X-Ray Crystal Structure of the Ternary Complex $[Cu(3'\text{-GMP})(phen)(H_2O)]_2 \cdot 7H_2O$ (GMP = guanosine monophosphate, phen = 1,10-phenanthroline): Unusual Absence of M–N(7) Bonding in a Metal–GMP Complex

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Summary The structure of $[Cu(3'\text{-GMP})(phen)(H_2O)]_2 \cdot 7H_2O$ (GMP = guanosine monophosphate, phen = 1,10-phenanthroline) represents the first example of a metal–GMP complex in which the N(7) atom of guanine is not co-ordinated to the metal atom, and provides evidence that the dominant form of metal–nucleotide binding in such ternary complexes is the 'phosphate only' bonding mode.

THE crystal structures of about fifteen metal complexes of guanosine monophosphate (GMP), and the closely related molecule inosine monophosphate (IMP), are now known.[1,2] Metal–nucleotide complexation has been shown to take place either through the nucleotide base, or concurrently through the base and the phosphate group. In all cases, metal binding to the N(7) atom of the purine ring appears to be the dominant factor in the solid state. We report the first example of a metal complex of a guanosine derivative in which metal–N(7) bonding is absent.

The ternary complex $[Cu(3'\text{-GMP})(phen)(H_2O)]_2$ (phen = 1,10-phenanthroline) was prepared by mixing solutions of $Cu(NO_3)_2$, phen and 3'-GMP (Na salt), all at 0·01 M, adjusting the pH to 6·8, and heating the solution to 80 °C. Bright blue-green plates appeared upon slow cooling of the reaction mixture. Crystals of $[Cu(3'\text{-GMP})(phen)(H_2O)]_2 \cdot 7H_2O$ are triclinic, space group $P\bar{1}$, with $a = 6{\cdot}857(1)$, $b = 13{\cdot}888(3)$, $c = 14{\cdot}815(2)$ Å, $\alpha = 108{\cdot}30(2)$, $\beta = 88{\cdot}96(2)$, $\gamma = 95{\cdot}48(2)°$, $U = 1333{\cdot}2(5)$ Å^3, $D_m = 1{\cdot}69$ and $D_c = 1{\cdot}71$ g cm^{-3} for one dimeric molecule per unit cell. Data were collected on a Syntex $P2_1$ automated diffractometer with Mo–K_α radiation up to a 2θ maximum of 45°. The structure was solved by conventional heavy-atom techniques and refined to final agreement values of $R = 0{\cdot}061$ and $R_w = 0{\cdot}076$ for 6660 reflections with $I > 3\sigma(I)$.

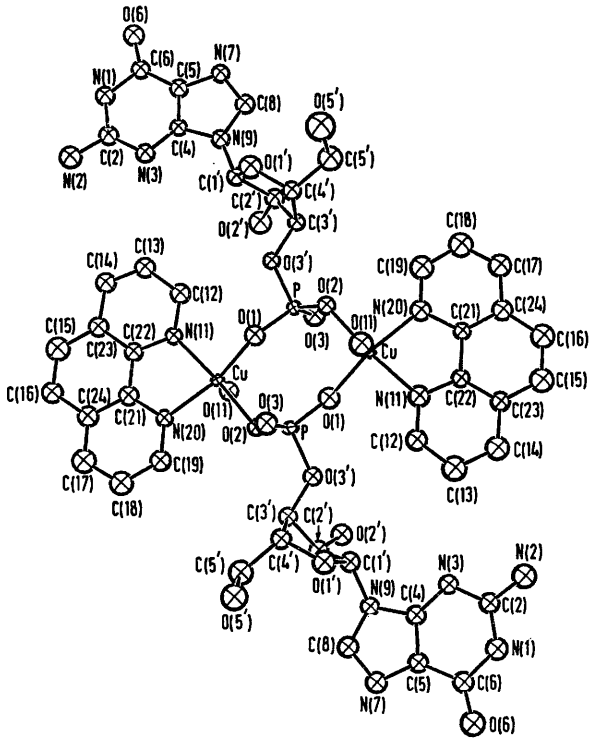

FIGURE. The molecular structure of $[Cu(3'\text{-GMP})(phen)(H_2O)]_2$.

The structure (Figure) has as its inner core a puckered eight-membered $(Cu–O–P–O)_2$ ring. Each Cu atom is in a square-pyramidal environment, with the axial position occupied by a water molecule. Average distances around Cu are: Cu–O(phos) = 1·929(6), Cu–N(phen) = 2·013(7), and Cu–O(water) = 2·472(6) Å. The ligands are arranged in such a way as to produce a pseudo centre of symmetry at the centre of the molecule; a true centre of symmetry, however, is not possible because of the chirality of the ribose groups. Both 3'-GMP ligands have similar nucleotide configurations; the conformations of the purine bases about the glycosidic C(1')–N(9) bonds are *anti*, those of the C(5')–O(5') bonds relative to the sugar rings are *gauche-trans*, and the ribose rings are in the C(2')-*endo* puckering mode.†

The most striking feature of the molecular structure is the fact that the nucleotide ligands co-ordinate to metal through the phosphate groups only. We had earlier found this mode of bonding in the complex $[Cu(5'\text{-UMP})(dpa)(H_2O)]_2$ (UMP = uridine monophosphate, dpa = 2,2'-dipyridylamine), which has a very similar geometry.[3] In $[Cu(3'\text{-GMP})(phen)(H_2O)]_2$, the N(7) atoms of guanine are hydrogen-bonded to water molecules of crystallization at an average distance of 2·96 Å.

Solution studies by Sigel and his co-workers[4] have shown that, in the presence of a second ligand (a π-aromatic base such as phenanthroline or bipyridyl), metal–nucleotide interactions take place predominantly at the phosphate group. The nucleotide base is believed not to bind to the metal ion, but to be stacked with the π-aromatic ring of the second ligand. Our earlier structure determination of $[Cu(5'\text{-UMP})(dpa)(H_2O)]_2 \cdot 5H_2O$,[3] which also shows the 'phosphate only' metal binding mode, was interpreted as a partial confirmation of this model. However, in that case it could have been argued that the poor co-ordinating tendency of the uracil base, whose N(3) atom carries a proton at neutral pH's, would have made metal–uracil binding highly unlikely anyway. In the present $[Cu(3'\text{-GMP})(phen)(H_2O)]_2$ complex, this objection is clearly invalid, since N(7) of guanine *is* a powerful ligating site. The fact that no M–N(7) bonding is found here strongly suggests that the metal–phosphate interaction is indeed the dominant bonding mode in ternary complexes of this type. The intramolecular base–base stacking which is believed to take place in solution is manifested in the solid as intermolecular stacking. In $[Cu(5'\text{-UMP})(dpa)(H_2O)]_2$ this stacking is of the AA–BB type (uracil–uracil, dpa–dpa),[3] whereas in $[Cu(3'\text{-GMP})(phen)(H_2O)]_2$ it is of the AB type (guanine–phenanthroline). Such stacking interactions contribute significantly towards the stability of the crystal lattice.

These results are further supported by an independent study by Aoki[5] on the structure of $[Cu(5'\text{-AMPH})(bpy)(H_2O)]_2(NO_3)_2 \cdot 6H_2O$ [AMPH = adenosine monophosphate (protonated form), bpy = 2,2'-bipyridyl] (prepared at pH 4), which shows a geometry very similar to that of the present compound. Again, the lack of metal binding to the nucleotide base is significant since adenosine monophosphate (AMP) is, like GMP, a ligand for which metal–purine binding is normally expected.[6] In this complex, intramolecular adenine–bipyridyl π–π overlap is found along with the usual intermolecular stacking. Of the four ternary complexes which have been structurally characterized, only the monomeric species $[Cu(5'\text{-IMPH})(bpy)(H_2O)_2](NO_3) \cdot H_2O$[7] [IMPH = inosine monophosphate (protonated form)] deviates from the 'phosphate only' bonding pattern; in that compound, metal–N(7) bonding is found and metal–phosphate bonding is not. However, in that case the phosphate group is almost certainly protonated, making it a less attractive ligand to the metal ion. In contrast, in $[Cu(5'\text{-AMPH})(bpy)(H_2O)]_2^{2+}$ the protonation of 5'-AMP is believed to take place at the N(1)

† 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.

site,[5] which would not significantly affect the strength of metal-phosphate binding. The three dimeric ternary complexes described here, plus the polymeric structure of $[Co_2(5'\text{-UMP})_2(H_2O)_4]_n$ recently reported by Goodgame, Skapski, and their co-workers,[8] represent the only known crystal structures in which the nucleotide ligands co-ordinate solely through the phosphate groups.

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