

Refined Crystal Structure of Tetra- μ -acetato-bisaquodicopper(II)

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The structure of the title compound has been refined from three-dimensional X-ray diffractometer data. Crystals are monoclinic, space group $C2/c$, with $Z = 4$ in a unit-cell of dimensions: $a = 13.168(2)$, $b = 8.564(2)$, $c = 13.858(2)$ Å, and $\beta = 117.02(1)^\circ$. Full-matrix least-squares refinement, using 1280 independent reflections, has reached R 0.047.

The refinement has, as expected, confirmed the original two-dimensional structure determination and much more accurate bond lengths and bond angles have been obtained: mean Cu-O(acetate) 1.969 Å, Cu-O(water) 2.156, and Cu \cdots Cu is 2.616 Å. The geometry of the acetate bridges is planar and bond lengths and angles are as expected.

THE structure of dimeric copper(II) acetate monohydrate was originally determined¹ from two-dimensional X-ray data. The structure has been the object of much interest ever since, because of the rather short Cu \cdots Cu separation. There has been considerable controversy regarding the origin of the antiferromagnetism of this compound, centred around the question of whether the spin exchange occurs through direct metal-metal bonding or *via* the bridging acetate groups.² While there has never been any doubt about the basic correctness of the original structure, the accuracy was limited, and certain aspects of the geometry of the acetate groups were rather unsatisfactory. This has prompted us to refine this structure on the basis of new diffractometer data.

EXPERIMENTAL

Dark green prisms were crystallised from water.

Crystal Data.— $C_8H_{10}Cu_2O_{10}$, $M = 399.2$, Monoclinic, $a = 13.168(2)$, $b = 8.564(2)$, $c = 13.858(2)$ Å, $\beta = 117.02(1)^\circ$, $U = 1392.2$ Å³, $Z = 4$, $D_c = 1.91$ g cm⁻³, $F(000) = 808$. Cu- K_α radiation, $\lambda = 1.5418$ Å; $\mu(\text{Cu-}K_\alpha) = 44.35$ cm⁻¹. Space group $C2/c$.

Accurate unit-cell dimensions agree reasonably well with previously published values.^{1,3} Two sets of intensity data were collected, since the first set proved to be unsatisfactory, probably due to serious extinction problems. A second set of data was collected from a smaller crystal ($0.13 \times 0.09 \times 0.06$ mm), which had been submitted to thermal shock in liquid nitrogen. This ensured a more pronounced mosaic structure, so as to eliminate extinction as much as possible. The crystal was mounted on a Siemens off-line four-circle diffractometer, and Cu- K_α radiation at a take-off angle of 4.5° , a nickel β filter, and a Na(Tl)I scintillation counter were used. The intensities of 1280 independent reflections were measured (to $\theta = 70^\circ$) using the θ - 2θ

scan technique with a 'five-value' measuring procedure.⁴ Of these 25 were judged to be unobserved as the net count was $< 2.58\sigma$. The data were scaled using a reference reflection and the Lorentz and polarization corrections were applied. At a later stage data were corrected for absorption according to the method of Busing and Levy⁵ with path-lengths determined by the vector analysis procedure of Coppens *et al.*⁶

Refinement of the Structure.—The crystal structure calculations system 'X-Ray '63'⁷ and its updated version of July 1970,⁸ were used to refine this structure.

Anisotropic refinement using the second set of data gave R 0.059, and from a difference Fourier all eight independent hydrogen atoms were located. When these were included in refinement as a fixed contribution, with isotropic temperature factors of their parent atoms R was reduced to 0.052. The data were now corrected for absorption and refinement as previously gave R 0.049. A weighting scheme of the type suggested by Hughes⁹ was now applied with $w = 1$ for $F < F^*$, $\sqrt{w} = F^*/F$ for $F \geq F^*$, with $F^* = 55$ found to be optimum, and R reached its final value of 0.047.

Full-matrix least-squares refinement was used, and the atomic scattering factors were from ref. 10 except those for hydrogen which were taken from ref. 11. The real and the imaginary parts of the anomalous dispersion correction for copper were from ref. 12. Final fractional co-ordinates of the non-hydrogen atoms are listed in Table 1, together with the co-ordinates of the original structure determination. Table 2 shows the coefficients in the expression for the anisotropic temperature factors $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$, and the root-mean-square amplitudes of vibration along the principal axes of the thermal ellipsoid. The co-ordinates of the hydrogen atoms are given in Table 3, and observed and the calculated structure amplitudes are listed in Supplementary Publication No. SUP 20827 (7 pp.).†

⁴ A. C. Skapski and P. G. H. Troughton, *Acta Cryst.*, 1970, B, **26**, 716.

⁵ W. R. Busing and H. A. Levy, *Acta Cryst.*, 1957, **10**, 180.

⁶ P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Cryst.*, 1965, **18**, 1035.

⁷ 'X-ray '63' system of programs, J. M. Stewart, University of Maryland Technical Report TR 64 6.

⁸ X-ray system, version of July 1970, eds. J. M. Stewart, F. A. Kundell, and J. C. Baldwin.

⁹ E. W. Hughes, *J. Amer. Chem. Soc.*, 1941, **63**, 1737.

¹⁰ D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

¹¹ R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

¹² D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

† See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. (Items less than 10 pp. are sent as full-size copies.)

¹ J. N. Van Niekerk and F. R. L. Schoening, *Acta Cryst.*, 1953, **6**, 227.

² B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, 1956, 3837; A. W. Schlenter, R. A. Jacobsen, and R. E. Rundle, *Inorg. Chem.*, 1966, **5**, 277; A. E. Hansen and C. J. Ballhausen, *Trans. Faraday Soc.*, 1964, **60**, 840; G. F. Kokoszka, M. Linzer, and G. Gordon, *Inorg. Chem.*, 1968, **7**, 1730; D. M. L. Goodgame, N. J. Hill, D. F. Marsham, A. C. Skapski, M. L. Smart, and P. G. H. Troughton, *Chem. Comm.*, 1969, 629; R. W. Jotham and S. F. A. Kettle, *Inorg. Chem.*, 1970, **9**, 1390.

³ R. B. Hull, *University of Pittsburgh Bull.*, 1938, **35**, 142.

DISCUSSION

The structure of the dimeric molecule is shown in Figure 1, together with the thermal vibration ellipsoids¹³

TABLE 1

Fractional atomic co-ordinates, with estimated standard deviations in parentheses. For comparison, the co-ordinates obtained by Van Niekerk and Schoening¹ are listed in the lower line

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Cu(1)	0.45004(4)	0.08401(6)	0.04496(4)
	0.450	0.088	0.044
O(1)	0.6836(2)	-0.0881(4)	0.1006(2)
	0.677	-0.100	0.101
O(2)	0.6000(2)	0.0603(4)	0.1759(2)
	0.598	0.050	0.175
O(3)	0.4922(3)	-0.2647(4)	-0.0003(3)
	0.492	-0.250	0.017
O(4)	0.4054(3)	-0.1201(4)	0.0753(3)
	0.400	-0.108	0.087
O(5)	0.3757(3)	0.2073(4)	0.1330(3)
	0.367	0.200	0.132
C(1)	0.6824(3)	-0.0214(5)	0.1804(3)
	0.697	-0.025	0.192
C(2)	0.7837(4)	-0.0380(7)	0.2888(4)
	0.807	-0.008	0.296
C(3)	0.4332(4)	-0.2477(5)	0.0507(3)
	0.427	-0.250	0.063
C(4)	0.3961(4)	-0.3963(6)	0.0836(4)
	0.385	-0.400	0.095

of the non-hydrogen atoms. The more important inter-atomic distances and bond angles are listed in Table 4.

Cr...Cr separation of 2.64 Å in chromium(II) acetate¹⁸ had been taken as evidence² for a weak Cr...Cr interaction, whereas a recent refinement of this structure¹⁴ has

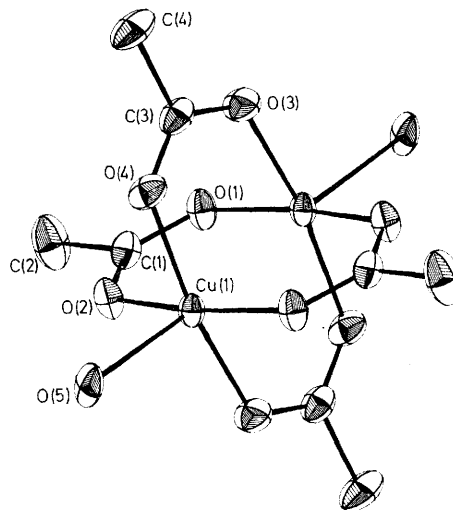


FIGURE 1 The centrosymmetric molecular structure of $[\text{Cu}_2(\text{CH}_3\text{CO}_2)_4\text{H}_2\text{O}]$. The thermal vibration ellipsoids are scaled to enclose 50% probability.

shown the distance to be very much shorter (2.362 Å) suggesting a multiple metal-metal bond.

In the case of dimeric copper acetate, there was no

TABLE 2

Atom	Final anisotropic thermal parameters and root-mean-square amplitudes of vibration (Å)						Min.	Inter.	Max.
	$10^5\beta_{11}$	$10^5\beta_{22}$	$10^5\beta_{33}$	$10^5\beta_{12}$	$10^5\beta_{13}$	$10^5\beta_{23}$			
Cu(1)	273(4)	689(8)	234(3)	20(4)	160(3)	4(4)	0.115	0.142	0.160
O(1)	28(2)	104(5)	26(2)	9(2)	14(2)	-2(2)	0.132	0.142	0.200
O(2)	32(2)	103(5)	24(2)	11(2)	12(2)	-6(2)	0.135	0.144	0.205
O(3)	58(2)	69(4)	52(2)	-6(3)	38(2)	3(2)	0.140	0.172	0.215
O(4)	46(2)	76(4)	50(2)	-2(2)	33(2)	13(2)	0.129	0.176	0.206
O(5)	65(3)	117(5)	39(2)	41(3)	41(2)	21(3)	0.106	0.161	0.258
C(1)	35(3)	87(6)	29(2)	-1(3)	17(2)	5(3)	0.140	0.156	0.182
C(2)	46(4)	189(10)	34(3)	27(5)	8(3)	-10(4)	0.152	0.186	0.285
C(3)	35(3)	83(6)	35(3)	-11(3)	15(2)	10(3)	0.135	0.158	0.202
C(4)	61(4)	96(7)	61(4)	-19(4)	33(3)	25(4)	0.124	0.214	0.248

A number of transition-metal carboxylates have the classic copper acetate dimeric structure.¹⁴⁻¹⁷ Some of the

TABLE 3

Fractional co-ordinates of the hydrogen atoms

Atom	<i>x</i>	<i>y</i>	<i>z</i>
H(21)[C(2)]	0.767	-0.044	0.357
H(22)[C(2)]	0.843	-0.088	0.292
H(23)[C(2)]	0.815	0.069	0.321
H(41)[C(4)]	0.415	-0.385	0.162
H(42)[C(4)]	0.439	-0.481	0.065
H(43)[C(4)]	0.313	-0.404	0.048
H(51)[O(5)]	0.390	0.168	0.195
H(52)[O(5)]	0.318	0.273	0.108

earlier structure determinations were somewhat inaccurate, for instance the distance quoted for the

¹³ C. K. Johnson, ORTEP, Thermal ellipsoid plotting program, Oak Ridge National Laboratory Report ORNL 3794.

¹⁴ F. A. Cotton, B. G. DeBoer, M. D. LaPrada, J. R. Pipal, and D. A. Ucko, *Acta Cryst.*, 1971, B, 27, 1664.

doubt that the original Cu...Cu distance of 2.64 Å was reasonably correct, since a number of related acetate bridged complexes, *i.e.* the monoclinic¹⁹ and orthorhombic²⁰ forms of pyridinecopper(II) acetate have almost identical metal-metal separation (2.630 and 2.645 Å). This refinement has shown that in copper acetate the Cu...Cu separation is slightly shorter than these values (2.616 Å) and is very similar to that found in copper(II) succinate dihydrate,¹⁷ 2.610 Å.

¹⁵ D. Lawton and R. Mason, *J. Amer. Chem. Soc.*, 1965, 87, 921.

¹⁶ M. R. Churchill and R. Mason, *Nature*, 1964, 204, 777.

¹⁷ B. H. O'Connor and E. N. Maslen, *Acta Cryst.*, 1966, 20, 824.

¹⁸ J. N. Van Niekerk, F. R. L. Schoening, and J. F. de Wet, *Acta Cryst.*, 1953, 6, 501.

¹⁹ G. A. Barclay and C. H. L. Kennard, *J. Chem. Soc.*, 1961, 5244.

²⁰ F. Hanic, D. Stempelova, and K. Hanicova, *Acta Cryst.*, 1964, 17, 633.

TABLE 4

Interatomic distances (Å) and angles (°) with standard deviations in parentheses

(a) Distances			
Cu(1)—O(1 ^I)	1.986(3)	Cu(1)—O(5)	2.156(4)
Cu(1)—O(2)	1.994(3)	Cu(1) ··· Cu(1 ^I)	2.616(1)
Cu(1)—O(3 ^I)	1.945(4)		
Cu(1)—O(4)	1.950(3)		
Mean Cu—O(acetate) 1.969			
C(1)—O(1)	1.251(6)	C(3)—O(3)	1.274(7)
C(1)—O(2)	1.268(6)	C(3)—O(4)	1.248(6)
Mean C—O 1.260			
C(1)—C(2)	1.495(5)	C(3)—C(4)	1.506(7)
Mean C—CH ₃ 1.501			
(b) Angles			
O(5)—Cu(1)—O(1 ^I)	98.4(2)	O(1 ^I)—Cu(1)—O(3 ^I)	87.5(2)
O(5)—Cu(1)—O(2)	93.0(2)	O(1 ^I)—Cu(1)—O(4)	91.1(1)
O(5)—Cu(1)—O(3 ^I)	97.7(2)	O(2)—Cu(1)—O(3 ^I)	90.1(2)
O(5)—Cu(1)—O(4)	93.3(2)	O(2)—Cu(1)—O(4)	89.1(1)
O(1 ^I)—Cu(1)—O(2)	168.6(2)	O(3 ^I)—Cu(1)—O(4)	168.9(2)
Cu(1 ^I)—O(1)—C(1)	121.9(3)	Cu(1 ^I)—O(3)—C(3)	120.7(3)
Cu(1)—O(2)—C(1)	124.9(3)	Cu(1)—O(4)—C(3)	124.9(4)
Mean Cu—O—C 123.1			
O(1)—C(1)—O(2)	124.2(4)	O(3)—C(3)—O(4)	125.4(5)
Mean O—C—O 124.8			
O(1)—C(1)—C(2)	118.7(4)	O(3)—C(3)—C(4)	115.8(4)
O(2)—C(1)—C(2)	117.0(4)	O(4)—C(3)—C(4)	118.8(5)
Mean O—C—C 117.6			
(c) Hydrogen-bonded contacts			
O(5) ··· O(1 ^{II})	2.939(5)	O(5)—H(52)—O(1 ^{II})	160
O(5) ··· O(2 ^{III})	2.817(5)	O(5)—H(51)—O(2 ^{III})	171

Superscripts refer to atoms in the following positions:

$$\text{I } 1-x, -y, -z \quad \text{II } x - \frac{1}{2}, \frac{1}{2} + y, z \quad \text{III } 1-x, y, \frac{1}{2} - z$$

Polymeric copper(I) acetate, whose structure has been reported recently,²¹ also contains bridging acetate groups,

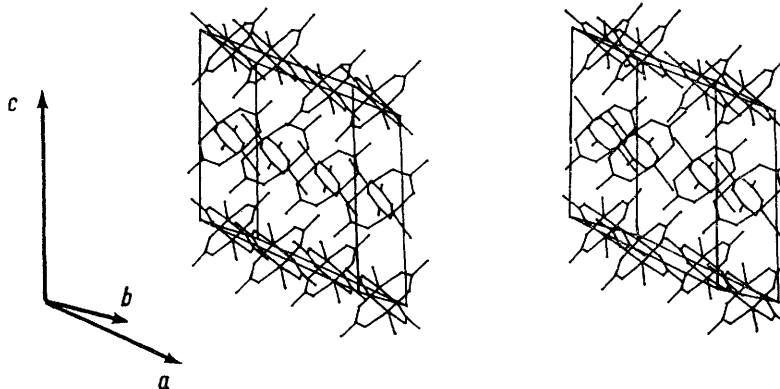


FIGURE 2 Stereoscopic view showing the packing of the molecules

with pairs of copper atoms separated by 2.544 Å. The likelihood of metal-metal bonding is more pronounced for monovalent copper, and even shorter Cu ··· Cu separations are known, *e.g.* 2.45 Å in the binuclear copper(I)

²¹ M. G. B. Drew, D. A. Edwards, and R. Richards, *J.C.S. Chem. Comm.*, 1973, 124.

derivative of diazoaminobenzene,²² and 2.38 Å in the tetranuclear (4-methyl-2-cupriobenzyl)dimethylamine.²³

The Cu—O(acetate) distances in the original structure seemed reasonable (1.95–1.99, mean 1.97 Å), and our refinement gives very similar distances (1.945–1.994 mean 1.969 Å). The mean value in copper succinate dihydrate is 1.975 Å. The original Cu—O(water) distance of 2.20 Å is shown to be somewhat shorter at 2.156 Å. The least accurate part of the previous determination was the geometry of the bridging acetate groups, which was clearly unsatisfactory, *e.g.* mean C—O 1.33 Å, and mean O—C—O angle 112°. Our refinement has revised these values to 1.260 Å and 124.8°.

Table 5 shows details of the planarity of various groups

TABLE 3

Planarity of groups of atoms in the structure. The equations of the planes are expressed as $Px + Qy + Rz = S$. Deviations (Å) of atoms from the planes are listed in square brackets

	<i>P</i>	<i>Q</i>	<i>R</i>	<i>S</i>
Plane (1): O(1 ^I), O(2), O(3 ^I), O(4)	-9.46	4.50	10.2	-3.61
[O(1 ^I) -0.004, O(2) -0.004, O(3 ^I) 0.004, O(4) 0.004, Cu(1) 0.192, O(5) 2.344]				
Plane (2): O(1), O(2), C(1), C(2)	7.25	6.98	-5.71	3.76
[O(1) 0.000, O(2) 0.000, C(1) 0.001, C(2) 0.000, Cu(1) -0.174, Cu(1 ^I) -0.109, O(5) -0.355, O(5 ^I) 0.072]				
Plane (3): O(3), O(4), C(3), C(4)	6.58	0.01	7.55	3.23
[O(3) 0.001, O(4) 0.001, C(3) -0.003, C(4) 0.001, Cu(1) 0.068, Cu(1 ^I) 0.045, O(5) 0.244, O(5 ^I) -0.131]				

Superscripts are defined as in Table 4.

of atoms in the structure. It can be seen that the two independent acetate groups form good planes.

The mode of packing of the dimeric molecules is shown as a stereoscopic¹³ pair of illustrations in Figure 2.

There are two independent hydrogen bonds in the structure in which the two hydrogen atoms of the water molecule participate. This hydrogen bonding is almost certainly responsible for the fact that the two acetate

²² I. D. Brown and J. D. Dunitz, *Acta Cryst.*, 1961, **14**, 480.

²³ J. M. Guss, R. Mason, I. Sotofte, G. van Koten, and J. G. Noltes, *J.C.S. Chem. Comm.*, 1972, 446.

oxygen atoms involved, O(1) and O(2), are slightly further away from the copper atom (by *ca.* 0.04 Å) than the other two oxygen atoms, O(3) and O(4).

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