X-Ray Crystal Structure of a Stable Metal–5′-Uridine Monophosphate (UMP) Complex, $[Cu(5'\text{-}UMP)(2,2'\text{-}dipyridylamine)(H_2O)]_2$

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Summary The ternary complex $[Cu(5'\text{-}uridine\ monophosphate)(2,2'\text{-}dipyridylamine)(H_2O)]_2\cdot5H_2O$ has been prepared and structurally characterized by *X*-ray crystallography; it contains UMP ligands which co-ordinate to copper through the phosphate groups but not through the uracil bases.

In the growing list of transition metal–nucleotide complexes that have been isolated and structurally characterized,[1] there is not a single example of a complex with UMP (uridine monophosphate). Nor is there an example of a nucleotide complex in which co-ordination takes place solely through the phosphate group. We here report the preparation and structure of a molecule containing both these features, the ternary complex $[Cu(5'\text{-}UMP)(dpa)(H_2O)]_2\cdot5H_2O$ (dpa = 2,2′-dipyridylamine).

The complex was prepared by vapour diffusion of an aqueous solution of $Cu(NO_3)_2$, $Na_2(5'\text{-}UMP)$, and dpa (each at 5×10^{-3}M) at pH 7 against Bu^tOH.[2] Crystals in the form of flat green plates appeared after *ca.* 5 weeks. *Crystal data*: monoclinic, space group $P2_1$, $a = 7{\cdot}739(3)$, $b = 18{\cdot}248(6)$, $c = 17{\cdot}473(7)$ Å, $\beta = 90{\cdot}04(2)°$, $Z = 2$, $D_m = 1{\cdot}65$, $D_c = 1{\cdot}663$ g cm^{-3}. Data were collected on a Nonius CAD-3 automated diffractometer with Mo-K_α radiation up to a 2θ limit of 45°. The structure was solved by heavy atom methods and refined to a present R factor of 0·083 for 2920 reflections with $I > 3\sigma(I)$.

The Figure shows a molecular plot of the dimeric molecule, which has no crystallographically-imposed element of symmetry. The most interesting feature of the molecular geometry is the fact that the uracil base is not co-ordinated

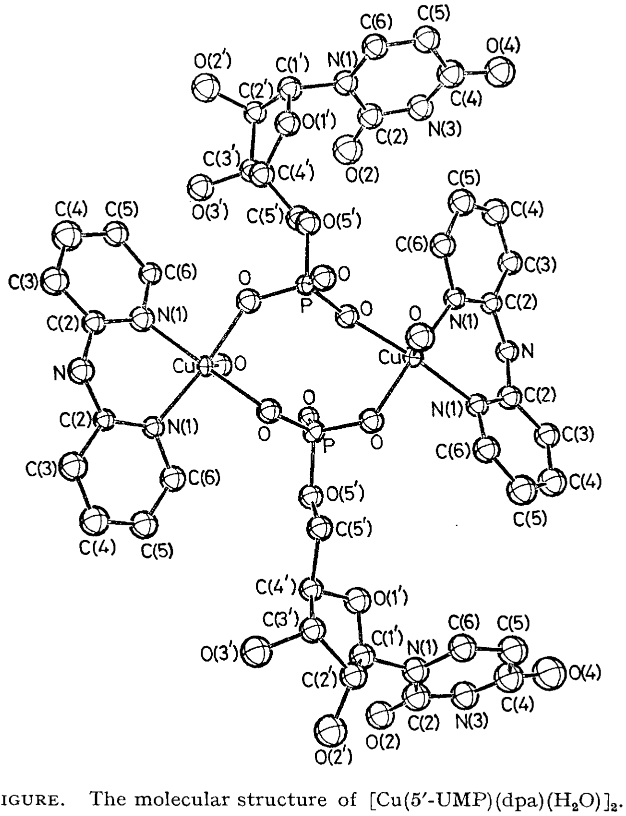

Figure. The molecular structure of $[Cu(5'\text{-}UMP)(dpa)(H_2O)]_2$.

to the metal atom. Instead, co-ordination takes place exclusively through the phosphate group, which forms a bridge between the copper atoms. Each Cu^{2+} ion has a square-pyramidal geometry, with the base defined by two oxygen atoms from different phosphate groups [Cu–O 1·934(12) Å] and two nitrogen atoms from a dipyridylamine ligand [Cu–N 1·987(14) Å]. In the axial position, a water molecule is co-ordinated at a considerably longer distance [Cu–H_2O 2·317(13) Å]. The copper atom is, as expected, located distinctly off the basal plane (*ca.* 0·2 Å) towards the axial water ligand. The two square pyramids are in a *transoid* arrangement, *i.e.* with the two axial groups pointing in opposite directions.†

The two ribose rings have unusual puckering modes: one is C(2′)-*exo* and the other is O(1′)-*endo*. Conformations about the glycosidic C(1′)–N(1) bonds are *syn* and *anti*, respectively.[3] Stacking interactions between the uracil bases of adjacent molecules (at 3·37 Å) and between the pyridine rings of adjacent dipyridylamine ligands (at 3·35 and 3·67 Å) serve to hold the crystal together in two directions. In the third direction, intermolecular contacts consist of a series of hydrogen bonds between co-ordinated water molecules and phosphate groups. The pyridine rings within an individual dipyridylamine ligand are inclined to each other at a dihedral angle of 21·3°.

It is interesting to compare the co-ordinating abilities of various pyrimidine-containing molecules. Cytosine and its derivatives are known to be reasonably good ligands, with primary co-ordination taking place at N(3) and occasionally reinforced by weaker interactions through O(2).[1] Uracil, thymine, and their derivatives are considerably poorer ligands, presumably because the nucleophilic N(3) position is protonated at $pH < 9$. The only two metal–uracil structures that have been reported show complexation through O(4),[4] but this is not evident in the present compound.

This structure shows that the 'phosphate-only' type of nucleotide–metal interaction, long believed to be prevalent in solution,[5] is indeed capable of existence. There are two conceivable reasons why the nucleotide in the present complex should prefer to bind through the phosphate rather than the base. It could be that this type of co-ordination is typical for mixed-ligand complexes containing an aromatic heterocyclic amine like dipyridyl or phenanthroline, or it could simply be due to the weak co-ordinating tendency of uracil. It will be interesting to see, in future structure determinations, if a pattern emerges on metal–nucleotide binding in ternary complexes.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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