X-Ray Crystal Structure of Copper(I) Acetate

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Summary The structure of copper(I) acetate is a polymeric planar chain, each copper atom being in a distorted square-planar environment bonded to three oxygen atoms and another copper atom [Cu–Cu = 2·544(4) Å].

THERE is considerable current interest in both the stereochemistry of copper(I) compounds[1] and in the various modes of co-ordination of carboxylate groups to metals.[2] Although a vast amount of information is available on copper(II) carboxylates, the chemistry of copper(I) carboxylates has been relatively neglected, even though such compounds are known, for example, to be involved in the decarboxylation of organic acids using copper(I) oxide[3] and in the formation of esters from carboxylic acids and alkyl halides[4] again in the presence of copper(I) oxide. Copper(I) acetate has also been used[5] in homogeneous catalytic hydrogenation reactions.

A crystal structure determination of copper(I) acetate has shown: (i) a unique square-planar environment for each copper atom, (ii) a new type of acetate co-ordination, (iii) binuclear units, further linked to other such units in a chain structure; each binuclear unit involving a copper–copper bond.

The acetate was prepared by reducing copper(II) acetate with copper foil in MeCN-AcOH-Ac_2O (20:4:1), under nitrogen. Precipitation of the product with ether, followed by a sublimation at 160° in an evacuated sealed tube, gave crystals suitable for *X*-ray investigation.

The crystals were monoclinic, space group $P2_1/m$, $a = 5{\cdot}20(1)$, $b = 6{\cdot}26(1)$, $c = 9{\cdot}90(1)$ Å, $\beta = 93{\cdot}7(1)°$, $D_c = 2{\cdot}53$, $D_m = 2{\cdot}49(5)$, $Z = 4$ for $C_2H_3CuO_2$, $M = 122{\cdot}6$, Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å.

The intensities of 316 independent reflections ($2\theta < 45°$) above background were measured on a GE XRD 5 manual diffractometer by the stationary-crystal–stationary-counter method and refined (Cu anisotropic, O,C isotropic) to R 0.063. There are two $C_2H_3O_2Cu$ units in the asymmetric unit, all atoms being in special positions (2*e*) with $y = \frac{1}{4}, \frac{3}{4}$.

This unit is centrosymmetric within experimental error around the midpoint of the Cu–Cu bond (see Figure: standard deviations: Cu–Cu, 0·004; Cu–O, 0·02; C–C, 0·03 Å; Cu–Cu–O, 0·3°; O–Cu–O, 0·6°; O–C–O, 1·5°). Thus only the mean dimensions need be discussed.

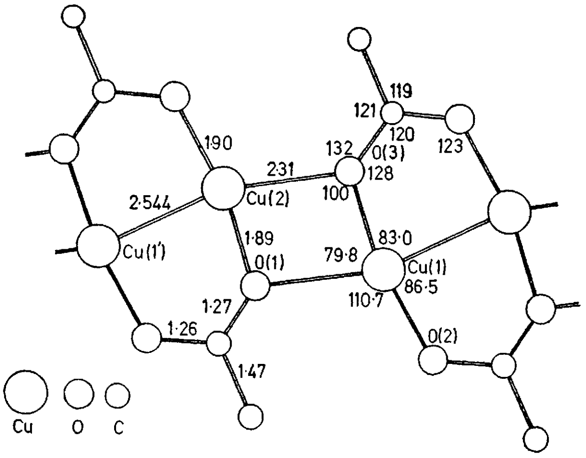

FIGURE. *Structure of* CuOAc; *distances in* Å, *angles in degrees, Primed atoms are symmetry related* (−1 + x, y, z) *to unprimed atoms* (x, y, z).

The Cu–Cu bond length of 2·544(4) Å can be compared with that found in $Cu_2(OAc)_4,2H_2O$,[6] (2·64 Å), and with the range of values (2·65–2·97 Å) found[7] in various copper(I) polynuclear cluster compounds. Shorter Cu–Cu distances have been found in the tetranuclear (4-methyl-2-cupriobenzyl)dimethylamine,[8] (2·38 Å), and in the binuclear copper(I) derivative of diazoaminobenzene,[9] (2·45 Å). The alternative Cu–Cu distance in the chain is 3·24 Å, indicating little, if any, direct metal–metal interaction in those parts of the chain polymer.

The square-planar configuration around the copper atoms is unusual, tetrahedral structures being much more commonly found, as for example in the dimeric dichlorotris-[(1,2-bisdiphenylphosphino)ethane]dicopper(I).[1c] Although the polymer itself is strictly planar, the configuration around each copper atom (three oxygen atoms and the other copper atom of the basic binuclear unit) is distorted owing to this polymeric chain formation. Thus the Cu(1)–O(1) bond is considerably longer [2·31(2) Å] than the other two bonds, Cu(1)–O(3), Cu(1)–O(2), which are equivalent at 1·90(2) Å, thus increasing the distances between adjacent acetate groups. Other distortions occur for the same reason; ∠O(1)–Cu(1)–O(2) 110·7° compared to the other *cis* angles subtended at the Cu atom which are less than 90°; Cu(2)–O(3)–C = 132°.

The co-ordination of the acetate group is of a type not previously found, since although the group is bidentate, bridging two copper atoms as found in several $M_2(OAc)_4L_2$ species[2] (M = V, Cr, Mo, Re, Ru, Rh, Cu; L = monodentate donor), one of the two oxygens, O(3), is further co-ordinated to another copper atom, Cu(2), such that this oxygen atom lies close to the Cu(1′)–Cu(2) axis with ∠O(3)–Cu(2)–Cu(1′) = 162·8(5)°.

The closest contacts between atoms in parallel planes are Cu · · · O 3·17, 3·37 Å and Cu · · · Cu 3·34 Å indicating just weak interaction.

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