Crystallographic data of three modifications of carbobenzoxy-* glycyl-L-prolyl-L-leucyl-glycyl-L-proline.

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Recently carbobenzoxy-glycyl-L-prolyl-L-leucyl-glycyl-L-proline has been synthesized, which is the simplest crystalline substrate for collagenase (Nagai & Noda, 1959; Nagai, Sakakibara, Noda & Akabori, 1960; Sakakibara & Nagai, 1960). Present account deals with the diffraction measurements of this crystalline compound. It is hoped that such structural studies will throw light on the structure of crystalline part of collagen because of their similar behavior towards the action of collagenase.

It was found that this substance shows at least three modifications. The crystal data of each modification were obtained from oscillation and Weissenberg photographs about the principal axes. Accurate measurement by counting procedure was made using single crystal orienter of G.E. XRD-6. Densities were obtained by flotation method. The results are listed in Table 1.

(1) α-Modification; very unstable platelet crystal obtained from water saturated ethyl acetate solution, easily turning opaque on exposure to the air. Photographs were taken with crystal sealed in glass capillary.

(2) β-Modification; stable platelet crystal, obtained from ethyl acetate solution containing water less than 1%.

(3) γ-Modification; very unstable cube-like crystal, obtained from ethyl acetate solution freed from water. Although photographs were also taken with crystal sealed in glass capillary, diffraction spots were accompanied by some streaks.

It may be added that no crystalline reflexion was observed when the solvent is completely taken off from the crystal in high vacuum.

From the cell dimensions and densities, apparent formula weights were calculated as shown in Table 1. These values obtained indicate that there must exist one molecule of ethyl acetate and three or four molecules of water per peptide as crystallization solvent, at least, in the α- and β-modifications. It was confirmed by Sakakibara & Nagai (1960) that ethyl acetate was actually present in these crystals.

Previously we have reported that the stepwise removal of the amino acid residues from this compound gave rise to regular decrease of axial length properly chosen (Sasada, Tanaka, Ogawa & Kakudo, 1961). From this it was considered to suggest that their molecules show some extended form in the crystals. If the pentapeptide molecule should assume also the extended form in the crystal, the length of an axis would have been expected to be about 32 Å. As the longest axis actually found is, however, 26 Å in the case of pentapeptide, we have to assume that the molecule is not fully extended, but that it somewhat curls up as a whole in the crystal. The density of this crystal is somewhat smaller than those of the lower peptides, and this may also have something to do with the above mentioned view.

It is observed that there are certain rational relations among the corresponding cell lengths of these three modifications. This suggests that in these three modifications the molecule has essentially the same shape. The occurrence of such polymorphism may be due to some complicated interaction between the peptide molecules and to that between the molecules and the solvent molecule of crystallization.

Table 1. *Crystallographic data of carbobenzoxy-glycyl-L-prolyl-L-leucyl-glycyl-L-proline* ($C_{28}H_{39}O_8N_5$, $M = 573$)

	α-Modification	β-Modification	γ-Modification
a	$13 \cdot 54 \pm 0 \cdot 07$ Å	$26 \cdot 28 \pm 0 \cdot 04$ Å	$26 \cdot 33$
b	$14 \cdot 73 \pm 0 \cdot 05$ Å	$14 \cdot 63 \pm 0 \cdot 02$ Å	$14 \cdot 43$
c	$10 \cdot 28 \pm 0 \cdot 03$ Å	$10 \cdot 30 \pm 0 \cdot 02$ Å	$10 \cdot 33$
β	$105 \cdot 6 \pm 0 \cdot 1°$	—	—
Space group	$P2_1$	$P2_12_12$	$P2_122$
Density	$1 \cdot 22_3$	$1 \cdot 21_7$	—
Z	2	4	4
Apparent formula weight	727	726	—

* Carbobenzoxy = benzyloxycarbonyl.

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On the symmetry and structure of the two modifications of anhydrous CoSO₄.

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In a recent paper by Pistorius (1961) are given the lattice constants and the space groups of the two polymorphic modifications of anhydrous $CoSO_4$, but a certain doubt is expressed in the choice of the most probable space

group. In view, however, of the complete structure determination of both forms (Rentzeperis, 1958b) the space groups can safely be taken as $D_{2h}^{17}-Cmcm$ for the low temperature β-CoSO$_4$ and $D_{2h}^{16}-Pnma$ for the high temperature α-CoSO$_4$. The first form, β-CoSO$_4$, belongs to the NiSO$_4$ series, i.e. is isostructural to NiSO$_4$ (Dimaras, 1957), MgSO$_4$ (Rentzeperis & Soldatos, 1958), MnSO$_4$ (Rentzeperis, 1958a), and FeSO$_4$ (Coing-Boyat, 1959). α-CoSO$_4$, on the other hand, is isostructural to CuSO$_4$ and ZnSO$_4$ (Kokkoros & Rentzeperis, 1958) and forms with them the chalcokyanite series.

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The unit cells and space groups of S$_4$N$_3$NO$_3$ and S$_2$N$_3$HBr$_4$.

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Muthmann & Seitter (1897) reported the preparation of a number of salts of the thiotrithiazyl ion, S$_4$N$_3^+$, and although these salts have been subject to a number of chemical studies (Goehring, 1956) no structural information is available for them. To determine the structure of the S$_4$N$_3^+$ ion we hoped to use S$_4$N$_3$Br, which is supposed to be made by reacting S$_4$N$_4$ with acetyl bromide. Good yields of the yellow S$_4$N$_3$Br were obtained at 0 °C., but the crystals were not suitable for X-ray use. Attempts to prepare S$_4$N$_3$Br by refluxing the reaction mixture gave S$_2$N$_3$HBr$_4$ instead.

S$_2$N$_3$HBr$_4$ forms dark purple, monoclinic crystals elongated in the c-direction and almost invariably twinned on (100). It melts sharply at 138 °C. Weissenberg photographs made with Cu $K\alpha$ radiation give

$$a = 10{\cdot}84, \ b = 10{\cdot}90, \ c = 10{\cdot}95 \text{ Å}; \ \beta = 96° \, 5'.$$

The calculated density is 2·20 g.cm.$^{-3}$; flotation measurements give a density of 2·12 g.cm.$^{-3}$. There are four molecules per unit cell, and the absence of $h0l$ reflections for h odd and $0k0$ reflections for k odd indicates the space group $P2_1/a$.

The compound S$_4$N$_3$NO$_3$ is being used for structural study because it crystallizes so readily. Magnificent yellow crystals, grown from a solution of S$_4$N$_3$Cl in concentrated nitric acid, form as plates whose principal faces are (010) and (100) or as needles elongated in the c-direction. It decomposes upon heating. The dimensions of the monoclinic unit cell are

$$a = 5{\cdot}84, \ b = 10{\cdot}50, \ c = 14{\cdot}32 \text{ Å}; \ \beta = 125°.$$

The space group is $P2_1/c$. Assuming four molecules per unit cell, one calculates a density of 2·13 g.cm.$^{-3}$. Flotation in dibromoalkanes shows the density to lie between 1·99 and 2·18 g.cm.$^{-3}$.

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Notes and News

Announcements and other items of crystallographic interest will be published under this heading at the discretion of the Editorial Board. The notes (in duplicate) should be sent to the General Secretary of the International Union of Crystallography (D. W. Smits, Mathematisch Instituut, University of Groningen, Reitdiepskade 4, Groningen, The Netherlands).

International Conference on Crystal-Lattice Defects

A conference under the above title is being planned by the Physical Society of Japan, to be held in Kyoto, Japan, 7–12 September 1962. The conference will cover point defects in metals, semi-conductors and ionic crystals. Suggested items of discussion will be electronic processes in imperfect crystals, properties of single and multiple point defects, radiation damage, association, dissociation and diffusion of point defects, etc. All correspondence should be addressed to Prof. R. R. Hasiguti, Department of Metallurgy, University of Tokyo, Bunkyo-ku, Tokyo, Japan.

Fifty Years of X-ray Diffraction

On the occasion of the 50th anniversary of the discovery of X-ray diffraction, the Ludwig-Maximilians-Universität at Munich, the Bayerische Akademie der Wissenschaften and the International Union of Crystallography are jointly organizing a Commemoration Meeting *Fifty Years of X-ray Diffraction*, which will be held in Munich from Wednesday 25 until Friday 27 July 1962. Following a commemoration session on Wednesday morning, invited lectures will be presented describing the development of the total field of X-ray diffraction.

In connection with the Commemoration Meeting, the International Union of Crystallography and the Sektion für Kristallkunde of the Deutschen Mineralogischen Gesellschaft will jointly organize a Symposium entitled *Recent Advances in the Experimental and Theoretical Methods of Crystal Structure Research*. This Symposium will take place from Friday afternoon 27 until Tuesday 31 July 1962; contributed papers will be welcome.

Those interested in the meetings are requested to register their names with the Chairman of the Local Committee (Prof. F. Bopp, Institut für Theoretische Physik der Universität München, Schellingstrasse 4–8, München 13, Germany) as soon as possible, preferably by filling in a pre-registration form which is attached to a First Notification. Further details about the meetings will be announced in a Second Circular which will be issued in December 1961, and which will contain a registration form.