Copper(II) Aspirinate

By LJUBICA MANOJLOVIĆ-MUIR*

(*Chemistry Department, The University of Glasgow, Glasgow, W.2*)

AN *X*-ray analysis of copper(II) aspirinate indicates that it belongs to a group of compounds which contain a Cu–Cu bond.

The compound was made by heating at about 50°, 1 mole of aspirin (acetylsalicylic acid) and ½ mole of copper salicylate tetrahydrate in 50% aqueous ethanol. Crystals, which appear on standing, are very small, dark blue prisms insoluble in water and in many common organic solvents.

There are four formula units of $Cu(C_9H_7O_4)_2$ in a monoclinic unit cell of dimensions: $a = 8{\cdot}208$,

* Present address: Department of Chemistry, Brookhaven National Laboratory, Upton, L.I., N.Y. 11973, U.S.A

$b = 10{\cdot}39$, $c = 21{\cdot}56$ Å, and $\beta = 104{\cdot}74°$. The space group is $P2_1/c$. The intensities of 1635 independent reflexions were measured on a linear diffractometer, using Mo-$K\alpha$ radiation, and the structure was solved by the heavy-atom method.

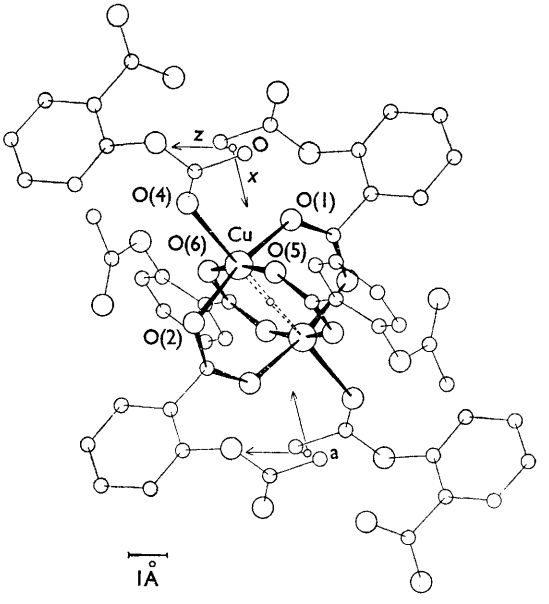

FIGURE. *The binuclear unit of copper(II) aspirinate viewed down the* b *axis.*

At the end of least-squares refinement of the positional and isotropic thermal parameters of the atoms the R factor is 10·0%.

The crystal structure contains binuclear units, $[Cu(C_9H_7O_4)_2]_2$, interconnected by Cu–O(4) bonds to form a polymeric system, the O(4) being part of the acetyl residue (see Figure). The stereochemistry of the binuclear unit resembles that found in copper(II) succinate dihydrate,[1] copper(II) acetate monohydrate,[2] orthorhombic monopyridinecopper(II) acetate,[3] and monoclinic monopyridinecopper(II) acetate.[4] The co-ordination of the copper atom is octahedral. Five of its nearest neighbours are oxygens, four of these belonging to four carboxyl groups, and the fifth to an acetyl group. The Cu–O bonds directed to O(1), O(2), O(5), and O(6) are nearly co-planar, with mean length 1·96 Å (the standard deviations of the individual bond lengths being ~0·02 Å). The Cu–O(4) bond is somewhat longer ($2{\cdot}24 \pm 0{\cdot}02_5$ Å), and approximately perpendicular to the O(1), O(2), O(5), O(6) plane. Copper is, therefore, surrounded by a tetragonal pyramid of oxygens; the distorted octahedron is completed by a centrosymmetrically related copper atom. The Cu–Cu distance is $2{\cdot}621 \pm 0{\cdot}008$ Å.

The bond lengths in the aspirin acid residue agree, within the experimental errors, with the corresponding lengths in potassium hydrogen diaspirinate[5] and in aspirin itself.[6]

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