Absence of Direct Metal–Nucleotide Interaction in the Crystal Structure of the Ternary System, $[Cu(bim)(H_2O)_5]^{2+}[5'\text{-IMP}]^{2-}\cdot 3H_2O$ (bim = benzimidazole; 5′-IMP = inosine 5′-monophosphate)

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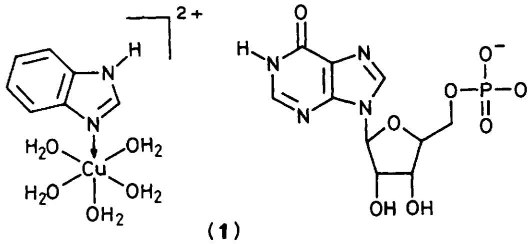
The unusual absence of direct metal–nucleotide binding in a metal-6-oxopurine nucleotide complex is demonstrated for the first time in the structure of $[Cu(bim)(H_2O)_5]^{2+}[5'\text{-IMP}]^{2-}\cdot 3H_2O$ (bim = benzimidazole; 5′-IMP = inosine 5′-monophosphate); the nucleotide base stacks with the bim ligand and the phosphate oxygens are involved in hydrogen bonds with the co-ordinated water molecules.

X-Ray structural studies have shown that the 6-oxopurine nucleotides, *viz.*, inosine monophosphate and the closely related guanosine monophosphate, co-ordinate solely through the N(7) atom of the base in the monomeric complexes of the type $[M(\text{nucleotide})(H_2O)_5]$, or concurrently through N(7) and phosphate oxygens in the case of polymeric complexes.[1] On the other hand, in ternary complexes containing a π-aromatic amine, they co-ordinate only through phosphate oxygens.[1,2] We report here the first example of a ternary system $[Cu(bim)(H_2O)_5]^{2+}[5'\text{-IMP}]^{2-}$ (**1**), in which both N(7) and phosphate co-ordination are absent.

The complex was prepared by mixing solutions of $Cu(NO_3)_2$, Na_2-5′-IMP, and bim in equimolar ratios. Vapour diffusion of the reaction mixture (pH 6.0) against t-butyl alcohol afforded light blue plate-like crystals after about one week. *Crystal data:* $C_{17}H_{33}CuN_6O_{16}P$, monoclinic, space group $P2_1$, $a = 7.013(2)$, $b = 13.179(9)$, $c = 14.565(9)$ Å, $\beta = 94.82(4)°$, $Z = 2$. Intensity data were collected on a Syntex $P2_1$ diffractometer with Mo-K_α radiation for $4.5<2\theta<45°$. The structure was solved by the heavy atom method and refined by full-matrix least-squares to an R value of 0.034 for 1761 reflections with $I>3\sigma(I)$.† The calculations were performed using the program SHELX-76.

The metal ion has a distorted (4 + 1 + 1) octahedral geometry (Figure 1) with the basal plane defined by the nitrogen atom, N(11) of the bim ligand and three water oxygen atoms, O(W1), O(W2), and O(W3) [Cu–N(bim) 1.948; Cu–(water)$_{av.}$ 2.017 Å]. The axial positions are occupied by water oxygens at longer distances [Cu–O(W4) 2.194; Cu–O(W5) 2.732 Å]. The most remarkable feature of the structure is that the nucleotide is not co-ordinated to the metal ion. Instead of binding to Cu^{II}, the N(7) atom of the base is linked to a lattice water molecule [N(7) · · · · O(W6) 2.85 Å], while the phosphate oxygens are involved in hydrogen bonds to co-ordinated as well as lattice water molecules. The screw-related bim ring overlaps with the purine base at an average distance of 3.5 Å and an angle of 22°. Unit cell translation along *a* gives rise to a stacking pattern of the type –ABABA– (A = nucleotide base; B = π-aromatic amine). The nucleotide adopts the energetically preferred conformation: the *anti* base with $\chi_{CN} = -96.9°$, C(3′)-*endo* sugar pucker, and *gauche–gauche* conformation about the C(4′)–C(5′) bond.



(**1**)

Solution studies on ternary complexes have suggested that in the presence of a π-aromatic amine, the metal ion prefers to bind at the phosphate group while the base of the nucleotide is involved in stacking interactions with the secondary ligand.[3] *X*-Ray structural studies on metal–nucleotide complexes containing various π-aromatic amines have confirmed this mode of binding in the solid state.[2] Apart from intramolecular stacking of AB type, which is believed to take place in solution, intermolecular stacking of AA/BB type has also been observed in these structures. Sigel and coworkers[4] have shown that the biologically important imidazole group would also impart similar discriminating qualities to metal ions. However, in the only metal–nucleotide complex containing imidazole structurally characterized so far, the nucleotide co-ordinates through N(7) atoms of the bases in *cis*-position instead of through the phosphate oxygens.[5]

The results obtained in the present study, which involves a derivative of imidazole, are novel in the sense that the

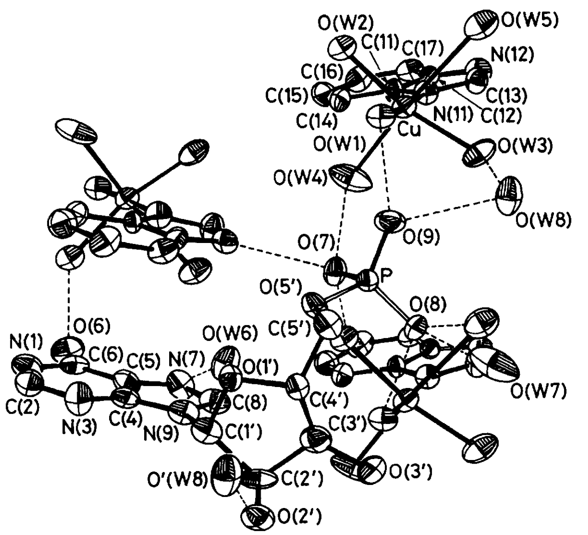


Figure 1. A view of the structure showing the stacking of bim and purine base. The sequence repeats by unit translation along *a* (vertical direction). Broken lines indicate hydrogen bonds. The correct optical form is identified from the known absolute configuration of (D)-ribose.

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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.

powerful ligand, 5′-IMP anion, is pushed out of the primary co-ordination sphere of the metal ion and intermolecular π–π overlapping interaction between the two constituents of the stacking adduct prevails over direct metal–nucleotide co-ordination. The neighbouring stacks of adducts are bridged by hydrogen bonds involving phosphate oxygens and co-ordinated water molecules. This mode of interaction in a ternary metal–nucleotide system, which represents a new structural type, is capable of existing in solution and, perhaps, should be borne in mind when interpreting solution results.

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References

1 R. W. Gellert and R. Bau, in 'Metal Ions in Biological Systems,' ed. H. Sigel, Marcel Dekker, New York, 1979, vol. 8, pp. 1—56; V. Swaminathan and M. Sundaralingam, *CRC Crit. Rev. Biochem.*, 1979, **6**, 245.
2 R. W. Gellert, B. E. Fischer, and R. Bau, *Biochem. Biophys. Res. Commun.*, 1979, **88**, 1443 and references cited therein.
3 H. Sigel, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 394; C. F. Nauman and H. Sigel, *J. Am. Chem. Soc.*, 1974, **96**, 2750; P. R. Mitchell and H. Sigel, *ibid.*, 1978, **100**, 1564.
4 H. Sigel, *Inorg. Chem.*, 1980, **19**, 1411 and references cited therein.
5 M. Damodara Poojary and H. Manohar, *Inorg. Chem.*, 1985, **24**, 1065.