Interaction of Metal Ions with 2'-Deoxyribonucleotides. Crystal and Molecular Structure of a Cobalt(II) Complex with 2'-Deoxyinosine 5'-Monophosphate†

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The crystal structure of the cobalt(II) complex with 2'-deoxyinosine 5'-monophosphate (5'-dIMP), $[Co(5'\text{-dIMP})(H_2O)_5]\cdot 2H_2O$, has been analysed by *X*-ray diffraction. The complex crystallizes in the space group $P2_12_12_1$ with $a = 6.877(3)$, $b = 10.904(2)$, $c = 25.421(6)$ Å, and $Z = 4$. The structure was solved by the heavy-atom method and refined to an *R* value of 0.043 using 1 776 unique reflections. The cobalt ion binds only to the 6-oxopurine base of the nucleotide at the N(7) position, the octahedral co-ordination of the metal being completed by five water oxygens. The phosphate oxygens are involved in hydrogen bonding with the co-ordinated water molecules. The structure is closely similar to that of the corresponding ribonucleotide complex. The nucleotide has the energetically preferred conformation: an *anti* base, a C(3')-*endo* sugar pucker, and a *gauche–gauche* conformation about the C(4')–C(5') bond. The significance of sugar puckering in the monomeric complexes of general formula $[M(5'\text{-nucleotide})(H_2O)_5]$ is explained in terms of the structural requirements for metal–water–phosphate bridging interactions.

Nucleotides play a key role in biology,[1-3] *e.g.*, in the information storage *via* RNA and DNA or in energy-transfer processes. The enzymes which require these nucleotides as substrates need metal ions for their activation.[1] Moreover, it has been shown that certain platinum complexes, notably *cis*-$[Pt(NH_3)_2Cl_2]$, are effective antitumour agents[3] and these drugs are widely believed to produce their effects *via* interaction with nucleic acids.[4] Consequently, metal ion–nucleotide complexes have been studied extensively both in solution and in the solid state.

The majority of metal–nucleotide complexes that have been structurally characterized contain a ribonucleotide.[5-7] However, information regarding the metal binding on deoxyribonucleotides, the building blocks of DNA, is limited. *X*-Ray studies carried out so far on metal complexes of deoxyribonucleotides are confined to Co^{II}[8,9] and Ni^{II}[9] complexes with 2'-deoxyguanosine 5'-monophosphate (5'-dGMP), and Cd^{II} complexes with 2'-deoxycytidine 5'-monophosphate (5'-dCMP)[10] and 2'-deoxyuridine 5'-monophosphate (5'-dUMP).[11] In this paper we report the preparation and *X*-ray structural study on a Co^{II} complex of 2'-deoxyinosine 5'-monophosphate (5'-dIMP), the first such study of a metal 5'-dIMP complex.

Experimental

Preparation of the Complex.—The complex was prepared by mixing aqueous solutions of cobalt nitrate hexahydrate (Sarabhai M. Chemicals, India) and the disodium salt of 5'-dIMP (Sigma), each at 0.03 mol dm^{-3}. The pH was adjusted to 6.5. The solution was stirred for 15 min and allowed to stand at room temperature. The violet plate-like crystals, which appeared after *ca.* one week were filtered off, washed with water and air-dried.

† *Supplementary data available* (No. SUP 56361, 8 pp.): thermal parameters, H-atom co-ordinates, torsion angles involving ribose and phosphate group, least-squares planes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Abbreviations used are those recommended by the IUPAC–IUB commission on Biochemical Nomenclature, *Eur. J. Biochem.*, 1970, **15**, 203.

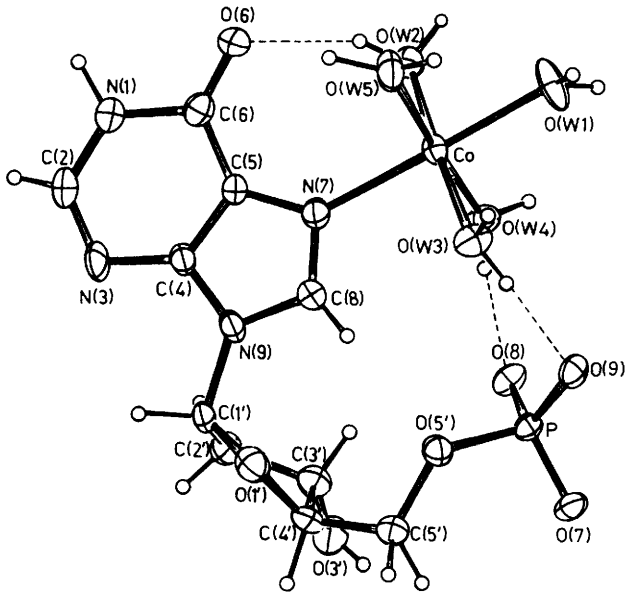

Figure 1. Structure of $[Co(5'\text{-dIMP})(H_2O)_5]$. Broken lines indicate hydrogen bonds; atoms not labelled represent hydrogens. Note the formation of a loose macrochelate through direct co-ordination of N(7) and hydrogen-bonded phosphate co-ordination of the metal

Crystal data.—$C_{10}H_{25}CoN_4O_{14}P$, $M = 514.9$, orthorhombic, space group $P2_12_12_1$ (D_2^4, no. 19), $a = 6.877(3)$, $b = 10.904(2)$, $c = 25.421(6)$ Å, $U = 1\,907.1$ Å^3, $Z = 4$, $D_c = 1.79$ g cm^{-3}, $F(000) = 1\,044$, Mo-K_α radiation, $\lambda = 0.7107$ Å, μ(Mo-K_α) = 10.5 cm^{-1}. Specimen: 0.30 × 0.11 × 0.52 mm, $2\theta_{max.} = 56°$.

Collection and Reduction of the X-Ray Intensity Data.—Unit-cell dimensions and their associated standard deviations were derived from a least-squares fit to the setting angles for 20 carefully selected and centred reflections on a Nonius CAD-4 automated diffractometer. Intensity data were collected in the $\omega/2\theta$ scan mode with a constant scan speed of 1° min^{-1}. The intensities of two standards were monitored after every 3 000 s

Table 1. Final fractional co-ordinates (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses for $[Co(5'\text{-dIMP})(H_2O)_5]\cdot 2H_2O$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Co	7 105(1)	1 812(1)	3 384(0)	N(9)	6 850(8)	4 498(4)	4 613(2)
P	7 655(2)	5 944(1)	2 778(1)	C(1′)	6 638(10)	5 822(5)	4 760(2)
O(5′)	6 224(6)	6 186(3)	3 275(1)	C(2′)	8 596(11)	6 480(2)	4 764(2)
O(7)	7 945(7)	7 160(4)	2 506(2)	C(3′)	8 736(10)	6 964(6)	4 202(3)
O(8)	9 518(6)	5 397(4)	2 992(2)	C(4′)	6 638(10)	7 311(5)	4 096(3)
O(9)	6 538(6)	5 004(4)	2 454(1)	C(5′)	6 009(10)	7 360(6)	3 527(2)
N(1)	7 143(9)	1 430(5)	5 442(2)	O(1′)	5 491(7)	6 386(4)	4 368(2)
C(2)	7 118(12)	2 526(6)	5 706(2)	O(3′)	1 003 7(8)	7 945(4)	4 165(2)
N(3)	7 097(9)	3 608(5)	5 488(2)	O(W1)	7 341(6)	801(4)	2 672(2)
C(4)	7 021(10)	3 531(5)	4 949(2)	O(W2)	9 048(7)	551(4)	3 682(2)
C(5)	7 091(11)	2 485(5)	4 642(2)	O(W3)	5 163(6)	3 058(4)	3 042(2)
C(6)	7 206(10)	1 307(6)	4 888(2)	O(W4)	9 452(6)	2 927(4)	3 184(2)
O(6)	7 310(9)	287(3)	4 684(2)	O(W5)	4 691(7)	635(4)	3 543(2)
N(7)	6 918(9)	2 796(4)	4 113(2)	O(W6)	−739(8)	3 570(4)	1 881(2)
C(8)	6 802(10)	4 002(5)	4 120(2)	O(W7)	2 328(8)	5 198(5)	3 756(2)

Table 2. Bond lengths (Å) with e.s.d.s in parentheses

Co–O(W1)	2.127(4)	Co–O(W2)	2.062(5)	N(9)–C(4)	1.362(7)	N(9)–C(1′)	1.498(7)
Co–O(W3)	2.094(4)	Co–O(W4)	2.083(4)	C(1′)–C(2′)	1.526(10)	C(2′)–C(3′)	1.526(9)
Co–O(W5)	2.137(5)	Co–N(7)	2.145(5)	C(3′)–C(4′)	1.516(9)	C(4′)–O(1′)	1.455(8)
N(1)–C(2)	1.372(8)	C(2)–N(3)	1.304(8)	O(1′)–C(1′)	1.411(8)	C(3′)–O(3′)	1.397(8)
N(3)–C(4)	1.372(7)	C(4)–C(5)	1.385(8)	C(4′)–C(5′)	1.512(3)	C(5′)–O(5′)	1.439(7)
C(5)–C(6)	1.431(8)	C(6)–O(6)	1.229(7)	P–O(5′)	1.622(4)	P–O(7)	1.510(4)
C(6)–N(1)	1.414(8)	C(5)–N(7)	1.391(7)	P–O(8)	1.514(5)	P–O(9)	1.524(4)
N(7)–C(8)	1.317(7)	C(8)–N(9)	1.367(7)				

Table 3. Bond angles (°) with e.s.d.s in parentheses

O(W1)–Co–O(W2)	85.2(2)	C(6)–N(1)–C(2)	124.8(5)	N(3)–C(4)–C(5)	127.8(5)
O(W1)–Co–O(W4)	90.0(2)	N(1)–C(6)–O(6)	120.4(5)	C(5)–C(6)–N(1)	110.5(5)
O(W1)–Co–N(7)	178.4(2)	C(6)–C(5)–N(7)	130.3(5)	C(5)–C(6)–O(6)	129.1(5)
O(W2)–Co–O(W4)	88.6(2)	N(7)–C(8)–N(9)	113.9(5)	C(4)–C(5)–N(7)	110.0(5)
O(W2)–Co–N(7)	93.2(2)	C(2′)–C(3′)–C(4′)	101.0(5)	C(5)–N(7)–C(8)	103.7(5)
O(W3)–Co–O(W5)	88.4(2)	C(4′)–O(1′)–C(1′)	109.5(5)	C(8)–N(9)–C(4)	105.7(5)
O(W4)–Co–O(W5)	176.7(2)	N(9)–C(1′)–C(2′)	111.6(5)	N(9)–C(4)–N(3)	125.6(5)
O(W5)–Co–N(7)	95.2(2)	O(3′)–C(3′)–C(4′)	114.0(5)	C(4)–N(9)–C(1′)	126.8(5)
O(W1)–Co–O(W3)	91.8(2)	C(5′)–C(4′)–O(1′)	109.0(5)	C(1′)–C(2′)–C(3′)	102.3(5)
O(W1)–Co–O(W5)	84.7(2)	C(5′)–O(5′)–P	123.6(4)	C(3′)–C(4′)–O(1′)	105.0(5)
O(W2)–Co–O(W3)	176.9(2)	O(5′)–P–O(8)	107.4(2)	N(9)–C(1′)–O(1′)	107.4(5)
O(W2)–Co–O(W5)	91.9(2)	O(7)–P–O(8)	113.5(3)	C(2′)–C(3′)–O(3′)	115.5(5)
O(W3)–Co–O(W4)	90.8(2)	O(8)–P–O(9)	110.9(2)	C(3′)–C(4′)–C(5′)	116.8(6)
O(W3)–Co–N(7)	89.8(2)	O(5′)–P–O(7)	107.1(2)	C(4′)–C(5′)–O(5′)	111.4(5)
O(W4)–Co–N(7)	88.0(2)	O(5′)–P–O(9)	103.0(2)	N(9)–C(4)–C(5)	106.7(5)
Co–N(7)–C(8)	120.9(4)	O(7)–P–O(9)	114.2(2)	C(8)–N(9)–C(1′)	127.4(5)
C(2)–N(3)–C(4)	111.7(5)	Co–N(7)–C(5)	135.0(4)	O(1′)–C(1′)–C(2′)	107.0(5)
C(4)–C(5)–C(6)	119.6(5)	N(1)–C(2)–N(3)	125.5(5)		

and showed no systematic variations over the duration of the experiment. Of the 2 737 reflections collected, 1 776 were deemed to be observed [$F_o > 3\sigma(F_o)$]. The intensities were corrected for Lorentz and polarization effects, but not for absorption.

Solution and Refinement of the Structure.—The structure was solved by the heavy-atom method and refined by full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms. All the hydrogen atoms were identified from difference Fourier syntheses. The thermal parameters of hydrogens were set equal to 1.5 $Å^2$ plus that of the heavy atoms to which they are bonded. The final values of the discrepancy indices were $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.043$ and $R' = [\Sigma w(|F_o| - |F_c|^2)/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.043$. The weighting scheme used was $w = 1.5/[\sigma^2(F) + 0.009|F|^2]$.

Computations were carried out on a DEC 1090 computer; SHELX 76[12] was used for structure solution and refinement. The curve for neutral scattering factors for Co was taken from ref. 13. The scattering factors as available in SHELX 76 were used for all other atoms. Anomalous dispersion corrections were applied to the scattering factors of all non-hydrogen atoms. Diagrams were drawn using the program ORTEP-II.[14] Final atomic co-ordinates are listed in Table 1.

Results and Discussion

The molecular structure of the complex is shown in Figure 1. Interatomic distances and angles are listed in Tables 2 and 3 respectively. Table 4 gives the possible hydrogen bonding contact distances.

Although the space group and cell parameters for the complex are similar to those of the 5′-IMP complexes,[15] the positional parameters obtained from the present study are different from the values reported for these complexes. The

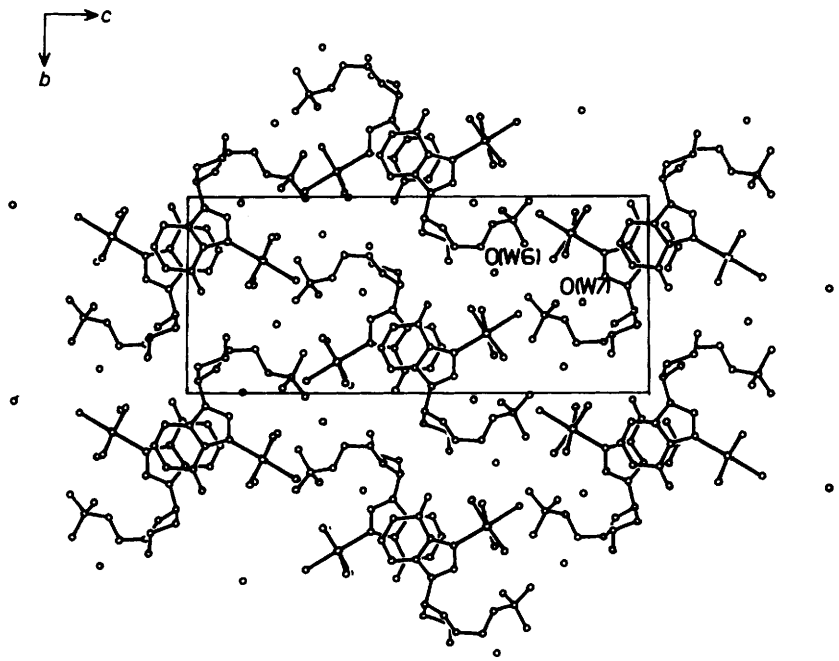

Figure 2. Packing diagram of $[Co(5'\text{-dIMP})(H_2O)_5]\cdot 2H_2O$ displaying the stacking of bases related by a two-fold screw axis. The unit cell shown runs from $y = 0$ to 1.0 and $z = -\frac{1}{2}$ to $+\frac{1}{2}$

complex, however, is isostructural with the corresponding ribonucleotide complexes. The reason for the different set of positional parameters in the present case may be attributed to a larger value for the torsion angle around the C(5′)–O(5′) bond (see below). The metal ion has an octahedral geometry with the six co-ordination sites occupied by five water oxygens and the N(7) atom of the purine base (Figure 1). The metal–nitrogen distance (2.145 Å) and the metal–oxygen distances (2.062–2.137 Å) are normal. The cobalt ion deviates by 0.12 Å away from the best plane through the nine-atom framework and is 0.058 Å off the best plane through the four oxygen atoms, O(W2), O(W3), O(W4), and O(W5).

The conformation about the glycosidic bond is *anti*[16] [χ_{CN} = O(1′)–C(1′)–N(9)–C(4) = −148.1°] and that about the C(4′)–C(5′) bond is *gauche–gauche*. The sugar ring is in the C(3′)-*endo* puckering mode. The C(3′) atom deviates by 0.59 Å from the best plane defined by O(1′), C(1′), C(2′), and C(4′) on the same side of C(5′). The conformation about the C(5′)–O(5′) bond, as defined by the torsion angle, φ = C(4′)–C(5′)–O(5′)–P, is −118.6°. This value is considerably larger than that reported for various nucleoside 5′-monophosphates, for most of which a φ value of *ca.* 175° is preferred.[17] This torsion angle shows greater tendency to deviate from 180° in nucleoside di- and triphosphates: *e.g.*, φ values of −138.4 (molecule A) and −142.4° (molecule B) have been observed in the structure of disodium adenosine 5′-triphosphate.[18] While the reasons for the large φ angle are not clear, a perusal of the torsion angles around the O(5′)–P bond shows that the phosphate group is rotated by 69.5° (mean value) about the O(5′)–P bond relative to its corresponding position in the Co(5′-IMP) complex (5′-IMP = inosine 5′-monophosphate). It may be that in an effort be that in an effort to establish the hydrogen-bonded phosphate co-ordination to the metal, the phosphate group has undergone a rotation consequent to changes in φ.

The bond lengths and bond angles of the nucleotide moiety are in overall agreement with those found in the corresponding ribonucleotide complexes mentioned above. The C(1′)–C(2′) bond length (1.526 Å) is smaller than that reported for ribonucleotide complexes. The corresponding values are 1.571 and 1.552 Å for the Co(5′-IMP) and Ni(5′-IMP) complexes respectively. The P–O(5′)–C(5′) bond angle (123.6°) is notably larger than that observed for the Co(5′-IMP) (118.0°) and Ni(5′-IMP) complexes (117.6°). The nine-atom framework shows a significant degree of puckering and the deviation is pronounced for the atoms N(1), N(3), C(5), and C(6) of the pyrimidine ring. The exocyclic atoms O(6) and C(1′) deviate by 0.07 and 0.10 Å respectively on the opposite side of the plane.

Table 4. Possible hydrogen-bonding contacts (Å)

N(1) · · · O(W7^{IV})	2.71	O(3′) · · · O(W6^{III})	2.79
O(W1) · · · O(8^{VI})	2.78	O(W1) · · · O(9^{V})	2.82
O(W2) · · · O(6^{I})	2.83	O(W2) · · · O(W6^{V})	2.84
O(W3) · · · O(7^{V})	2.73	O(W3) · · · O(9^{I})	2.76
O(W4) · · · O(7^{VI})	2.64	O(W4) · · · O(8^{I})	2.74
O(W5) · · · O(9^{V})	2.76	O(W6) · · · O(7^{V})	2.91
O(W6) · · · O(9^{II})	2.84	O(W7) · · · O(5^{I})	3.14
O(W7) · · · O(8^{II})	2.75		

Symmetry codes: I x, y, z; II $x-1, y, z$; III $1-x, y+\frac{1}{2}, \frac{1}{2}-z$; IV $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; V $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; VI $2-x, y-\frac{1}{2}, \frac{1}{2}-z$.

The packing of the molecules (Figure 2) appears to be governed by base stacking and intermolecular hydrogen bonds. Further stabilization of the structure is provided by hydrogen bonding of the complex to lattice water molecules. There is an infinite stack of overlapping bases related by a two-fold screw axis along *a*. The two overlapping bases are inclined to each other by approximately 7°. The mean separation between the overlapping bases is 3.49 Å.

There are significant differences in the hydrogen-bonding scheme, as compared to the 5′-IMP complexes of Co^{II} and Ni^{II}. The sugar hydroxyl oxygen atom O(2′) in the latter complexes is connected to a lattice water through a hydrogen bond, while the O(3′) atom donates a proton to the phosphate oxygen atom. In the Co(5′-dIMP) complex the position of the above lattice water

has changed sufficiently so that in the absence of O(2′) it accepts a proton from the O(3′) atom. Therefore, the sugar–phosphate hydrogen-bonded interaction observed in the Co(5′-IMP) and Ni(5′-IMP) complexes is not possible in the present case. Similarly the ligand water, which donates protons to O(6) of the base and sugar oxygens in the ribonucleotide complexes, donates to the lattice water instead. Apart from the above mentioned differences in hydrogen bonding and the torsion angle φ, the structure of the Co(5′-dIMP) complex is essentially similar to that of the Co(5′-IMP) and Ni(5′-IMP) complexes.

Conclusions

While the 5′-dGMP complexes of Co^{II} and Ni^{II} are isomorphous with the corresponding ribonucleotide complexes,[19–22] the present structure is only isostructural with 5′-IMP complexes of Co^{II} and Ni^{II}. In the absence of a 2′-hydroxyl group as in the Co(5′-dGMP) complex, a channel is formed in the lattice without disturbing the overall structure and even the hydrogen-bonding scheme observed in the analogous ribonucleotide complexes. The difference in the hydrogen-bonding scheme in the Co(5′-dIMP) complex, as compared to the corresponding ribonucleotide complexes, is mainly due to the lattice water molecules. These results suggest that the contribution of the 2′-hydroxyl group towards the stabilization of these structures is not significant.

It is well known that the sugar in the deoxyribonucleotides has greater flexibility and hence the latter can show a broader range of sugar puckering compared to ribonucleotides. However, it has been observed that deoxyribonucleosides show a definite preference for a C(2′)-*endo* pucker while ribonucleosides, especially pyrimidine nucleosides, prefer a C(3′)-*endo* pucker. Swaminathan and Sundaralingam[7] have pointed out that the fundamental conformational preference of the sugar moieties in nucleosides and nucleotides is less affected by the 5′-phosphate group than by the 2′-hydroxyl group. They also suggest that metal binding by itself does not affect the preferred nucleotide conformation. The deoxyribose sugar, in the structure presented here and in the structures of 5′-dGMP complexes of Co^{II} and Ni^{II}, is in the C(3′)-*endo* puckering mode, as is also observed in the above mentioned ribonucleotide complexes. On the other hand, in the Fe^{II} complex of 5′-IMP, $[Fe(5'\text{-IMP})(H_2O)_5]\cdot 2H_2O$,[23] which also belongs to the group mentioned above, both C(3′)-*endo* and C(2′)-*endo* conformations coexist in the structure. Out of the three crystallographically independent molecules, two have the ribose rings with C(3′)-*endo* puckering, while the other one has the sugar with C(2′)-*endo* puckering. There is thus a definite preference for the C(3′)-*endo* pucker in the structure. The above findings, therefore, suggest that, in the solid state, for the transition metal complexes containing a 5′-nucleotide of the general formula $[M(5'\text{-nucleotide})(H_2O)_5]$, irrespective of the presence of the 2′-hydroxyl group, the C(3′)-*endo* puckering mode is generally favoured.

An important factor contributing to the stability of these complexes is, clearly, two strong metal–water–phosphate bridging interactions resulting in a type of loose six-membered chelate. These interactions apparently require the ribose ring to adopt a particular puckering mode, so as to bring effectively the phosphate group in the proximity of the metal ion. Thus one may conclude that, in systems with the above type of structure, the conformation of the sugar moiety is largely a consequence of the stereochemical requirement for the stability of the complex, rather than the conformational preference of the nucleotide.

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