STRUCTURAL STUDIES OF METAL-RIBONUCLEOTIDE COMPLEXES

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by

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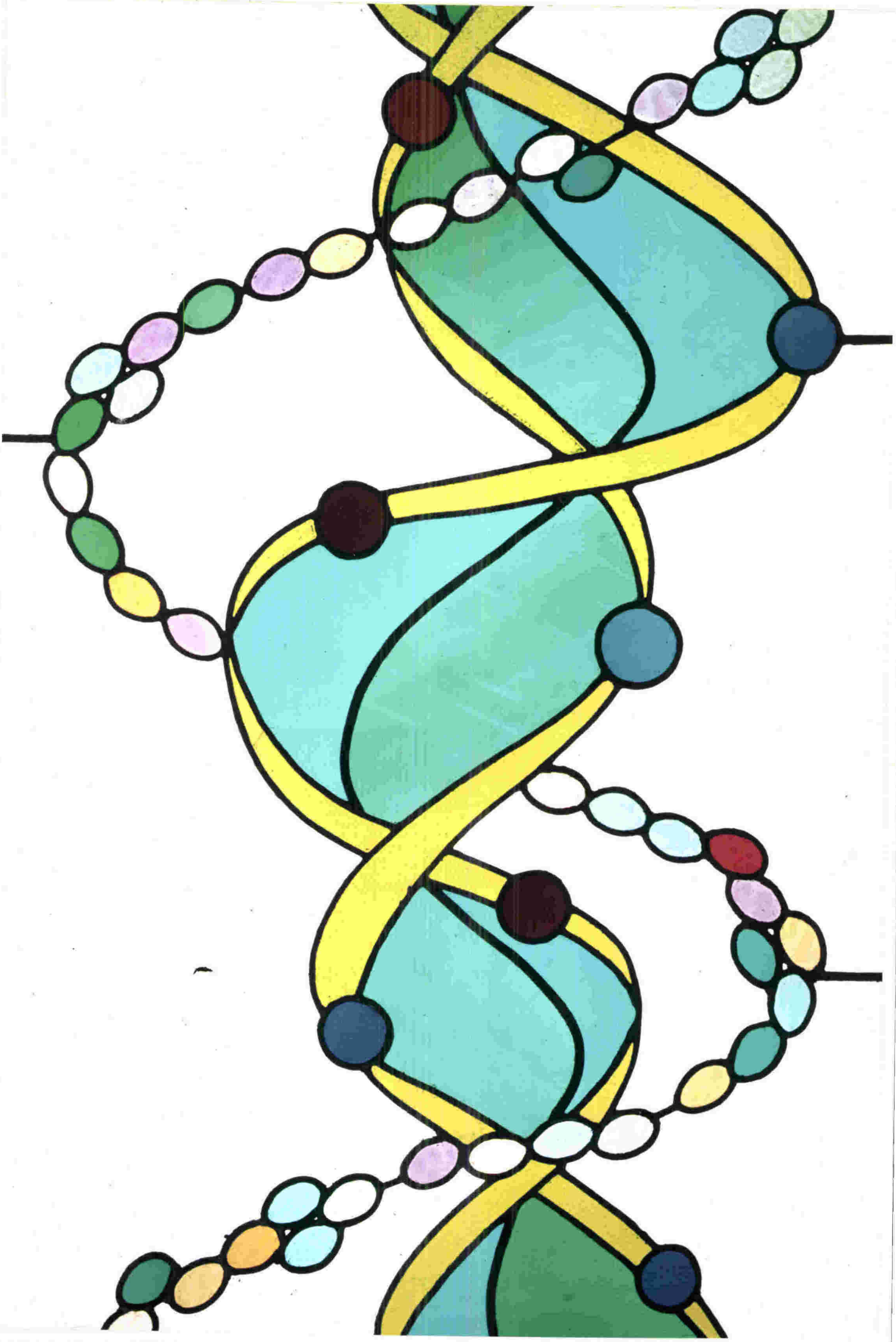

ABSTRACT

The crystal and molecular structures of five binary complexes between transition-metal ions and 5'-ribonucleotides have been determined by X-ray crystallographic means. All data were collected by diffractometry and the structures refined by the full-matrix least-squares method.

The complex $Ni(C_{10}H_{11}N_4O_8P)(H_2O)_5.2H_2O$ crystallizes in the orthorhombic space group $P2_12_12_1$ with four molecules in a unit cell of dimensions a = 6.853(1), b = 10.812(2), c = 25.925(3) Å. Refinement converged with R and R_w values of 0.054 and 0.059 respectively.

The structure is monomeric with nickel octahedrally co-ordinated to N(7) of the base and to five water molecules. The monomer is stabilized by three intramolecular hydrogen bonds involving co-ordinated water molecules, phosphate oxygens, and the exocyclic O(6) atom of the base.

The complex of empirical formula $Co(C_9H_{12}N_3O_8P)(H_2O)$ crystallizes in the monoclinic space group $P2_1$ with two formula units in a unit cell of dimensions a = 10.002(1), b = 7.459(2), c = 9.429(1) Å, $\beta = 96.58(1)^{\circ}$. The final R and R_w values were 0.073 and 0.063 respectively.

The structure is polymeric in two dimensions. The cobalt is in a distorted tetrahedral environment, being co-ordinated to N(3) of the base, two oxygens of two

different phosphate groups, and a water molecule. There is a weak interaction between the metal ion and the exocyclic O(2) atom of the base.

The complex of empirical formula $Cd(C_9H_{12}N_3O_8P)(H_2O).H_2O$ crystallizes in the orthorhombic space group $P2_12_12_1$ with four formula units in a unit cell of dimensions $a = 5.294(1)$, $b = 17.070(1)$, $c = 16.371(1)$ Å. Final R and R_w values of 0.038 and 0.045 respectively were obtained.

The structure is polymeric in three dimensions. The cadmium is in a distorted square-pyramidal environment, being co-ordinated to N(3) of the base, three oxygen atoms of three phosphate groups, and a water molecule. There is a weak interaction between the metal ion and the O(2) atom of the base.

The complex of empirical formula $Cu(C_{10}H_{11}N_4O_8P).H_2O$ crystallizes in the orthorhombic space group $P2_12_12_1$ with four formula units in a unit cell of dimensions $a = 17.412(3)$, $b = 15.772(3)$, $c = 5.077(1)$ Å. Refinement returned R and R_w values of 0.083 and 0.061 respectively.

The structure is polymeric in one dimension. The copper is co-ordinated to N(7) of the base and three oxygens of three phosphate groups. Weak axial bonds to a further phosphate oxygen and the exocyclic O(6) atom of the base complete the pseudo octahedral co-ordination geometry (4 + 1 + 1).

The complex of empirical formula $Cu_3(C_{10}H_{12}N_5O_8P)_3$-$(H_2O)_8.4H_2O$ crystallizes in the orthorhombic space group $P2_12_12$ with four formula units in a unit cell of dimensions a = 20.813(4), b = 23.356(3), c = 11.392(1) Å. The final R and R_w values were 0.11 and 0.09 respectively.

The structure consists of irregular helical chains. Each of the three independent coppers is in a square-pyramidal environment, with N(7) of the bases occupying the axial positions. Whereas the square-planes of two of the coppers each consists of one phosphate oxygen and three water molecules, that of the third consists of two oxygens from two phosphates, and two water molecules. The structure is stabilized by intramolecular hydrogen bonds involving co-ordinated water molecules, phosphate oxygens, and the exocyclic O(6) atoms of the bases.

A system has been devised for classifying the structures of binary metal/ribonucleotide complexes.

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