

Crystal Structure of a Copper–Nucleoside Analogue

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Summary The purine base in a copper–nucleoside analogue has been shown to possess only one binding site, N(7), indicating that the direction of the co-ordinating orbital on the imidazole nitrogen is not compatible with the formation of a chelate structure involving N(7) and O(6).

THE present structure determination is the third in a series on metal complexes of purine derivatives.^{1,2} Previously the copper complex of the unsubstituted hypoxanthine molecule has been shown to possess a dinuclear structure where N(3) and N(9) co-ordinate to copper.² The co-ordination in the

present compound, where N(9) is carrying a methyl group, is more relevant to biological systems since in naturally occurring nucleosides N(9) is blocked by a ribose residue.

Bis-(9-methyl-6-oxopurine)copper(II) dichloride pentahydrate, $[(C_6H_6N_4O)_2Cu]Cl_2 \cdot 5H_2O$, was synthesized according to Weiss and Venner.³ Large, light blue crystals were easily obtained. The space group is monoclinic, $C2/c$ with $Z = 4$ and $a = 16.85$, $b = 8.53$, $c = 14.30$ Å and $\beta = 91.05^\circ$. Data were collected on a Siemens AED 4-circle diffractometer using niobium-filtered Mo- K_α radiation. Within a sphere, $\sin \theta/\lambda \leq 0.64$, 2242 independent reflections were measured. Of these 228 were not significantly above the background. The structure was solved by the heavy-atom method and refined by full-matrix least-squares procedure to a final R value of 0.027.

The geometry of the complex is shown projected on to the plane through the purine moiety (Figure). The copper atoms, at centres of symmetry, have (4+2) co-ordination with Cu–N(7) 2.055, Cu–O(3) 1.971, and Cu–Cl 2.785 Å. The base co-ordinates only through the imidazole nitrogen N(7). The absence of a chelate structure involving N(7) and O(6) may be explained by geometric factors. To accommodate the copper ion in a chelate structure the co-ordinating orbital on N(7) must be appreciably bent. By constructing a hypothetical structure with Cu–O(6) and Cu–N(7) bond lengths of 2.0 Å the angle C(5)–N(7)–Cu becomes approximately 90° , thus differing by 40° from the angle obtained when the direction of the Cu–N(7) bond bisects the external angle C(5)–N(7)–C(8). In the actual structure the corresponding angle is 135.0° and the distance $Cu \cdots O(6)$ is 3.74 Å.

In charged metal complexes of adenine and guanine where the substituent on C(6) is an amino-group the bases are found to be mono-dentate ligands with either N(7) or N(9) as binding site.^{4,5} The absence of a chelate structure in these compounds has been related to the basic properties of the C(6) amino-group; however, in view of the present investigation steric factors are probably decisive.

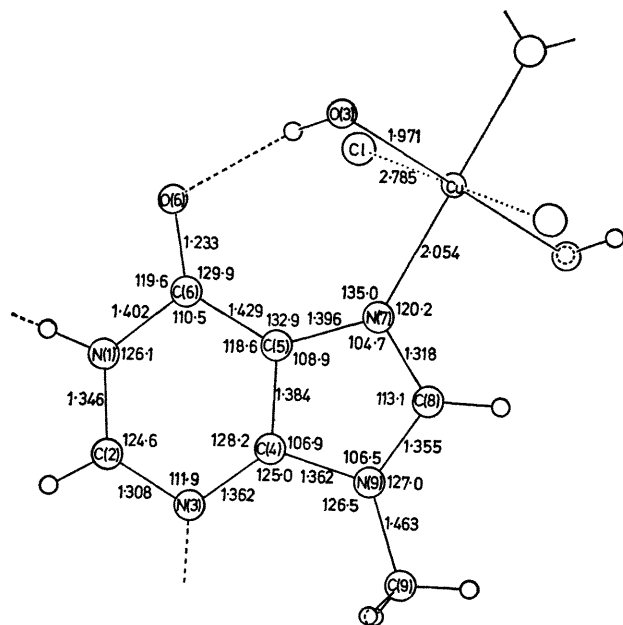


FIGURE. The 9-methylhypoxanthine–copper(II) complex projected onto a plane through the purine moiety.

Estimated standard deviations: Cu–Cl 0.001, Cu–O(N) 0.002, C–X (X = C, N, O) 0.003 Å.

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² E. Sletten, *Acta Cryst.*, 1970, **B26**, 1609.

³ R. Weiss and H. Venner, *Z. physiol. Chem.*, 1965, **340**, 138.

⁴ J. A. Carrabine and M. Sundaralingam, *J. Amer. Chem. Soc.*, 1970, **92**, 369.

⁵ L. Srinivasan and M. R. Taylor, *Chem. Comm.*, 1970, 1668.

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