Transition-metal–Nucleotide Complexes. *X*-Ray Crystal and Molecular Structure of the Complex Between Nickel(II) and Inosine 5′-Monophosphate [Ni(imp)$(H_2O)_5$,$2H_2O$]

By GEORGE R. CLARK* and JOHN D. ORBELL

(*Department of Chemistry, University of Auckland, Private Bag, Auckland, New Zealand*)

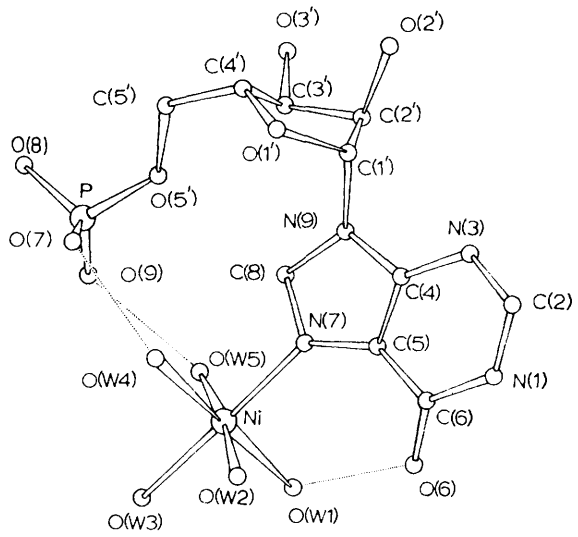
Summary. A crystal and molecular structure determination of the transition metal–nucleotide complex, Ni(imp)-$(H_2O)_5$,$2H_2O$ shows that the octahedral nickel ion is co-ordinated to the N(7) atom of the hypoxanthine unit and to five water molecules and that hydrogen bonding occurs between two of the co-ordinated water molecules and two of the phosphate oxygen atoms; the structure previously proposed is shown to be incorrect.

THERE is much conflicting evidence[1] on the sites and nature of the binding of metal ions to the nucleic acids and their constituents. We have determined the crystal and molecular structure of the complex between nickel ions and the nucleotide inosine 5′-monophosphate.

Blue needles of the complex $(C_{10}H_{11}N_4O_8P)Ni(H_2O)_7$ were obtained by the method of Ogawa and Sakaguchi.[2] The structure of the product was established by i.r. spectroscopy and elemental analysis. The crystals are orthorhombic, $a = 6{\cdot}853(1)$, $b = 10{\cdot}812(2)$, $c = 25{\cdot}925(3)$ Å, $Z = 4$, space group $P2_12_12_1$.

Intensity data were collected on a Hilger-Watts 4-circle diffractometer using Zr-filtered Mo-K_α radiation. A total of 1471 unique reflections with $I > 3\sigma(I)$ were recorded. The structure was solved by Patterson and Fourier syntheses and has been partially refined by least-squares techniques. The nickel and phosphorus atoms have been assigned anisotropic temperature parameters, all other non-hydrogen atoms have been assigned isotropic temperature parameters. The hydrogen atoms have yet to be located. R at this stage is 0·085.

The structure of the molecule, a divalent zwitterion, is shown in the Figure. The nickel ion is directly bonded to the N(7) position of the hypoxanthine unit, the octahedral



FIGURE

co-ordination being completed by five water molecules. The asymmetric unit also contains two water molecules of crystallisation (not shown in the diagram) and hence the

correct molecular formula is $Ni(C_{10}H_{11}N_4O_8P)(H_2O)_5,2H_2O$. The most significant intramolecular hydrogen bonds are those linking co-ordinated water molecules with the oxygen atom of the hypoxanthine group and two oxygen atoms of the phosphate O(W1)–O(6) 2·83, O(W4)–O(7) 2·65, O(W5)–O(9) 2·73 Å.

The ten atoms of the purine ring system are statistically non-planar. The relative orientiation of base and sugar, as defined by the torsion angle Φ_{CN}[3,4] is $-33·8°$. Hence the nucleotide displays the *anti*-conformation. The ribose ring is puckered [(C(3′) *endo*, displacement of C(3′) from the best plane defined by O(1′), C(1′), C(2′), and C(4′) is 0·59 Å]. The conformation about the C(4′)–C(5′) bond is *gauche–gauche*.[5]

Bond distances and angles within the molecule are mostly as expected. The Ni–H_2O bonds average 2·06 Å, Ni–N(7) = 2·11 Å. Co-ordination of the metal ion to N(7) appears to have had little effect on the geometry of the purine ring system. The exocyclic bond N(9)–C(1′) (1·52 Å) is rather long, as is C(5′)–O(5′) (1·48 Å), but detailed comparisons will be deferred until refinement has been completed. The ester P–O bond length is 1·62 Å, other P–O bonds are all 1·51 Å.

On the basis of i.r. spectra investigations, Ogawa and Sakaguchi concluded[2] that the nickel atom binds to the phosphate group in this complex. They could reach no conclusions regarding co-ordination to the hypoxanthine ring. Our analysis has shown that the nickel atom does co-ordinate to N(7) of the base, but does not bond directly to the phosphate group. However, the molecule is stabilised by water bridges between the nickel ion and two of the phosphate oxygen atoms, and this may be the basis of misinterpretation. It would seem likely that similar interactions may occur in the many other metal–nucleotide complexes where metal–phosphate bonding has either been proposed or tacitly assumed.

(*Received, 5th November* 1973; *Com.* 1514.)

[1] R. M. Izatt, J. J. Christensen, and J. H. Rytting, *Chem. Rev.*, 1971, **71**, 439; Y. A. Shin, J. M. Heim, and G. L. Eichhorn, *Bioinorg. Chem.*, 1972, **1**, 149; T A. Glassman, C. Cooper, L. W. Harrison, and T. J. Swift, *Biochem.*, 1971, **10**, 843.
[2] M. Ogawa and T. Sakaguchi, *Chem. Pharm. Bull.* (*Japan*), 1971, **19**, 1650.
[3] J. Donohue and K. N. Trueblood, *J. Mol. Biol.*, 1960, **2**, 363.
[4] A. E. V. Haschemeyer and A. Rich, *J. Mol. Biol.*, 1967, **27**, 369.
[5] E. Shefter and K. N. Trueblood, *Acta Cryst.*, 1965, **18**, 1067.