STRUCTURE OF ANHYDROUS COPPER ALKANOATES

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Abstract

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STRUCTURE OF ANHYDROUS COPPER ALKANOATES

As is known, copper acetate monohydrate in the crystalline state consists of dimeric molecules in which two copper atoms are located at a very short distance ([1]) and are linked by exchange forces, which leads to the appearance of an upper triplet state ($S = 1$) and a lower singlet state ($S = 0$). The combined action of the crystal field, anisotropic exchange, and dipole interactions splits the triplet state into a doublet and a singlet. The electron paramagnetic resonance (EPR) spectrum of this salt in the 9000 MHz range consists of two lines, one of which is located in a very weak magnetic field, and the other at about 4500 oersted ([2]).

The study of the EPR spectra of single crystals of copper propionate monohydrate ([3]) and copper *n*-butyrate monohydrate ([4]) showed that in these compounds as well the molecules are dimeric. Yu. V. Yablokov and A. V. Ablov found that the EPR spectra of polycrystalline samples of copper acetate and propionate monohydrates also consist of two lines observed at the same magnetic-field values ([5]).

Anhydrous copper alkanoates, analogously to the monohydrates, in polycrystalline samples have these same two lines in their EPR spectra and, consequently, contain pairs of exchange-bonded copper ions. However, in these spectra a third intense line is also observed, the nature of which is not yet clear.

Salts of monobasic fatty acids with divalent and trivalent metals are known as metallic soaps. They possess very interesting properties and find diverse applications in practice. Very little is known about the structure of these soaps. As an initial stage in the study of their structure, an X-ray structural investigation was carried out on anhydrous copper salts of the two lowest representatives of the fatty acids: propionic and *n*-butyric.

Copper propionate and *n*-butyrate monohydrates were dehydrated by heating at 120° and dissolved in the corresponding anhydrous acids. By very slow isothermal evaporation of the acids at room temperature, single crystals of the anhydrous salts were obtained, most of the crystals possessing internal strains.

Both salts crystallize as elongated plates of dark-green color and possess two perfect cleavage planes. From oscillation and rotation X-ray photographs obtained in RKOP and RKV-86 cameras (the latter with a NaCl standard), and from zero- and upper-layer line scans obtained on RGIK and KFOR X-ray goniometers, the parameters of the triclinic unit cells were determined:

	a, Å	b, Å	c, Å	α	β	γ
$Cu(CH_3CH_2COO)_2$	5.01	8.58	9.69	87°50′	90°	75°50′
$Cu(CH_3CH_2CH_2COO)_2$	5.20	8.85	11.50	94°	90°	74°50′

The piezoelectric effect found,* much smaller than that of quartz, was attributed by us to the effect of destruction of the crystal. A statistical analysis of the intensities, taking into account the heavy atom in a general position

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([6]) made it possible to select for further study the centrosymmetric space group $P\bar{1}$. The experimental material consisted, for $Cu(CH_3CH_2COO)_2$, of a set of layer-line scans (Hkl) $(H = 0, 1, 2, 3$; Mo radiation), and for $Cu(CH_3CH_2CH_2COO)_2$, of a set of $(0kl)$, $(1kl)$, and $(h0l)$ lines (Cu radiation). Intensities were estimated visually according to the standard blackening scale with an interval of $\sqrt[4]{2}$.

At the first stage of the investigation, projections of the Patterson function $P(vw)$ and $P(uw)$ were constructed for copper butyrate, and $P(vw)$ and $P_1(uw)$ for copper propionate. Analysis of these projections made it possible to locate the Cu atom unambiguously and to establish that in the structures there are pairs of copper ions at a Cu–Cu distance of ~ 2.7 Å ([7]), and that both salts have a similar structure, the additional chain link $-CH_2 - CH_3$ in copper butyrate being located in a plane parallel to (yz). To determine the coordinates of the light atoms from the contributions of the copper atoms, electron-density projections were constructed on the (yz) and (xy) planes for copper butyrate and on the (yz) plane for copper propionate. The low resolution of the peaks in the projections made it necessary to resort to generalized Raman–Srinivasan syntheses ([8–10]). Using reflections of the $(0kl)$ zone for both compounds, projections of generalized α- and β-syntheses were constructed with the coefficients

$$\alpha_{\text{gen}} = F^2(hkl) \cdot F_{\text{Cu}}(hkl),$$

$$\beta_{\text{gen}} = F^2(hkl)/F_{\text{Cu}}(hkl),$$

Fig. 1. Structure of the $Cu_2(COOR)_4$ complex

Figure 1: Fig. 1. Structure of the $Cu_2(COOR)_4$ complex

where $F^2(hkl)$ is the structure factor and $F_{Cu}(hkl)$ is the structure amplitude calculated from the coordinates of the copper atom. The somewhat higher resolving power of the β-synthesis made it possible to determine the y, z coordinates of all nonoverlapping light atoms. Further refinement of the structure was carried out by the method of successive approximation of Fourier syntheses calculated using programs of the Institute of Chemical Physics, Academy of Sciences of the USSR ([11]). The coordinates of overlapping atoms were refined by difference electron-density syntheses. As a result, the discrepancy factor calculated for copper propionate from 390 nonzero reflections of the $(0kl)$ and $(1kl)$ zones ($\sin\theta/\lambda \leq 0.64$ Å^{-1}) is 0.14; for copper butyrate, the factor calculated from 104 nonzero reflections of the $(0kl)$ zone ($\sin\theta/\lambda \leq 0.52$ Å^{-1}) is 0.20. The third coordinate x was determined from weighted electron-density projections.

At present the structures are being refined using three-dimensional experimental material.

Fig. 1. Structure of the $Cu_2(COOR)_4$ complex

Both compounds form cross-shaped centrosymmetric dimers (Fig. 1). Four oxygen atoms of four carboxyl groups form around the copper a slightly distorted square (Cu–O distances $\sim$ 1.90–2.04 Å). The copper atom is located outside the plane of these four oxygen atoms. The coordination of copper to six is completed by a copper ion at a distance of 2.58 Å and by the oxygen of the carboxyl group of the neighboring "dimer" (Cu–O $\sim$ 2.35 Å). The dimers are linked into chains parallel to the X axis. On the basis of the presence of perfect cleavage planes parallel to (010) and (001), it may be assumed that only weak intermolecular interactions exist between the chains.

The structures of anhydrous copper propionate and n-butyrate have much in common with the known structures of copper acetate monohydrate $Cu_2(CH_3COO)_4 2H_2O$ ([1]), copper acetate pyridinate $Cu_2(CH_3COO)_4 2Py$ ([12], [13]), and copper acetate quinolinate $Cu_2(CH_3COO)_4 2C_9H_7N$ ([14]). In all these

In these compounds there is a "motif" $Cu_2(CO_2R)_4$, consisting of two closely spaced copper atoms surrounded by four carboxylate ions. The indicated compounds differ only in the nature of the sixth ligand of copper (the oxygen of water, the nitrogen of pyridine or quinoline, the oxygen of the carboxyl group of a neighboring dimer). Despite the difference in the atoms by which the sixth ligands are bound to the copper atom, the Cu–Cu distances differ very little (from 2.58 to 2.64 Å).

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Note: Figure translations are in progress. See original paper for figures.