Crystal Structures of Copper(II) α-Hydroxy- and α-Alkoxy-carboxylates

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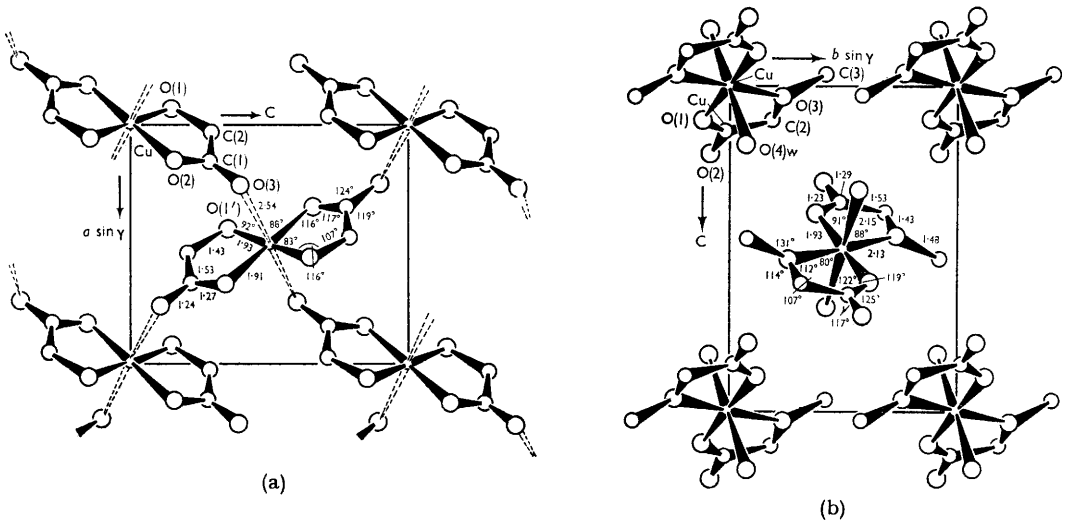
MANY crystalline copper(II) carboxylates with magnetic moments ~1·45 B.M. at room temperature are assumed[1] to have structures similar to those of the acetate monohydrate and monopyridine dimers. Although potentially bidentate copper carboxylates with moments ~2 B.M. are presumably monomeric, it cannot be assumed that the ligands necessarily chelate. Thus, the crystalline salicylate tetrahydrate contains unidentate salicylate ions.[2] Differential proton relaxation indicates[3] that glycollate, methoxyacetate, mandelate, and β-hydroxybutyrate chelate Cu^{II} in aqueous solution, but it does not follow that these ligands are all bidentate in the solid state. Thus, our solid sample of the β-hydroxybutyrate is blue–green with a magnetic moment[4] of 1·34 B.M. at room temperature ($-2J = 328$ cm.$^{-1}$; $g = 2·08$) and must be dimeric.

Crystalline copper glycollate, methoxyacetate dihydrate, and mandelate are all pale blue, do not have the 375 mμ band supposedly indicative of a Cu–Cu bond and have magnetic moments of 1·88, 1·93, and 1·88 B.M. Although the O–H stretching bands of mulls of the anhydrous glycollate and mandelate are broad, it is not clear whether these monomeric species are chelates or not. We now report the crystal structures of the glycollate and methoxyacetate dihydrate determined from single-crystal oscillation and Weissenberg photographs.

(a) Bisglycollatocopper(II), $C_4H_6O_6Cu$, $M = 213·6$. Monoclinic, $a = 7·93 \pm 0·02$, $b = 5·08 \pm 0·02$, $c = 8·68 \pm 0·03$ Å, $\gamma = 111·1 \pm 0·1°$; $D_m = 2·164$ (by flotation), $Z = 2$; *space group* $P2_1/a$ (C_{2h}^5, no. 14); Cu-K_α radiation, $\mu = 46·0$ cm.$^{-1}$

(b) Bismethoxyacetatocopper(II) dihydrate, $C_6H_{14}O_8Cu$, $M = 277·6$. Monoclinic, $a = 6·92 \pm 0·02$, $b = 7·24 \pm 0·02$, $c = 10·10 \pm 0·03$ Å, $\gamma = 96·7 \pm 0·1°$; $D_n = 1·820$ (by flotation), $Z = 2$; *space group* $P2_1/n$ (C_{2h}^5, no. 14, non-standard setting); Cu-K_α radiation, $\mu = 33·8$ cm.$^{-1}$

602 and 722 independent reflections were estimated visually from multiple film packs. Trial structures determined from the Patterson functions were refined to convergence by the least-squares method using the full matrix and assuming independent isotropic temperature-factors for all atoms. The residual R was 0·136 for



FIGURE

(a) *The molecular arrangement projected down the* b*-axis in copper*(II) *glycollate showing the sheet co-ordination polymer. Layers are held together by hydrogen bonds* 2·57Å *in length between the carboxyl oxygen* O(3) *and the hydroxyl group* O(1)′ *of a chelate in the next layer.*

(b) *The molecular arrangement projected down the* a*-axis in copper*(II) *methoxyacetate.*

the glycollate and 0·115 for the methoxyacetate. The standard deviations in interatomic distances are ~0·01 Å between Cu and light atoms and ~0·02 Å between pairs of light atoms. Hydrogen atoms were not located. Projections of the two structures, showing the planar five-membered chelate rings, are given in the Figure. There is a great similarity between these structural types and those observed[5] for amino-acid complexes of copper.

In the glycollate structure there are four short Cu–O contacts of ~1·93 Å in the chelate ring and two long contacts (2·54Å) to carboxyl oxygens in neighbouring molecules. By contrast, in the methoxyacetate, there are two short contacts (again of 1·93 Å), to carboxyls and two long contacts of ~2·14 Å to the methoxy-groups in the chelate ring. Six-fold co-ordination about the copper is completed by two waters, also at ~2·14 Å. The latter uncommon type of tetragonal distortion occurs[6] in K_2CuF_4 and $MCuF_3$. The greater length and presumably smaller strength of the Cu←OMe bond in comparison with Cu←OH is in keeping with the ligational enthalpies in solution.[7]

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