X-Ray Crystal Structures of Zinc–Adenine and Zinc–Guanine Complexes

By LATA SRINIVASAN and MAX R. TAYLOR*

(*School of Physical Sciences, The Flinders University of South Australia, Bedford Park, South Australia* 5042)

Summary Crystal structure analyses of zinc complexes of adenine and guanine have shown that zinc is co-ordinated to N(7) and N(9), respectively, with no metal–amino-nitrogen bond in either case.

THE co-ordination of bivalent metal ions to nucleotides and nucleotide bases is of importance in biochemical systems.[1] In particular, it has been suggested that Zn^{2+} ions are co-ordinated to the bases when they take part in the reversible winding and unwinding of DNA.[2] Here we report the results of two crystal structure analyses, one of a zinc–adenine complex and the other of a zinc–guanine complex. We believe that the zinc–adenine structure is the first to show co-ordination of a metal ion to a site of a purine base that is available for co-ordination under biologically significant conditions.

Following the method of Weitzel and Spehr[3] good crystals were obtained by slow evaporation of 2 : 1 mixtures of zinc chloride and base in acid solution. *Crystal data*: (I) trichloroadeniniumzinc, $C_5H_6N_5Cl_3Zn$, monoclinic, $P2_1/c$, $Z = 4$, $a = 10{\cdot}85$, $b = 5{\cdot}93$, $c = 15{\cdot}73$ Å, $\beta = 90°57'$; (II) trichloroguaniniumzinc $C_5H_6N_5OCl_3Zn$, monoclinic, $P2_1/n$, $Z = 4$, $a = 8{\cdot}84$, $b = 11{\cdot}70$, $c = 10{\cdot}36$ Å, $\beta = 100°06'$. Three-dimensional intensity data were recorded from two different crystals in each case on an automatic two-circle diffractometer.[4] Refinement by full-matrix least-squares methods has given $R = 0{\cdot}034$ (I) and $R = 0{\cdot}08$ (II).

Both compounds exist as discrete molecules in the crystals with zinc tetrahedrally co-ordinated to three chlorine atoms and one nitrogen atom in each case. In (I) the base is co-ordinated to zinc through N(7) and carries one positive charge, being protonated at N(1). The N(7)–Zn bond is at an angle of 8° to the adenine ring. The

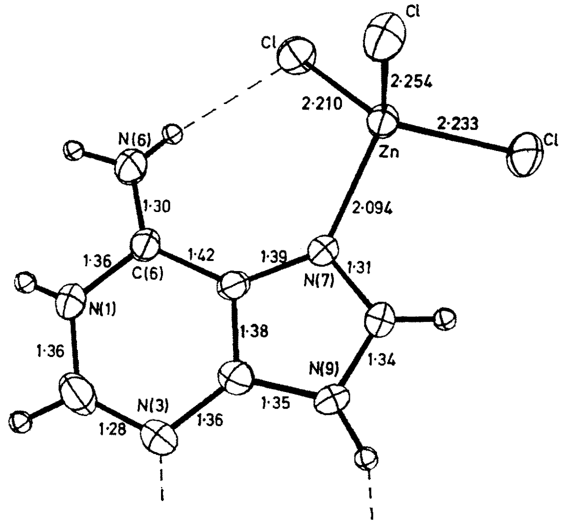

Figure. *The trichloroadeniniumzinc molecule.* ***Hydrogen bonds are dashed.*** *E.s.d.'s of interatomic distances*: Zn–Cl, **0·002;** Zn–N, 0·006, C–C(N), 0·007Å.

C(6)–N(6) bond length (Figure) indicates that, as a result of protonation at N(1) and metal co-ordinated at N(7), the N(6) lone pair has become delocalised to such an extent that the C(6)–N(6) bond has more double bond character than many of the C–N bonds within the purine ring. The resultant residual positive charge on the amino-group prohibits the co-ordination of N(6) to zinc in spite of their proximity and the possibility of forming a chelate. In (II), zinc is bound to N(9) of the base and the base is protonated at N(3) and N(7) giving it a net positive charge. The protonation and co-ordination of the base are similar to that found in a copper(II) chloride–guanine complex.[5] The molecules are linked by strong hydrogen bonds.

Both structures support previous evidence that the amino-group of nucleotide bases is not co-ordinated to bivalent metal ions.[5]

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