The Crystal Structure of a Copper–Cytoside Complex

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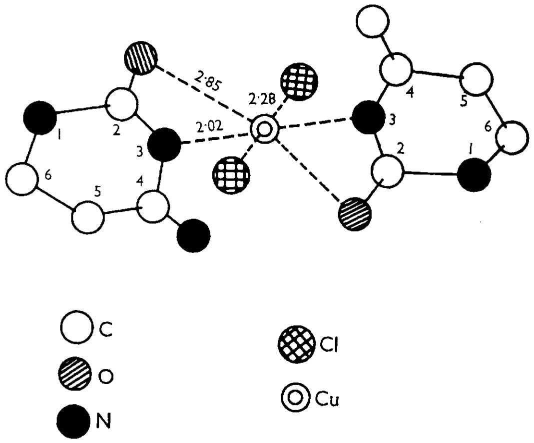
CURRENT interest in metal ion–nucleic acid interactions[1] has prompted us to undertake an *X*-ray diffraction study of metal complexes with nucleic acid bases, nucleosides, and nucleotides. We report the crystal structure of a 2:1 cytosine–copper chloride complex, bis-(4-aminopyrimidine-2-one)copper(II) chloride, which represents the first unequivocal case of copper–pyrimidine bonding.

Light-blue, translucent crystals of $(C_4N_3H_5O)_2CuCl_2$ were prepared in a manner similar to that of Melzer.[2] From oscillation and Weissenberg photographs, the following crystal data were obtained: monoclinic, $P2_1/c$, $a = 8{\cdot}37$, $b = 13{\cdot}78$, $c = 13{\cdot}66$ Å, $\beta = 128°$, Cu-K_α ($\lambda = 1{\cdot}5418$ Å) radiation; $D_m = 1{\cdot}96$ (flotation method) $D_c = 1{\cdot}90$, assuming four molecules of $(C_4N_3H_5O)_2CuCl_2$ per unit cell.

Multiple-film equi-inclination Weissenberg data were collected for five layers on a crystal oscillating about the *a*-axis. Visual intensities were measured for 558 observed reflections, and Lorentz and polarization corrections were made in the usual way. The structure solution was achieved using the heavy-atom method, with subsequent full-matrix least-squares refinement yielding the present discrepancy index R of approximately 0·15.

The co-ordination about the copper atom, together with pertinent bond lengths are shown in the Figure. The very distorted octahedral arrangement is such that the co-ordination can be considered as essentially square planar, involving two chloride ions, and the N(3) atoms of the two cytosine bases, which are in a *trans*-configuration. The O(2) atoms of the bases are only weakly bonded (if at all), approaching the copper on opposite sides, at an average distance of 2·85 Å. The most significant aspect of the co-ordination is that the principal bonding site, N(3), on the cytosine is normally involved in hydrogen bonding to guanine in the Watson–Crick double helix. Analogous bonding of copper to the DNA bases can be invoked to explain the selective destabilization of DNA by copper.



FIGURE

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[1] G. L. Eichhorn, American Chemical Society, Advances in Chemistry, Series No. 62, Werner Centennial, 1967, p. 378; S. Hiai, *J. Mol. Biol.*, 1965, **11**, 672; H. Venner and Ch. Zimmer, *Biopolymers*, 1966, **4**, 321.

[2] M. S. Melzer, *Chem. Comm.*, 1967, 1053.