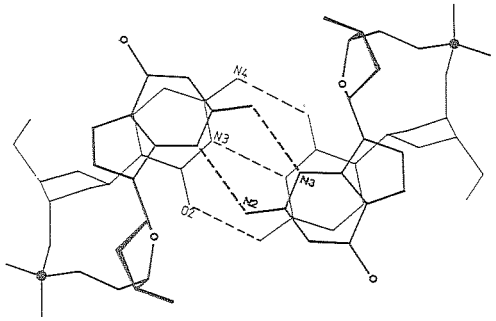
03.2-03 THE CRYSTAL STRUCTURE OF AMMONIUM DEOXY-CYTIDYLYL-(3',5')-DEOXYGUANOSINE TRIHYDRATE

William B.T. Cruse, Ernst Egert and Olga Kennard, University of Cambridge, Cambridge CB2 1EW, U.K.

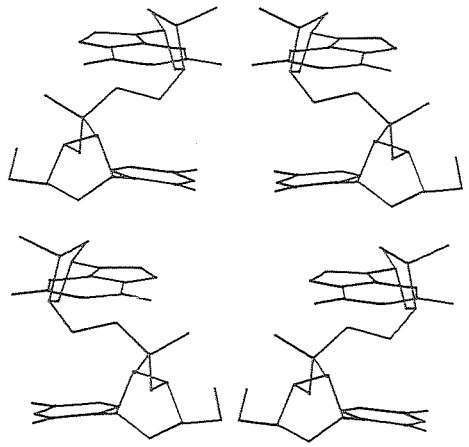
Although self-complementary oligonucleotides are often assumed to form Watson-Crick dimers, ammonium deoxy-CpG, forms self base-pairs when crystallized from aqueous acetone at pH4. The crystals are tetragonal, space group $P4_32_12$, with a=b=11.078 Å, c=45.826 Å and Z=8. The structure was solved by tangent expansion of phases based on phosphorous and refined to a final R of 6%

The deoxy-CpG dimers utilize the two-fold symmetry axis normal to [110]. Guanine bases pair via two hydrogen bonds. Cytosine bases pair by an additional hydrogen bond arising from the hemi-protonation of N(3). The cytosine base C(2)-N(3) and N(3)-C(4) distances of 1.384(9) and 1.344(9)Å can be correlated with other protonated cytidinium structures.

The structure displays normal nucleoside conformational features. The sugar puckers are C(2)'-endo with glycosidic torsion angles of 54.6° for C and 94.4° for G.



The extent of the base-base and base-sugar stacking is shown in the two Figures. There is pronounced stacking between but not within deoxy-CpG dimers.



The hydrogen bond donors not involved in base-pairing interact with solvent or phosphate oxygen atoms. Ionic interactions between the phosphate and the partially disordered ammonium ion are mediated by water molecules. A zero charge balance within the lattice is accountable if the ammonium nitrogen atoms, related by the dyad axis normal to [110]and separated by 2.824 Å, share a proton.

The observed conformation in ammonium deoxy-CpG does not lead to the construction of an unhindered helix.

03.2-04 INFERENCE OF PROTONATION SITES IN NUCLEOTIDE STRUCTURE ANALYSIS. R. Taylor & O. Kennard, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

The recent interest in the structure determination of increasingly large oligonucleotides has prompted an examination of the reliability with which protonation sites may be inferred from the base dimensions. To this end, the Cambridge Structural Database has been used to determine the distribution of the molecular geometries of protonated and neutral base residues in precisely determined mononucleoside structures. The possibility of partial protonation represents a complicating factor which has been taken into account. The influence of the degree of protonation on the geometry of the terminal phosphate group has also been investigated.

The distributions derived from this work should be of use in the solution and refinement of macromolecular structures containing nucleoside residues.

03.2-05 A CRYSTAL STRUCTURE CONTAINING THE N(7)-H ISOMER OF ADENINE. By Max R. Taylor and J.A. Westphalen, School of Physical Sciences, The Flinders University of South Australia, Bedford Park, S.A., Australia.

Crystals with the empirical formula $(C_5H_6N_5)_2.ZnCl_4.H_2O$ may be obtained on evaporation of an acidified aqueous solution of adenine and zinc chloride. The x-ray structure determination of these crystals has revealed that they contain equal numbers of free adeninium cations and discrete trichloroadeninium zinc-(II) molecules. The latter molecules appear to be identical in stereochemistry to those in the structure of trichloroadeninium zinc(II) determined earlier (M.R. Taylor, Acta Cryst. (1973) B29, 884) where Zn is coordinated to the base through N(7).

The free adeninium cations are unusual in that they are in the isomeric form where H is attached to N(7) and not N(9). A similar isomer is found in the structure of purine (D.G. Watson, R.M. Sweet and R.E. Marsh, Acta Cryst. (1965) 19, 573).

The structure consists of layers of metal complex alternating with layers of cations. There are no direct links between the coordinated and uncoordinated cations. The free adeninium cations are neatly hydrogen bonded to one another in infinite chains along a screw axis via $-NH_2$ and N(1)-H (donors) and N(3) and N(9) (receptors) respectively. The lengths of these hydrogen bonds are 2.908Å and 2.777Å respectively.

The crystals are in space group $P2_1/c$ with a = 15.191Å b = 11.984Å c = 10.509Å β = 100.88° Z = 4. R = 0.041.