Crystallographic Studies of Interactions between Nucleotides and Metal Ions. II. The Crystal and Molecular Structure of the 1:1 Complex of Cadmium(II) with Guanosine 5'-Phosphate

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The crystal and molecular structure of the 1:1 complex of cadmium(II) with guanosine 5'-phosphate [$(C_{10}H_{12}N_5O_8P)Cd(H_2O)_5.3H_2O$] has been determined from three-dimensional X-ray diffraction data. The compound crystallizes in the monoclinic space group $C2$ with four molecules in a cell of dimensions $a=27\cdot849$ (7), $b=11\cdot361$ (5), $c=6\cdot774$ (3) Å and $\beta=92\cdot78$ (3)°. The structure was refined by block-diagonal least-squares methods to $R=0\cdot060$ for 1707 independent reflexions. The cadmium ion has an octahedral coordination of six neighbours, five of which are water O atoms and the remaining site is occupied by N(7) of the guanine molecule. Coordination of the cadmium ion to N(7) significantly affects the geometry of the purine ring system. The torsion angle about the glycosidic bond N(9)–C(1'), φ_{CN}, is $13\cdot0°$, corresponding to the *anti* conformation. The ribose conformation can be described as C(3')-*endo*. The conformation about C(4')–C(5') is the commonly observed *gauche–gauche*. The sugar phosphate assumes the extended conformation. There are three intramolecular hydrogen bonds, which stabilize the molecular structure. The purine bases are parallel to each other about 3·4 Å apart, generating infinite stacks along the c axis, the base planes being arranged nearly normal to this axis.

Introduction

There is an increasing interest in the stereochemistry of nucleic acid–metal ion interactions. The present structural investigation was undertaken as part of a series of crystallographic studies of metal–nucleotide complexes. The crystal structures of cobalt–inosine 5'-phosphate(5'-IMP–Co) and nickel–inosine 5'-phosphate (5'-IMP–Ni) complexes have been reported (Aoki, 1975). Cadmium is recognized as an important contaminant in both aquatic and terrestrial environments, and is toxic to animals in quite small quantities. In this connexion, it is interesting to investigate the interaction between the cadmium ion and nucleic acid components. We report here the crystal structure of the cadmium–guanosine 5'-phosphate (5'-GMP–Cd) complex.

Recently de Meester, Goodgame, Skapski & Smith (1974) reported the crystal structure of the nickel–guanosine 5'-phosphate (5'-GMP–Ni) complex and de Meester, Goodgame, Jones & Skapski (1974) gave crystal data for the manganese–guanosine 5'-phosphate(5'-GMP–Mn) complex. The present crystal structure was found to be isostructural with the nickel and manganese analogues.

Experimental

White crystals of formula $Cd(C_{10}H_{12}N_5O_8P).8H_2O$ were obtained by adding an aqueous solution of the disodium salt of guanosine 5'-phosphate to that of cadmium nitrate tetrahydrate in an equimolar ratio at pH 4·5. A crystal with dimensions $0\cdot15 \times 0\cdot15 \times 0\cdot17$ mm was mounted along **c**. All the subsequent X-ray measurements were made on a Rigaku automated diffractometer using Ni-filtered Cu $K\alpha$ radiation. Unit-cell dimensions were determined by least-squares analysis of the angular positions of 20 high-angle reflexions. In Table 1 the crystal data of the cadmium complex are compared with those of the analogous nickel and manganese complexes.

X-ray diffraction peak counts were measured using the 2θ–ω scan mode, a scan rate of 2° min^{-1} and background counts of 10 s at each scan limit. 2184 unique reflexions were measured to the limit $2\theta = 130°$, of which 477 reflexions had $|F_o| < 3\sigma(|F_o|)$ and hence were considered unobserved. The data were corrected for Lorentz and polarization effects. Absorption corrections with spherical approximations ($\mu = 102\cdot5$ cm^{-1} for Cu $K\alpha$ radiation and $\mu R = 0\cdot82$ assuming an approximate crystal radius of 0·008 cm) were originally applied, but since, after refinement, these corrections were found to increase R slightly, they were omitted. This may indicate that spherical approximations to the crystal shape are inadequate, but for the present study no further investigations were made.

Structure determination and refinement

The position of the Cd atom was readily deduced from a three-dimensional sharpened Patterson map. The subsequent Fourier synthesis phased by the Cd atom showed the whole geometry of the guanosine 5'-phosphate molecule and eight water O atoms. The structure was refined by block-diagonal least-squares methods with anisotropic temperature factors for all atoms, to $R=0\cdot07$. A difference Fourier map was then calculated, from which the positional parameters for all

the H atoms of the guanosine 5'-phosphate molecule except two bonded to the amino nitrogen atom N(2) were readily determined, but those of the water molecules could not be identified clearly. These H atoms were included in the subsequent refinement with isotropic temperature factors. During the final stages of the refinement, a weighting scheme of the form $\sqrt{w} = 1\cdot0$ for $|F_o| \le 35\cdot0$ and $\sqrt{w} = 35\cdot0/|F_o|$ for $|F_o| > 35\cdot0$ was employed, and convergence was attained at $R = 0\cdot060$ for 1707 observed reflexions. On the final cycle of refinement no parameter shift was larger than 0·3 e.s.d.'s.

No dispersion correction for Cd atomic scattering factors was applied. Final atomic parameters are listed in Table 2 along with their estimated standard deviations.* Atomic scattering factors were obtained from *International Tables for X-ray Crystallography* (1962).

* A table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31450 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Comparison of the crystal data of the cadmium complex of guanosine 5'-phosphate with those of the nickel and manganese derivatives*

	$C_{10}H_{12}N_5O_8PCd.8H_2O$ (5'-GMP-Cd)	$C_{10}H_{12}N_5O_8PNi.8H_2O$ (5'-GMP-Ni)	$C_{10}H_{12}N_5O_8PMn.8H_2O$ (5'-GMP-Mn)
System	Monoclinic	Monoclinic	Monoclinic
a	27·849 (7) Å	27·604 (4) Å	27·809 (3) Å
b	11·361 (5)	11·087 (2)	11·230 (1)
c	6·774 (3)	6·715 (2)	6·757 (1)
β	92·78 (3)°	93·94 (1)°	93·11 (1)°
U	2141·9 Å³	2050·2 Å³	2107·0 Å³
Space group	$C2$	$C2$	$C2$
Z	4	4	4
	Present work	de Meester *et al.* (1974)	de Meester *et al.* (1974)

Table 2. *Final atomic parameters and standard deviations*

Positional parameters of non-hydrogen atoms have been multiplied by 10^4. Positional parameters of hydrogen atoms have been multiplied by 10^3. Anisotropic thermal parameters have been multiplied by 10^4. The anisotropic temperature factor is of the form $T = \exp\left[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\right]$, and for the hydrogen atoms $T = \exp\left[-B(\sin\theta/\lambda)^2\right]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cd	1450 (0)	7500 (0)	2643 (1)	6 (0)	31 (1)	116 (2)	0 (0)	1 (0)	1 (2)
P	2422 (1)	3817 (3)	2426 (5)	4 (0)	25 (3)	72 (7)	2 (1)	3 (1)	4 (4)
O(5')	1937 (4)	3070 (10)	1873 (15)	7 (1)	48 (9)	104 (23)	−5 (3)	−10 (4)	44 (12)
O(7)	2855 (4)	2957 (10)	2446 (16)	4 (1)	38 (8)	146 (25)	3 (3)	4 (4)	4 (11)
O(8)	2433 (4)	4698 (10)	758 (15)	7 (1)	41 (9)	139 (24)	−2 (3)	2 (5)	27 (12)
O(9)	2371 (4)	4361 (10)	4446 (15)	14 (2)	33 (9)	106 (24)	2 (3)	7 (5)	−12 (12)
N(1)	−438 (4)	6508 (13)	2422 (20)	5 (2)	57 (12)	146 (31)	6 (4)	−3 (5)	16 (16)
C(2)	−559 (5)	5298 (15)	2445 (20)	7 (2)	50 (13)	66 (30)	−4 (4)	2 (6)	−7 (15)
N(3)	−249 (5)	4439 (11)	2597 (18)	8 (2)	29 (10)	122 (29)	−2 (3)	−2 (6)	−5 (14)
C(4)	212 (6)	4814 (15)	2653 (20)	9 (2)	44 (13)	57 (28)	0 (4)	1 (6)	3 (15)
C(5)	370 (5)	5977 (14)	2532 (21)	7 (2)	38 (12)	101 (31)	−7 (4)	5 (6)	5 (16)
C(6)	21 (5)	6915 (12)	2468 (20)	4 (2)	17 (10)	112 (33)	6 (4)	−2 (6)	−0 (15)
N(7)	848 (4)	6021 (12)	2633 (20)	6 (2)	29 (10)	192 (33)	−3 (3)	13 (6)	−4 (15)
C(8)	989 (6)	4905 (14)	2888 (26)	6 (2)	26 (12)	233 (45)	−1 (4)	11 (8)	−5 (19)
N(9)	611 (4)	4183 (11)	2897 (20)	5 (2)	30 (10)	171 (32)	4 (3)	9 (6)	6 (14)
O(6)	90 (4)	7994 (11)	2448 (21)	8 (2)	43 (9)	312 (39)	9 (3)	3 (6)	3 (16)
N(2)	−1044 (6)	5069 (16)	2338 (21)	11 (2)	69 (14)	151 (35)	−3 (4)	3 (7)	9 (19)
C(1')	631 (6)	2885 (13)	3295 (23)	10 (2)	21 (11)	139 (35)	−1 (4)	24 (7)	1 (14)
C(2')	547 (6)	2145 (15)	1353 (26)	10 (3)	41 (15)	197 (43)	−8 (4)	1 (8)	−5 (18)
C(3')	1057 (5)	1855 (12)	838 (23)	7 (2)	11 (11)	157 (38)	−2 (4)	−0 (7)	−0 (16)
C(4')	1323 (6)	1744 (14)	2901 (27)	8 (2)	22 (12)	216 (45)	1 (4)	−6 (8)	−3 (18)
O(1')	1089 (3)	2602 (14)	4075 (14)	6 (1)	53 (10)	151 (22)	1 (4)	−2 (4)	3 (18)
O(2')	278 (4)	1117 (12)	1866 (22)	7 (2)	47 (10)	349 (41)	−3 (4)	−4 (6)	11 (18)
O(3')	1064 (4)	840 (11)	−349 (18)	11 (2)	38 (9)	201 (30)	−3 (3)	1 (6)	−9 (14)
C(5')	1842 (6)	1983 (15)	2909 (26)	10 (2)	23 (10)	193 (43)	−1 (5)	−9 (8)	7 (19)
W(1)	931 (4)	8550 (12)	721 (18)	6 (2)	71 (12)	202 (30)	−1 (3)	−3 (5)	48 (16)
W(2)	1239 (4)	8163 (12)	5757 (18)	6 (2)	82 (12)	179 (29)	−1 (4)	2 (5)	−36 (16)
W(3)	1783 (4)	6509 (10)	35 (16)	8 (2)	41 (9)	131 (25)	3 (3)	7 (5)	−6 (12)
W(4)	1954 (5)	6429 (12)	4710 (21)	19 (2)	48 (11)	253 (36)	12 (4)	−43 (8)	−44 (16)
W(5)	1977 (3)	9022 (10)	2435 (17)	4 (1)	46 (9)	190 (28)	−7 (3)	2 (5)	−8 (13)
W(6)	3154 (4)	8527 (11)	2445 (17)	11 (2)	59 (11)	130 (26)	−1 (4)	2 (5)	−8 (14)
W(7)	3189 (5)	6105 (14)	2364 (22)	13 (2)	69 (13)	308 (41)	−15 (4)	20 (7)	−29 (19)
W(8)	4462 (6)	4936 (17)	4127 (25)	14 (2)	117 (19)	318 (45)	−10 (5)	9 (8)	52 (25)

Table 2 (cont.)

	x	y	z	B (Å²)
H(N1)	−68 (7)	659 (19)	203 (27)	4·2 (44)
H(C8)	129 (4)	475 (12)	340 (17)	0·9 (22)
H(C1')	42 (4)	272 (11)	442 (15)	1·5 (23)
H(C2')	40 (4)	268 (12)	30 (15)	0·9 (22)
H(C3')	112 (4)	225 (13)	7 (18)	0·5 (27)
H(C4')	128 (4)	103 (12)	362 (17)	0·2 (22)
H(O2')	7 (6)	105 (17)	64 (22)	3·1 (39)
H(O3')	126 (6)	89 (16)	−109 (22)	2·2 (34)
H(C5')	203 (5)	140 (13)	155 (20)	0·6 (27)
H'(C5')	209 (6)	192 (14)	416 (23)	2·4 (34)

Results and discussion

The molecular structure with the bond lengths, bond angles and atomic numbering scheme are shown in Fig. 1. Standard deviations are approximately 0·01 Å for Cd–N, Cd–W (water oxygen atom) and P–O bonds and 0·02 Å for C–C (or N or O) bonds, and 0·4° for W–Cd–W, 0·5° for N–Cd–W, 0·6° for O–P–O and 1° for other angles involving C, N and O atoms. The structure consists of a $(C_{10}H_{12}N_5O_8P)Cd(H_2O)_5$ unit and three water molecules of crystallization (not shown in Fig. 1).

The guanine ring

Interest focuses on the detailed structure of the guanine ring geometry. As Fig. 1 shows, the coordination of N(7) to the Cd atom has its most significant effect on the guanine ring geometry, especially on the imidazole ring; the C(5)–N(7) bond is shorter by 0·06 Å (3·2 e.s.d.'s) than the corresponding average bond length of 1·391 Å for all the molecules in related structures such as guanosine 5'-phosphate trihydrate (Murayama, Nagashima & Shimizu, 1969), sodium guanosine 3',5'-cyclic phosphate tetrahydrate (Chwang & Sundaralingam, 1974), disodium deoxyguanosine 5'-phosphate tetrahydrate (Young, Tollin & Wilson, 1974) and guanosine dihydrate (Thewalt, Bugg & Marsh, 1970); in addition C(8)–N(9) and N(9)–C(4) are also shorter by 0·04 Å (2·0 e.s.d.'s) and 0·05 Å (2·6 e.s.d.'s) than the average corresponding bond lengths of 1·374 and 1·381 Å, respectively. Thus four C–N bonds of the imidazole ring have an almost equivalent length of 1·33 Å. The internal ring angle at the position N(9) has increased by 3° (2·2 e.s.d.'s) and the external ring angle at the position C(4) has increased by 3° (2·0 e.s.d.'s) from the average corresponding bond angles of 106·2 and 125·8°, respectively. The decrease in the C(8)–N(9) and N(9)–C(4) bonds and the increase in the C(8)–N(9)–C(4) and N(9)–C(4)–N(3) angles, however, may be explained by the error in the atomic position of N(9). No other lengths and angles differ by more than 2 e.s.d.'s.

Table 3 shows that there is also a significant difference between the planarities of the guanine rings. The atoms comprising the purine nucleus in the crystal structures mentioned above, are all essentially coplanar, except for those of the present complex and guanosine

Table 3. *Deviations of atoms from the least-squares planes of the guanine and ribose rings* (Å)

(1) Plane through the guanine molecule

N(1)	0·037*
C(2)	−0·016*
N(3)	−0·019*
C(4)	−0·021*
C(5)	−0·043*
C(6)	0·030*
N(7)	−0·041*
C(8)	0·032*
N(9)	0·042*
N(2)	−0·035
O(6)	0·082
C(1')	0·216
A	−0·0031
B	0·0623
C	0·9981
D	2·1259

(2) Plane through the six-membered ring of the guanine molecule

N(1)	0·009*
C(2)	−0·021*
N(3)	0·008*
C(4)	0·016*
C(5)	−0·026*
C(6)	0·013*
N(7)	−0·005
C(8)	0·100
N(9)	0·110
	0·0116
	0·0427
	0·9990
	1·9918

(3) Plane through the five-membered ring of the guanine molecule

C(4)	−0·009*
C(5)	0·012*
N(7)	−0·010*
C(8)	0·005*
N(9)	0·003*
N(1)	0·161
C(2)	0·060
N(3)	0·002
C(6)	0·147
A	−0·0231
B	0·1018
C	0·9945
D	2·3117

(4) Plane through the ribose ring

C(1')	0·004*
O(1')	−0·004*
C(2')	−0·002*
C(3')	−0·548
C(4')	0·002*
O(2')	1·362
O(3')	−0·150
C(5')	−0·801
C(3')-*endo*	
	−0·3931
	−0·7371
	0·5497
	−1·9273

(5) The dihedral angle between planes (2) and (3): 4·0°

(6) The dihedral angle between planes (1) and (4): 59·7°

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 in Å, measured relative to crystallographic a^*, b and c axes respectively.

N(7) – Cd–W(2)	91 2
N(7) – Cd–W(4)	92 2
N(7) – Cd–W(5)	174 2
W(1) – Cd–W(2)	99 8
W(1) – Cd–W(3)	94 9
W(1) – Cd–W(4)	177 4
W(2) – Cd–W(3)	165 2
W(3) – Cd–W(5)	92 1
W(4) – Cd–W(5)	93 6

O(5)–P–O(9) 108
O(7)–P–O(8) 112

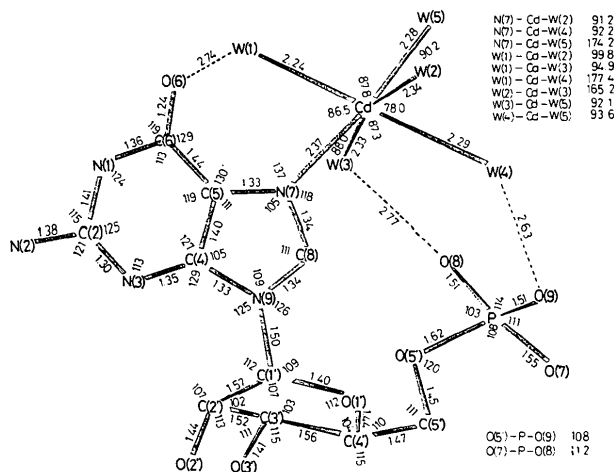Fig. 1. Bond lengths and bond angles, not involving hydrogen atoms in the 5'-GMP–Cd.(H₂O)₅ unit. Intramolecular hydrogen bonds are also shown as broken lines.

3',5'-cyclic phosphate. In the present complex there is a marked degree of puckering, in which C(5), N(7) and N(9) of the imidazole ring are deviated the most. The pyrimidine and imidazole portions of the purine system are each planar within the limits of the error in the atomic positions of the respective atoms; they are, however, tilted from coplanarity about the C(4)–C(5) bond by 4·0°. The exocyclic atoms O(6) and C(1') show even greater displacements of 0·08 and 0·22 Å, respectively, on the same side of the plane, while N(2) is displaced by 0·04 Å on the opposite side.

There is a significant metal-bonding effect on the purine geometry in the present complex, although this is only a minor effect for metals belonging to the first long period, such as those in 5'-IMP–Co, 5'-IMP–Ni, 5'-GMP–Ni, 9-methylhypoxanthine–Cu (Sletten, 1971) and adenine–Zn (Taylor, 1973) complexes, in which N(7) is the sole binding site of the metal ion to the base. In order to verify if this effect is characteristic of metals other than those which belong to the first long period, we will conduct further investigations.

The ribose ring

There are no significant departures in the bond lengths and bond angles from the normal values within experimental errors. As shown in Table 3, the conformation of the ribose ring is C(3')-*endo*, where C(3') is displaced by 0·55 Å on the same side as C(5') and N(9) from the least-squares plane formed by the four remaining ring atoms. This deviation from the plane is similar to the values of 0·560 Å in the 5'-IMP–Co complex and 0·566 Å in the 5'-IMP–Ni complex. The torsion angles around the ribose ring together with those of the phosphate group are listed in Table 4, and are similar to those in 5'-IMP–Co and 5'-IMP–Ni complexes. The orientation of the C(5')–O(5') bond relative to the ribose ring, described by the torsion angles $\varphi_{OO} = -67\cdot6°$ and $\varphi_{OC} = 48\cdot6°$, is *gauche–gauche* with O(5') located above the sugar.

Table 4. *Torsion angles* (°) *around the ribose and phosphate group*

C(8)–N(9)–C(1')–O(1')	(φ_{CN})	13·0
C(8)–N(9)–C(1')–C(2')		−104·8
C(4')–O(1')–C(1')–C(2')		−0·7
O(1')–C(1')–C(2')–C(3')		−21·1
C(1')–C(2')–C(3')–C(4')		32·9
C(2')–C(3')–C(4')–O(1')		−34·2
C(3')–C(4')–O(1')–C(1')		21·8
N(9)–C(1')–C(2')–C(3')		97·7
N(9)–C(1')–C(2')–O(2')		−144·0
O(2')–C(2')–C(3')–O(3')		42·4
O(2')–C(2')–C(3')–C(4')		−81·2
C(2')–C(3')–C(4')–C(5')		−154·3
O(3')–C(3')–C(4')–C(5')		85·4
C(5')–C(4')–O(1')–C(1')		144·7
O(1')–C(4')–C(5')–O(5')	(φ_{OO})	−67·6
C(3')–C(4')–C(5')–O(5')	(φ_{OC})	48·6
C(4')–C(5')–O(5')–P	(φ_{OP})	153·7
C(5')–O(5')–P——O(7)		49·4
C(5')–O(5')–P——O(8)		168·1
C(5')–O(5')–P——O(9)		−70·6

The phosphate group

The phosphate group is present as the divalent anion $ROPO_3^{2-}$, as in 5'-IMP–Co, 5'-IMP–Ni, 5'-GMP–Ni, disodium deoxyguanosine 5'-phosphate and calcium thymidylate (Trueblood, Horn & Luzzati, 1961). It is difficult, however, to determine which two bonds should be P–O$^-$ bonds and which the P=O bond, since no distinct difference among the three P–O bonds is observed. The best explanation may be that the phosphate group as a whole is a divalent anion. It is in the extended conformation relative to C(5')–O(5'), with the torsion angle $\varphi_{OP} = 153\cdot7°$.

Conformation of the guanosine 5'-phosphate molecule

The orientation of the ribose ring relative to the purine base, described in terms of the torsion angle φ_{CN} about the glycosidic bond for the sequence of atoms C(8)–N(9)–C(1')–O(1') (Sundaralingam & Jensen, 1965) is 13·0°; the nucleotide is then in the *anti* conformation. The dihedral angle between the base and ribose planes is 59·7°.

Cadmium ion coordination

The coordination about the cadmium ion is shown in Fig. 1. The Cd atom is octahedrally coordinated with the six coordination sites occupied by the five water O atoms and N(7) of the guanine ring, but is not coordinated directly to the phosphate O atoms. The overall coordination geometry of the complex is similar to those found in 5'-GMP–Ni, 5'-IMP–Co and 5'-IMP–Ni complexes and suggests that this type of coordination may be of widespread occurrence *in vivo*, where the metal ion could be highly hydrated.

Table 5. *Deviations of atoms from the least-squares planes* (Å)

The atoms marked * were included in the calculations of the least-squares planes.

(1) Plane through the guanine ring †		(2) Plane through the four water oxygen atoms, $W(1)$, $W(2)$, $W(3)$ and $W(4)$	
Cd	−0·017	$W(1)$	0·002*
$W(1)$	−0·168	$W(2)$	−0·002*
$W(2)$	2·167	$W(3)$	−0·002*
$W(3)$	−1·900	$W(4)$	0·002*
$W(4)$	1·232	Cd	0·029
$W(5)$	−0·126	N(7)	−2·340
P	−0·564	$W(5)$	2·302
		A	0·6850
		B	0·7240
		C	−0·0813
		D	8·7688

(3) The dihedral angle (°) between the planes (1) and (2): 92·2.

† Plane 1 in Table 3.

The Cd atom lies 0·02 Å off the best plane through the guanine ring on the opposite side of O(6) and is 0·03 Å off the best plane through the four oxygen

atoms, $W(1)$, $W(2)$, $W(3)$ and $W(4)$, on the same side as $W(5)$ (Table 5). The Cd–N(sp^2) bond length of 2·37 Å is in good agreement with that of 2·35 Å reported in the crystal structure of dichlorodipyridinecadmium(II) (Paulus, 1969). The Cd–W coordination bond lengths fall in a fairly narrow range, from 2·24 to 2·34 Å (Table 6) while Harrison & Trotter (1972) have noted that Cd–O (including water O atoms) bond lengths vary quite markedly, 1·98–3·00 Å.

Fig. 2. shows the dimensions of the coordination octahedron of 5'-GMP–Cd, 5'-IMP–Co and 5'-IMP–Ni complexes for comparison and average values of their structural parameters are listed in Table 7. Differences in metal–N(7) and in metal–W bond lengths correspond to those in the ionic radii rather than those in the covalent radii of metals; ionic radii: Cd^{II} 0·97, Co^{II} 0·72 and Ni^{II} 0·69 Å, and covalent radii: Cd 1·48, Co 1·32 and Ni 1·39 Å (Pauling, 1960).

The $W(2)$–$W(4)$ separation, 2·91 Å, is apparently shorter than other W–W separations, which may be due to their hydrogen bonding with the same phosphate oxygen O(7) [at IV(001)] (Fig. 3). This structure is also found in both 5'-IMP–Co and 5'-IMP–Ni complexes.

Crystal packing and hydrogen bonding

The molecular packing is shown in Fig. 3. Probable hydrogen bonds are listed in Table 8 and are also
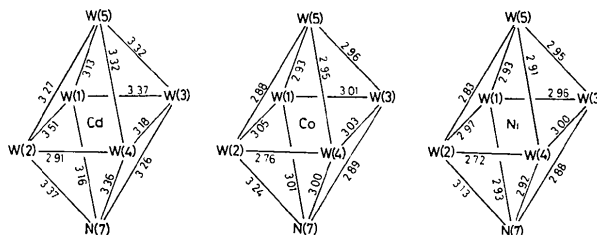
Fig. 2. Comparison of the dimensions of the octahedral coordination of [nucleotide–metal(II)] (H$_2$O)$_5$ units. (a) 5'-GMP–Cd.(H$_2$O)$_5$, (b) 5'-IMP–Co.(H$_2$O)$_5$ and (c) 5'-IMP–Ni.(H$_2$O)$_5$. $W(1)$, $W(2)$, $W(3)$ and $W(4)$ in (b) and (c) correspond to $W(2)$, $W(1)$, $W(4)$ and $W(3)$, respectively, in the original paper (Aoki, 1975).

Table 6. *Comparison of* Cd–W (*water oxygen atom*) *coordination bond lengths* (Å)

Compound	Range of Cd–W	Mean*	
5'-GMP–Cd	2·24–2·34 (1)	2·30 (4)	Present work
Cd(NO$_3$)$_2$.4H$_2$O	2·26–2·33 (2)	2·30 (5)	Matković, Ribar, Zelenco & Peterson (1966)
Cd(AcO)$_2$.2H$_2$O	2·299–2·325 (4)	2·31 (2)	Harrison & Trotter (1972)
Cd[(CHCO$_2$)$_2$]$_2$.4H$_2$O	2·226–2·317 (5)	2·28 (4)	Post & Trotter (1974)

* E.s.d.'s for average lengths are calculated via the 'scatter' formula, σ (mean) $= [\sum(x_i - \bar{x})^2/(N-1)]^{1/2}$, where x_i is the ith of N equivalent measurements and $\bar{x}$ is the mean value.

Table 7. *Average values for various structural parameters of* [nucleotide–metal(II)] (H$_2$O)$_5$ *units*

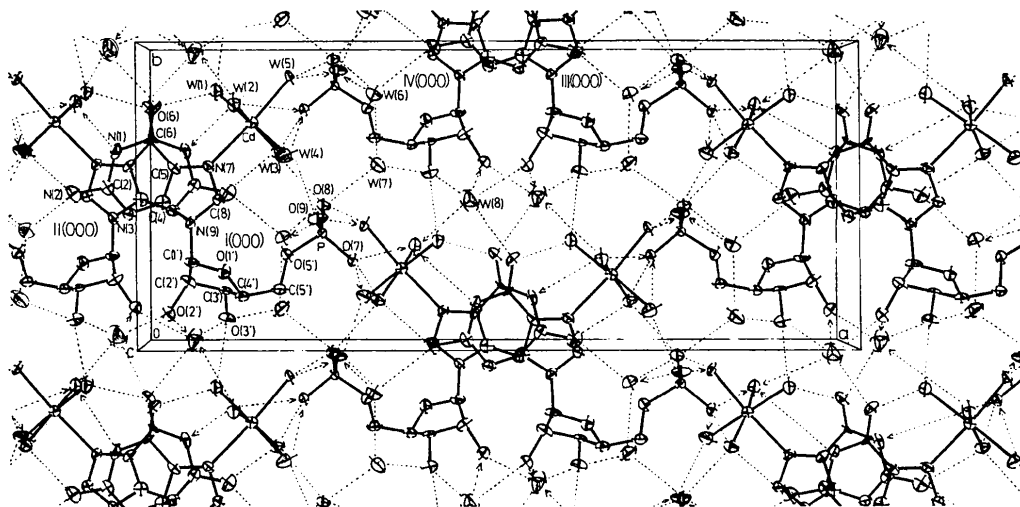|		5'-GMP–Cd	5'-IMP–Co	5'-IMP–Ni
M–N(7)	length (Å)	2·37 (1)	2·162 (9)	2·105 (10)
M–W	length (Å)	2·30 (4)	2·09 (2)	2·06 (2)
N(7)–W	separation (Å)	3·29 (10)	3·04 (14)	2·97 (12)
W–W	separation (Å)	3·25 (18)	2·95 (8)	2·91 (8)
N(7)–M–W	chelate angle (°)	90 (3)	91 (5)	91 (4)
W–M–W	chelate angle (°)	90 (6)	90 (4)	90 (4)

Fig. 3. Stereoscopic view of the crystal structure along **c**. Hydrogen bonds are shown by broken lines.

Table 8. *Presumed hydrogen bonds*

Hydrogen bond from	To	Of molecule	Code No.	Distance (Å)	Angle (°) subtended at the donor atom*	
N(1)	W(2)	II (001)	1	3·210 (19)	C(2)—N(1)···1	113·2 (10)
					C(6)—N(1)···1	117·6 (10)
N(2)	W(3)	II (000)	2	3·030 (19)	C(2)—N(2)···2	124·6 (11)
N(2)	W(6)	III (1̄10)	3	2·841 (21)	C(2)—N(2)···3	152·5 (12)
O(2')†	W(8)	III (1̄10)	4	3·108 (22)	2····N(2)····3	80·3 (5)
O(2')†	W(8)	IV (01̄0)	5	3·083 (22)	C(2')—O(2')···4	150·6 (11)
O(3')	W(7)	IV (01̄0)	6	2·562 (19)	4····O(2')···5	61·6 (5)
W(1)	O(6)	I (000)	7	2·743 (17)	C(3')—O(3')···6	104·1 (9)
W(1)	O(3')	I (010)	8	2·728 (18)	Cd—W(1)···7	99·8 (5)
					Cd—W(1)···8	124·6 (6)
W(2)	O(7)	IV (001)	9	2·761 (15)	7····W(1)···8	117·6 (6)
W(2)	W(8)	IV (001)	10	2·808 (22)	Cd—W(2)···9	96·1 (5)
					Cd—W(2)···10	117·4 (6)
W(3)	O(7)	IV (000)	11	2·591 (15)	9····W(2)···10	132·2 (6)
W(3)	O(8)	I (000)	12	2·767 (16)	Cd—W(3)···11	111·7 (5)
					Cd—W(3)···12	120·4 (5)
W(4)	O(7)	IV (001)	13	2·628 (17)	11···W(3)···12	108·3 (5)
W(4)	O(9)	I (000)	14	2·629 (18)	Cd—W(4)···13	101·3 (6)
					Cd—W(4)···14	133·9 (7)
W(5)	O(8)	IV (000)	15	2·886 (16)	13···W(4)···14	124·4 (7)
W(5)	O(9)	IV (001)	16	2·747 (15)	Cd—W(5)···15	129·9 (5)
					Cd—W(5)···16	117·6 (5)
W(6)†	O(8)	IV (000)	17	2·969 (16)	15···W(5)···16	99·2 (5)
W(6)†	O(5')	IV (000)	18	2·972 (15)	17···W(6)···18	48·7 (4)
W(6)	O(9)	IV (001)	19	2·790 (16)	17···W(6)···19	96·3 (5)
W(7)	O(8)	I (000)	20	2·820 (18)	19···W(6)···18	141·3 (6)
W(7)	W(6)	I (000)	21	2·751 (20)	20···W(7)···21	123·2 (6)
W(8)	O(6)	III (01̄0)	22	3·068 (22)	22···W(8)···23	100·9 (6)
W(8)	O(3')	IV (000)	23	3·065 (20)		

* Some of the atoms are designated by the code number.
† Hydrogen atoms on these atoms probably take part in bifurcated hydrogen bonds.

shown as broken lines in Fig. 3, where the positions of the molecules are denoted as follows: (I) x,y,z; (II) $-x,y,-z$; (III) $\frac{1}{2}+x,\frac{1}{2}+y,z$; (IV) $\frac{1}{2}-x,\frac{1}{2}+y,-z$, with the x, y and z coordinates as given in Table 2. The translations along the three edges of the unit cell are indicated in parentheses. The packing is mainly dominated by hydrophilic interactions or hydrogen bonds, although the guanine rings stack through hydrophobic interactions. The purine bases are parallel to each other, 3·3 Å apart, related by the twofold axis along **b** at $(0,y,\frac{1}{2})$, and 3·5 Å apart, related by the twofold axis at $(0,y,0)$, and tilted from the *ab* plane by only 3·5°, generating infinite stacks with a high degree of base overlap along **c**.

All the O and N atoms except N(3) and O(1') participate in hydrogen bonding in a different manner with water molecules. There is no inter-base hydrogen bond. Three molecules of water of crystallization, $W(6)$, $W(7)$ and $W(8)$, take part in the crystal structure by linking adjacent nucleotide molecules through bridging hydrogen bonding. The cadmium ions are not bonded directly to the phosphate O atoms, but are connected to them *via* three water ligands. These are of the type

$$Cd\cdots O-H\cdots O-P-$$
$$|$$
$$H$$
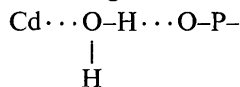
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