit  $\text{Cu}_2(\text{O}_2\text{CCH}_3)_4 \cdot 2\text{H}_2\text{O}$  plus four hydrogen-bonded oxygen atoms of adjacent units. The 50% probability ellipsoids (Johnson, 1970*a*) from the preliminary refinement are shown. Atoms may be identified by reference to Fig. 2, which shows the unit in about the same orientation with atoms labelled.

rigid and riding motions as appropriate. The C-H bond lengths corrected in this manner are included in Table 3.

The  $\beta_{ij}^R$ 's of the methyl hydrogen atoms were used as constants in further least-squares refinement with a special version of the program *ORFLS* which incorporates the torsional-oscillator model. Except for the parameters  $\delta^2$  and  $U_{ij}$  of the methyl hydrogen atoms, the same parameters were adjusted as in the standard refinement. In the final refinement cycle the largest ratio of parameter shift to standard error was 0.04. The final measures of goodness of fit are shown in Table 2.

We consider that the improvement in the fit of the  $F_o^2$ 's to the  $F_o^2$ 's resulting from the use of the torsional-oscillator model is significant, mainly from the fact that the calculated C-H bond lengths became much more nearly acceptable (see Table 3 and *Discussion* below). To weigh the significance of the improved fit, one may also use the *R*-factor ratio test (Hamilton, 1965). The hypothesis is that the thermal motion of the six methyl hydrogen atoms is properly taken into account by use of the usual six-parameter anisotropic temperature factors. The hypothesis is not linear and its dimension is not well defined, since there must be some redun-

dance between the 24 new parameters ( $\delta^2$ 's and  $U_{ij}$ 's) and the 36  $\beta_{ij}$ 's of hydrogen atoms used in estimating the  $\beta_{ij}^R$ 's; however, as a basis of discussion one may take the dimension to be 24. For this dimension and 2167 degrees of freedom, the 0.005 probability point,  $\mathcal{R}_{24, 2167, 0.005}$ , is 0.01. The observed ratio,  $\mathcal{R}$ , is 1.08. Therefore, the hypothesis may be strongly rejected, especially so as 24 is probably an overestimate of the dimension.

The final parameters and their standard errors are represented in Table 5. The Table includes for each methyl hydrogen atom the  $\beta_{ij}$ 's from the preliminary standard refinement and the  $\beta_{ij}^R$ 's from the segmented-body analysis, as well as the  $\delta^2$ 's and  $U_{ij}$ 's of the new model. It also includes the nuclear scattering lengths,\*

\* In reply to a question from a referee, we note that there are six correlation coefficients among the scattering lengths and between the scattering lengths and other parameters that exceed 0.3 in magnitude. The largest in magnitude is the 0.701 between the scale factor and the scattering length of the oxygen atoms. Although some of the coefficients are moderately large, the validity of our least-squares refinement is in no way impaired by them. There are, in fact, 69 correlation coefficients among other parameters spanning the same range of magnitude.

Table 5. *Structure parameters for copper acetate monohydrate, with standard errors in parentheses*

(a) Coordinates ( $\times 10^5$ ) of all atoms; anisotropic thermal parameters  $\beta_{ij}$  ( $\times 10^5$ ) of all atoms except methyl hydrogen atoms; thermal parameters  $\delta$  ( $^\circ$ ) ( $\times 10$ ) and  $U_{ij}$  ( $\text{\AA}^2$ ) ( $\times 10^4$ ) of the methyl hydrogen atoms.

Atom	X	Y	Z	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Cu	45018 (06)	8393 (11)	4504 (06)	262 (05)	549 (10)	242 (05)	31 (06)	128 (03)	12 (06)
O(1)	68393 (10)	-8857 (18)	10069 (09)	311 (07)	937 (17)	269 (06)	121 (10)	97 (05)	-8 (09)
O(2)	60004 (10)	6002 (18)	17564 (09)	330 (07)	1008 (20)	269 (06)	88 (09)	79 (05)	-74 (09)
O(3)	49239 (13)	-26436 (17)	-30 (13)	544 (10)	633 (16)	508 (08)	-74 (10)	296 (08)	37 (10)
O(4)	40512 (13)	-12053 (17)	7491 (13)	487 (09)	733 (17)	538 (09)	-8 (10)	307 (08)	102 (10)
O(W)	37544 (15)	20799 (20)	13294 (12)	703 (12)	1098 (21)	432 (09)	391 (13)	401 (09)	206 (11)
C(1)	68233 (08)	-2060 (13)	18032 (08)	275 (05)	757 (13)	232 (05)	30 (07)	69 (04)	14 (07)
C(2)	78455 (12)	-3672 (23)	28871 (10)	457 (08)	1741 (27)	304 (06)	306 (13)	-7 (06)	-40 (11)
C(3)	43418 (09)	-24892 (14)	5032 (09)	318 (06)	641 (13)	337 (06)	-68 (08)	109 (05)	112 (07)
C(4)	39634 (12)	-39571 (18)	8397 (12)	572 (09)	909 (19)	587 (09)	-167 (11)	246 (07)	240 (10)
H(1)	31355 (26)	27868 (36)	11251 (24)	694 (20)	1250 (40)	606 (18)	290 (24)	347 (16)	87 (21)
H(2)	38439 (27)	15823 (37)	19846 (22)	789 (22)	1416 (43)	506 (16)	235 (25)	400 (16)	182 (21)
				$\delta$	$U_{11}$	$U_{22}$	$U_{12}$		
H(3)	85209 (40)	-10261 (100)	28429 (35)	249 (7)	138 (15)	43 (25)	-42 (15)		
H(4)	81516 (50)	7686 (71)	32482 (47)	219 (6)	113 (19)	66 (37)	6 (22)		
H(5)	75600 (52)	-9478 (138)	34442 (41)	270 (8)	123 (19)	51 (42)	-36 (23)		
H(6)	30405 (36)	-40780 (65)	3624 (54)	192 (5)	90 (20)	143 (26)	-21 (19)		
H(7)	43554 (59)	-49805 (47)	6749 (64)	232 (5)	139 (18)	123 (33)	-28 (19)		
H(8)	41575 (95)	-38648 (80)	16938 (46)	283 (8)	200 (23)	11 (32)	-76 (22)		

(b) For the methyl hydrogen atoms, the anisotropic thermal parameters  $\beta_{ij}$  ( $\times 10^4$ ) from the preliminary refinement and the parameters  $\beta_{ij}^R$  ( $\times 10^4$ ) from the segmented-body analysis. The parameters  $\beta_{ij}$  and  $\beta_{ij}^R$  are for temperature-factor expressions of the form  $\exp[-h^2\beta_{11} - k^2\beta_{22} - l^2\beta_{33} - 2hk\beta_{12} - 2hl\beta_{13} - 2kl\beta_{23}]$ .

Atom	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	$\beta_{11}^R$	$\beta_{22}^R$	$\beta_{33}^R$	$\beta_{12}^R$	$\beta_{13}^R$	$\beta_{23}^R$
H(3)	85 (03)	473 (17)	81 (03)	124 (07)	-16 (3)	-67 (6)	44	196	46	42	-7	-13
H(4)	119 (05)	260 (12)	117 (05)	29 (07)	-54 (4)	-73 (7)	39	239	59	16	-7	-65
H(5)	133 (06)	658 (28)	64 (03)	-6 (11)	6 (3)	119 (8)	100	264	29	69	17	36
H(6)	82 (03)	224 (09)	183 (07)	-56 (05)	41 (4)	60 (7)	54	111	109	-29	46	-8
H(7)	168 (07)	114 (06)	267 (10)	20 (05)	147 (7)	74 (6)	48	69	70	-13	10	27
H(8)	375 (15)	288 (13)	89 (04)	-156 (12)	105 (7)	21 (6)	133	138	69	-34	56	35

(c) Neutron scattering lengths, in units of  $10^{-12}$  cm.

Scattering amplitudes C, 0.661 Cu, 0.760 (4) O, 0.578 (3) H, -0.371 (3)

Table 6. Structure-factor table
See text for explanation.

Table with multiple columns of numerical data representing structure factors for various hkl reflections. The table is organized into several sections, each starting with a header row indicating the reflection indices (h, k, l) and their corresponding Miller indices. The data values are arranged in columns, with some cells containing asterisks or other symbols indicating specific conditions or errors.

which are not significantly different from those in the compilation published by the Neutron Diffraction Commission (1969).

The observed structure-factor magnitudes  $|F_o|$  and the calculated structure factors  $F_c$  are listed in Table 6, both on the absolute scale in units of  $10^{-13}$  cm. For each reflection for which  $F_o^2$  is greater than or equal to  $\sigma(F_o^2)$ , the standard error  $\sigma(F_o)$ , computed as  $\sigma(F_o^2)/2|F_o|$ , is given in units of  $10^{-14}$  cm; for the other reflections the errors  $\sigma(F_o^2)$  are given (in units of  $10^{-25}$  cm<sup>2</sup>), with minus signs attached to indicate that the reflections are weak. The 113 reflections marked *U* were omitted in the final refinement cycles because their phase signs were considered undetermined. The 35 reflections of highest intensity, marked *X*, were omitted to minimize effects of extinction (mild effects amounting in no case to a reduction of intensity or more than about 11%). Reflection  $4,0,\bar{2}1$  was also omitted because its intensity measurement was considered unreliable.

### Discussion

#### *The torsional oscillations and the CH<sub>3</sub> groups*

Table 4 compares the root-mean-square torsional amplitudes,  $\delta$ 's, found for the individual methyl hydrogens with corresponding estimates made from the largest principal-axis displacements calculated from the  $\beta_{ij}$ 's from the normal refinement and with the two amplitudes for CH<sub>3</sub> groups calculated by the segmented-body analysis previously described. The spread of the individual amplitudes from the torsional-oscil-

lator model within each methyl group, especially within the C(4) methyl, is a little disappointing, but the general agreement with the other estimates is encouraging.

The C-H bond lengths calculated directly from the parameters derived in the torsional-oscillator refinement are clearly to be preferred over any values that we have been able to calculate from the parameters from the normal refinement (see Table 3). There is a range of 0.039 Å in the bond lengths, but the r.m.s. deviation from the average is only two or three times the standard error of an individual length. The average length 1.093 Å is close to the mean separation  $1.107 \pm 0.001$  Å reported by Bartell, Kuchitsu & DeNeui (1961) from an electron-diffraction study of gaseous methane. We judge that so far as the accuracy of the C-H bond lengths is concerned the results from use of the new model are moderately satisfactory.

The model appears to be at least as successful in this application as the King & Lipscomb (1950) model has been as applied to the motion of the cyclopentadienyl rings in (C<sub>5</sub>H<sub>5</sub>FeS)<sub>4</sub> (Schunn, Fritchie & Prewitt, 1965) and to the motion of the methyl groups in hexamethylbenzene (Hamilton, Edmonds & Tippe, 1969). In each case physically realistic bond lengths have been obtained by taking explicit account in the least-squares refinement of curvilinear motions of atoms.

It is of interest also to compare the C-H distances with those resulting from a refinement performed by our colleague Dr C. K. Johnson which was based on the same set of data but which used the three-cumulant

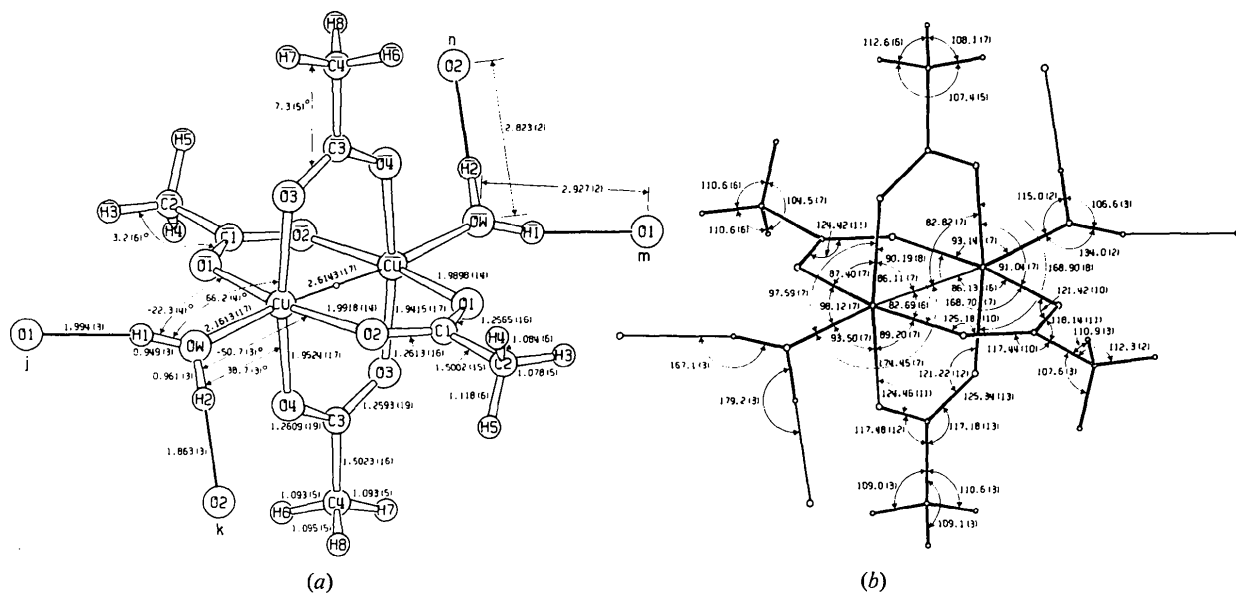


Fig. 2. The geometry of the dinuclear unit in copper(II) acetate monohydrate and of the hydrogen bonds. (a) Interatomic distances (Å) and selected torsion angles. Each of the latter is distinguished by a degree symbol (°) and by a double-headed arrow pointing to two bonds at opposite ends of the particular bond about which the torsion angle is measured. The letters *j*, *k*, *m*, and *n* adjacent to the oxygen atoms hydrogen-bonded to the water molecules identify symmetry transformations (see Table 8). The superscript bars in some of the atom symbols denote inversion through the center at  $\frac{1}{2}, 0, 0$  (transformation *i*). (b) Valence angles and angles of hydrogen bonds (°).

model (Johnson, 1969, 1970*b*). The fit of parameters to data in his refinement is better than in ours (see Table 2); but it is not clear what part of the improvement is to be attributed to use of the three-cumulant model for the methyl hydrogens, since the model was also used for all of the other atoms. Johnson's refinement also included calculation of extinction corrections, which may well affect the goodness-of-fit parameters without making the structure parameters any more reliable than those from our refinement, in which the data which seemed to be affected by the moderate degree of extinction were omitted. The intermode C–H distances calculated from Johnson's parameters by use of the Edgeworth expansion are included in Table 3. These are the distances between the most probable positions for the atoms, which in principle, subject to the tests of experience, might be expected to be the best measures of the C–H bond distances. In each methyl group two of the C–H intermode distances are nearly correct and one is much too short, for reasons not known.

The angle parameters which describe each methyl group are given in Fig. 2. They describe somewhat distorted methyl groups, though the distortion for the C(2) methyl is not quite so great as appeared from the parameters of the normal least-squares refinement. The angle distortions and the variations in C–H bond lengths probably reflect imperfections in the torsional-oscillator model in its present form. Another indication of imperfection of the model is the fact that the three  $U_{ij}$ 's in Table 5 for atom H(8) do not define a positive-definite quadratic form. The  $U_{ij}$ 's of the other five hydrogen atoms seem generally reasonable.

Possibly it would be preferable to use a model in which a single parameter  $\delta^2$  is used for each methyl group, perhaps with constraint to the ideal trigonal geometry (point group  $3m$ ). With only a single  $\delta^2$  it might be possible to adjust simultaneously six ordinary  $\beta_{ij}$ 's for each atom without encountering a singular matrix, thereby taking care of the other modes of motion.

Final Fourier difference syntheses were made through the center of each methyl hydrogen atom in the plane perpendicular to the appropriate C–C axis. The peaks (see Fig. 3) are somewhat smeared out, consistent with the large-amplitude oscillations. They do not have exactly the sausage-like shapes that might be expected for pure oscillatory motion, probably because of the perturbing effects of other modes of motion. The general shapes and orientations of the low-lying contours are strikingly similar to those of the corresponding Edgeworth density maps computed from the parameters of the three-cumulant refinement (see Fig. 2 of Johnson, 1969).

Comparison of the final structure parameters with those obtained from our preliminary refinement shows that there are only slight effects on the parameters derived for the other atoms when the model is changed for the methyl hydrogens. Specifically, the only changes in coordinates as large as their standard errors were

changes of  $1.3\sigma_x$  and  $1.1\sigma_y$  for atom C(4). There were five comparable changes in the  $\beta_{ij}$ 's, two each for C(1) and C(3) and one for H(2). Other changes were on the average much smaller. Clearly the large-amplitude torsional motions of the methyl hydrogens constituted no serious problem so far as the determination of reliable parameters for the other atoms was concerned.

#### The dinuclear complex unit

The structure of the dinuclear complex unit in Cu(II) acetate monohydrate is described in detail by the bond lengths, valence angles, and torsion angles (Klyne & Prelog, 1960) in Fig. 2. Various least-squares best planes and deviations from them are shown in Table 7. Table 8 defines the symmetry transformations implied by the superscript letters used in the atom symbols in this paper.

The vector  $\text{Cu} \rightarrow \text{Cu}'$  within the dinuclear unit makes angles of  $44.05(6)$ ,  $123.36(6)$ , and  $134.88(6)^\circ$  with the axial vectors **a**, **b**, and **c**, respectively. The angle  $123.36^\circ$  corresponds to angles between the Cu–Cu axes and the (010) plane of  $\pm 33.36^\circ$ , remarkably close to the values  $\pm 33.3^\circ$  recently reported by Gregson, Martin & Mitra (1971) from measurements of magnetic anisotropy and to the values  $\pm 33^\circ$  from studies of electron spin resonance (Bleaney & Bowers, 1952; Koszka, Allen & Gordon, 1965). The projection of  $\text{Cu} \rightarrow \text{Cu}'$  on the  $xz$  plane of the unit cell makes an angle  $32.36(5)^\circ$  with **c**, in agreement with the value  $33^\circ$  reported from both anisotropy and e.s.r. measurements.

The Cu–Cu' distance is  $2.6143(17) \text{ \AA}$ , significantly closer than the  $2.64 \text{ \AA}$  reported by van Niekerk & Schoening to the distance  $2.556 \text{ \AA}$  in metallic copper. This fact strengthens somewhat the arguments for direct electronic interaction between the two Cu atoms in the unit. Since the Cu–Cu' distance is hardly distinguishable from the distance  $2.6010(1) \text{ \AA}$  found by O'Connor & Maslen (1966) in Cu(II) succinate dihydrate, the explanation of these authors for the fact that the succinate has a slightly lower magnetic moment at room temperature than the acetate seems invalid.

Variations of length among chemically equivalent bonds are comparable in the acetate and succinate complexes, and the average Cu–O, C–O, and C–C

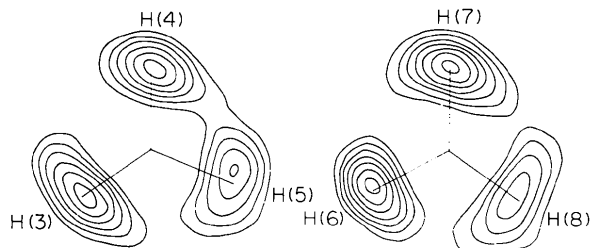


Fig. 3. Final difference maps showing nuclear scattering density in each group of three methyl hydrogen atoms. Contours are all negative; the outermost contour is at the level  $-0.2 \times 10^{12} \text{ cm}^{-2}$ ; the contour interval is  $0.1 \times 10^{12} \text{ cm}^{-2}$ .



distances are in close agreement. The most striking structural difference between the acetate and succinate dinuclear units appears for the bond length Cu–O(*W*),

Table 7. Equations of least-squares best planes through various groups of atoms, and deviations (Å) from the best planes

In each equation *X*, *Y*, and *Z* represent fractional coordinates in the crystal system; their coefficients are the components referred to the reciprocal base vectors of the unit normal from origin to plane. Positive deviations are in the direction of this normal. For each plane, only the atoms not marked with asterisks were used in establishing the equation.

Plane	Equations and deviations			
1	6.6833 <i>X</i> + 7.0910 <i>Y</i> – 6.1349 <i>Z</i> = 3.3417 Å			
	Cu	–0.0141 Å	C(1)*	–0.0339 Å
	Cu <sup>i</sup>	0.0140	C(2)*	–0.1299
	O(1)	–0.0165	O( <i>W</i> )*	–0.1733
	O(2)	0.0166		
2	6.4376 <i>X</i> – 0.2240 <i>Y</i> + 7.6885 <i>Z</i> = 3.2188 Å			
	Cu	0.0067 Å	C(3)*	0.0189 Å
	Cu <sup>i</sup>	–0.0067	C(4)*	0.0669
	O(3)	0.0079	O( <i>W</i> )*	0.1737
	O(4)	–0.0078		
3	7.2030 <i>X</i> + 6.9829 <i>Y</i> – 5.7795 <i>Z</i> = 3.7267 Å			
	O(1)	–0.0007 Å	C(1)	0.0020 Å
	O(2)	–0.0007	C(2)	–0.0006
4	6.5746 <i>X</i> + 0.0388 <i>Y</i> + 7.5547 <i>Z</i> = 3.2248 Å			
	O(3)	–0.0001 Å	C(3)	0.0002 Å
	O(4)	–0.0001	C(4)	–0.0001
5	9.4515 <i>X</i> – 4.4899 <i>Y</i> – 10.177 <i>Z</i> = 3.6110 Å			
	O(1 <sup>i</sup> )	0.0033 Å	O(3 <sup>i</sup> )	–0.0034 Å
	O(2)	0.0032	O(4)	–0.0032
			Cu*	–0.1913
6	7.4160 <i>X</i> + 6.9275 <i>Y</i> – 5.6238 <i>Z</i> = 3.5859 Å			
	Cu	0.0809 Å	Cu <sup>i</sup>	–0.0809 Å
	O(1 <sup>i</sup> )	–0.0621	O(1 <sup>j</sup> )	0.0621
	O( <i>W</i> )	–0.1084	O( <i>W</i> <sup>i</sup> )	0.1084
	H(1)	0.0373	H(1 <sup>i</sup> )	–0.0373
7	5.9121 <i>X</i> + 7.3099 <i>Y</i> – 6.0868 <i>Z</i> = 2.9576 Å			
	Cu	0.0433 Å	O( <i>W</i> <sup>k</sup> )	0.0210 Å
	O(2)	–0.0405	H(2 <sup>k</sup> )	0.0031
	O( <i>W</i> )	–0.0268		
8	5.8085 <i>X</i> + 6.1040 <i>Y</i> + 3.9547 <i>Z</i> = 3.9754 Å			
	O(1 <sup>j</sup> )	0.0026 Å	H(1)	–0.0081 Å
	O(2 <sup>k</sup> )	–0.0031	H(2)	0.0080
	O( <i>W</i> )	0.0006		

Table 8. Definition of symmetry transformations implied by the superscript letters *i, j, ... n* used in the atom designations

Superscript	Atom position		
none	<i>x</i>	<i>y</i>	<i>z</i>
<i>i</i>	1 – <i>x</i>	– <i>y</i>	– <i>z</i>
<i>j</i>	–½ – <i>x</i>	½ + <i>y</i>	<i>z</i>
<i>k</i>	1 – <i>x</i>	<i>y</i>	½ – <i>z</i>
<i>l</i>	½ – <i>x</i>	½ – <i>y</i>	– <i>z</i>
<i>m</i>	¾ – <i>x</i>	–½ – <i>y</i>	– <i>z</i>
<i>n</i>	<i>x</i>	– <i>y</i>	–½ + <i>z</i>

which is 2.1613 (14) Å in the acetate and 2.102 (7) Å in the succinate. This difference, which amounts to about eight times its standard error, is highly significant.

In the acetate the bond lengths Cu–O(1<sup>i</sup>) and Cu–O(2) of 1.9898 (11) and 1.9918 (11) Å are significantly longer than the bonds lengths Cu–O(3<sup>i</sup>) and Cu–O(4) of 1.9415 (14) and 1.9524 (14) Å. A reasonable explanation is that the bonds Cu–O(1<sup>i</sup>) and Cu–O(2) are weakened relative to Cu–O(3<sup>i</sup>) and Cu–O(4) because there are hydrogen bonds (see further discussion below) to O(1) and O(2) but not to O(3) and O(4). A closely similar pattern of metal–oxygen bond lengths is observable in the isostructural Cr(II) compound (Cotton *et al.*, 1971). The lengthening effect of hydrogen bonding on the Rh–O distances is not so clearly observable in the Rh(II) compound, though there is a suggestion of it, as there is also in Cu(II) succinate dihydrate.

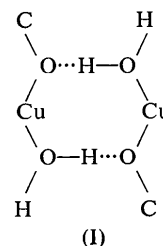
The acute angle between the least-squares best planes of the two atomic groups Cu, Cu<sup>i</sup>, O(1), O(2) and Cu, Cu<sup>i</sup>, O(3), O(4) (see planes 1 and 2 of Table 7) is 88.3°; the corresponding angle\* between the best planes (planes 3 and 4) of the two groups CCO<sub>2</sub> is 83.5°.

In each of the two acetate groups, one of the hydrogen atoms is nearly eclipsed with respect to one of the oxygen atoms (see torsion angles in Fig. 2). The conformations about the C–C bonds are thus consistent with those found for the corresponding bonds in gaseous acetaldehyde (Kilb, Lin & Wilson, 1957), gaseous acetic acid (Derissen, 1970), crystalline acetic acid (Nahringbauer, 1970; Jönsson, 1971), hydrazinium acetate (Abdel-Hady, Nahringbauer & Olovsson, 1969), and the 1:1 complex of ammonium acetate and acetic acid (Nahringbauer, 1969).

#### The water molecule, hydrogen bonding, and molecular packing

Fig. 4 shows a stereoscopic view of the crystal structure in a direction about 20° from *b*. The structure is held together by a three-dimensional network of hydrogen bonds from the water molecules to the oxygen atoms O(1) and O(2) of one of the two acetate groups.

Two kinds of ring structure with linkages generally as shown in (I) are formed by the hydrogen bonds. One kind of ring structure involves atoms H(1) and O(1);



\* This angle was incorrectly given as 88° in our preliminary report (Chidambaram & Brown, 1972).

the rings are nearly plane arrangements (see plane 6, Table 7) about the symmetry centers at  $\frac{1}{4}, \frac{1}{4}, 0$  and equivalent positions. This arrangement resembles the centrosymmetric configuration often produced by dimerization of carboxylic acids in the crystalline state (Jeffrey & Sax, 1963). Each dinuclear unit  $\text{Cu}_2(\text{O}_2\text{CCH}_3)_4 \cdot 2\text{H}_2\text{O}$  is connected to two of its neighbors in this mode of H-bonding, so that infinite chains of the units are formed.

The other type of hydrogen-bonded ring structure involves H(2) and O(2); the rings are symmetrical about the twofold axes at  $\frac{1}{2}, y, \frac{1}{4}$  and equivalent locations. Each dinuclear unit in a given chain held together by the first kind of hydrogen bonding described is also connected by bonds of this second type to two other units, each in a different chain. Within the reference ring structure of twofold symmetry, the atoms Cu, O(2), O(W), O(W<sup>k</sup>), and H(2<sup>k</sup>) are very nearly coplanar (plane 7, Table 7), and so of course are the atoms Cu<sup>k</sup>, O(2<sup>k</sup>), O(W), O(W<sup>k</sup>) and H(2). The obtuse angle between the best planes of the two groups of atoms is 117.8°.

The angles and distances describing the water molecule and the two crystallographically distinct kinds of hydrogen bonds are included in Fig. 2. The hydrogen bonds involved in the centrosymmetric rings discussed above are slightly bent, having O-H...O angles of 167.0 (3)°; the other bonds, those of the rings about twofold axes, have angles of 179.3 (4)°.

In each hydrogen bond the O-H bond of the water molecule is oriented nearly along the line of the bisector of the obtuse angle Cu-O-C at the acceptor oxygen atom - that is, nearly along the axis of a lone pair of electrons if the oxygen atoms are considered to be in  $sp^2$  hybridization. Thus, the angles Cu-O(1<sup>i</sup>)...H(1<sup>i</sup>) and C(1<sup>i</sup>)-O(1<sup>i</sup>)...H(1<sup>i</sup>) are 115.24 (11) and 123.17 (12)°; and the angles Cu-O(2)...H(2<sup>k</sup>) and C(1)-O(2)...H(2<sup>k</sup>) are 116.56 (12) and 118.20 (13)°. The O(1<sup>i</sup>)...H(1<sup>i</sup>) line makes an angle 4.2° with respect to the plane of Cu-O(1<sup>i</sup>)-C(1<sup>i</sup>), and the O(2)...H(2<sup>k</sup>) line

makes an angle 2.6° with respect to the plane of Cu-O(2)-C(1). The approximate trigonal symmetry of the bonds about the oxygen atoms recalls the similar configurations about the acceptor atoms in dimers of carboxylic acids and in hydrogen-bonded carboxylate ions, for example, in ammonium oxalate monohydrate (Robertson, 1965) and in potassium oxalate monohydrate (Chidambaram, Sequeira & Sikka, 1964; Hodgson & Ibers, 1969; Sequeira, Srikanta & Chidambaram, 1970). It supports the view of Robertson (1964) that lone pairs of oxygen atoms in  $sp^2$  hybridization are of stereochemical significance in the hydrogen bonding of carboxyl and carboxylate groups. However, the degree of significance of the lone-pair directions continues to be under discussion (Donohue, 1968; Chidambaram, Balasubramanian & Ramachandran, 1970).

The apparent O-H distances within the water molecule are 0.949 (3) and 0.961 (3) Å; after correction by use of the 'riding' model (Busing & Levy, 1964), which should be a fair approximation in this case, the distances become 0.959 and 0.971 Å. The H-O-H angle is 106.6 (3)° (uncorrected). These molecular parameters show that the molecule is very little perturbed from the structure in the gaseous state, which is described by the parameters 0.9572 (3) Å and 104.52 (5)° from the infrared spectroscopic analysis of Benedict, Gailar & Plyler (1956). The water oxygen atom is trigonally coordinated; the bisector of its lone pairs makes an angle of 20.9 (2)° with the bond O(W)-Cu, which is bent out of the plane of the water molecule by 18.3°. The coordination is thus approximately type *D* in the classification scheme of Chidambaram, Sequeira & Sikka (1964). A similar situation was described by Cotton *et al.* in the Cr(II) compound.

The three atoms of the water molecule and the two acceptor oxygen atoms to which it is hydrogen bonded are very nearly coplanar (plane 8, Table 7). The angle O(1<sup>i</sup>)...O(W)...O(2<sup>k</sup>) is 97.7 (1)°. The bending of the bond O(W)-H(1)...O(1<sup>i</sup>) is an accommodation to the difference between the angles H-O-H and O...O...O.

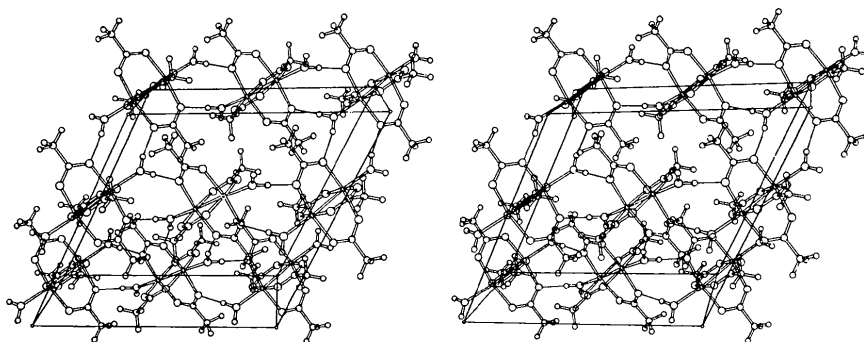


Fig. 4. Stereoscopic view of the crystal structure of copper(II) acetate monohydrate. The direction of view is about 20° away from the direction of the axis *b*. Axis *c* is approximately horizontal from left to right, and axis *a* runs from top to bottom about 25° from the vertical. The parallelepiped shown is symmetrical about the point  $\frac{1}{2}, 0, \frac{1}{2}$ , with edges equal to *a*, *b*, and *c* on the scale of the drawing.

The angles which the  $p$ - $p$  vector  $H(1) \rightarrow H(2)$  of the water molecule makes with respect to the axial vectors  $\mathbf{a}$ ,  $\mathbf{b}$ , and  $\mathbf{c}$  are 75.2, 132.4, and 59.9°. The projection of the  $p$ - $p$  vector on the  $xz$  plane makes an angle of 47.3° with respect to  $\mathbf{c}$ . These angles confirm the essential correctness of the orientation deduced by Kawamori (1966) in an n.m.r. study. The  $H(1) \cdots H(2)$  distance is 1.531 (4) Å, to be compared with Kawamori's value  $1.58 \pm 0.02$  Å.

We thank Drs H. A. Levy and C. K. Johnson for helpful advice and discussion.

### References

- ABDEL-HADY, S., NAHRINGBAUR, I. & OLOVSSON, I. (1969). *Acta Chem. Scand.* **23**, 2764–2772.
- BACON, G. E. (1962). *Neutron Diffraction*. Oxford Univ. Press.
- BAIRD, M. C. (1968). In *Progress in Inorganic Chemistry*, Vol. 9, pp. 1–159. Edited by F. A. COTTON. New York: Interscience.
- BARCLAY, G. A. & KENNARD, C. H. L. (1961). *J. Chem. Soc.*, pp. 5244–5251.
- BARTELL, L. S., KUCHITSU, K. & DE NEUI, R. J. (1961). *J. Chem. Phys.* **35**, 1211–1218.
- BENEDICT, W. S., GAILAR, N. & PLYLER, E. K. (1956). *J. Chem. Phys.* **24**, 1139–1165.
- BLEANEY, B. & BOWERS, K. D. (1952). *Proc. Roy. Soc. A* **214**, 451–465.
- BROWN, G. M. & CHIDAMBARAM, R. (1969). *Acta Cryst.* **B25**, 676–687.
- BROWN, G. M. & LEVY, H. A. (1964). *J. Phys. Radium*, **25**, 497–502.
- BROWN, G. M. & WALKER, L. A. (1966). *Acta Cryst.* **20**, 220–229.
- BUSING, W. R., ELLISON, R. D., LEVY, H. A., KING, S. P. & ROSEBERRY, R. T. (1968). *The Oak Ridge Computer-Controlled X-ray Diffractometer*. Report ORNL-4143, Oak Ridge National Laboratory.
- BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 180–182.
- BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142–146.
- BUSING, W. R., SMITH, H. G., PETERSON, S. W. & LEVY, H. A. (1964). *J. Phys. Radium*, **25**, 495–496.
- CHIDAMBARAM, R. & BROWN, G. M. (1972). *Cryst. Struct. Commun.* **1**, 269–272.
- CHIDAMBARAM, R., BALASUBRAMANIAN, R. & RAMACHANDRAN, G. N. (1970). *Biochim. Biophys. Acta*, **221**, 182–195.
- CHIDAMBARAM, R. & BROWN, G. M. (1973). *Acta Cryst.* **B29**, 2388–2392.
- CHIDAMBARAM, R., SEQUEIRA, A. & SIKKA, S. K. (1964). *J. Chem. Phys.* **41**, 3616–3622.
- COTTON, F. A., DEBOER, B. G., LAPRADE, M. D., PIPAL, J. R. & UCKO, D. A. (1971). *Acta Cryst.* **B27**, 1664–1671.
- CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 757–758.
- DRISSEN, J. L. (1970). Cited by NAHRINGBAUR (1970).
- DONOHUE, J. (1968). *Acta Cryst.* **B24**, 1558–1560.
- EL SAFFAR, Z. M. & BROWN, G. M. (1970). *Acta Cryst.* **B27**, 66–73.
- GOODGAME, D. M. L., HILL, N. J., MARSHAM, D. F., SKAPSKI, A. C., SMART, M. L. & TROUGHTON, P. G. H. (1969). *Chem. Commun.* pp. 629–630.
- GREGSON, A. K., MARTIN, R. L. & MITRA, S. (1971). *Proc. Roy. Soc. A* **320**, 473–486.
- HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.
- HAMILTON, W. C., EDMONDS, J. W. & TIPPE, A. (1969). *Discuss. Faraday Soc.* **48**, 192–204.
- HANIC, F., ŠTEMPELOVÁ, D. & HANICOVÁ, K. (1964). *Acta Cryst.* **17**, 633–639.
- HODGSON, D. J. & IBERS, J. A. (1969). *Acta Cryst.* **B25**, 469–477.
- International Tables for X-ray Crystallography* (1952). Vol. I. Birmingham: Kynoch Press.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- JEFFREY, G. A. & SAX, M. (1963). *Acta Cryst.* **16**, 430.
- JOHNSON, C. K. (1969). *Acta Cryst.* **A25**, 187–194.
- JOHNSON, C. K. (1970a). *ORTEP*. Report ORNL-3794 (2nd rev.), Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- JOHNSON, C. K. (1970b). In *Thermal Neutron Diffraction*, pp. 132–160. Edited by B. T. M. WILLIS. Oxford Univ. Press.
- JOHNSON, C. K. (1970c). In *Crystallographic Computing*, pp. 207–219. Edited by F. R. AHMED. Copenhagen: Munksgaard.
- JÖNSSON, P.-G. (1971). *Acta Cryst.* **B27**, 893–898.
- KATO, M., JONASSEN, H. B. & FANNING, J. C. (1964). *Chem. Rev.* **64**, 99–128.
- KAWAMORI, A. (1966). *J. Phys. Soc. Japan*, **21**, 1096–1103.
- KILB, R. W., LIN, C. C. & WILSON, E. B. JR (1957). *J. Chem. Phys.* **26**, 1695–1703.
- KING, M. V. & LIPSCOMB, W. N. (1950). *Acta Cryst.* **3**, 155–158.
- KLYNE, W. & PRELOG, V. (1960). *Experientia*, **16**, 521–523.
- KOKOSZKA, G. F., ALLEN, H. C. & GORDON, G. (1965). *J. Chem. Phys.* **42**, 3693–3697.
- NAHRINGBAUR, I. (1969). *Acta Chem. Scand.* **23**, 1653–1666.
- NAHRINGBAUR, I. (1970). *Acta Chem. Scand.* **24**, 453–462.
- NEUTRON DIFFRACTION COMMISSION (1969). *Acta Cryst.* **A25**, 391–392.
- NIKERK, J. N. VAN & SCHOENING, F. R. L. (1953). *Acta Cryst.* **6**, 227–232.
- NIKERK, J. N. VAN, SCHOENING, F. R. L. & DE WET, J. F. (1953). *Acta Cryst.* **6**, 501–504.
- O'CONNOR, B. H. & MASLEN, E. N. (1966). *Acta Cryst.* **20**, 824–835.
- OLDHAM, C. (1968). In *Progress in Inorganic Chemistry*, Vol. 10, pp. 223–258. Edited by F. A. COTTON. New York: Interscience.
- PETERSON, S. W. (1962). Unpublished compilation.
- PETERSON, S. W. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 70–76.
- ROBERTSON, J. H. (1964). *Acta Cryst.* **17**, 316.
- ROBERTSON, J. H. (1965). *Acta Cryst.* **18**, 410–417.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
- SCHUNN, R. A., FRITCHIE, C. J. & PREWITT, C. T. (1966). *Inorg. Chem.* **5**, 892–899.
- SEQUEIRA, A., SRIKANTA, S. & CHIDAMBARAM, R. (1970). *Acta Cryst.* **B26**, 77–80.
- WORSHAM, J. E. JR & BUSING, W. R. (1969). *Acta Cryst.* **B25**, 572–578.