

03.5- 3 CRYSTAL STRUCTURE AND CONFORMATION OF THE CYCLIC DIPEPTIDE: CYCLO-(D-PHENYLALANYL-L-PROLYL), R. Ramani, Molecular Biophysics Unit, Indian Institute of Science, Bangalore, K. Venkatesan, Dept. of Organic Chemistry, Indian Institute of Science, Bangalore-560012, INDIA and

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The crystal structure of Cyclo-(D-phenylalanyl-L-Prolyl) has been determined from three-dimensional X-ray diffraction data and refined to a final R index of 3.0% for 1439 observed reflections by least-squares method. The standard deviation in the bond distances on an average is 0.003 Å. The space group is $P2_1$, with $a = 8.083$, $b = 6.632$, $c = 12.090$ Å, $\beta = 96.34^\circ$ and $Z = 2$. The molecular packing coefficient is about 0.72, with pairs of molecules held together by an N-H...O type of hydrogen bond between the peptide nitrogen and oxygen (2.855 Å). The molecule is in the folded conformation ($\chi = -75.0^\circ$) with the aromatic side chain facing the diketopiperazine ring. The DKP ring assumes a boat conformation with the α -carbon atoms deviating about 0.2 Å from a least-squares plane through the two peptide bonds. The pyrrolidine ring assumes a half chair conformation with an approximate C2 symmetry.

03.5- 4 THE STRUCTURE OF A COPPER-BINDING TRIPEPTIDE, Cu-GLYCYL-GLYCYL-L-HISTIDINE METHYL AMIDE, N. Camerman, Dept. of Biochemistry, Univ. of Toronto, Toronto, Canada and A. Camerman, Depts. of Neurology and Pharmacology, Univ. of Washington, Seattle, Wash. USA.

Glycyl-glycyl-L-histidine methyl amide is a copper-binding tripeptide designed and synthesized by Sarkar to mimic the copper-binding site of serum albumen.

Reddish-purple crystals of the copper-tripeptide complex (Cu-GGH), grown at physiological pH, are triclinic, with cell dimensions $a = 9.990$, $b = 9.986$, $c = 7.682$ Å, $\alpha = 107.40^\circ$, $\beta = 91.72^\circ$, $\gamma = 96.49^\circ$, space group $P1$, $Z = 2$ units of Cu-GGH and two water molecules per cell. The structure was solved by interpretation of a Cu-phased Fourier map containing a great deal of false symmetry, after multiple attempts with direct phasing methods failed. Refinement proceeded to $R = 0.036$.

The conformations of the two Cu-GGH units are virtually identical. Each copper is tetradentate chelated by the amino terminal nitrogen, the next two imino nitrogens, and a histidyl nitrogen of a single tripeptide molecule in a mildly distorted square planar arrangement. The Cu...N distances range between 1.89 - 2.04 Å, with N...Cu...N angles of 165° and 176° . There appear to be weak highly-distorted octahedral interactions involving the copper atoms, water molecules, and carbonyl oxygens of other Cu-GGH units.

03.5- 5 THE CRYSTAL AND MOLECULAR STRUCTURE OF MONO-SODIUM GLUTAMATE MONOHYDRATE: A MODEL OF METAL INTERACTION WITH PROTEIN. S. T. Rao and M. Mallikarjunan, Department of Biochemistry, University of Wisconsin, Madison, Wisconsin 53706 U.S.A.

The crystals of the title compound ($C_5H_9NO_4 \cdot H_2O \cdot Na \cdot H_2O$) belong to the orthorhombic space group $P2_12_12_1$ with unit cell dimensions of $a = 17.954(2)$, $b = 15.241(2)$ and $c = 5.559(1)$ Å. There are two independent molecules in the asymmetric unit. The intensity data were collected on a diffractometer and the structure was solved by direct methods. Least squares refinement with anisotropic thermal parameters for the heavier atoms resulted in $R = 0.032$ for 1404 observed reflections. In both the molecules, the amino nitrogen atom lies in the plane of the α -carboxyl group. The conformation about the C^a-C^b bond is different ($\chi_1 = -60.4/58.5^\circ$) in the two molecules while that about the C^b-C^{\gamma} is essentially the same ($\chi_2 = -167.1/171.0^\circ$). Each Na⁺ ion is coordinated to six oxygen ligands (distances range from 2.327 Å to 2.574 Å) forming distorted octahedra. Two oxygen atoms are coordinated both the Na⁺ ions and are common apices to the two polyhedra. The implications of these for the interactions of similar ions to glu residues in proteins will be discussed. The structure is stabilized by a tightly knit hydrogen bonding network.

03.5- 6 STRUCTURAL STUDIES ON CRYSTALLINE COMPLEXES BETWEEN AMINO ACIDS. CRYSTAL STRUCTURE OF ARGININE GLUTAMATE MONOHYDRATE, T. N. Bhat and M. Vijayan, Department of Physics and Molecular Biophysics Unit, Indian Institute of Science, Bangalore 560012, India.

Crystalline complexes between amino acids and short peptides would serve as good model systems for studying the atomic details of non-covalent interactions in protein structures. The crystal structure of such a complex, namely, arginine glutamate monohydrate, $C_6H_{15}N_4O_2 \cdot C_5H_8NO_4 \cdot H_2O$, has been determined by the symbolic addition procedure using photographic data. The crystals are orthorhombic, space group $P2_12_12_1$, with $a = 5.05$, $b = 9.85$, $c = 32.50$ Å and $Z = 4$. The current R value is 0.12. Further refinement of the structure is in progress.

The arginine molecule in the structure carries a net positive charge while the glutamate carries a net negative charge. The conformation of the arginine molecule is different from those reported previously whereas the glutamate has an extended conformation as found in its hydrochloride (Sequeira, Rajagopal and Chidambaram, Acta Cryst. B28, 2514, 1972). The crystal structure is stabilized by ionic interactions, and N-H...O and O_w-H...O hydrogen bonds. The most significant feature of the structure is a specific ion-pair interaction involving two nearly parallel N-H...O hydrogen bonds between the guanidyl group of arginine and the side chain carboxylate group of the glutamate; such interactions between guanidyl and carboxylate groups, which could be observed only at a much lower resolution in protein electron-density maps, are important for the stability of protein structures.