Crystallographic Studies of Interaction between Nucleotides and Metal Ions. I. Crystal Structures of the 1 : 1 Complexes of Cobalt and Nickel with Inosine 5′-Phosphate

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The crystal structures of the 1 : 1 complexes of inosine 5′-phosphate with cobalt ($C_{10}H_{11}O_8N_4PCo,7H_2O$) and inosine 5′-phosphate with nickel($C_{10}H_{11}O_8N_4PNi,7H_2O$) have been determined from single-crystal X-ray data collected on an automated diffractometer. The both isomorphous crystals belong to orthorhombic system, space group $P2_12_12_1$ with four formula units in the unit cell of dimensions $a=10.859$, $b=25.987$, $c=6.845$ Å for the cobalt complex and $a=10.812$, $b=25.898$, $c=6.845$ Å for the nickel complex respectively. The structure of the cobalt complex was determined by three-dimensional Patterson and Fourier methods and that of the nickel complex was elucidated from that of the cobalt complex. Both were refined by the block-diagonal least-squares method including anisotropic temperature factors. The final R values were 0.051 and 0.075 for the cobalt and nickel complexes, respectively. All of the 25 hydrogen atoms in the case of the cobalt complex and 22 hydrogen atoms in the case of the nickel complex were found. The hypoxanthine bases related by the two-fold screw axis parallel to c are extensively overlapped at a distance of 3.42 Å for both complexes. The nucleotides have the preferred *anti* conformation about the glycoside linkage with the ribose ring showing the C(3′)-*endo* pucker. The torsion angles around the C(5′)—O(5′) bond are 161.6° (cobalt complex) and 162.0° (nickel complex). In the both complexes, therefore, the phosphate group has the extended conformation. The metals are not directly bonded to the phosphate oxygen atoms but are bonded to the nitrogen atom N(7) of the base and to five water oxygen atoms. There is extensive hydrogen bonding involving the hypoxanthine ring, the phosphate anion, the hydroxyl groups of the furanose ring and seven water molecules in the crystal.

It has now been widely recognized that metal ions have profound effects on the structure and function of nucleic acids and their constituents. They stabilize or destabilize the manifold structure of nucleic acid[1,2] and alter the coding specificity in protein synthesis.[3]

The other interesting area of metallonucleic acid chemistry includes the use of heavy metals to determine the sequence of nucleic acid biopolymers by electron microscope techniques[4,5] and to determine the structure of tRNA by X-ray method.[6] We have investigated the crystal structures of 1 : 1 metal complexes of inosine 5′-phosphate(5′-IMP) in order to obtain the fundamental and precise informations regarding interaction of transition metals with the component of nucleic acid, where inosine is present as minor base in the triplet anticodon of yeast tRNAs such as alanine tRNA, serine tRNA1, serine tRNA2 and valine tRNA.

The crystal structures of 5′-IMP containing alkali metals such as barium and sodium have been investigated by Nagashima and Iitaka,[7] and Rao and Sundaralingam.[8]

After we had completed those structure determinations it came to our attention that Clark and Orbell had reported the brief communication on the same crystal structure of the inosine 5′-phosphate–nickel complex.[9] Their data are in agreement with those obtained from our X-ray crystallographic studies.

Experimental

Violet crystals of ($C_{10}H_{11}O_8N_4PCo$, $7H_2O$) and light green crystals of ($C_{10}H_{11}O_8N_4PNi$, $7H_2O$) were prepared by adding aqueous solution of cobalt nitrate hexahydrate and nickel nitrate hexahydrate to that of disodium inosine 5′-phosphate in an equivalent mole ratio, adjusting to pH 4.5 with dilute nitric acid. They were grown from an aqueous solution by slow evaporation. The elementary analysis revealed that the ratio of inosine 5′-phosphate to metal is 1 : 1 for both complexes.

The unit-cell dimensions were determined from high-order reflexions on a Rigaku four-circle automated diffractometer.

	Crystal data	
	$C_{10}H_{11}O_8N_4PCo$, $7H_2O$(5′-IMP-Co)	$C_{10}H_{11}O_8N_4PNi$, $7H_2O$(5′-IMP-Ni)
System	Orthorhombic	Orthorhombic
a	10.859±0.005 Å	10.812±0.005 Å
b	25.987	25.898
c	6.845	6.845
U	1931.6 Å^3	1916.1 Å^3
F(000)	1100	1104
Space group	$P2_12_12_1$	$P2_12_12_1$
Number of independent non-zero reflexions used for the structure determination	1424	1500

Three-dimensional intensity data in the 2θ-range from 0 to 50° for the cobalt complex with Zr-filtered Mo$K\alpha$ radiation and 130° for the nickel complex with Ni-filtered Cu$K\alpha$ radiation were collected on a Rigaku four-circle automated diffractometer. A 2θ-ω scan technique at a rate of 2°/min for the cobalt complex and 4°/min for the nickel complex was employed for the data collection. Background counts of 10 s were measured at each beginning and end of the scan. Three standard reflections were checked at an interval of every 52 reflections and they showed fluctuations in intensity of only ±2.0% for the cobalt complex and ±2.8% for the nickel complex. The data were corrected for Lorentz and polarization effects, but no absorption corrections were made ($\mu=10.8$ cm^{-1} (Co complex for Mo $K\alpha$ radiation) and 20.9 cm^{-1} (Ni complex for Cu $K\alpha$ radiation) and approximate crystal dimensions of $0.1\times0.2\times0.3$ mm (Co complex) and $0.1\times0.1\times0.2$ mm (Ni complex)). A reflection was considered unobserved if the intensity was smaller than 3.0 times its standard deviation. On this basis, 1424 reflections out of the total of 2067 reflections (Co complex) and 1500 out of the total of 1986 reflections (Ni complex) were adopted in the subsequent refinement of the structure.

TABLE 1. FINAL ATOMIC PARAMETERS AND STANDARD DEVIATIONS FOR $C_{10}H_{11}O_8N_4PCo$, $7H_2O$

Atom	X	Y	Z	β_{11} or B(Å^2)	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	0.0783(2)	0.3547(1)	0.2756(2)	0.0032(1)	0.0008(0)	0.0111(3)	−0.0002(1)	−0.0000(2)	−0.0001(1)
P	0.4204(3)	0.2436(1)	0.2287(5)	0.0034(2)	0.0008(0)	0.0073(6)	0.0000(1)	−0.0007(5)	−0.0000(1)
O(5′)	0.5000(8)	0.2921(3)	0.3027(13)	0.0046(8)	0.0010(1)	0.0130(22)	−0.0002(3)	0.0015(12)	−0.0001(5)
O(7)	0.5081(7)	0.1974(3)	0.2238(12)	0.0038(7)	0.0009(1)	0.0068(17)	0.0006(2)	0.0007(11)	−0.0002(4)
O(8)	0.3685(8)	0.2574(4)	0.0296(12)	0.0052(9)	0.0017(2)	0.0048(18)	0.0010(3)	−0.0005(10)	−0.0000(5)
O(9)	0.3225(7)	0.2377(3)	0.3872(12)	0.0025(7)	0.0011(2)	0.0105(19)	0.0004(3)	0.0012(10)	−0.0002(5)
N(1)	0.1837(9)	0.5530(4)	0.2995(16)	0.0056(10)	0.0008(2)	0.0159(26)	0.0006(3)	0.0004(16)	−0.0000(6)
C(2)	0.3060(12)	0.5645(4)	0.2913(23)	0.0069(13)	0.0006(2)	0.0206(36)	−0.0005(4)	−0.0026(22)	0.0004(8)
N(3)	0.3930(9)	0.5299(3)	0.2885(17)	0.0044(10)	0.0008(2)	0.0159(25)	0.0000(3)	0.0012(15)	0.0012(6)
C(4)	0.3479(11)	0.4815(4)	0.2911(18)	0.0047(11)	0.0009(2)	0.0083(25)	−0.0002(4)	−0.0017(18)	0.0001(6)
C(5)	0.2274(10)	0.4652(4)	0.2891(20)	0.0030(10)	0.0008(2)	0.0146(28)	0.0002(3)	0.0001(18)	−0.0002(7)
C(6)	0.1332(12)	0.5036(5)	0.3027(18)	0.0050(11)	0.0013(2)	0.0081(27)	0.0005(4)	−0.0000(17)	0.0005(7)
O(6)	0.0212(8)	0.4982(4)	0.3154(14)	0.0052(8)	0.0011(2)	0.0225(28)	0.0010(3)	0.0006(13)	0.0015(6)
N(7)	0.2230(9)	0.4118(3)	0.2859(16)	0.0053(9)	0.0007(1)	0.0107(22)	0.0002(3)	0.0018(15)	0.0004(5)
C(8)	0.3371(10)	0.3971(5)	0.2726(22)	0.0033(10)	0.0011(2)	0.0191(35)	0.0006(4)	0.0011(21)	−0.0015(8)
N(9)	0.4159(9)	0.4374(3)	0.2752(16)	0.0032(7)	0.0007(1)	0.0157(24)	−0.0001(3)	−0.0032(18)	0.0012(5)
C(1′)	0.5530(9)	0.4364(4)	0.2480(21)	0.0033(10)	0.0009(2)	0.0167(34)	−0.0003(3)	−0.0030(19)	−0.0007(7)
C(2′)	0.6249(12)	0.4326(5)	0.4465(24)	0.0027(11)	0.0010(2)	0.0283(46)	0.0004(4)	−0.0037(20)	0.0005(8)
C(3′)	0.6391(11)	0.3741(5)	0.4631(19)	0.0031(11)	0.0010(2)	0.0142(31)	0.0004(4)	−0.0023(16)	−0.0023(7)
C(4′)	0.6570(10)	0.3559(4)	0.2502(19)	0.0056(11)	0.0007(2)	0.0147(31)	0.0008(4)	0.0012(19)	0.0010(8)
C(5′)	0.6193(11)	0.3015(4)	0.2097(20)	0.0063(12)	0.0008(2)	0.0114(29)	−0.0006(4)	0.0030(18)	0.0000(7)
O(1′)	0.5800(9)	0.3921(3)	0.1372(12)	0.0049(8)	0.0011(1)	0.0130(19)	0.0005(3)	−0.0001(14)	0.0004(4)
O(2′)	0.7458(9)	0.4530(3)	0.4099(18)	0.0057(9)	0.0006(1)	0.0430(37)	0.0001(3)	−0.0033(17)	−0.0011(6)
O(3′)	0.7425(8)	0.3628(3)	0.5819(12)	0.0047(8)	0.0011(2)	0.0137(21)	−0.0003(3)	−0.0016(12)	−0.0003(5)
W(1)	−0.0207(9)	0.3841(4)	0.0331(15)	0.0075(10)	0.0016(2)	0.0165(25)	−0.0005(4)	−0.0033(14)	0.0011(6)
W(2)	−0.0236(8)	0.3966(3)	0.4766(15)	0.0046(9)	0.0011(2)	0.0233(28)	0.0001(3)	0.0031(14)	−0.0020(6)
W(3)	0.1729(8)	0.3155(4)	0.0568(12)	0.0028(8)	0.0017(2)	0.0098(20)	0.0009(3)	−0.0018(11)	−0.0014(5)
W(4)	0.1788(8)	0.3175(3)	0.4993(12)	0.0055(9)	0.0010(1)	0.0094(20)	−0.0001(3)	0.0035(12)	0.0006(5)
W(5)	−0.0529(8)	0.2966(3)	0.2850(13)	0.0068(9)	0.0014(2)	0.0097(19)	−0.0015(3)	0.0034(13)	−0.0004(5)
W(6)	0.8993(9)	0.1557(3)	0.2383(17)	0.0108(12)	0.0011(2)	0.0252(28)	−0.0005(3)	−0.0056(19)	0.0010(6)
W(7)	0.7265(11)	0·5578(4)	0.3873(16)	0.0110(14)	0.0020(2)	0.0218(29)	0.0006(5)	0.0013(18)	0.0013(7)
H(N1)	0.125(12)	0.592(5)	0.321(19)	4.7(3.4)					
H(C2)	0.325(10)	0.603(4)	0.306(17)	2.4(2.8)					
H(C8)	0.369(11)	0.361(5)	0.276(22)	4.8(3.4)					
H(C1′)	0.575(12)	0.470(4)	0.152(17)	3.5(2.9)					
H(C2′)	0.576(13)	0.454(5)	0.578(19)	4.7(3.3)					
H(C3′)	0.547(9)	0.363(4)	0.517(15)	1.1(2.4)					
H(C4′)	0.764(14)	0.364(6)	0.207(23)	7.0(4.2)					
H(C5′)	0.612(12)	0.290(4)	0.047(19)	3.6(3.1)					
H′(C5′)	0.685(12)	0.273(5)	0.270(24)	5.5(3.7)					
H(O2′)	0.727(12)	0.491(5)	0.441(17)	2.8(3.1)					
H(O3′)	0.732(10)	0.324(4)	0.613(14)	0.8(2.2)					
H(W1)	−0.061(10)	0.352(4)	−0.095(15)	2.2(2.5)					
H′(W1)	−0.019(11)	0.422(4)	0.040(17)	2.5(2.8)					
H(W2)	−0.085	0.380	0.490	3.0					
H′(W2)	−0.066(12)	0.422(5)	0.463(19)	4.3(3.2)					
H(W3)	0.096(13)	0.303(5)	−0.039(20)	4.5(3.4)					
H′(W3)	0.226(13)	0.294(5)	0.053(20)	4.1(3.6)					
H(W4)	0.119(9)	0.310(3)	0.562(14)	0.4(2.0)					
H′(W4)	0.224(15)	0.290(5)	0.489(24)	7.0(4.5)					
H(W5)	−0.112(15)	0.292(5)	0.131(23)	7.0(4.3)					
H′(W5)	−0.097(10)	0.280(4)	0.385(15)	1.1(2.3)					
H(W6)	0.817	0.169	0.365	3.0					
H′(W6)	0.913(16)	0.190(6)	0.138(24)	8.9(4.5)					
H(W7)	0.776(13)	0.581(5)	0.344(19)	4.9(3.6)					
H′(W7)	0.644(14)	0.553(5)	0.331(23)	7.3(4.4)					

The temperature factors for the heavier atoms are of the form, $T=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$, and those for the hydrogen atoms are, $T=\exp[-B(\sin\theta/\lambda)^2]$. The hydrogen atoms H(W2) and H(W6) were found on the final difference electron density map and their atomic parameters were not refined.

Table 2. Final atomic parameters and standard deviations for $C_{10}H_{11}O_8N_4PNi$, $7H_2O$

Atom	X	Y	Z	β_{11} or B(Å^2)	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0.0812(2)	0.3547(1)	0.2740(4)	0.0047(1)	0.0010(0)	0.0239(5)	−0.0001(1)	0.0003(3)	−0.0001(1)
P	0.4211(3)	0.2423(1)	0.2288(5)	0.0021(2)	0.0004(0)	0.0135(8)	0.0001(1)	0.0001(5)	−0.0001(2)
O(5′)	0.5005(7)	0.2914(3)	0.3020(16)	0.0029(7)	0.0004(1)	0.0237(29)	−0.0003(2)	0.0017(13)	−0.0010(5)
O(7)	0.5084(7)	0.1967(3)	0.2218(16)	0.0030(7)	0.0005(1)	0.0181(26)	0.0001(2)	0.0009(13)	−0.0006(5)
O(8)	0.3689(8)	0.2554(4)	0.0346(14)	0.0032(2)	0.0011(2)	0.0123(24)	0.0009(3)	0.0022(12)	−0.0003(5)
O(9)	0.3231(8)	0.2374(3)	0.3896(15)	0.0037(8)	0.0006(1)	0.0158(24)	−0.0002(3)	0.0030(12)	0.0003(5)
N(1)	0.1827(10)	0.5525(4)	0.2916(20)	0.0045(9)	0.0005(1)	0.0196(32)	0.0006(3)	−0.0013(17)	0.0001(7)
C(2)	0.3071(13)	0.5639(5)	0.2844(28)	0.0053(12)	0.0006(2)	0.0247(44)	−0.0005(4)	−0.0004(23)	0.0014(9)
N(3)	0.3936(9)	0.5295(4)	0.2790(20)	0.0038(9)	0.0008(2)	0.0206(33)	−0.0003(3)	0.0016(17)	0.0018(7)
C(4)	0.3487(11)	0.4807(5)	0.2770(24)	0.0029(10)	0.0006(2)	0.0189(37)	0.0001(3)	−0.0010(20)	0.0010(8)
C(5)	0.2254(10)	0.4642(5)	0.2828(22)	0.0023(9)	0.0008(2)	0.0121(30)	0.0002(4)	0.0001(17)	0.0002(7)
C(6)	0.1323(12)	0.5033(5)	0.2942(24)	0.0036(10)	0.0006(2)	0.0209(39)	0.0003(4)	0.0023(20)	0.0008(8)
O(6)	0.0181(8)	0.4964(3)	0.3077(17)	0.0027(7)	0.0008(1)	0.0275(33)	0.0007(3)	−0.0006(14)	0.0004(6)
N(7)	0.2210(9)	0.4113(4)	0.2773(20)	0.0020(8)	0.0006(1)	0.0209(32)	−0.0001(3)	−0.0020(16)	0.0009(7)
C(8)	0.3379(10)	0.3965(4)	0.2708(27)	0.0026(9)	0.0004(2)	0.0270(44)	0.0001(3)	−0.0000(22)	−0.0008(8)
N(9)	0.4182(8)	0.4369(3)	0.2707(18)	0.0014(7)	0.0006(1)	0.0196(29)	−0.0003(3)	0.0005(17)	0.0002(6)
C(1′)	0.5546(10)	0.4354(4)	0.2387(23)	0.0021(9)	0.0004(2)	0.0200(37)	−0.0003(3)	0.0034(19)	0.0012(8)
C(2′)	0.6279(12)	0.4329(6)	0.4334(26)	0.0022(10)	0.0010(2)	0.0236(45)	−0.0004(4)	−0.0012(20)	0.0002(9)
C(3′)	0.6417(11)	0.3749(5)	0.4551(24)	0.0019(10)	0.0006(2)	0.0211(39)	−0.0003(4)	−0.0004(18)	−0.0002(7)
C(4′)	0.6586(10)	0.3561(4)	0.2439(25)	0.0025(9)	0.0005(2)	0.0254(43)	0.0003(3)	0.0050(20)	0.0012(9)
C(5′)	0.6201(11)	0.3016(5)	0.2032(26)	0.0027(10)	0.0007(2)	0.0233(43)	0.0002(4)	−0.0041(19)	0.0001(8)
O(1′)	0.5828(8)	0.3910(3)	0.1319(15)	0.0035(7)	0.0006(1)	0.0199(25)	0.0003(3)	−0.0003(14)	−0.0001(5)
O(2′)	0.7484(8)	0.4524(4)	0.3956(22)	0.0021(8)	0.0008(2)	0.0493(46)	−0.0005(3)	−0.0039(17)	0.0002(7)
O(3′)	0.7450(9)	0.3631(3)	0.5829(18)	0.0043(8)	0.0004(1)	0.0296(32)	0.0000(3)	−0.0029(16)	−0.0010(6)
W(1)	−0.0187(9)	0.3850(4)	0.0415(18)	0.0040(8)	0.0011(2)	0.0251(32)	0.0003(3)	−0.0023(15)	0.0012(6)
W(2)	−0.0179(8)	0.3970(3)	0.4728(17)	0.0029(8)	0.0009(2)	0.0235(30)	−0.0004(3)	0.0015(14)	−0.0010(6)
W(3)	0.1721(8)	0.3169(4)	0.0568(15)	0.0027(7)	0.0009(1)	0.0180(26)	0.0001(3)	−0.0027(13)	−0.0004(6)
W(4)	0.1791(8)	0.3179(3)	0.4954(14)	0.0038(7)	0.0008(1)	0.0128(22)	0.0003(3)	0.0006(12)	0.0002(5)
W(5)	−0.0519(8)	0.2971(3)	0.2804(16)	0.0050(8)	0.0009(1)	0.0156(24)	−0.0014(3)	0.0008(14)	−0.0008(6)
W(6)	0.8991(11)	0.1542(3)	0.2426(21)	0.0108(12)	0.0008(1)	0.0315(36)	0.0004(4)	−0.0017(23)	0.0004(7)
W(7)	0.7231(12)	0.5571(4)	0.3817(21)	0.0106(13)	0.0011(2)	0.0316(39)	0.0004(4)	−0.0005(21)	0.0006(8)
H(N1)	0.141(10)	0.574(4)	0.257(19)	1.0(2.3)					
H(C2)	0.324(9)	0.603(4)	0.301(16)	2.4(2.0)					
H(C8)	0.368(13)	0.368(5)	0.222(25)	3.9(3.7)					
H(C1′)	0.563(9)	0.460(4)	0.140(15)	1.3(2.0)					
H(C2′)	0.592(11)	0.441(4)	0.550(16)	1.0(2.2)					
H(C3′)	0.584(10)	0.360(4)	0.465(16)	0.5(2.2)					
H(C4′)	0.737(11)	0.370(4)	0.200(19)	1.9(2.6)					
H(C5′)	0.594(9)	0.299(4)	0.081(15)	2.0(2.0)					
H′(C5′)	0.675(9)	0.277(4)	0.227(17)	0.1(2.0)					
H(O2′)	0.741(12)	0.477(5)	0.367(20)	1.9(2.8)					
H(O3′)	0.768(14)	0.327(6)	0.589(23)	3.0(3.6)					
H(W1)	−0.078(11)	0.380(5)	−0.088(19)	1.1(2.6)					
H′(W1)	−0.068(11)	0.417(5)	0.034(18)	1.0(2.4)					
H(W3)	0.125(10)	0.308(4)	−0.092(17)	0.8(2.3)					
H′(W3)	0.233	0.293	0.030	3.0					
H(W4)	0.154(17)	0.311(7)	0.594(28)	3.3(5.0)					
H′(W4)	0.197(13)	0.297(5)	0.406(22)	3.7(3.2)					
H(W5)	−0.036(13)	0.292(5)	0.163(22)	3.5(3.5)					
H′(W5)	−0.080(14)	0.265(5)	0.362(21)	2.5(3.3)					
H(W6)	0.841	0.149	0.410	3.0					
H′(W6)	0.874	0.187	0.140	3.0					
H′(W7)	0.697(15)	0.569(6)	0.262(29)	5.1(4.6)					

The temperature factors for the heavier atoms are of the form, $T=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$, and those for the hydrogen atoms are, $T=\exp[-B(\sin\theta/\lambda)^2]$. The hydrogen atoms H′(W3), H(W6) and H′(W6) were found on the final difference electron density map and their atomic parameters were not refined. Three hydrogen atoms bonded to W(2) and W(7) were not clearly found on the difference map.

TABLE 3. COMPARISON OF BOND LENGTHS AND ANGLES OF DIFFERENT COMPOUNDS INVOLVING INOSINE MOIETY

Compound	5′-IMP-Co	5′-IMP-Ni	5′-IMP-Na	Inosine, $2H_2O$		Inosine
Space group	$P2_12_12_1$	$P2_12_12_1$	$C222_1$	$P2_1$		$P2_1$
No. of molecules in the unit cell	4	4	8	4		2
				Molecule I	Molecule II	
Bond lengths						
N (1) - C (2)	1.362 (16) Å	1.377 (17) Å	1.38 (2) Å	1.360 (6) Å	1.351 (6) Å	1.355 (5) Å
C (2) - N (3)	1.305 (15)	1.292 (17)	1.27	1.307	1.308	1.308
N (3) - C (4)	1.351 (14)	1.356 (16)	1.30	1.362	1.364	1.365
C (4) - C (5)	1.375 (16)	1.399 (16)	1.33	1.382	1.367	1.374
C (5) - C (6)	1.432 (17)	1.430 (17)	1.44	1.429	1.436	1.433
C (6) - O (6)	1.227 (15)	1.251 (15)	1.22	1.221	1.235	1.233
C (6) - N (1)	1.397 (16)	1.386 (16)	1.36	1.401	1.390	1.397
C (5) - N (7)	1.388 (14)	1.373 (16)	1.40	1.371	1.379	1.371
N (7) - C (8)	1.300 (15)	1.321 (15)	1.43	1.311	1.301	1.307
C (8) - N (9)	1.353 (15)	1.358 (14)	1.33	1.359	1.369	1.372
N (9) - C (4)	1.369 (14)	1.361 (15)	1.39	1.372	1.370	1.372
N (9) - C (1′)	1.500 (14)	1.491 (14)	1.46	1.460	1.452	1.477
C (1′) - C (2′)	1.571 (20)	1.552 (22)	1.54	1.525	1.516	1.530
C (2′) - C (3′)	1.532 (18)	1.518 (19)	1.52	1.517	1.529	1.525
C (3′) - C (4′)	1.545 (18)	1.536 (23)	1.56	1.526	1.525	1.522
C (4′) - O (1′)	1.478 (15)	1.441 (16)	1.44	1.452	1.450	1.459
O (1′) - C (1′)	1.409 (14)	1.396 (15)	1.43	1.416	1.410	1.417
C (2′) - O (2′)	1.437 (16)	1.422 (16)	1.41	1.417	1.407	1.420
C (3′) - O (3′)	1.417 (15)	1.451 (17)	1.41	1.418	1.412	1.413
C (4′) - C (5′)	1.496 (17)	1.498 (17)	1.48	1.513	1.503	1.506
C (5′) - O (5′)	1.465 (15)	1.483 (16)	1.45	1.437	1.418	1.428
P - O (5′)	1.610 (9)	1.614 (9)	1.62 (1)			
P - O (7)	1.533 (8)	1.515 (8)	1.53			
P - O (8)	1.518 (9)	1.483 (10)	1.53			
P - O (9)	1.527 (9)	1.533 (10)	1.52			
N (1) - H	1.22 (12)	0.75 (11)		1.00 (5)	1.06 (5)	0.84 (5)
C (2) - H	1.04 (10)	1.05 (9)		0.93	1.07	0.98
C (8) - H	1.00 (13)	0.88 (15)		0.92	0.94	0.99
C (1′) - H	1.12 (11)	0.94 (10)		1.01	1.01	1.04
C (2′) - H	1.19 (13)	0.91 (11)		1.05	0.96	1.01
C (3′) - H	1.11 (10)	0.74 (11)		0.94	0.99	0.95
C (4′) - H	1.22 (15)	0.97 (12)		1.02	0.97	0.96
C (5′) - H	1.16 (13)	0.88 (11)		1.00	0.90	0.97
C (5′) - H′	1.11 (14)	0.88 (10)		1.01	1.06	0.99
O (2′) - H	1.02 (12)	0.67 (10)		0.78	0.84	0.88
O (3′) - H	1.05 (9)	0.97 (14)		0.83	0.79	0.90
Bond angles						
N (1) - C (2) - N (3)	123.7 (12)°	124.0 (14)°	123 (1)°	126.2 (5)°	126.7 (5)°	124.6 (3)°
C (2) - N (3) - C (4)	112.3 (11)	112.6 (12)	114	111.2	110.7	111.9
N (3) - C (4) - C (5)	129.2 (11)	128.7 (12)	127	127.7	128.0	128.5
C (4) - C (5) - C (6)	117.7 (11)	117.2 (12)	122	119.7	119.5	118.3
C (5) - C (6) - N (1)	111.0 (11)	111.9 (12)	107	110.6	110.7	111.0
C (6) - N (1) - C (2)	125.9 (11)	125.5 (12)	126	124.5	124.4	125.4
C (4) - C (5) - N (7)	110.0 (10)	109.6 (11)	111	110.6	111.6	111.6
C (5) - N (7) - C (8)	105.2 (10)	104.9 (11)	103	104.3	103.4	103.8
N (7) - C (8) - N (9)	112.0 (11)	112.9 (12)	108	113.5	113.8	113.6
C (8) - N (9) - C (4)	107.9 (10)	106.7 (11)	110	106.0	105.8	105.7
N (9) - C (4) - C (5)	104.8 (10)	105.9 (11)	107	105.6	105.3	105.4
N (3) - C (4) - N (9)	125.7 (11)	125.5 (12)	127	126.7	126.7	126.1
C (5) - C (6) - O (6)	129.3 (12)	126.7 (13)	132	128.1	128.6	128.4
N (1) - C (6) - O (6)	119.7 (11)	121.4 (12)	121	121.2	120.6	120.6
C (6) - C (5) - N (7)	132.2 (11)	133.2 (12)	126	129.7	128.8	130.1
C (8) - N (9) - C (1′)	127.8 (10)	127.7 (11)	126	128.9	125.9	128.1

Table 3. Continued

Compound	5′-IMP-Co	5′-IMP-Ni	5′-IMP-Na	Inosine, $2H_2O$		Inosine
Space group	$P2_12_12_1$	$P2_12_12_1$	$C222_1$	$P2_1$		$P2_1$
No. of molecules in the unit cell	4	4	8	4		2
				Molecule I	Molecule II	
C (4)-N (9)-C (1′)	124.1 (10)	124.9 (11)	124	125.1	128.3	126.0
O (1′)-C (1′)-C (2′)	108.1 (10)	107.7 (11)	104	105.1	105.1	106.8
C (1′)-C (2′)-C (3′)	100.1 (10)	100.1 (11)	102	101.4	100.6	100.6
C (2′)-C (3′)-C (4′)	104.3 (10)	103.5 (11)	102	102.7	102.5	101.5
C (3′)-C (4′)-O (1′)	103.1 (9)	103.6 (10)	105	105.8	106.9	104.0
C (4′)-O (1′)-C (1′)	110.9 (9)	111.2 (10)	111	109.9	108.1	109.6
N (9)-C (1′)-O (1′)	106.7 (9)	108.3 (10)	107	107.6	107.3	108.4
N (9)-C (1′)-C (2′)	112.8 (10)	112.3 (11)	114	113.4	114.4	111.5
C (1′)-C (2′)-O (2′)	106.3 (11)	107.3 (12)	111	113.9	114.4	109.6
O (2′)-C (2′)-C (3′)	106.7 (11)	106.3 (12)	112	115.6	112.2	107·5
C (2′)-C (3′)-O (3′)	109.1 (10)	110.0 (11)	107	112.0	111.2	115.9
O (3′)-C (3′)-C (4′)	112.2 (10)	114.1 (11)	111	107.8	109.1	114.2
C (3′)-C (4′)-C (5′)	115.5 (10)	116.1 (12)	119	117.4	115.8	114.1
C (5′)-C (4′)-O (1′)	110.4 (10)	109.6 (11)	112	107.8	108.8	110.0
C (4′)-C (5′)-O (5′)	108.7 (10)	108.9 (11)	109	111.2	112.5	112.0
C (5′)-O (5′)-P	118.0 (7)	117.6 (8)	114			
O (5′)-P-O (7)	106.7 (5)	107.1 (5)	107			
O (5′)-P-O (8)	107·3 (5)	107.6 (5)	104			
O (5′)-P-O (9)	103.2 (5)	103.1 (8)	107			
O (7)-P-O (8)	113.4 (5)	113.7 (9)	113			
O (7)-P-O (9)	111.7 (5)	112.9 (5)	112			
O (8)-P-O (9)	113.8 (5)	113.5 (5)	112			
H-N (1)-C (6)	124 (6)	116 (9)		119.5 (5)	118.2 (5)	112 (3)
H-N (1)-C (2)	109 (6)	115 (9)		115.8	117.4	122
H-C (2)-N (1)	114 (6)	112 (6)		109.9	115.2	120
H-C (2)-N (3)	122 (6)	123 (6)		123.8	118.1	115
H-C (8)-N (7)	127 (8)	128 (10)		119.9	125.0	123
H-C (8)-N (9)	120 (8)	115 (10)		126.6	121.2	123
H-C (1′)-N (9)	106 (6)	101 (6)		109.1	104.0	113
H-C (1′)-O (1′)	106 (6)	99 (6)		107.2	112.7	105
H-C (1′)-C (2′)	117 (6)	127 (6)		114.0	113.4	111
H-C (2′)-C (1′)	114 (6)	121 (7)		106.9	108.4	109
H-C (2′)-C (3′)	117 (6)	101 (7)		112.9	105.3	115
H-C (2′)-O (2′)	111 (6)	118 (7)		106.2	114.6	114
H-C (3′)-C (2′)	101 (5)	117 (8)		112.2	111.6	110
H-C (3′)-C (4′)	111 (5)	91 (8)		112.8	110.6	108
H-C (3′)-O (3′)	118 (5)	119 (8)		109.1	111.3	107
H-C (4′)-C (3′)	107 (7)	106 (7)		112.9	107.9	109
H-C (4′)-C (5′)	112 (7)	122 (7)		108.5	109.6	111
H-C (4′)-O (1′)	108 (7)	96 (7)		103.2	107.5	108
H-C (5′)-C (4′)	117 (6)	109 (7)		109.3	104.2	113
H-C (5′)-O (5′)	108 (6)	98 (7)		109.0	115.4	110
H-C (5′)-H′	103 (10)	110 (9)		104.6	106.9	113
H′-C (5′)-C (4′)	113 (7)	117 (7)		108.5	105.6	104
H′-C (5′)-O (5′)	107 (7)	112 (7)		113.9	111.5	104
H-O (2′)-C (2′)	98 (7)	106 (11)		113.3	111.4	111
H-O (3′)-C (3′)	103 (5)	115 (9)		107.9	117.8	106
	Present study	Present study	Rao and Sundaralingam (1969)	Thewalt, Bugg, and Marsh (1970)		Munns and Tollin (1970)

Determination and Refinement of the Structure

The structure was established by heavy atom method. Approximate positional parameters of the cobalt atom were determined from (1/2, v, w), (u, 1/2, w) and (u, v, 1/2) Harker sections. The Fourier synthesis based on the phases of the cobalt atom revealed the complete molecular structure and seven water oxygen atoms. The refinement was carried out using the block-diagonal least-squares method. Five cycles of isotropic and five cycles of anisotropic refinement reduced R value to 0.08. The least-squares weighting was that similar to Hugehes,[10] where $\sqrt{w}=50/|F_o|$ for $|F_o|>50$, $\sqrt{w}=1.0$ for $|F_o|\leq 50$. At this stage a difference Fourier synthesis could locate 23 hydrogen atoms out of 25. Three more cycles of refinement including hydrogen atoms with isotropic thermal parameters gave final R value of 0.051. Finally, two remaining hydrogen atoms could be found from the subsequent difference Fourier synthesis. The final atomic parameters are given in Table 1 together with their standard deviations.

The structure of the nickel complex was elucidated from that of the cobalt complex. Five cycles of isotropic block-diagonal least-squares refinement using the atomic parameters of the cobalt complex as starting parameters reduced the R value to 0.134. Subsequent five cycles of anisotropic refinement decreased R to 0.088. In a difference Fourier synthesis calculated at this stage, 19 hydrogen atoms in the asymmetric unit were actually located and their positions were in accord with the stereochemistry of the molecule, and they were included in the refinement with isotropic temperature factors. Three cycles of refinement, including all atoms brought R to 0.075; an additional final cycle gave no significant changes in positional or thermal parameters. Finally, a difference Fourier synthesis was computed in order to locate the six remaining hydrogen atoms, three of which were actually located. The weighting scheme was; $\sqrt{w}=25/|F_o|$ for $|F_o|>25$, $\sqrt{w}=1.0$ for $|F_o|\leq 25$. The refined atomic parameters are given in Table 2. Complete lists of the observed and calculated structure factors are preserved by the Chemical Society of Japan.[11]

The atomic scattering factors used in the present structure determination were; for hydrogen atoms those cited as Q–1 in International Tables for X-ray Crystallography,[12] for carbon SX–6, for nitrogen SX–7, for oxygen SX–8, for phosphorus SX–70, for cobalt SX–27 and for nickel SX–28.

Discussion of the Structure

The bond lengths and bond angles of the inosine 5′-phosphate molecules along with their estimated standard deviations are listed in Table 3. In this table the values are compared with those of the inosine molecules in monosodium inosine 5′-phosphate (5′-IMP–Na),[8] inosine dihydrate (Inosine, $2H_2O$)[13] and inosine.[14] Figure 1 is a perspective view of the molecule in the cobalt complex showing the numbering

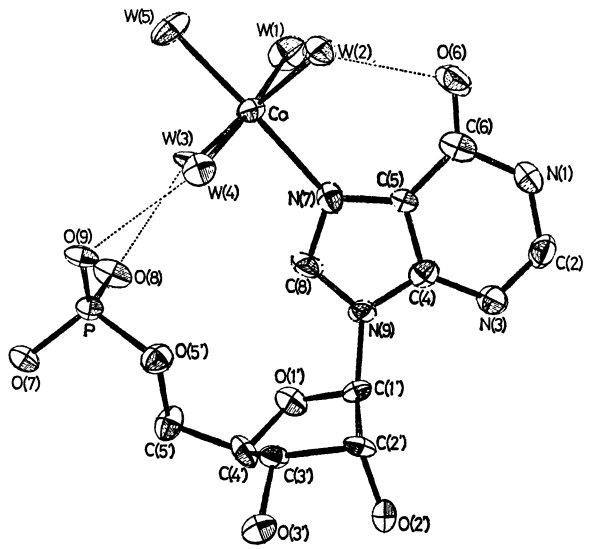

Fig. 1. Perspective view of the molecule in the cobalt complex showing the numbering system and the anisotropic thermal motion of the non-hydrogen atoms represented by 50% probability ellipsoids.

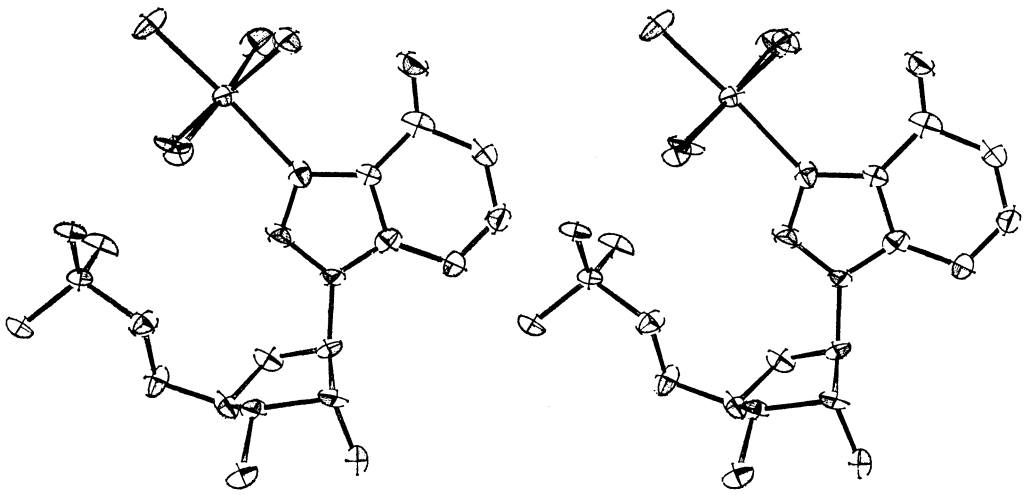

Fig. 2. Stereoscopic view of the structure of the molecule in the cobalt complex.

Table 4. Least-squares planes through the base and sugar

	5′-IMP-Co	5′-IMP-Ni	5′-IMP-Na	Inosine, $2H_2O$		Inosine
				Molecule I	Molecule II	
(1) Plane through the hypoxanthine ring						
N(1)	−0.015* Å	−0.006* Å	0.002* Å	−0.009* Å	0.008* Å	0.020* Å
C(2)	−0.028*	−0.011*	−0.002*	−0.001*	−0.009*	0.020*
N(3)	0.013*	0.005*	0.004*	0.037*	0.005*	−0.010*
C(4)	0.045*	0.000*	−0.020*	0.023*	0.011*	−0.008*
C(5)	−0.007*	−0.001*	0.060*	0.030*	−0.001*	−0.010*
C(6)	0.020*	0.018*	−0.024*	−0.010*	−0.001*	−0.045*
N(7)	0.006*	−0.012*	−0.018*	0.023*	−0.001*	0.023*
C(8)	−0.028*	−0.002*	0.003*	0.012*	0.004*	0.004*
N(9)	−0.005*	0.008*	−0.005*	−0.002*	0.012*	−0.014*
O(6)	0.064	0.069	−0.091	−0.042	−0.010	−0.161
C(1′)	−0.134	−0.155	−0.072	−0.061	−0.018	−0.149
A	0.0383	0.0371	0.875	0.0533	0.0319	0.7237
B	−0.0265	−0.0207	0.118	0.0577	0.0124	−0.4684
C	0.9989	0.9991	−0·446	0.9790	0.9845	−0.5068
D	1.7586	1.7759	0.741	4.0891	6.9433	−1.2786
(2) Plane through the ribose ring						
C(1′)	−0.025*	−0.030*	0.012*	−0.004*	0.028*	0.042*
O(1′)	0.026*	0.032*	−0.020*	0.007*	0.045*	−0.043*
C(2′)	0.014*	0.017*	0.610	−0.589	−0.605	−0.025*
C(3′)	−0.560	−0.566	−0.011*	0.004*	−0.026*	0.626
C(4′)	−0.015*	−0.019*	0.018*	−0.007*	0.043*	0.026*
O(2′)	1.402	1.386	0.232	−0.319	−0.287	−1.379
O(3′)	−0.108	−0.168	−1.334	1.353	1.279	0.440
C(5′)	−0.839	−0.836	1.105	−1.178	−1.025	0.845
	C(3′)-*endo*	C(3′)-*endo*	C(2′)-*endo*	C(2′)-*endo*	C(2′)-*endo*	C(3′)-*endo*
A	0.8074	0.8013	0.666	−0.6207	−0.4733	0.7363
B	0.4288	0.4259	−0.728	−0.4972	0.7752	−0.2892
C	−0.4051	−0.4202	−0.166	0.6887	0.4816	0.6329
D	9.0486	8.9507	−5.188	−4.3651	5.3742	0.9278
(3) The dihedral angle between planes, (1) and (2)						
	67.3°	66.5°	55.2°	52.2°	62.0°	69.7°
	Present study	Present study	Rao and Sundaralingam (1969)	Thewalt, Bugg and Marsh (1970)		Munns and Tollin (1970)

The atoms marked * were included in the calculations of the least-squares planes. The equation of the least-squares plane is defined by $AX+BY+CZ=D$, where X, Y and Z are the orthogonal coordinates measured in Å units along the crystallographic a, b and c axes, respectively.

Table 5. Comparison of the conformations of 5′-IMP molecules

	ϕ_{OO}	ϕ_{OC}	Conformation about the C(4′)-C(5′) bond	ϕ_{CN}	ϕ_{OP}	Displaced suger atom
5′-IMP-Co	−71.7°	44.7°	*gg*	25.4°	161.6°	C(3′)-*endo*
5′-IMP-Ni	−73.7	43.1	*gg*	24.0	162.0	C(3′)-*endo*
5′-IMP-Ba						
molecule I	58	49	*gg*	−46	170	C(2′)-*endo*
molecule II	57	51	*gg*	−34	160	C(2′)-*endo*
5′-IMP2-Na	61	56	*gg*	−43	172	C(2′)-*endo*
5′-IMP-Na	−63	59	*gg*	41	176	C(2′)-*endo*

ϕ_{OO}: torsion angle O(1′)-C(4′)-C(5′)-O(5′), defined by Shefter and Trueblood (1965).
ϕ_{OC}: torsion angle C(3′)-C(4′)-C(5′)-O(5′), defined by Shefter and Trueblood (1965).
ϕ_{CN}: torsion angle C(8)-N(9)-C(1′)-O(1′), defined by Sundaralingam and Jensen (1965).
ϕ_{OP}: torsion angle C(4′)-C(5′)-O(5′)-P.

system. A stereoscopic view of the structure of the molecule in the cobalt complex is also shown in Fig. 2. Aspects of the coordination and the conformation of the inosine 5′-phosphate molecule in the cobalt and nickel complexes are similar to each other.

The Hypoxanthine Ring. The bond lengths and bond angles in the both hypoxanthine rings are in over all agreement with those found in the compounds mentioned above. A common and characteristic feature of the hypoxanthine moieties is regarding angles around the C(6)–O(6) bond; the C(5)–C(6)–O(6) angle is apparently larger than the N(1)–C(6)–O(6), differences of which are distributed in the range of 6—11°. This may be due to the effect of the steric interaction between the oxygen atom O(6) and the nitrogen atom N(7).

The least-squares plane through the nine atoms of the base, excluding the substituent atom O(6), and the deviations of atoms from this plane are given in Table 4, comparing with those of the compounds mentioned above. The atoms composing the purine ring show a significant degree of puckering, which has been often found in purine and pyrimidine derivatives.

The binding of the metal to N(7) has little effect on the base geometry as shown in Tables 3 and 4.

The Ribose Ring. The bond lengths and bond angles in the ribose ring have their usual values.[15] The conformational parameters of the ribose ring for the inosine 5′-phosphate molecule are listed in Table 5, comparing with those of monosodium inosine 5′-phosphate,[8] disodium inosine 5′-phosphate (5′-IMP–2Na)[7] and barium inosine 5′-phosphate (5′-IMP–Ba).[7] An important stereochemical parameter in nucleosides and nucleotides is the glycosyl torsion angle ϕ_{CN},[15] C(8)–N(9)–C(1′)–O(1′), which describes the relative orientation of the base with respect to the sugar. Those angles are 25.4° (Co complex) and 24.0° (Ni complex), therefore, the conformation about the glycosyl bond is *anti* in both complexes.

The ribose carbon atom C(1′) is out of the base plane by 0.134 Å (Co complex) and 0.155 Å (Ni complex) and the glycosidic C(1′)–N(9) bond makes an angle of about 5.0° (Co complex) and 6.0° (Ni complex) with the base plane. As shown in Table 4, the ribose ring is puckered with C(3′) displaced by the best four-atom plane of the furanose ring by 0.560 Å (Co complex) and 0.566 Å (Ni complex) on the same side as C(5′), the conformation of the ribose ring is, therefore, C(3′)-*endo*. When refered to the three-atom plane C(1′), O(1′) and C(4′), the conformation is C(3′)-*endo*-C(2′)-*exo* for both complexes, where C(3′) and C(2′) are displaced by 0.465 and 0.122 Å (Co complex) and 0.477 and 0.151 Å (Ni complex).

Dihedral angles between the base and the ribose planes are 67.3° (Co complex) and 66.5° (Ni complex) (Table 4).

The ribose ring conformation can also be described in terms of torsion angles around the ring bonds. The conformation around the C(4′)–C(5′) bond, described by the angles ϕ_{OO},[16] O(1′)–C(4′)–C(5′)–O(5′) and ϕ_{OC},[16] C(3′)–C(4′)–C(5′)–O(5′), is *gauche-gauche* for both complexes.

The Phosphate Group. The ester linkage, C(5′)–O(5′), shows the elongated conformation as usual, the torsion angle ϕ_{OP}, C(4′)–C(5′)–O(5′)–P, being 161.6° (Co complex) and 162.0° (Ni complex).

It may be noted that both phosphorus atoms in the cobalt and nickel complexes lie approximately in the base plane; only 0.188 Å (Co complex) and 0.173 Å (Ni complex) off the base plane.

Coordination Geometry about the Metal Atom. The coordination geometries about (a) the cobalt and (b) nickel atoms are shown in Fig. 3, together with the bond lengths and bond angles within the metal coordination spheres. They are approximately octahedral with the six coordination sites occupied by the five oxygen atoms of the water molecules and the nitrogen atom N(7) of the hypoxanthine moiety, a site which is accessible and presumedly favorable in the biopolymer, and are similar to that found in the cobalt-theophylline complex.[5] Other two cases of the transition metal binding to N(7) of the purine base have been reported in the zinc–adenine[17] and the copper–9-methylhypoxanthine[18] complexes. Although in the vitamine B_{12} derivatives,[19] the analogous N(7) site of the dimethylbenzimidazole base is coordinated to the cobalt atom which is chelated to the corrine nucleus in a manner similar to that of the present complexes, it is to our knowledge the first case in the crystal structure of nucleotides that the transition metal directly bonds to the base. Bond lengths and bond angles of the cobalt complex agree in general

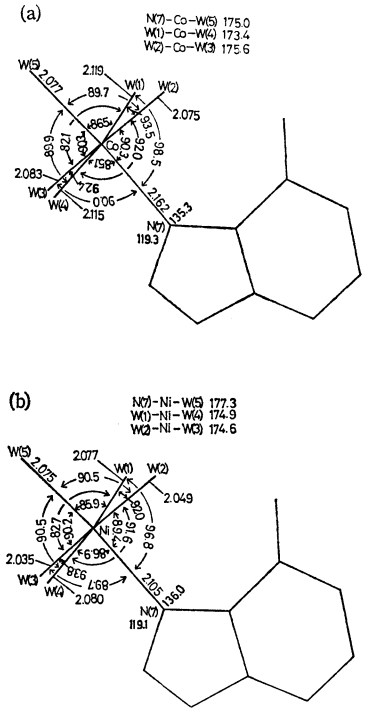

Fig. 3. The coordination geometries around (a) the cobalt atom and (b) the nickel atom. The bond lengths and angles within the metal coordination spheres are shown. The average estimated standard deviations are 0.009 Å for Metal-W bonds and 0.010 Å for Metal-N bonds and 0.4° for W-Metal-W and W-Metal-N angles and 0.8° for C-N-Metal angles.

Table 6. Deviations of the atoms from the least-squares planes (Å)

Atom	5′-IMP-Co	5′-IMP-Ni
(1) Plane through the hypoxanthine ring[a]		
Metal	−0.086	−0.060
W(1)	−1.805	−1.706
W(2)	1.218	1.237
W(3)	−1.516	−1.489
W(4)	1.511	1.513
W(5)	−0.036	−0.039
(2) Plane through the four water oxygen atoms, W(1), W(2), W(3) and W(4)		
W(1)	−0.036*	−0.043*
W(2)	0.033*	0.040*
W(3)	0.037*	0.043*
W(4)	−0.034*	−0.039*
Metal	0.033	0.026
N(7)	2.180	2.122
W(5)	−2.044	−2.047
A	0.6681	0.6745
B	0.7414	0.7365
C	−0.0499	−0.0512
D	7.2853	7.2365
(3) The dihedral angle between the planes, (1) and (2)	87.5°	87.6°

The atoms marked * were included in the calculations of the least-squares planes. The equation of the least-squares plane is defined by $AX+BY+CZ=D$, where X, Y and Z are the orthogonal coordinates measured in Å units along the crystallographic a, b and c axes, respectively.

a) This plane is identical with that in Table 4.

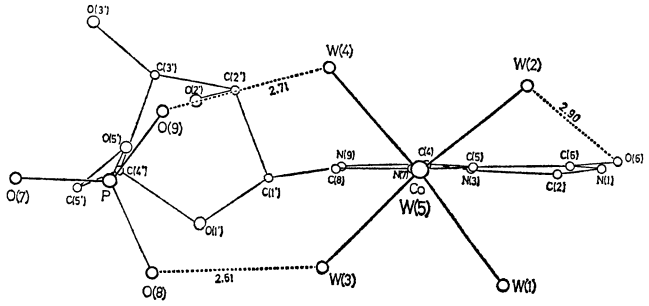

Fig. 4. A view of the cobalts complex down the W(5)-Co bond. Note the dispositions of the hypoxanthine ring system, and in particular the intramolecular hydrogen bonds from W(3) and W(4) to O(8) and O(9) of the phosphate group respectively.

with those of the nickel complex. However, each bond length in the nickel complex is smaller than the corresponding one in the cobalt complex. The metal–oxygen coordination distances range from 2.075 to 2.119 Å with an average value of 2.094 Å for the cobalt complex and from 2.035 to 2.080 Å with that of 2.063 Å for the nickel complex. The metal–nitrogen coordination distances are 2.162 Å for the cobalt complex and 2.105 Å for the nickel complex. These values of the nickel complex in the present study are in good agreement with those of the same nickel complex reported by Clark and Orbell[9]; (Ni–H_2O)average= 2.06 Å and Ni–N(7)=2.11 Å. As shown in Table 6, the cobalt and nickel atoms involving the water oxygen W(5) lie in the base plane. The cobalt and nickel atoms are also in the least-squares plane through four water oxygen atoms, W(1), W(2), W(3) and W(4), which is approximately perpendicular to the base plane.

Table 7. Bond lengths and angles involving hydrogen atoms in water molecules

Bond length	5′-IMP-Co	5′-IMP-Ni
W(1)-H	1.28(11) Å	1.10(13) Å
W(1)-H′	0.98(11)	0.98(12)
W(2)-H	0.80	—
W(2)-H′	0.80(12)	—
W(3)-H	1.14(14)	1.16(12)
W(3)-H′	0.81(13)	0.92
W(4)-H	0.80(10)	0.75(19)
W(4)-H′	0.88(15)	0.85(14)
W(5)-H	1.24(16)	0.83(15)
W(5)-H′	0.94(10)	1.05(14)
W(6)-H	1.29	1.31
W(6)-H′	1.13(16)	1.14
W(7)-H	0.86(13)	—
W(7)-H′	0.98(15)	0.92(19)
Bond angle		
H-W(1)-H′	133(8)°	75(9)°
H-W(2)-H′	88	—
H-W(3)-H′	108(12)	90
H-W(4)-H′	108(12)	125(17)
H-W(5)-H′	109(11)	117(13)
H-W(6)-H′	107	120
H-W(7)-H′	121(12)	—

A notable feature of the metal coordination is that metals are not directly attached to the phosphate oxygen atoms, as is found for sodium ion in the crystal structures of disodium inosine 5′-phosphate[7] and monosodium inosine 5′-phosphate[8] and for barium ion in those of barium inosine 5′-phosphate,[7] barium uridine 5′-phosphate[16] and barium 5′-ribophosphate,[20] whereas in the structures of calcium thymidylate[21] and disodium adenosine triphosphate,[22] metal ions bond directly to the phosphate oxygen atoms.

Figure 4 is a view of the cobalt complex down to W(5)–Co bond. The hypoxanthine ring has positioned itself nearly symmetrically between the bonds Co–W(3) and Co–W(4), but asymmetrically between the bonds Co–W(1) and Co–W(2). This may be due to the intramolecular hydrogen bond from the water W(2) to the carbonyl oxygen O(6) of the base. Figure 5 is the arrangement of the molecules in the unit cell in projection down the c axis for the cobalt complex. Cobalt atom interacts indirectly with phosphate oxygens through the water molecules.

Molecular Packing and Hydrogen Bonds. In Fig. 5, the close contacts are shown by broken lines, which may represent hydrogen bonds. The positions of the molecules are denoted as following: I at x, y, z; II at

Table 8. Hydrogen bond distances and angles

Donor (D)	Acceptor (A)	Of molecule	Distance (D)·····(A)		Distance H·····(A)		Angle H–(D)·····(A)	
			5′-IMP-Co	5′-IMP-Ni	5′-IMP-Co	5′-IMP-Ni	5′-IMP-Co	5′-IMP-Ni
N(1)	W(6)	IV(000)	2.830(13) Å	2.788(14) Å	1.72(12) Å	2.13(10) Å	18(6)°	24(9)°
O(2′)	W(7)	I(000)	2.734(14)	2.726(14)	1.78(12)	2.09(12)	17(7)	15(11)
O(3′)	O(9)	III(000)	2.761(12)	2.744(12)	1.87(10)	1.78(14)	26(5)	4(9)
W(1)	O(7)	III($\bar{1}0\bar{1}$)	2.769(13)	2.795(14)	1.74(11)	2.37(12)	27(5)	56(6)
W(1)	W(7)	II(00$\bar{1}$)	2.876(15)	2.885(16)	2.54(12)	2.09(12)	60(7)	29(7)
W(2)	O(6)	I(000)	2.901(13)	2.838(13)	2.43(12)	—	7(9)	—
W(2)	O(2′)	I($\bar{1}$00)	2.938(13)	2.953(13)	2.23(13)	—	24(9)	—
W(2)	O(3′)	I($\bar{1}$00)	2.783(13)	2.812(13)	2.03	—	16	—
W(3)	O(7)	III($\bar{1}0\bar{1}$)	2.646(11)	2.625(14)	1.58(14)	1.54(11)	13(7)	16(5)
W(3)	O(8)	I(000)	2.613(12)	2.662(13)	1.82(14)	1.76	9(10)	10
W(4)	O(7)	III($\bar{1}$00)	2.679(12)	2.701(13)	1.91(10)	2.03(19)	13(7)	22(14)
W(4)	O(9)	I(000)	2.707(12)	2.701(12)	1.86(15)	2.05(13)	12(10)	34(9)
W(5)	O(8)	III($\bar{1}0\bar{1}$)	2.708(12)	2.688(14)	1.71(15)	2.10(14)	27(7)	38(10)
W(5)	O(9)	III($\bar{1}$00)	2.767(12)	2.780(14)	1.85(10)	1.99(15)	9(6)	34(8)
W(6)	O(8)	III(00$\bar{1}$)	2.927(13)	3.031(15)	1.86(16)	1.91	14(8)	8
W(6)	W(4)	III(000)	3.074(13)	3.065(15)	1.80	2.05	7	31
W(7)	O(3′)	II(10$\bar{1}$)	2.956(14)	2.928(16)	2.32(13)	—	36(9)	—

Table 9. Hydrogen bond directions around the donor atom

Hydrogen bond from	to Atom	Of molecule	Code No.	Angles subtended at the donor atom[a]	5′-IMP-Co	5′-IMP-Ni
N(1)	W(6)	IV(000)	1	C(2)-N(1)···1	95.7(8)°	96.0(9)°
				C(2)-N(1)···1	138.0(8)	131.1(9)
O(2′)	W(7)	I(000)	2	C(2′)-O(2′)···2	107.9(8)	105.6(9)
O(3′)	O(9)	III(000)	3	C(3′)-O(3′)···3	119.3(7)	118.5(8)
W(1)	O(7)	III($\bar{1}0\bar{1}$)	4	4···W(1)···5	105.6(4)	103.2(5)
W(1)	W(7)	II(00$\bar{1}$)	5	Metal-W(1)···4	99.0(4)	98.8(4)
				Metal-W(1)···5	148.7(5)	152.2(6)
W(2)	O(6)	I(000)	6	6···W(2)···7	68.3(3)	66.8(4)
W(2)	O(2′)	I($\bar{1}$00)	7	7···W(2)···8	54.5(3)	54.6(4)
W(2)	O(3′)	I($\bar{1}$00)	8	6···W(2)···8	122.6(4)	121.0(5)
				Metal-W(2)···6	97.8(4)	98.5(4)
				Metal-W(2)···7	127.8(5)	126.0(5)
				Metal-W(2)···8	119.5(4)	119.2(5)
W(3)	O(7)	III($\bar{1}0\bar{1}$)	9	9···W(3)···8	115.2(4)	114.7(4)
	O(8)	I(000)	10	Metal-W(3)···9	104.5(4)	105.6(4)
				Metal-W(3)···10	137.3(4)	135.8(5)
W(4)	O(7)	III($\bar{1}$00)	11	11···W(4)···12	119.3(4)	118.6(4)
W(4)	O(9)	I(000)	12	Metal-W(4)···11	102.8(4)	103.8(4)
				Metal-W(4)···12	116.3(4)	116.9(4)
W(5)	O(8)	III($\bar{1}0\bar{1}$)	13	13···W(5)···14	108.9(4)	109.5(4)
W(5)	O(9)	III($\bar{1}$00)	14	Metal-W(5)···13	124.6(4)	124.6(5)
				Metal-W(5)···14	126.5(4)	125.9(5)
W(6)	O(8)	III(00$\bar{1}$)	15	15···W(6)···16	95.9(4)	95.8(4)
W(6)	W(4)	III(000)	16	W(6)···16-Metal	136.2(4)	135.5(5)

a) Some of the atoms are designated by Code No.

1/2−x, 1−y, 1/2+z; III at 1/2+x, 1/2−y, 1−z and IV at 1−x, 1/2+y, 1/2−z, with the x, y and z coordinates as given in Tables 1 and 2. The translations along the three edges of the unit cell are indicated in parentheses.

The packing of the molecules seems to be governed by the base stacking and intermolecular hydrogen bonds. Further stabilization of the structure is provided by hydrogen bonding of the complex to two water molecules of crystallization. The bond lengths and bond angles involving hydrogen atoms in water molecules are listed in Table 7. The lengths and the

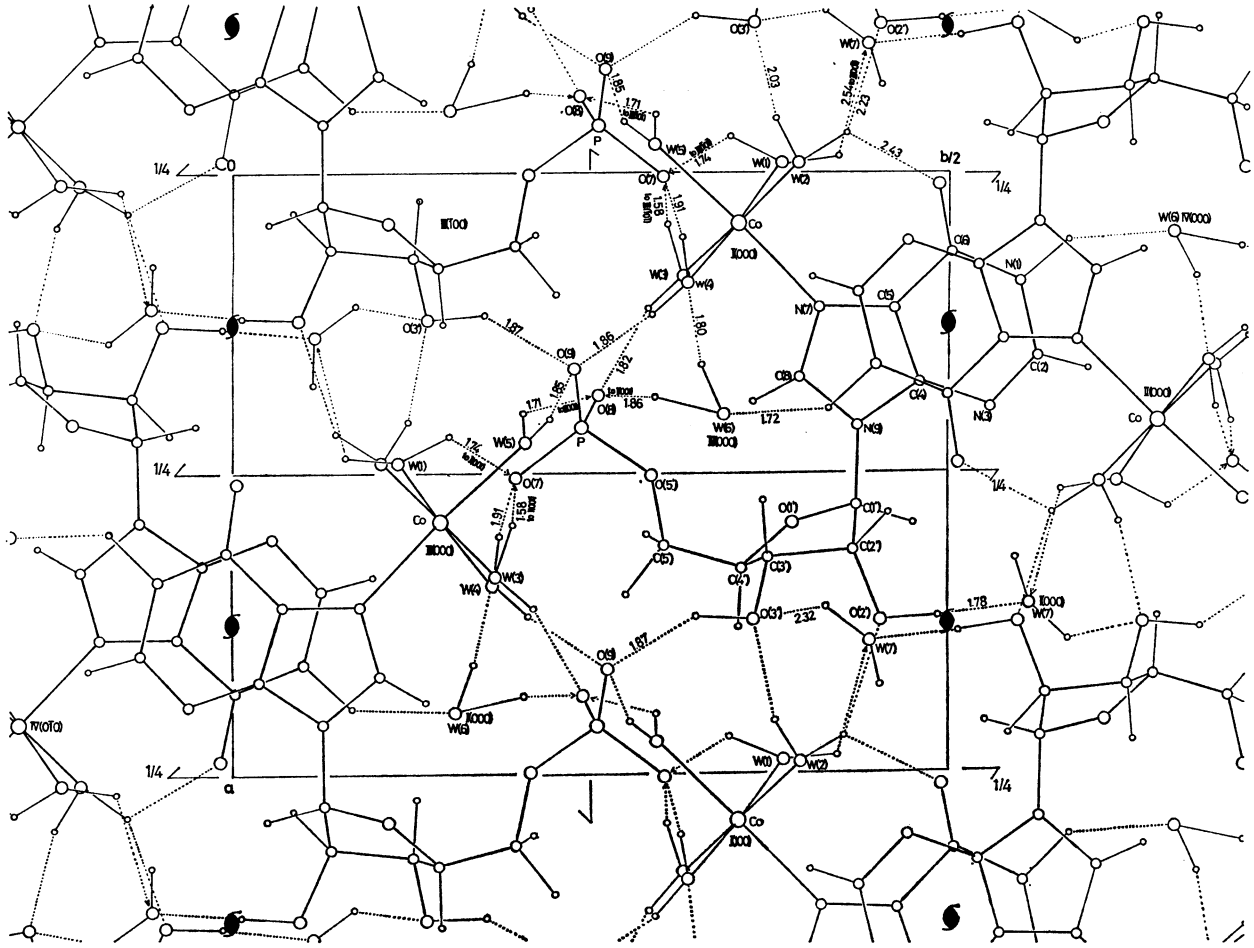

Fig. 5. Projection of the crystal structure of the cobalt complex along the c axis. Hydrogen bonds are shown by broken lines.

directions of the hydrogen bonds are summarized in Tables 8 and 9.

There is an infinite stack of relatively extensive overlapping bases about a two-fold screw axis along the c axis. Adjacent bases are rotated by 180° from each other, which favours dipole-dipole interactions. It is well known that this type of purine superposition may be an important stabilizing force in the inosine and guanosine structures.[23] The hypoxanthine rings lie in the ab plane so that they are stacked with a separation of 3.42 Å along the c axis in both complexes, this value is normal for the perpendicular distance between the base planes.

As expected, the highest concentrations of water molecules are seen around the metal and the anionic phosphate group of the nucleotide. The base, sugar and phosphate moieties are all hydrogen bonded to different degrees with the water molecules, but there is only one hydrogen bond which does not involve a water molecule, that from O(3′) to the phosphate oxygen O(9) (III(000)), and there are no interbase hydrogen bonds. The phosphate groups are running parallel to the a axis about the two-fold screw axis (at x, 1/4, 0) forming hydrogen-bonded ribons, $-(-\text{P}-\text{O}(7)\cdots\text{W}(3)\cdots\text{O}(8)-)-_n$.

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