Transition-metal–Nucleotide Complexes. *X*-Ray Crystal and Molecular Structures of the Cobalt(II) and Cadmium(II) Complexes of Cytosine 5′-Monophosphate, $[Co(CMP)(H_2O)]$ and $[Cd(CMP)(H_2O)]\cdot H_2O$

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Summary Crystal and molecular structure determinations of the transition-metal–nucleotide complexes $Co(CMP)(H_2O)$ and $Cd(CMP)(H_2O)\cdot H_2O$ show the former to be two-dimensionally polymeric with the tetrahedral cobalt ion directly bonded to two phosphate oxygen atoms, N(3) of the pyrimidine, and one water molecule and the latter to be three-dimensionally polymeric with the distorted square-pyramidal cadmium ion directly bonded to three phosphate oxygen atoms, N(3) of the pyrimidine ring, and one water molecule.

To further understand the nature and sites of metal ion binding to nucleic acids and their constituents[1] we have determined the crystal and molecular structures of complexes between the nucleotide cytosine 5′-monophosphate and the metal ions cobalt(II) and cadmium(II).

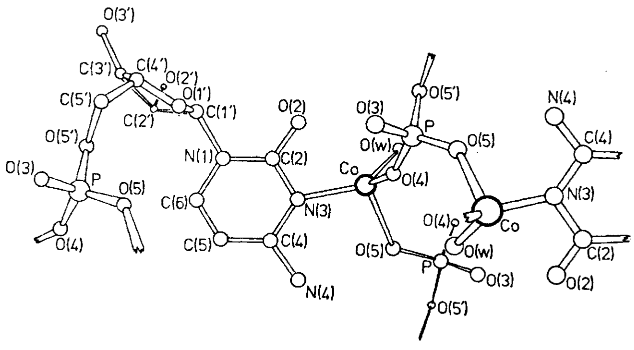

FIGURE 1. A section of the structure of $Co(CMP)(H_2O)$.

The complexes were prepared using the method of Ogawa and Sakaguchi[2] and analysed as $(C_9H_{12}N_3O_8P)Co(H_2O)$ and $(C_9H_{12}N_3O_8P)Cd(H_2O)_2$. The cobalt complex is monoclinic, $a = 10{\cdot}002(1)$, $b = 7{\cdot}459(2)$, $c = 9{\cdot}429(1)$ Å, $\beta = 96{\cdot}58(1)^\circ$, $Z = 2$, space group $P2_1$; the cadmium complex is orthorhombic, $a = 5{\cdot}294(1)$, $b = 17{\cdot}070(1)$, $c = 16{\cdot}371(1)$ Å, $Z = 4$, space group $P2_12_12_1$.

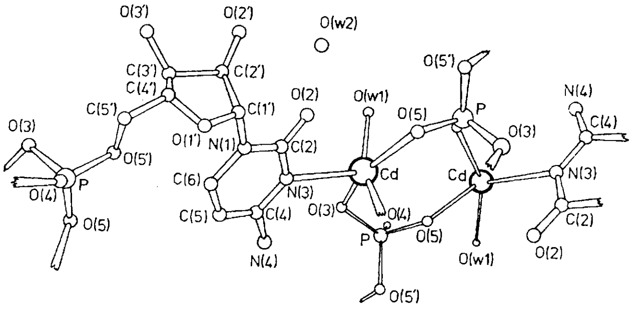

FIGURE 2. A section of the structure of $Cd(CMP)(H_2O).H_2O$.

Intensity data were collected on a Hilger-Watts 4-circle diffractometer using Ni-filtered Cu-K_α radiation. Totals of 871 and 1104 unique observed reflections $[I > \sigma(I)]$ were recorded for the cobalt and cadmium complexes respectively. Both structures were solved by Patterson and Fourier syntheses and have been partially refined by least-squares techniques. The metal 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 $0{\cdot}092$ for the cobalt complex and $0{\cdot}071$ for the cadmium complex.

A section of the structure of the cobalt complex is shown in Figure 1. The complex is polymeric in two dimensions, the layers being linked by hydrogen bonds. The tetrahedral cobalt ion is bonded to the N(3) position of the pyrimidine ring, to two oxygen atoms of different phosphate groups, and to a water molecule. A feature of the structure is the spiralling sequences of atoms –Co–O(4)–P–O(5)–Co–O(4)– which form elongated cylinders throughout the crystal. In Figure 1 the broken bond from the right-hand cobalt atom extends to the atom one unit cell above O(4) to perpetuate the spiral. A consequence of the molecular geometry is that the pyrimidine bases partially overlay one another along the *b* direction at a separation distance of 3·73 Å, the stacking being stabilised mainly by the interaction between the amino group [N(4)] and the neighbouring π-electron systems. This type of base stacking has been predicted[3] and frequently observed.[4]

The cadmium complex is three-dimensionally polymeric. A segment of its structure is shown in Figure 2. For clarity the large number of hydrogen bonds have again been omitted. The distorted square-pyramidal cadmium atom is bonded to N(3) of the pyrimidine ring, to three oxygen atoms of different phosphate groups and to a water molecule. The correct empirical formula is thus $Cd(C_9H_{12}N_3O_8P)(H_2O).H_2O$. The crystals of this complex also possess cylindrical channels extending through the entire crystal, but now the spirals of –Cd–O(5)–P–O(3)–Cd)– atoms are cross-linked by additional phosphate bridges through O(4). There is no base stacking.

In both complexes the nucleotide geometries are similar to those found in structural studies of other nucleosides and nucleotides, and thus the geometry has not been markedly affected by co-ordination to the metal atoms. The six atoms of each pyrimidine ring are statistically non-planar, and both nucleotides display the *anti*-conformation. The relative orientations of base and sugar as defined by the torsion angle χ_{CN}[5] are 68·1° and 12·8° for cobalt and cadmium complexes respectively. Both ribose rings are puckered [Co, C(2′) *endo*, displacement of C(2′) from the best plane defined by O(1′), C(1′), C(3′), C(4′) is 0·48 Å; Cd, C(3′) *endo*, displacement of C(3′) from the best plane defined by O(1′), C(1′), C(2′), C(4′) is 0·56 Å]. In both complexes the conformation about the C(4′)–C(5′) bond is gauche–gauche.[6]

Bond distances and angles within both complexes are mostly as expected but detailed comparisons will be deferred until refinement has been completed.

On the basis of i.r. spectra investigations Ogawa and Sakaguchi concluded[2] that the metal atoms bind to both the phosphate group and the cytosine base in these two complexes. Our analysis has verified this conclusion and has established the site of base co-ordination to be N(3). The direct binding to the phosphate oxygen atoms is in contrast to that found for the nickel(II) inosine 5′-monophosphate complex[1] where the nickel atom bonds only indirectly to the phosphate *via* water bridges.

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