X-Ray Crystal Structure of the 1:1 Manganese–Cytosine 5′-Phosphate Complex: Metal Bonding to Both O(2) of the Base and Phosphate

By KATSUYUKI AOKI

(*The Institute of Physical and Chemical Research, Wako-shi, Saitama* 351, *Japan*)

Summary The *X*-ray crystal structure analysis of the 1:1 complex of manganese and cytosine 5′-phosphate shows the complex to be a three-dimensional polymer with the metal bonded to O(2) of the base, four oxygen atoms of the three phosphate groups, and one water molecule.

CONSIDERABLE interest has been focussed on metal-ion interaction with nucleic acids. The crystal structure determination of metal complexes of nucleotides is important in establishing the sites of binding of the constituent base, sugar, and phosphate units, and the stereochemistry of the complexes formed. We report the crystal structure of the 1:1 manganese–cytosine 5′-phosphate complex as a part of a series of crystallographic studies of metal nucleotide complexes.[1]

The complex (small pink needles) was prepared in a manner similar to that of Ogawa and Sakaguchi[2] and analysed as $C_9H_{12}N_3O_8PMn,2{\cdot}5H_2O$. *Crystal data* (from Weissenberg and precession photographs): orthorhombic, space group $P2_12_12_1$, $a = 15{\cdot}44(2)$, $b = 19{\cdot}54(2)$, $c = 5{\cdot}08(1)$

Å, $Z = 4$, $D_m = 1{\cdot}84$ (by flotation), $D_c = 1{\cdot}824$ g cm.$^{-3}$ Multiple-film equi-inclination Weissenberg data were collected for five layers along the *c*-axis using Cu-K_α radiation. Intensities were measured for 586 observed reflections and were corrected for Lorentz and polarization factors in the usual way. The structure was solved by the heavy-atom method and partially refined by block-diagonal least-squares yielding the present discrepancy index R of 0·117, where the metal and phosphate group were refined anisotropically and all other non-hydrogen atoms isotropically.

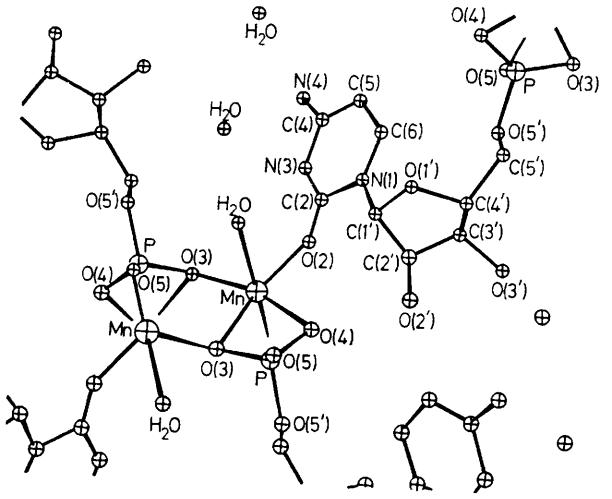

FIGURE. A section of the structure of $[(C_9H_{12}N_3O_8P)Mn(H_2O)]$, $1{\cdot}5H_2O$. Hydrogen bonds are omitted.

A section of the structure of the complex is shown in the Figure. A notable structural feature of the complex is that the O(2) and not the N(3) position of the pyrimidine ring is involved in the co-ordination sphere: there are seven other reported structures of metals with cytosine nucleotides,[3] where each metal is primarily bonded to the N(3) position of the pyrimidine ring and O(2) is only weakly bonded. The co-ordination about the manganese atom is square-bipyramidal, involving the O(2) atom of the pyrimidine base, a water molecule, and four oxygen atoms of the three different phosphate groups, two of which bridge across two manganese atoms: Mn–O(2) 2·08(3), Mn–(phosphate oxygen) average value 2·21(9), and Mn–(H_2O) 2·40(3) Å. The complex is a three-dimensional polymer. The crystal of the complex possesses cylindrical channels with a helical sequence of –Mn–O(3)–Mn–O(3)–atoms throughout the crystal. There is no stacking in the base. Bond distances and angles within the molecule have their usual values, and thus co-ordination of the metal ion to O(2) scarcely affects the geometry of the pyrimidine ring system. The conformation about the glycosyl bond is *anti*: χ_{CN}[4] = − 170·3°. The ribose ring is puckered with C(3′) displaced by 0·61 Å on the same side as C(5′), and hence C(3′) is *endo*. The conformation about the exocyclic bond C(4′)—C(5′) is the commonly observed *gauche–gauche* one.[5]

It should be noted that co-ordination of the metal to the O(2) atom has little effect on the carbonyl stretching band in the i.r. spectra and this may be the cause of misinterpretation by Ogawa and Sakaguchi,[2] who concluded on the basis of i.r. studies that the metal atom does not bind to the base.

(*Received, 4th June* 1976; *Com.* 640.)

[1] K. Aoki, *Bull. Chem. Soc. Japan*, 1975, **48**, 1260; K. Aoki, *Acta Cryst.*, 1976, **B32**, 1454; K. Aoki, G. R. Clark, and J. D. Orbell, *Biochim. Biophys. Acta*, 1976, **425**, 369.
[2] M. Ogawa and T. Sakaguchi, *Yakugaku Zassi*, 1972, **92**, 1166.
[3] J. A. Carrabine and M. Sundaralingam, *Chem. Comm.*, 1968, 746; G. R. Clark and J. D. Orbell, *ibid.*, 1975, 697; K. Saito, R. Terashima, T. Sakaki, and K. Tomita, *Biochem. Biophys. Res. Comm.*, 1974, **61**, 83; D. J. Szalda, L. G. Marzilli, and T. J. Kistenmacher, *ibid.*, 1975, **63**, 601; T. J. Kistenmacher, D. J. Szalda, and L. G. Marzilli, *Acta Cryst.*, 1975, **B31**, 2416; D. J. Szalda, L. G. Marzilli, and T. J. Kistenmacher, *Inorg. Chem.*, 1975, **14**, 2076: K. Aoki, *Biochim. Biophys. Acta*, 1976, **447**, 379.
[4] W. Saenger, *Angew. Chem.*, 1973, **85**, 680.
[5] E. Shefter and K. N. Trueblood, *Acta Cryst.*, 1965, **18**, 1067.