THE CRYSTAL AND MOLECULAR STRUCTURE OF CYTOSINE-GLYCYLGLYCINE-COPPER(II) COMPLEX, A BIOLOGICALLY IMPORTANT TERNARY COORDINATION COMPLEX

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SAMMARY: The title compound was prepared and studied to gain some insight into the structural basis for the protein-nucleic acid-metal ion interaction. The crystal structure has been determined from three-dimensional diffractometer X-ray data using Cu Kα radiation. The crystals are monoclinic, space group $P2_1/c$, with cell dimension; a=10.642(1)Å, b=8.081(1)Å, c=17.792(1)Å, β=124.29(1)°, z=4. Amino and amide nitrogen, carboxyl O(8) of glycylglycine, N(3) of cytosine and O(2) of adjacent cytosine molecule coordinate to the central copper ion to form a square pyramid. An additional weak interaction in complex molecule between copper and O(2) of cytosine is also observed. The complex molecules are held together by hydrogen- and coordination-bonds in crystalline state.

The mutual interaction between each component in ternary coordination complex such as protein, nucleic acid and metal ion is probably one of the most important factors for the conformational stability of macromolecules and the control of many biological reactions in living cell. Furthermore, an understanding of the effects of bound ligands on ternary complex formation is stereochemically most interest because many enzymic and other catalytic processes requiring metal ions are thought to involve such complex as an intermediate.

Continued from the preceding paper[1] on adenine-glycylglycine-Cu(II) complex, we describe here briefly the crystal and molecular structure of cytosine-glycylglycine-Cu(II) complex which is the first case of pyrimidine base-dipeptide-metal complex determined by X-ray diffraction method.

The crystals were prepared by slightly modified procedure from that reported by Sakaguchi and Tanno[2]. Glycylglycine-Cu(II) and cytosine were dissolved in 30% aqueous ethanol in a 1:1 ratio and reacted at 60°C for two hours. The violet blue needle crystals were obtained by slow evaporation at room temperature and they are monoclinic and space group is $P2_1/c$ with four units of the chemical formula, $C_8H_{11}N_5O_4Cu\cdot 2H_2O$, in the unit cell: a=10.642(1)Å, b=8.081(1)Å, c=17.792(1)Å and β=124.29(1)°. The intensity data for 1758 independent reflections were collected by a computer-controlled four-circle diffractometer(Rigaku Denki Co.) with ω-2θ scan technique.

The structure was solved by the heavy atom method and the non-hydrogen atoms of the complex were found easily from successive Fourier syntheses calculated with phases based on the copper position. The crystal structure was refined by the block-diagonal least-squares method to an R-factor of 0.09.

The molecular structure of the complex viewed down the b-axis is shown in Fig.1 with the interatomic distances.

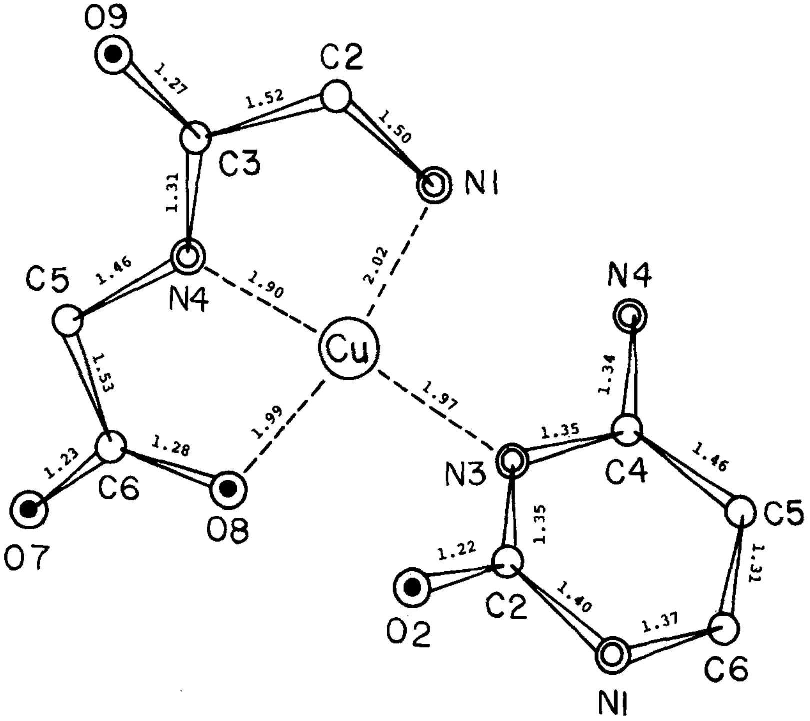

Fig.1

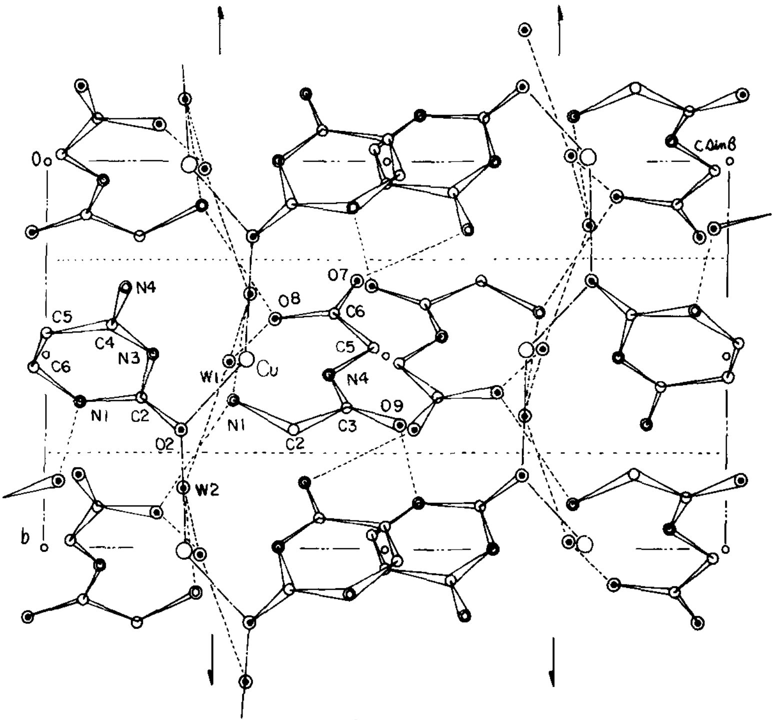

Fig.2

The coordination bond around the central copper ion forms a square plane by three Cu-N bonds(amino N(1) and amide N(4) of glycylglycine and N(3) of cytosine) and one Cu-O bond (carboxyl O(8) of glycylglycine). Moreover, O(2) of adjacent cytosine molecule related by two-fold screw axis cordinate also to the central copper with a distance of 2.73Å. This means that five ligands bound to copper ion form a square pyramid. The dihedral angle between the square plane formed by strong coordination bond and the cytosine base plane is ca. 115°, caused the O(2) of cytosine to deviate about 0.2Å out of the least-squares plane of pyrimidine ring and to have a short distance(2.81Å) from the central copper ion. Carrabine and Sundaralingam[3] cited that the similar short contact found in cytosine-Cu(II) complex is due to a weak coordination bond. However, the angle of 53° between this weak bond and the sqare plane deviates considerably from a right angle and it is still obscure whether it really a weak coordination bond is.

The molecular arrangement in crystalline state projected down the a-axis is shown in Fig.2. There is no stacking between the adjacent cytosine molecules. The interesting point in a mode of hydrogen bond is that the amino nitrogen N(4) of cytosine is hydrogen bonded to the carboxyl O(7) of the adjacent glycylglycine molecule related by glide plane. this fact suggests that on ternary complex formation the amino nitrogen N(4) of cytosine residue in nucleic acid may form directly a hydrogen bond to an acceptor in protein as well as N(3) of cytosine residue indirectly connected to protein through metal ion. Each complex molecule is held together by hydrogen bonds and weak coordination bonds to form a three-dimensional network as shown by the broken lines in Fig.2.

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