

03.2-2 TERNARY METAL COMPLEXES WITH DEOXYRIBONUCLEOTIDES. X-RAY STRUCTURES OF NICKEL(II) ETHYLENEDIAMINE-2'-DEOXYGUANOSINE 5'-MONOPHOSPHATE AND COPPER(II)-BENZIMIDAZOLE-2'-DEOXYGUANOSINE 5'-MONOPHOSPHATE. By N. Shahina Begum, M. Damodara Poojary and H. Manohar, Department of Inorganic & Physical Chemistry, Indian Institute of Science, Bangalore-560012, India.

Very little structural information is available regarding metal binding to deoxyribonucleotides, the building blocks of DNA. Two ternary transition metal complexes of 5'-dGMP have been synthesised and their crystal structures elucidated. These represent the first structural studies on ternary deoxyribonucleotide systems.

- (1)  $[\text{Ni}(\text{en})_{1.3}(\text{H}_2\text{O})_{1.4}(\text{H}_2\text{O})_2]^{2+}[\text{Ni}(5'\text{-dGMP})_2(\text{en})_{0.7}(\text{H}_2\text{O})_{0.6}(\text{H}_2\text{O})_2]^{2-} \cdot 7\text{H}_2\text{O}$  (en = ethylenediamine),  $a = 8.810(1)$ ,  $b = 25.090(4)$ ,  $c = 21.084(1)$  Å, space group  $C222_1$ ,  $Z = 4$ , observed reflections 1211,  $R = 0.087$ .
- (2)  $\text{Cu}(\text{bim})(5'\text{-dGMP}) \cdot 8\text{H}_2\text{O}$  (bim = benzimidazole),  $a = 7.069(6)$ ,  $b = 13.959(10)$ ,  $c = 14.204(12)$  Å,  $\alpha = 75.12(6)$ ,  $\beta = 94.15(6)$ ,  $\gamma = 97.98(6)^\circ$ , space group  $P1$ ,  $Z = 2$ , observed reflections 2913, present  $R = 0.062$ .

In compound (1), contrary to expectation, en and dGMP do not coordinate to the same metal. One of the  $\text{Ni}^{2+}$  ions is coordinated by two nucleotides in *cis* geometry through N(7) atoms of the base. The remaining octahedral coordination sites are occupied by water oxygens. Two water oxygens are partially replaced by en nitrogens. The ternary ligand, en, is labilised from the metal ion on nucleotide coordination and binds to a second  $\text{Ni}^{2+}$  ion, which has an octahedral coordination of four nitrogens from two en moieties and two water oxygens. The nitrogens are replaced by water oxygens with partial occupancies. The structure is similar to those of  $\text{Co}^{3+}$  and  $\text{Ni}^{2+}$  en complexes of 5'-IMP and 5'-GMP. (M.D. Poojary and H. Manohar, J.C.S. Chem. Comm. 533, 1982). The mode of metal binding to nucleotides in these compounds is similar to that observed in  $[\text{Pt}(\text{NH}_3)_2(5'\text{-IMP})_2]^{2+}$ , the intrastrand cross-linking model for Pt binding to DNA. However, an important difference is that in the present case the labilisation is incomplete, the en group coordinating both the metal ions with partial occupancies.

Compound (2) has two molecules in the unit cell with similar gross geometries.  $\text{Cu}^{2+}$  has a square-pyramidal coordination, with bim coordinating through a nitrogen and the nucleotide through N(7). The remaining three sites are occupied by water oxygens. This is a novel result since earlier crystallographic, as well as solution, studies on ternary metal nucleotide complexes with  $\pi$ -aromatic amines have shown phosphate binding to the metal.

Thus, while a common binding site, N(7), is observed in the two structures, the metal environment differs drastically in the two cases. Details of the structures will be presented.

03.2-3 PARALLEL PACKING OF ALPHA-HELICES IN CRYSTALS OF Boc-Trp-Ile-Ala-Aib-Ile-Val-Aib-Leu-Aib-Pro-Ala-Aib-Pro-Aib-Pro-Phe-OMe $\cdot$ 4H $_2$ O $\cdot$ 2CH $_3$ OH. By I. L. Karle, J. Flippen-Anderson, M. Sukumar and P. Balaram, Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, D. C. 20375, U.S.A. and Indian Institute of Science, Bangalore, India.

The title compound, a synthetic apolar analog of membrane active peptides found in spores in soil, crystallizes in space group  $P1$  with  $Z=1$  and cell parameters  $a=9.086$  Å,  $b=10.410$  Å,  $c=28.188$  Å,  $\alpha=86.13^\circ$ ,  $\beta=87.90^\circ$  and  $\gamma=89.27^\circ$ ;  $R=7.3\%$  for 7180 data ( $F_o > 3\sigma$ ), 0.91 Å resolution. The backbone makes a continuous spiral that begins as a  $3_{10}$  helix at the N terminus, changes to an alpha-helix for two turns, and ends in a spiral of three beta-bends in a ribbon. Each of the beta-bends contains a Pro residue at one of the corners. There are ten intramolecular  $\text{NH}\cdots\text{OC}$  hydrogen bonds in the helix. There is a direct head-to-tail hydrogen bond between the NH in the Trp(1) side-chain and the CO in Aib(14) in succeeding molecules, as well as a direct head-to-tail N(1)H $\cdots$ OC(16) bond. Two H $_2$ O and two CH $_3$ OH solvent molecules fill additional space with appropriate hydrogen bonding in the head-to-tail region and two additional H $_2$ O molecules form hydrogen bonds with carbonyl oxygens near the kink in the helix at Pro(10).

Since there is only one peptide molecule per cell in space group  $P1$ , the molecules repeat only by translation, and consequently, the alpha-helical portions must be parallel to each other. There is only hydrophobic contact between the bulky side groups on adjacent helices, except in the kinked region. Similar parallel packing of alpha-helices has been found in the decapeptide consisting of the same 1-10 residues in space group  $P1$  (Karle, Sukumar, Balaram, PNAS 1986, 83, 9284-8) and also very probably in a  $P2_1$  polymorph. In proteins antiparallel packing has been found almost exclusively.

03.2-4 CRYSTAL STRUCTURE AND MOLECULAR CONFORMATION OF A TRIPEPTIDE N-BOC-L-PHE-DEHYDRO-PHE-L-VAL-OCH $_3$ . By T.P. Singh and M. Haridas, Department of Biophysics, All-India Institute of Medical Sciences, New Delhi-110029. V.S. Chauhan and A. Kumar, Department of Chemistry, University of Delhi, Delhi-110007, India.

The tripeptide N-Boc-L-Phe-dehydro-Phe-L-Val-methyl ester: C $_{29}$ H $_{37}$ N $_3$ O $_6$  was synthesized as a model peptide to produce specific  $\beta$ -turn with the help of dehydro-Phe. This peptide crystallizes in the triclinic space group  $P1$  with  $a=6.085(2)$  Å,  $b=9.515(4)$  Å,  $c=13.243(5)$  Å,  $\alpha=105.16(3)^\circ$ ,  $\beta=92.69(3)^\circ$ ,  $\gamma=104.9(3)^\circ$  and  $Z=1$ . The structure was solved by direct methods using MULTAN 80. The structure was refined by block-diagonal least-squares method to an  $R$  value of 0.075 for 2438 observed reflections. The bond lengths and angles, in general, are in good agreement with the standard values. The peptide backbone adopts the  $\beta$  conformation as a result of deprotonation at C $^\alpha$  and C $^\beta$  atoms in the dehydro-Phe residue. The backbone conformations around the C $^\alpha$  atoms are *cis*, and the corresponding moieties are non planar. The backbone segments between the C $^\alpha$  atoms have extended *trans* conformations with highly planar configurations. The chain conformation angles  $\phi_1$ ,  $\psi_1$ ,  $\omega_1$ ,  $\phi_2$ ,  $\psi_2$ ,  $\omega_2$ ,  $\phi_3$  and  $\psi_3$  are  $-45.4(11)^\circ$ ,  $-45.6(6)^\circ$ ,  $-179.3(4)^\circ$ ,  $-46.5(5)^\circ$ ,  $-38.0(6)^\circ$ ,  $165.3(9)^\circ$ ,  $51.7(5)^\circ$  and  $43.0(6)^\circ$  respectively. The phenyl rings of Phe and dehydro-Phe are essentially planar and their planes are inclined with respect to each other at  $69.7(5)^\circ$ . The C $^\beta$ -C $^\gamma$  bonds in Phe and dehydro-Phe are *trans* with respect to the N-C $^\alpha$  bonds with  $\chi_1$  torsion angle (about C $^\alpha$ -C $^\beta$ ) of  $-176.3(1)^\circ$  and  $-179.4(5)^\circ$  respectively. The C $^\gamma$ -C $^\alpha$  bonds have torsion angles of  $-56.8(7)^\circ$  and  $-170.0(16)^\circ$  in Phe and dehydro-Phe respectively. The  $\beta$ -turn conformation is stabilized by an intramolecular hydrogen bond N $_3$ -H $_3$   $\cdots$  O $_2$  of distance 3.116(6) Å. The molecules are held in the crystal structure by a network of hydrogen bonds and the van der Waals forces.