

**03.2-20** THE STRUCTURE OF THE 1:1 MIXTURE OF CYCLO(L-ALA-L-PRO-L-PHE-L-PRO) AND CYCLO(L-ALA-L-PRO-D-PHE-L-PRO). By C. C. Chiang and I. L. Karle, Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, D. C. 20375.

The conformation of the synthetic cyclic tetrapeptide (Ala-Pro-Phe-Pro),  $C_{22}H_{28}N_4O_4$ , was established by x-ray diffraction methods. Although the synthesis was designed to produce only the LLLL isomer, the crystal structure analysis showed that the unit cell contained both the LLLL and LLDL isomers. The mixture crystallizes in the space group  $P2_12_12_1$  with  $a = 20.532(7)$ ,  $b = 22.228(9)$  and  $c = 9.429(2)$  Å. The structure was solved by the symbolic addition procedure for phase determination followed by the tangent formula method of phase refinement. The two independent molecules in the asymmetric unit were found to be diastereoisomers. This structure represents the first cyclic tetrapeptide with all L peptide groups. The four peptide units in both molecules adopt the cis trans cis trans conformation. The molecule with all L peptide groups has an approximate 2-fold rotation axis perpendicular to the average plane of the ring. No intramolecular hydrogen bonding was found in either molecule. Several intermolecular hydrogen bonds involving the isomers result in the stacking of alternate molecules along the c-axis.

**03.2-21** CYCLO(L-PROLYL-GLYCYL)<sub>3</sub>-DMF COMPLEX.\* K.I. Varughese, S. Aimoto and G. Kartha, Center for Crystallographic Research, Roswell Park Memorial Institute, Buffalo, New York 14263 U.S.A.

Cyclo(L-prolyl-glycyl)<sub>3</sub> is a synthetic cyclic hexapeptide which exhibits selective ion binding properties and has been extensively studied by Blout and coworkers (1). It is known that the conformation this peptide assumes is strongly influenced by the polarity of the medium and also the interactions with ions. We have investigated the structure and conformation of this cyclic peptide and its ion complex and report here the crystallographic results of a 1:2 complex of cyclo-(pro-gly)<sub>3</sub> with N,N-dimethylformamide (DMF).

The DMF complex crystallizes in orthorhombic space group  $P2_12_12_1$  with  $a = 9.025(1)$ ,  $b = 22.441(4)$ ,  $c = 15.059(7)$  and one molecule of peptide and two molecules of DMF in the asymmetric unit. The crystals are unstable in the air, easily losing its solvent, and resulting in a unit cell of appreciably smaller b-axis ( $20.42$  Å) and poorer diffraction characteristics. Hence the crystals were sealed in capillary for data collection. Diffraction data were collected to a Bragg angle of  $75^\circ$  (CuK $\alpha$ ), and the structure solved by multiresolution methods and refined to an R index of 6.6% for 3293 observed reflections. The conformation of the hexapeptide is asymmetric and out of six peptide bonds in the molecule one is in the cis conformation and to this extent the structure is similar to that found on crystallization from aqueous medium (2). Out of two DMF molecules in the asymmetric unit, only one is bonded to the peptide. None of the peptides are unusually nonplanar, the maximum deviation in  $w$  is  $7^\circ$ .

(1) Madison et al., JACS 96, 6724 (1974).

(2) Kartha et al., ACA Abst. (March 1980), p. 19.

\*Work supported by NIH Grant GM-22490.

**03.2-22** A MAGNESIUM COMPLEX OF CYCLO(Pro-Gly)<sub>3</sub>.\* G. Kartha, S. Aimoto and K.I. Varughese, Center for Crystallographic Research, Roswell Park Memorial Institute, 666 Elm St., Buffalo, NY 14263 USA.

The synthetic hexapeptide cyclo(Pro-Gly)<sub>3</sub> binds group I and II cations selectively and the binding induces significant conformational changes on the peptide (1). We have examined the crystal structure of this peptide and some of its cation complexes. Here we report on the crystal structure of its  $Mg^{2+}$  complex with perchlorate as anion.

The magnesium complex crystallizes in space group  $P2_1$ ,  $a = 12.677(2)$ ,  $b = 12.340(5)$ ,  $c = 21.502(2)$  and  $\beta = 92.69(1)$ . The asymmetric unit cell contains 2 molecules of the hexapeptide, 2 cations and 4 anions in addition to 9 molecules of water. The diffraction data were collected on an ENRAF NONIUS CAD-4 automated diffractometer to Bragg angle of  $75^\circ$  (CuK $\alpha$ ) yielding 7232 unique reflections of which 6107 were considered observed and used in structure analysis and refinement. The structure was solved by locating the cations on a sharpened Patterson map and subsequent series of structure factor and fourier cycles to locate the 57 non-hydrogen atoms in the asymmetric unit. The structure was refined by block diagonal least squares and at present the R index is  $\cdot 10$ .

Both the peptide molecules in the asymmetric unit cell have an approximate three-fold symmetric conformation with the cation in each case sandwiched between three glycyl oxygen atoms of the peptide and three water molecules. All peptides are in the trans conformation. The magnesiums have octahedral coordination with the six oxygen atoms at the average distance of  $2.06$  Å.

(1) V. Madison, M. Atreyi, C.M. Deber and E.R. Blout, J. Am. Chem. Soc. 96, 6724 (1974). \*Work supported by NIH Grant GM-22490.

**03.3-01** CRYSTAL STRUCTURE OF DL-N-ETHYLNOR-PHENYLEPHRINE HYDROCHLORIDE. By Rekha R. Pattanayek, J.K. Dattagupta and N.N. Saha, Saha Institute of Nuclear Physics, 92 A.P.C. Road, Calcutta-700009, India.

The crystal and molecular structure of a sympathomimetic amine, DL-N-Ethylnorphenylephrine ( $C_{10}H_{15}NO_2$ ), has been determined in the form of its hydrochloride. The crystals were kept inside a sealed glass capillary for data collection since they were highly unstable under normal atmospheric conditions. The crystals belong to monoclinic space group  $P2_1/n$  with two molecules per asymmetric unit. The unit cell dimensions are  $a = 5.168$ ,  $b = 11.430$ ,  $c = 38.328$  Å and  $\beta = 93.7^\circ$ . The structure was solved both by direct methods and heavy-atom method. Atomic parameters of all the atoms in the asymmetric unit were refined by full-matrix least-squares method using 2699 diffractometric data. In both the molecules the ethylamine side chain is in the extended form, the C-C-C-N<sup>+</sup> torsion angles being  $175.6^\circ$  and  $178.3^\circ$  respectively. The angles between the plane passing through these side chain atoms and that of the phenyl ring are  $84^\circ$  and  $118^\circ$ . The distance of the amino N atom from the centre of the benzene ring is  $5.09$  and  $5.21$  Å for the two molecules. The crystal structure is stabilised by a network of N-H...Cl, O-H...Cl and O-H...O hydrogen bonds. Conformational aspects in general will be discussed.