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THE CRYSTAL AND MOLECULAR STRUCTURE OF CHLOROGLYCYL-GLYCINATOCOPPER(II) MONOHYDRATE

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Crystals of chloroglycylglycinatocopper(II) monohydrate crystallized from acid solution are monoclinic, space group $P2_1/c$, with 8 formula units in a cell. The copper(II)-glycylglycine chelate has a dimeric structure, in which the peptide is bonded to two copper atoms - to one through the terminal nitrogen and the peptide oxygen and to the other through the terminal oxygen. The copper atom is five-coordinated and has a distorted square pyramidal coordination polyhedron.

Two types of structure have been presented for the copper(II) chelate of glycylglycine formed in acid solution. One involves bidentate chelation of glycylglycine through the amino nitrogen and the peptide oxygen,[1-6] whereas the other involves terdentate chelation of glycylglycine through the amino nitrogen, the amide nitrogen and the carboxylic oxygen.[7-9] Both postulations have, at this moment, no decisive evidences for supporting the respective structures.

In view of the above argument, X-ray structure analysis of copper(II)-glycylglycine chelate obtained from acid solution is supposed to be significant, though the structure of chelate in crystalline state is not necessarily the same as that in dilute solution.

Chloroglycylglycinatocopper(II) monohydrate was prepared and purified according to the direction of Bair and Larsen.[10] Blue crystals of $C_4H_7N_2O_3CuCl \cdot H_2O$ are formed in the monoclinic space group $P2_1/c$: $a = 12.858(2)$, $b = 9.537(2)$, $c = 15.479(3)$ Å, $\beta = 120°10'(1')$, $U = 1629.8$ Å^3, $D_m = 2.00$ g/cm^3, $Z = 8$, $D_c = 2.02$ g/cm^3. The three-dimensional intensity data were collected with a Hilger and Watts automatic four-circle diffractometer Y-290. Integrated intensities were measured up to $\theta = 23°$ by the θ-2θ scan technique with Mo-K_α radiation and a scintillation counter. The pulse-height analyser and a zirconium filter were used. The structure was solved by the usual Patterson and Fourier method and refined by a block-diagonal least-squares technique with anisotropic thermal parameters for all atoms. R-factor for 2000 reflections was 5.8%, excluding the hydrogen atoms.

It has been disclosed as the result of structural analysis that the copper(II)-glycylglycine chelate has a dimeric structure as shown in Fig. 1. The glycyl-

glycinate ligands are coordinated to one copper(II) atom through the amino nitrogen and peptide oxygen atoms and to the other copper(II) atom through the carboxylic oxygen atom in the dimeric structure having C_2-like symmetry.

The coordination polyhedron around the copper atom is a distorted square pyramid, the base of which is formed by the amino nitrogen and peptide oxygen atoms of one peptide, the carboxylic oxygen atom of a second peptide and a chloride ion. The apex of the pyramid is occupied by the water oxygen atom. The copper atom is slightly displaced from the base plane in the direction of the water oxygen.

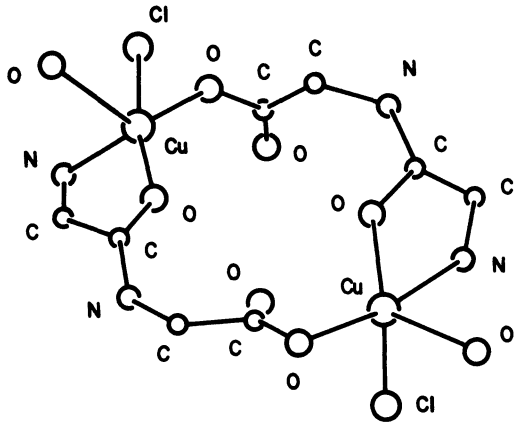

FIGURE 1. A perspective view of the molecular structure.

The average bond lengths in the peptide groups (C_α-CO-NH-C_α') are C_α-C = 1.53 Å, C-O = 1.25 Å, C-N = 1.32 Å and C_α'-N = 1.48 Å, and in the carboxyl groups C-O = 1.23 Å, 1.28 Å (bonded to the copper atom). The peptide groups are almost planar and the configurations of the C-O and N-H bonds are trans.

The structure of the copper(II)-glycylglycine chelate in this work is essentially the same as that of copper(II)-triglycine[11] obtained from acid solution, and is contrasted to the monomeric structure of the cationic bis(glycylglycinato)-cobalt(III) complex[12] in which the glycylglycinate ligand is coordinated to the cobalt(III) atom as a terdentate ligand.

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