Interaction of Metal Ions with 6-Oxopurine Nucleotides. Part 2.[1] *X*-Ray Structures of Ternary Nickel(II) Complexes with 2′-Deoxyguanosine 5′-Monophosphate or Guanosine 5′-Monophosphate†

Noor Shahina Begum, M. Damodara Poojary, and Hattikudur Manohar*
Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India

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The ternary metal nucleotide complexes $[Ni(en)_{1.3}(H_2O)_{1.4}(H_2O)_2][Ni(5'\text{-dGMP})_2(en)_{0.7}(H_2O)_{0.6}(H_2O)_2]\cdot 7H_2O$ (**1**) and $[Ni(en)_2(H_2O)_2][Ni(5'\text{-GMP})_2(H_2O)_4]\cdot 6H_2O$ (**2**) (en = ethylenediamine, 5′-dGMP = 2′-deoxyguanosine 5′-monophosphate, 5′-GMP = guanosine 5′-monophosphate) have been prepared and their structures analyzed by *X*-ray diffraction methods. Both compounds crystallise in the space group $C222_1$ with a = 8.810(1), b = 25.090(4), c = 21.084(1) Å, and Z = 4 for (**1**) and a = 8.730(1), b = 25.691(4), c = 21.313(5) Å, and Z = 4 for (**2**). The structures were deduced from the analogous Co^{III} complexes and refined by full-matrix least-squares methods to final R values of 0.087 and 0.131 for 1 211 and 954 reflections for (**1**) and (**2**) respectively. An interesting feature of the deoxyribonucleotide complex (**1**) is that en is not totally labilized from the metal centre on nucleotide co-ordination, as observed in corresponding ribonucleotide complexes. Apart from extensive intra- and inter-molecular hydrogen bonding, the structures are stabilized by significant intracomplex base–base and base–sugar interactions. The nucleotides in both complexes have an *anti* base, C(2′)-*endo* sugar pucker, and *gauche–gauche* conformation about the C(4′)–C(5′) bond.

As part of our ongoing studies on ternary metal complexes with 6-oxopurine nucleotides,[2–4] we reported the crystal structures of Co^{III} complexes containing ethylenediamine (en) in Part 1 of this series.[1] In this paper we describe the syntheses and structures of ternary Ni^{II} complexes of 2′-deoxyguanosine 5′-monophosphate (5′-dGMP) or guanosine 5′-monophosphate (5′-GMP) containing the same ternary ligand. The complex involving 5′-dGMP was studied in order to understand the co-ordinating behaviour of a deoxyribonucleotide in a ternary metal system. This represents the first structural study of such a system.

Experimental

Preparation of the Complexes.—$[Ni(en)_{1.3}(H_2O)_{1.4}(H_2O)_2][Ni(5'\text{-dGMP})_2(en)_{0.7}(H_2O)_{0.6}(H_2O)_2]\cdot 7H_2O$ (**1**). Light blue crystals of $[Ni(en)(H_2O)_4][NO_3]_2$ were obtained by slow evaporation of an aqueous equimolar mixture of $Ni(NO_3)_2\cdot 6H_2O$ and en. An aqueous solution of this complex and $Na_2(5'\text{-dGMP})$ were then mixed in an equimolar ratio and the pH adjusted to 6.5 using dilute HNO_3. On vapour diffusion against t-butyl alcohol the reaction mixture afforded light blue plate-like crystals after two weeks. The crystals were filtered off, washed with water, and air dried.

$[Ni(en)_2(H_2O)_2][Ni(5'\text{-GMP})_2(H_2O)_4]\cdot 6H_2O$ (**2**). $[Ni(en)(H_2O)_4]SO_4$ was prepared by mixing aqueous solutions of $NiSO_4\cdot 6H_2O$ and en in an equimolar ratio. On slow evaporation of the reaction mixture, light greenish blue thin plate-like crystals appeared after 3 d. The ternary nucleotide complex was obtained by mixing aqueous solutions of $[Ni(en)(H_2O)_4]SO_4$ and $Na_2(5'\text{-GMP})$, both at 5×10^{-3} mol dm^{-3}. On vapour diffusion against t-butyl alcohol the reaction mixture yielded light green thin plate-like crystals after one week. These were filtered off, washed with water, and air dried. The quality of the crystals was, however, not high. The best among these was chosen for *X*-ray data collection.

Collection and Reduction of X-*Ray Intensity Data.*—Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer with Ni-filtered Cu-K_α radiation for compound (**1**) and with graphite-monochromated Mo-K_α radiation for compound (**2**). The data were corrected for Lorentz and polarization effects. An absorption correction was applied for compound (**1**) using φ-scan data.[5] In the final stages of the refinement both data sets were corrected for secondary extinction effects [$g = 1.05 \times 10^{-6}$ for (**1**) and 1.55×10^{-6} for (**2**)]. Crystal data, and a summary of data collection and structure refinement are given in Table 1.

Structure Solution and Refinement.—*Compound* (**1**). Atomic co-ordinates from the isomorphous compound $[Co(en)_2(H_2O)_2][Co(5'\text{-GMP})_2(H_2O)_4]Cl_2\cdot 4H_2O$ reported in Part 1[1] were employed, except those of the carbon atoms of en and the lattice water oxygens. Four cycles of isotropic least-squares refinement (R = 0.18) followed by a difference Fourier synthesis yielded three oxygen atoms of lattice waters in general positions and one at a special position. A further difference synthesis after including these atoms revealed the appearance of a new peak at bonding distance (1.45 Å) from the atom assumed to be O(W2). This peak, together with its two-fold symmetry equivalent, completed a satisfactory geometry for an en group co-ordinated to Ni(1), identifying the water oxygens to be nitrogens and the new peaks to be carbons. However, the peak heights corresponding to the carbon atoms of en co-ordinated both to Ni(1) and Ni(2) were lower than expected (*ca.* 60%) suggesting partial occupancy of the group. On the basis of further refinement and the results of chemical analysis the en group around Ni(1) was assigned an occupancy of 0.7 while that around Ni(2) was assigned 0.65. In the absence of en, water molecules located at nearly the same positions as the nitrogens of en obviously co-ordinate the metal ions Ni(1) and Ni(2). As in the case of the Co^{III} complexes,[1] the carbon atoms of en, *i.e.* C(13), C(14), and C(15), were disordered and the bond lengths associated with C(15), in particular, were unsatisfactory. Therefore these atoms were fixed at the positions identified in

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† *Supplementary data available*: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

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

Table 1. Crystal data for $[Ni(en)_{1.3}(H_2O)_{1.4}(H_2O)_2][Ni(5'\text{-}dGMP)_2(en)_{0.7}(H_2O)_{0.6}(H_2O)_2]\cdot 7H_2O$ (**1**) and $[Ni(en)_2(H_2O)_2][Ni(5'\text{-}GMP)_2(H_2O)_4]\cdot 6H_2O$ (**2**)

Compound	(1)	(2)
Formula	$C_{24}H_{64}N_{14}Ni_2O_{27}P_2$	$C_{24}H_{62}N_{14}Ni_2O_{28}P_2$
M	578.96	598.17
Crystal system	Orthorhombic	Orthorhombic
Space group	$C222_1$	$C222_1$
a/Å	8.810(1)	8.730(1)
b/Å	25.090(4)	25.691(4)
c/Å	21.084(1)	21.313(5)
U/Å^3	4 660.62	4 780.75
Z	4	4
D_m/Mg m^{-3}	1.65	1.65
D_c/Mg m^{-3}	1.65	1.66
F(000)	2 544	2 608
μ/cm^{-1}	24.77	9.16
λ/Å	1.5418	0.7107
Crystal dimensions/mm	0.18 × 0.30 × 0.55	0.12 × 0.20 × 0.19
2θ range/°	0—140	2—48
Scan mode	ω–2θ	ω–2θ
Scan speed/° min^{-1}	4	1
Scan width, Δ θ	0.75 + 0.45 tan θ	0.75 + 0.45 tan θ
No. of reflections measured	2 540	2 170
No. of reflections used [$I \geqslant 3\sigma(I)$]	1 211	954
$R[=\Sigma \lvert F_o - \lvert F_c\rvert\rvert/\Sigma F_o]$	0.087	0.131
$R'\{=[\Sigma w(F_o - \lvert F_c\rvert)^2/\Sigma wF_o^2]^{\frac{1}{2}}\}$	0.093	0.138

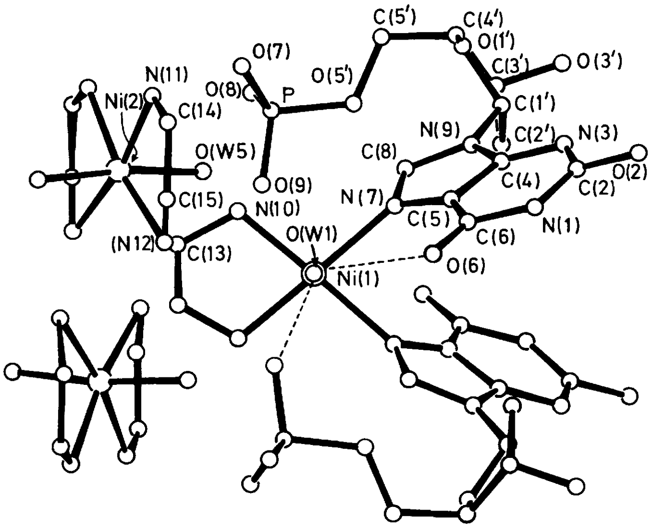

Figure 1. Structure of $[Ni(en)_{1.3}(H_2O)_{1.4}(H_2O)_2][Ni(5'\text{-}dGMP)_2(en)_{0.7}(H_2O)_{0.6}(H_2O)_2]\cdot 7H_2O$ (**1**). The occupancy of en co-ordinated to Ni(1) is 0.7 and that around Ni(2) is 0.65. In the absence of en, water oxygens (with partial occupancy) located at nearly the same positions as the nitrogens of en co-ordinate to the Ni atoms

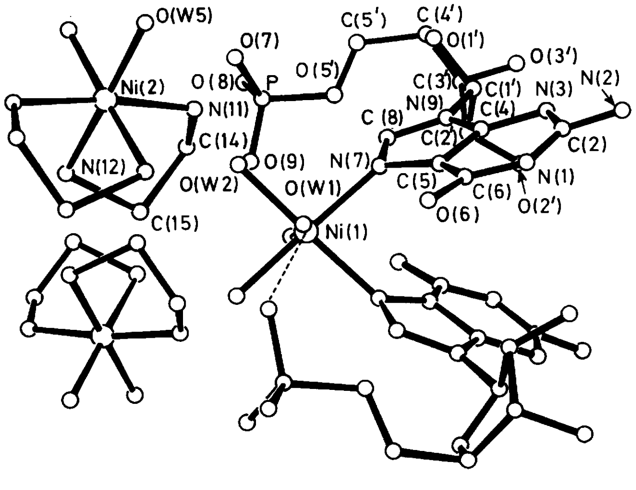

Figure 2. Structure of $[Ni(en)_2(H_2O)_2][Ni(5'\text{-}GMP)_2(H_2O)_4]\cdot 6H_2O$ (**2**)

the Fourier map in further cycles of refinement. Hydrogens of the nucleotide, except those associated with the sugar hydroxyl group, were fixed on the basis of geometrical considerations. The contributions from the hydrogen atoms with $U_{iso} = 0.05$ Å^2 were included in the subsequent cycles but not refined. Three cycles of refinement with anisotropic thermal parameters for all the atoms, except the disordered ones and the lattice water oxygens, produced convergence. A final difference Fourier map was essentially featureless except for some residual electron density around the disordered atoms. The positional parameters for the non-hydrogen atoms are given in Table 2.

Compound (**2**). As in the case of (**1**), the structure of (**2**) was elucidated from that of the isomorphous Co^{III} complex.[1] Three cycles of isotropic least-squares refinement using the positional parameters of all the atoms excepting those of the carbon atoms of en and the lattice water oxygens reduced the *R* value to 0.17. A difference Fourier synthesis at this stage revealed the positions of the remaining non-hydrogen atoms. However, difficulty in identifying the carbon atoms of the en group was encountered. Smeared out electron density corresponding to these atoms in the neighbourhood of expected positions indicated disorder of the group. Different possible positions were attempted for the carbon atoms. However, refinement of these positions resulted in an unsatisfactory geometry of the en ring. Therefore the carbon atoms were fixed in positions so as to give a reasonable geometry. Hydrogen atoms of the nucleotide molecule, except the sugar hydroxyl hydrogens, were fixed on the basis geometrical considerations. Their U_{iso} values were set equal to 0.05 Å^2. The refinement was concluded after two more cycles with anisotropic thermal parameters for the Ni and P

Table 2. Final fractional co-ordinates (× 10^4) with e.s.d.s in parentheses for (**1**)

Atom	*x*	*y*	*z*
Ni(1)	0	1 630(2)	2 500
Ni(2)	−2 882(5)	0	5 000
P	3 450(6)	1 340(2)	4 546(2)
O(5′)	3 646(17)	1 977(6)	4 459(6)
O(7)	4 552(17)	1 087(6)	4 085(6)
O(8)	3 769(17)	1 198(5)	5 230(5)
O(9)	1 795(17)	1 262(6)	4 363(6)
N(1)	1 743(22)	3 343(9)	1 357(7)
C(2)	2 576(25)	3 685(11)	1 726(9)
N(2)	2 998(29)	4 177(8)	1 461(10)
N(3)	3 049(21)	3 599(8)	2 310(7)
C(4)	2 657(22)	3 105(7)	2 474(10)
C(5)	1 805(23)	2 694(9)	2 151(8)
C(6)	1 359(29)	2 811(13)	1 506(14)
O(6)	690(20)	2 527(7)	1 126(7)
N(7)	1 618(20)	2 257(6)	2 517(9)
C(8)	2 349(31)	2 372(8)	3 080(8)
N(9)	2 939(21)	2 876(8)	3 067(7)
C(1′)	3 768(28)	3 139(9)	3 572(9)
C(2′)	2 735(24)	3 153(8)	4 207(8)
C(3′)	3 997(23)	3 120(9)	4 687(8)
C(4′)	5 201(27)	2 800(8)	4 414(8)
O(1′)	5 042(18)	2 829(6)	3 730(6)
O(3′)	4 518(16)	3 658(5)	4 815(7)
C(5′)	5117(27)	2 198(8)	4 581(9)
N(10)[a]	1 472(40)	1 040(17)	2 564(18)
N(11)[b]	−4 668(37)	−245(13)	4 456(16)
N(12)[b]	−1 321(33)	−330(12)	4 313(14)
C(13)[a,c]	675	546	2 667
C(14)[b,c]	−4 195	−346	3 813
C(15)[b,c]	−2 456	−329	3 519
O(W1)	172(18)	1 593(6)	1 510(6)
O(W2)[d]	1 919(56)	1 067(24)	2 413(24)
O(W3)	4 324(37)	1 523(12)	1 947(14)
O(W4)	3 407(35)	5 171(12)	579(16)
O(W5)	−2 769(17)	−682(6)	5 546(7)
O(W6)	3 716(35)	321(12)	3 426(14)
O(W7)	0	4 884(23)	2 500
O(W11)[e]	−4 229(50)	−475(18)	4 449(21)
O(W12)[e]	−958(47)	−353(16)	4 563(21)

[a] Occupancy 0.7. [b] Occupancy 0.65. [c] Position fixed. [d] Occupancy 0.3. [e] Occupancy 0.35.

Table 3. Final fractional co-ordinates (× 10^4) with e.s.d.s in parentheses for (**2**)

Atom	*x*	*y*	*z*
Ni(1)	0	1 665(2)	2 500
Ni(2)	−2 959(9)	0	5 000
P	−3 528(10)	1 393(4)	437(5)
O(5′)	3 674(29)	2 017(9)	4 495(12)
O(7)	4 539(29)	1 128(8)	4 105(12)
O(8)	4 045(22)	1 237(7)	5 209(10)
O(9)	1 865(31)	1 274(9)	4 427(12)
N(1)	1 742(31)	3 343(10)	1 369(12)
C(2)	2 563(42)	3 667(14)	1 688(18)
N(2)	2 986(37)	4 101(11)	1 441(14)
N(3)	3 076(31)	3 617(10)	2 299(12)
C(4)	2 577(40)	3 109(12)	2 507(22)
C(5)	1 776(57)	2 736(18)	2 184(21)
C(6)	1 417(50)	2 867(16)	1 556(21)
O(6)	766(35)	2 551(11)	1 172(15)
N(7)	1 671(30)	2 273(9)	2 504(16)
C(8)	2 440(36)	2 380(11)	3 063(16)
N(9)	2 929(33)	2 870(10)	3 082(13)
C(1′)	3 755(37)	3 152(12)	3 579(16)
C(2′)	2 657(39)	3 162(12)	4 170(17)
O(2′)	1 869(28)	3 620(9)	4 150(12)
C(3′)	4 094(40)	3 138(13)	4 669(17)
O(3′)	4 584(23)	3 657(8)	4 781(10)
C(4′)	5 320(30)	2 814(10)	4 440(12)
O(1′)	5 099(35)	2 828(9)	3 765(12)
C(5′)	5 083(62)	2 237(16)	4 612(20)
N(11)	−2 810(33)	677(10)	4 514(13)
N(12)	−1 295(35)	−310(11)	4 440(15)
C(14)*	−1 967	644	3 924
C(15)*	−395	280	4 132
O(W1)	−160(34)	1 601(9)	3 484(12)
O(W2)	1 685(38)	1 091(10)	2 521(20)
O(W3)	−650(60)	6 539(21)	1 983(26)
O(W4)	3 266(71)	474(24)	3 403(32)
O(W5)	387(42)	4 702(12)	4 460(17)
O(W6)	−3 377(67)	532(27)	6 903(30)

* Position fixed.

Table 4. Bond lengths (Å) involving the non-hydrogen atoms, with e.s.d.s in parentheses

	(**1**)	(**2**)		(**1**)	(**2**)
Ni(1)–N(7)	2.12(1)	2.13(2)	Ni(1)–O(W1)	2.09(1)	2.11(2)
Ni(1)–O(W2)	2.17(3)	2.08(3)	Ni(1)–N(10)	1.99(3)	—
Ni(2)–N(11)	2.04(3)	2.02(2)	Ni(2)–N(12)	2.16(3)	2.04(3)
Ni(2)–O(W5)	2.06(1)	1.99(3)	Ni(2)–O(W11)	2.04(4)	—
Ni(2)–O(W12)	2.12(4)	—	N(1)–C(2)	1.37(2)	1.29(4)
C(2)–N(2)	1.40(3)	1.28(4)	C(2)–N(3)	1.32(2)	1.38(4)
N(3)–C(4)	1.33(3)	1.44(4)	C(4)–C(5)	1.45(2)	1.37(6)
C(5)–C(6)	1.44(3)	1.41(6)	C(6)–O(6)	1.22(3)	1.28(5)
C(6)–N(1)	1.41(3)	1.31(4)	C(5)–N(7)	1.35(2)	1.37(5)
N(7)–C(8)	1.38(3)	1.39(4)	C(8)–N(9)	1.36(2)	1.33(3)
N(9)–C(4)	1.39(2)	1.40(5)	N(9)–C(1′)	1.45(2)	1.47(4)
C(1′)–C(2′)	1.62(2)	1.58(4)	C(2′)–C(3′)	1.50(2)	1.64(5)
C(2′)–O(2′)	—	1.36(4)	C(3′)–C(4′)	1.45(3)	1.44(4)
C(3′)–O(3′)	1.45(2)	1.42(4)	C(4′)–O(1′)	1.45(2)	1.45(3)
O(1′)–C(1′)	1.41(2)	1.49(4)	C(5′)–O(5′)	1.43(3)	1.37(5)
C(4′)–C(5′)	1.55(3)	1.54(4)	P–O(5′)	1.63(1)	1.61(2)
P–O(7)	1.51(1)	1.48(2)	P–O(8)	1.51(1)	1.50(2)
P–O(9)	1.52(1)	1.51(3)	N(10)–C(13)	1.41(7)	—
N(11)–C(14)	1.45	1.46	N(12)–C(15)	1.96	1.83
C(14)–C(15)	1.65	1.71	N(10′)–C(13′)	1.41(7)	—
C(13)–C(13′)	1.38(1)	—			

atoms and isotropic thermal parameters for the rest. The positional parameters for the non-hydrogen atoms are given in Table 3.

The program SHELX 76[6] was used for the structure solution and refinement. Scattering factors for the H, C, N, O, and P atoms were used as available in the SHELX 76 program and for Ni from 'International Tables'.[7] Complex scattering factors for Ni and P were employed. Diagrams were drawn using the program ORTEP-II.[8]

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

Results and Discussion

The molecular structures of compounds (**1**) and (**2**) together with the atomic numbering schemes are shown in Figures 1 and 2 respectively. Bond distances are given in Table 4 and bond angles in Table 5.

The structures of (**1**) and (**2**) are essentially isostructural except for the nature of en co-ordination in (**1**). The co-ordination geometry and mode of nucleotide binding are similar to those of the Co^{III} complexes discussed in Part 1.[1] While in the structure of (**2**), the en groups co-ordinate to only one of the metal ions [Ni(2)], as in the Co^{III} complexes,[1] an important difference in the structure of (**1**) is that the en groups co-ordinate

Table 5. Bond angles (°) involving the non-hydrogen atoms, with e.s.d.s in parentheses

	(1)	**(2)**		**(1)**	**(2)**
N(7)–Ni(1)–O(W1)	90.1(6)	95.7(12)	N(7)–Ni(1)–O(W2)	87.8(14)	92.0(11)
N(7)–Ni(1)–N(7′)	84.3(6)	86.1(10)	N(7)–Ni(1)–O(W1)	95.6(6)	92.0(10)
N(7)–Ni(1)–O(W2′)	170.2(14)	177.9(10)	O(W1)–Ni(1)–O(W2)	89.9(14)	88.3(14)
O(W1)–Ni(1)–O(W1′)	174.9(5)	171.0(10)	O(W1)–Ni(1)–O(W2′)	86.8(14)	85.4(10)
O(W2)–Ni(1)–O(W2′)	100.5(19)	89.9(11)	N(11)–Ni(2)–N(12)	89.9(12)	89.4(12)
N(11)–Ni(2)–O(W5)	95.8(10)	94.6(12)	N(11)–Ni(2)–N(11′)	79.1(13)	172.6(11)
N(11)–Ni(2)–N(12′)	169.0(11)	85.3(11)	N(11)–Ni(2)–O(W5′)	88.5(10)	94.6(12)
N(12)–Ni(2)–O(W5)	91.5(9)	134.5(13)	N(12)–Ni(2)–N(12′)	101.0(10)	89.3(12)
N(12)–Ni(2)–O(W5′)	85.0(8)	91.6(13)	O(W5)–Ni(2)–O(W5′)	174.4(6)	70.3(14)
N(10)–Ni(1)–N(10′)	82.7(16)	—	N(10)–Ni(1)–O(W1)	94.7(12)	—
N(10)–Ni(1)–O(W1′)	81.4(12)	—	N(10′)–Ni(1)–O(W1)	81.4(12)	—
N(10′)–Ni(1)–O(W1′)	94.7(12)	—	Ni(1)–N(7)–C(5)	132.3(14)	132.6(27)
Ni(1)–N(7)–C(8)	118.9(14)	118.4(21)	N(1)–C(2)–N(2)	117.9(18)	—
Ni(1)–N(10)–C(13)	109.6(1)	—	N(10)–C(13)–C(13′)	110.0(15)	—
N(1)–C(2)–N(3)	126.5(23)	127.9(32)	N(2)–C(2)–N(3)	115.6(21)	111.8(31)
C(2)–N(3)–C(4)	108.4(19)	105.9(28)	N(3)–C(4)–C(5)	132.5(19)	129.2(40)
C(4)–C(5)–C(6)	116.0(20)	114.9(41)	C(5)–C(6)–N(1)	109.6(22)	117.3(38)
C(6)–N(1)–C(2)	126.5(19)	124.1(32)	C(5)–C(6)–O(6)	129.0(27)	123.3(39)
N(1)–C(6)–O(6)	121.3(24)	119.4(38)	C(4)–C(5)–N(7)	112.0(16)	113.0(38)
C(6)–C(5)–N(7)	132.0(21)	131.3(41)	C(5)–N(7)–C(8)	105.4(16)	102.7(28)
N(7)–C(8)–N(9)	110.7(16)	111.6(27)	C(8)–N(9)–C(4)	109.3(16)	108.5(28)
N(9)–C(4)–C(5)	102.6(16)	104.0(31)	N(9)–C(4)–N(3)	124.8(18)	126.6(32)
C(8)–N(9)–C(1′)	126.8(16)	130.3(28)	C(4)–N(9)–C(1′)	123.9(18)	121.2(26)
O(1′)–C(1′)–C(2′)	105.3(15)	105.8(25)	C(1′)–C(2′)–C(3′)	98.0(16)	93.0(25)
C(2′)–C(3′)–C(4′)	107.7(16)	111.6(27)	C(3′)–C(4′)–O(1′)	107.3(16)	102.9(24)
C(4′)–O(1′)–C(1′)	109.9(15)	112.5(24)	N(9)–C(1′)–O(1′)	108.8(17)	107.5(24)
N(9)–C(1′)–C(2′)	109.5(18)	106.5(25)	C(2′)–C(3′)–O(3′)	107.9(17)	107.6(25)
O(3′)–C(3′)–C(4′)	110.9(17)	112.0(27)	O(2′)–C(2′)–C(1′)	—	107.2(26)
O(2′)–C(2′)–C(3′)	—	115.9(26)	C(3′)–C(4′)–C(5′)	114.4(18)	112.0(29)
C(5′)–C(4′)–O(1′)	105.6(15)	103.9(24)	C(4′)–C(5′)–O(5′)	112.3(18)	118.3(36)
C(5′)–O(5′)–P	117.3(11)	117.5(19)	O(5′)–P–O(7)	105.8(7)	110.5(14)
O(5′)–P–O(8)	108.1(5)	108.1(11)	O(5′)–P–O(9)	101.5(7)	105.0(14)
O(7)–P–O(8)	111.6(7)	109.3(11)	O(7)–P–O(9)	113.4(6)	110.6(15)
O(8)–P–O(9)	113.5(7)	116.1(12)	Ni(2)–N(11)–C(14)	111.0(18)	114.9(16)
N(11)–C(14)–C(15)	128.0(13)	102.3(11)	C(14)–C(15)–N(12)	98.8(9)	101.5(10)
C(15)–N(12)–Ni(2)	104.4(13)	101.1(13)	O(W11)–Ni(2)–O(W12)	88.5(17)	—
O(W11)–Ni(2)–O(W5)	82.1(13)	—	O(W11)–Ni(2)–O(W5′)	100.2(11)	—
O(W12)–Ni(2)–O(W5)	81.8(12)	—	O(W12)–Ni(2)–O(W5)	93.7(12)	—
O(W11)–Ni(2)–O(W11′)	109.0(17)	—	O(W12)–Ni(2)–O(W12′)	74.0(16)	—
O(W11′)–Ni(2)–O(W12)	162.4(16)	—			

both Ni(1) and Ni(2) with partial occupancies. In the absence of en, water oxygens at nearly the same positions as the en nitrogens complete an octahedral co-ordination around the metal. While the co-ordinating distances, Ni(1)–N(7) 2.12(1) in (**1**) and 2.13(2) Å in (**2**), are slightly shorter than those observed for the Co^{III} complexes,[1] the Ni(1)–O(H$_2$O)$_{av}$ distances, 2.12 in (**1**) and 2.08 Å in (**2**), compare well. The Ni(2)–N(en)$_{av}$ [2.10 in (**1**) and 2.03 Å in (**2**)] and Ni(2)–O(H$_2$O)$_{av}$ [2.05 Å in (**1**) and 1.99 Å in (**2**)] distances are normal. When en co-ordinates to Ni(1) in (**1**) [Ni(1)–N(10) 1.99 (3) Å], the co-ordination around Ni(1) resembles that of [Cu(5′-GMP)$_2$(en)(H$_2$O)$_2$]$^{2-}$.[9]

The structural similarities shown by the Na$^+$ salts,[10,11] Pt^{II} complexes,[12–17] Co^{III}(en) complexes, and here the Ni^{II}(en) complexes of 6-oxopurine nucleotides are highly significant in terms of the possible effect on polynucleotide structure due to intrastrand cross-linking by a metal complex. The important structural parameters, *i.e.* the N(7) ··· N(7′) distance [2.85 in (**1**) and 2.92 Å in (**2**)] and the dihedral angle between purine planes [44.4 in (**1**) and 41.0° in (**2**)], are in good agreement with those for the analogous bis(nucleotide) metal complexes given in Table 6 of Part 1.[1] The bond distances and angles in the nucleotide moieties of (**1**) and (**2**) are normal within the limits of experimental error. The e.s.d.s in the bond parameters of (**2**) are comparatively higher. This may be due to the poor quality of the data, as indicated earlier.

The sugar moiety in both (**1**) and (**2**) displays the C(2′)-*endo* puckering mode, a commonly observed conformation for bis(nucleotide) metal complexes. The orientation of the sugar with respect to the purine framework is *anti*. The conformation about the C(4′)–C(5′) bond is *gauche–gauche*.

There are significant intramolecular purine–purine stacking interactions: O(6) ··· C(8) 3.18 and C(5) ··· N(7) 3.28 Å for (**1**); corresponding distances in (**2**) are 3.27 and 3.30 Å. Sugar–base interactions within the complex include: O(1′) ··· N(1) 3.12, O(1′) ··· C(5) 3.36, O(1′) ··· C(6) 3.21, and O(1′) ··· C(2) 3.15 Å for (**1**); 3.07, 3.40, 3.12, and 3.12 Å for (**2**). In the crystal extensive intra- and inter-molecular hydrogen bonding is observed. The hydrogen bonding scheme is similar to that observed in the Co^{III} complexes, except for the absence in (**1**) of the hydrogen bond associated with the 2′-hydroxyl group. The crystal packing (see Figure 3) is also similar.

A possible mechanism for the *cis* binding of nucleotides and subsequent ligand separation in the case of Co^{III} ternary complexes has been given in Part 1.[1] While a similar mechanism can be expected to hold in the case of the Ni^{II} complexes also, it may be noted that the *trans* labilization is not complete in complex (**1**). In this context, this compound has a close similarity to [Cu(5′-IMP)$_2$(im)$_{0.8}$(H$_2$O)$_{1.2}$(H$_2$O)$_2$]$^{2-}$,[3] where the *trans* positions are partially occupied by imidazole (im) groups instead of en as in the present case.

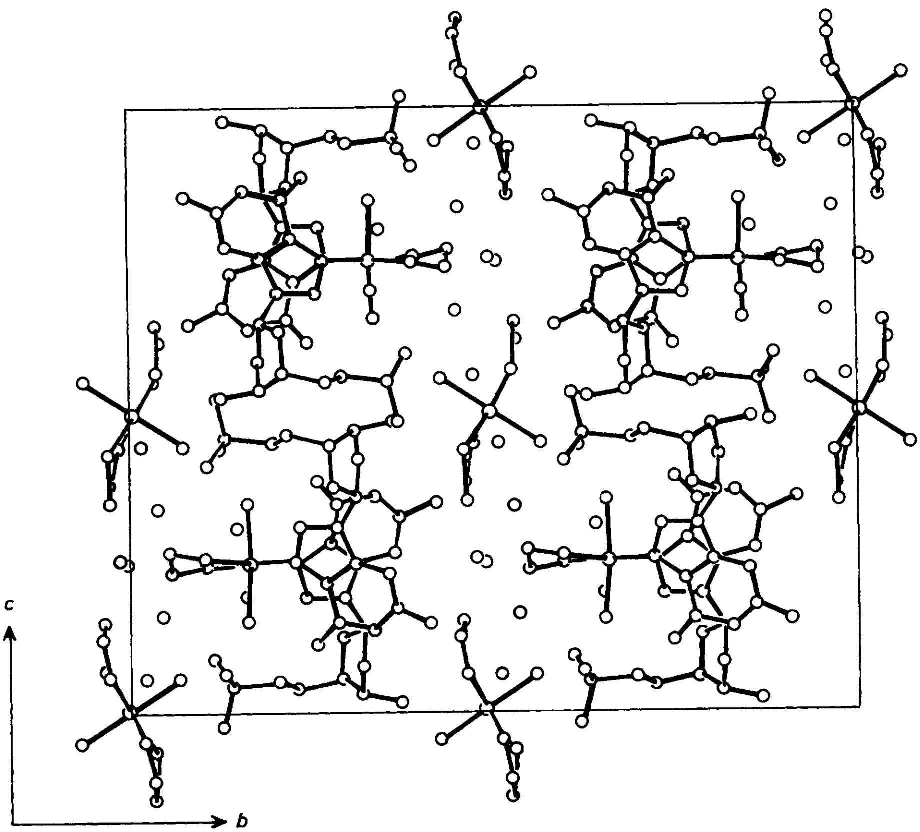

Figure 3. Packing of (**1**) viewed down *a*. The packing in (**2**) is similar

The ternary complexes of 5′-IMP or 5′-GMP with Co^{III} and 5′-GMP with Ni^{II} are isostructural. The overall structure in the case of the Ni^{II} (en) complex with 5′-dGMP is also very close to those of ribonucleotide complexes. Such a similarity in the structures of 6-oxopurine ribo- and deoxyribo-nucleotide metal complexes has also been observed in their respective binary complexes.[18] It therefore appears that the co-ordination behaviour of deoxy- and ribo-6-oxopurine nucleotides is similar both in their binary and ternary complexes. However, further structural studies are needed before this conclusion can be generalized.

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