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Abstract

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ELECTRON-DIFFRACTION DETERMINATION OF THE STRUCTURE OF COPPER *DL*- α -ALANINATE

In the present work the study of copper salts of α -amino acids has been continued ⁽¹⁾. It was shown in ⁽²⁾ that *DL*- α -alanine gives two copper salts, differing not only in their properties but also in composition. In addition to the hydrate $\text{Cu}(\text{H}_2\text{NCH}(\text{CH}_3)\text{COO})_2 \cdot \text{H}_2\text{O}$, which consists of dark-blue crystals, often in the form of needles ⁽³⁾, there also exists an anhydrous blue-violet salt $\text{Cu}(\text{H}_2\text{NCH}(\text{CH}_3)\text{COO})_2$.

Since the latter separates in the form of very thin, brittle plates, tightly adhering to one another, it is practically impossible to investigate it by the X-ray method. These plates proved, however, to be convenient for an electron-diffraction study.

Specimens were prepared on a celluloid substrate by deposition from dilute aqueous solutions. A well-textured polycrystal giving electron-diffraction patterns suitable for investigation was obtained as follows: a drop of the solution was applied to the substrate and dried at a temperature of 40–50°; then a second drop was applied to the same specimen and again dried. In this way 5–6 drops were applied successively. Gradually, from drop to drop, new crystals grow on the substrate between the crystals formed earlier. The crystallites occupy all possible directions in azimuth, forming a textured polycrystal.

On an EG electron diffractograph of the design of the Institute of Crystallography of the USSR Academy of Sciences, electron-diffraction patterns from the textured polycrystal and spot electron-diffraction patterns were obtained. The assignment of these electron-diffraction patterns to crystals of the anhydrous form of copper alaninate was confirmed by taking Debye patterns. It is possible that the initial substance crystallizes partly in the form of the monohydrate, but since electron-diffraction patterns are recorded in high vacuum, the monohydrate crystals rapidly lose water. It was shown in ⁽²⁾ that dehydrated monohydrate crystals are identical with plates of the anhydrous form.

Indexing of the electron-diffraction patterns ⁽⁴⁾ showed that the crystals belong to the monoclinic system with the following unit-cell constants: $a = 9.57 \pm 0.03 \text{ \AA}$; $b = 5.03 \pm 0.01 \text{ \AA}$; $c = 9.45 \pm 0.02 \text{ \AA}$; $\beta = 91^\circ 54' \pm 25'$. The constants

b and c were determined from spot electron-diffraction patterns, and a and β from the reflexions of “oblique texture” photographs (texture axis a^*).

On the oblique-texture electron-diffraction patterns, extinctions of $h0l$ -reflexions with $l = 2n + 1$ and of $0k0$ -reflexions with $k = 2n + 1$ were observed (on the spot electron-diffraction patterns such weak reflexions appeared, which may be explained as the result of secondary scattering of electrons). The indicated extinctions lead to the space group $P2_1/c$. The number of formula units in the cell is $z = 2$ ⁽⁴⁾.

For the determination of the structure, reflexions from oblique-texture electron-diffraction patterns were used. It is known that the intensity of reflexions of such electron-diffraction patterns amounts to hundredths and tenths of a percent of the intensity of the primary beam, and for these electron-diffraction patterns in most cases the basic condition of the kinematic nature of scattering is fulfilled ⁽⁴⁾.

The integrated intensity of most reflections was estimated by the multiple-exposure method using a microphotometric method. Taking the intensity of the measured reflections as blackening standards, we determined the intensity of the remaining reflections. In solving the structure, 197 reflections were used (of these, 162 were independent).

From comparison of the plot of the dependence of the mean intensity value \bar{I}/K on $\sin \theta/\lambda$ with the curves $f_{\text{el.av}}^2$ and $f_{\text{el.av}}$, it was established that the scattering is kinematic ⁽⁵⁾.

By three-dimensional Patterson synthesis the coordinates of the copper atom were determined: $000; 0^1/2^1/2$ (in ⁽²⁾ preliminary data were reported which indicated that the copper atoms are located on twofold axes). The position of the copper atom was determined from reflections of spot electron diffraction patterns.

Table 1

| Atoms | x/a | y/b | z/c |
|----------------|--------|---------|---------|
| Cu | 0.0000 | 0.0000 | 0.0000 |
| O ₁ | 0.0458 | 0.1916 | -0.1783 |
| O ₂ | 0.1998 | 0.2250 | -0.3421 |
| N ₁ | 0.1708 | -0.2365 | -0.0503 |
| C ₁ | 0.1583 | 0.1001 | -0.2334 |
| C ₂ | 0.2504 | -0.1250 | -0.1702 |
| C ₃ | 0.3456 | -0.3171 | -0.2532 |

Fig. 1

By the “heavy atom” method, using only those reflections in which copper atoms participate, the coordinates of the ligands of the Cu atom (two O atoms and

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

two N atoms) were determined by three-dimensional synthesis. Fig. 2 gives a projection of the structure potential onto the face ac , in the calculation of which several theoretical amplitudes were used (Φ_{100} , Φ_{200} , Φ_{400} , Φ_{500}), which on electron diffraction patterns of oblique textures fall into the dead zone. In all, 21 Φ_{h0l} were used. As is seen, for exact identification of the atoms of the complex from the projection, 21 reflections are insufficient (the peaks corresponding to atoms C_1 and C_2 overlap). Further, by the method of successive approximations using the three-dimensional set Φ_{hkl} , the remaining atoms were clearly revealed. The structure was refined by the method of successive approximations to $R = 19.3\%$.

After introduction of a general temperature correction $B = 2.00 \text{ \AA}^2$, the R -factor decreased to 18.9%.

Table 1 gives the coordinates of the basis atoms of the structure of DL - α -copper alaninate (see Fig. 1).

At $B = 2.00 \text{ \AA}^2$, $(\sin \theta / \lambda)_{\max} = 0.45 \text{ \AA}^{-1}$, $R = 19\%$, according to the error formula (⁴), the probable error proved to be, for atoms O, C, N: $\Delta x_O = 0.031 \text{ \AA}$; $\Delta x_C = 0.038 \text{ \AA}$; $\Delta x_N = 0.034 \text{ \AA}$.

The interatomic distances and valence angles in the structure are as follows:

| | | |
|--|--|--|
| Cu -N ₁ 2.09 ± 0.03 Å | O ₁ -Cu -N ₁ 83°33' | O ₁ -C ₁ -O ₂ 115°36' |
| Cu -O ₁ 2.00 ± 0.03 | O ₃ -Cu -N ₁ 96°27' | O ₂ -C ₁ -C ₂ 118°53' |
| N ₁ -C ₂ 1.49 ± 0.05 | Cu -N ₁ -C ₂ 112°23' | O ₁ -C ₁ -C ₂ 125°13' |
| C ₂ -C ₁ 1.54 ± 0.05 | Cu -O ₁ -C ₁ 112°00' | N ₁ -Cu -O ₅ 82°50' |
| C ₁ -O ₁ 1.30 ± 0.04 | N ₁ -C ₂ -C ₁ 105°38' | N ₂ -Cu -O ₅ 97°10' |
| C ₁ -O ₂ 1.29 ± 0.04 | C ₁ -C ₂ -C ₃ 126°36' | O ₁ -Cu -O ₅ 92°44' |
| C ₂ -C ₃ 1.56 ± 0.05 | N ₁ -C ₂ -C ₃ 118°2' | O ₃ -Cu -O ₅ 87°16' |
| Cu ...O ₅ 2.76 ± 0.03 | | |
| N ₁ -O ₁ 2.73 ± 0.04 | | |
| N ₁ -O ₃ 3.05 ± 0.04 | | |

The molecule of copper DL - α -alaninate is centrosymmetric, as are the other molecules of copper salts of racemic amino acids studied so far (⁶⁻⁸). Around the copper atom, two enantiomorphic alaninate ions are arranged in the trans position.

Fig. 2

Each copper atom is surrounded by two oxygen atoms and two nitrogen atoms in a distorted square. The equation of the plane of the square is

$$5.173x + 2.812y + 4.379z = 0.$$

The atoms O_2 , C_1 , C_2 , C_3 are displaced from this plane by $\delta_{O_2} = 0.02 \text{ \AA}$; $\delta_{C_1} = 0.01 \text{ \AA}$; $\delta_{C_2} = 0.03 \text{ \AA}$; $\delta_{C_3} = 0.03 \text{ \AA}$. As can be seen, within the limits of experimental error the molecule tends toward a planar form. The same tendency of the molecule toward a planar form is also seen in the structure of copper *L*- α -alaninate⁽⁹⁾. The rather large distance $Cu \dots O_5 = 2.76 \text{ \AA}$ makes it possible to regard the coordination polyhedron of the copper atom as a planar square. The atoms of the carboxyl group and the α -carbon atom C_2 are coplanar.

Weak bonds $Cu \dots O_5 = 2.76 \text{ \AA}$ unite the complexes into separate helices parallel to the *b* axis. Within a helix a weak hydrogen bond $N_1-H \dots O_5 = 3.25 \text{ \AA}$ is formed. The linkage of the helices with one another is effected through van der Waals forces between the methyl groups ($C_2-C_9 = 3.88 \text{ \AA}$).

The interatomic distances and valence angles in the structure of the plate form of copper *DL*- α -alaninate are close to the analogous values observed in the structures of the copper salts of *L*-alanine and *D*-alanine^(9,10).

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1. B. K. Vainshtein, I. A. D' yakon, A. V. Ablov, *Kristallografiya*, **12**, 354 (1967).
2. A. V. Ablov, L. F. Chapurina et al., *ZhNKh*, **11**, 2620 (1966).
3. A. Streecke, *Liebigs Ann.*, **75**, 27 (1850).
4. B. K. Vainshtein, *Structural Electron Diffraction*, Publ. House of the Academy of Sciences of the USSR, 1956.
5. B. K. Vainshtein, A. N. Lobachev, *Kristallografiya*, **1**, 472 (1956).
6. A. A. Mathieson, H. K. Welsh, *Acta Crystallogr.*, **5**, 599 (1952).

7. A. J. Stosick, *J. Am. Chem. Soc.*, **67**, 362 (1945).
 8. G. A. Barclay, F. S. Stephens, *J. Chem. Soc.*, 1963, 2027.
 9. A. Dijkstra, *Acta Crystallogr.*, **20**, 588 (1966).
 10. R. D. Gillard, R. Mason et al., *Chem. Comm.*, No. 6, 1955 (1966).
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