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Metal–Ribose Binding in a Transition-Metal–Nucleotide Complex. Preparation and Structure of a Polymeric Copper(II) Complex of Guanosine 2′-Monophosphate

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Abstract

$[\{Cu(2'\text{-GMP})_2(H_2O)_3\}.5H_2O]_n$ (1) was crystallized from an aqueous solution of $Cu(NO_3)_2$ and guanosine 2′-monophosphate at a pH of 4·5. (1), $C_{20}H_{32}CuN_{10}O_{19}P_2.5H_2O$, $M_r = 932{\cdot}1$, is triclinic, $P\bar{1}$, with $a = 11{\cdot}289\ (2)$, $b = 10{\cdot}093\ (2)$, $c = 11{\cdot}831\ (2)$ Å, $\alpha = 107{\cdot}99\ (1)$, $\beta = 114{\cdot}40\ (1)$, $\gamma = 114{\cdot}97\ (1)°$, $U = 902{\cdot}3\ (2)$ Å^3, $Z = 1$, $D_c = 1{\cdot}71$ Mg m^{-3}, μ(Mo $K\alpha$) = 0·74 mm^{-1}. The structure was refined to $R = 0{\cdot}056$ and $R_w = 0{\cdot}048$ for 3906 independent reflections. Structural units are linked into a polymeric chain by O—Cu bonds involving the ribose O(5′) of one of the two 2′-GMP molecules. The coordination of the Cu atom is distorted [4 + 2]-octahedral. It is bound to three different 2′-GMP molecules *via* two mutually *trans* equatorial Cu—N(7) bonds and one axial Cu—O(5′) bond. The coordination sphere is completed by three coordinated water molecules. The axial Cu—O(5′) bond is 0·138 Å longer than the opposite Cu—O bond to a coordinated water molecule. The 2′-GMP molecule which binds to Cu *via* O(5′) displays unusual molecular conformations, namely a *syn* glycosidic torsion angle χ_{CN} of $-112{\cdot}8\ (6)°$, a C(2′)-*endo*—C(3′)-*exo* conformation for the ribose and values for ψ_{OO} and ψ_{OC} of 129·9 (6) and $-113{\cdot}2\ (6)°$ for the conformation of the C(5′)—O(5′) bond relative to the ribose ring. For the second 2′-GMP molecule χ_{CN} is 35·8 (6)°, the conformation of the ribose is C(2′)-*endo*, and ψ_{OO} and ψ_{OC} are respectively $-79{\cdot}4\ (5)$ and 41·9 (6)°. There are five non-coordinated water molecules.

Introduction

Binding studies of metal ions and metal complexes to nucleic acid derivatives are of great current interest. Nucleotides contain three characteristic ligating regions which are capable of metal binding: (1) the heterocyclic ring N atoms and the exocyclic functional groups of the purine and pyrimidine bases, (2) the phosphate O atoms and (3) the hydroxyl O atoms of the ribose moiety. X-ray structural studies of more than 30 binary and ternary mononucleotide–transition-metal complexes have shown the first two modes of binding to predominate (Gellert & Bau, 1979; Swaminathan & Sundaralingam, 1979). All the binary guanosine 5′-monophosphate (5′-GMP) and adenosine 5′-monophosphate (5′-AMP) complexes which have been studied display covalent binding to N(7) of the purine base, sometimes strengthened by additional metal–phosphate bonding to a second nucleotide molecule. In contrast, ternary Cu complexes of purine nucleotides, in which the third component is an aromatic base such as bipyridyl or *o*-phenanthroline (= phen), have been found to display metal–phosphate O atom bonding only. In the only transition-metal complex of a mononucleotide triphosphate which has been characterized by X-ray analysis, the ternary complex $[Cu(ATP)(phen)]_2.7H_2O$, the Cu is coordinated by all three phosphate functions of the same ATP molecule (Sheldrick, 1981).

On the basis of these structural studies, the ribose group must be regarded as a poor ligand for transition metals at neutral or acid pH values (under which conditions crystalline complexes have been synthesized). Only one complex is known in which the ribose hydroxyl functions are involved in coordination to a divalent metal ion, the polymeric $[Cd_2(5'\text{-IMP})_3(H_2O)_6]_n$, in which a multiplicity of metal-binding sites is observed, namely the ribose O(2′) and O(3′) as well as phosphate O atoms and the base N(7) (Goodgame, Jeeves, Reynolds & Skapski, 1975). It might be supposed that the potential chelating site of the *cis*-diol 2′,3′-hydroxy groups in the ribose residue of 5′-nucleotides would be competitive with the base N and phosphate and water O atoms in conditions of relatively low water content such as crystals, and in basic solutions, since the ribose hydroxy groups undergo deprotonation at about pH 12·5. However, the Cd–ribose interaction in the above derivative is not particularly strong, as evidenced by the rather long Cd—O(ribose) lengths of 2·42 and 2·32 Å [in comparison to Cd—O(water) distances of 2·27–2·32 Å and a Cd—O(phosphate) distance of 2·23 Å] and the small O(2′)–Cd–O(3′) angle of 68·3°.

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Alkali and alkaline-earth metals generally coordinate the phosphate and ribose O atoms in their nucleotide salts. It is possible that steric factors may play a role in the non-observance of metal–ribose binding in crystals of transition-metal complexes of 5′-nucleotides. In 2′- and 3′-nucleotides the 5′-hydroxyl function is not directly bonded to the ribose ring. We present here the synthesis and X-ray structure of a polymeric Cu^{II} complex of guanosine 2′-monophosphate (= 2′-GMP), $[\{Cu(2'\text{-GMP})_2(H_2O)_3\}.5H_2O]_n$ (1), in which the Cu is coordinated by N(7) of the two guanosine bases and by one ribose O(5′) but not by phosphate O atoms. This study also represents the first structural characterization of a purine 2′-nucleotide.

Experimental

Preparation of $[\{Cu(2'\text{-GMP})_2(H_2O)_3\}.5H_2O]_n$ (1)

A solution of 0·10 g of copper nitrate trihydrate in 5 ml of water was added to a solution of 0·337 g of the disodium salt of 2′-GMP (Sigma Chemical Co.). A green gelatinous precipitate which formed immediately was redissolved by addition of HNO_3 to give a clear solution of pH 4·5. This was heated to 353 K for 30 min and then allowed to stand at room temperature. Clusters of chunky green crystals formed after about 24 h. These were filtered off and washed with H_2O and methanol. Microanalysis was carried out by Beller (Göttingen). Calculated for $[Cu(2'\text{-GMP})_2(H_2O)_3].5H_2O$: C 25·8; H 4·5; N 15·0%. Found: C 26·0; H 4·5; N 15·1%.

Data collection

Refinement data for (1) are summarized in Table 1. Cell parameters were determined by least squares from the settings for 15 reflections $\pm(hkl)$ measured on a Syntex $P2_1$ four-circle diffractometer. Intensities were collected with graphite-monochromated Mo $K\alpha$ radiation (λ = 0·71069 Å). Measurements were carried out in the θ–2θ mode at scan speeds varying linearly between 2·02° min^{-1} (for 150 counts s^{-1} and below) and 11·72° min^{-1} (for 4000 counts s^{-1} and above). The angular 2θ range traversed was from 1·0° below the $K\alpha_1$ to 1·0° above the $K\alpha_2$ reflection. The net intensity of each reflection (scaled to counts per minute) was assigned a standard deviation, based on the counting statistics, of $(I) = t(N_s + N_b)^{1/2}$, where t is the scan rate, N_s the gross count and N_b the total background count. Lorentz and polarization but no absorption corrections were applied. Only those reflections with $F^2 \geq 2{\cdot}0\sigma(F^2)$ were retained in the refinement.

Table 1. *Refinement data for* (1)

2θ range	$2\theta \leq 60°$
F^2 rejection criterion	$<2{\cdot}0\sigma(F^2)$
Number of reflections	3906
R	0·056
$R_w = \sum w^{1/2}\Delta/\sum w^{1/2}F_o$	0·048
k	1·5438
q	0·0002

Structure solution and refinement

The structure was solved from difference syntheses and refined by blocked full-matrix least squares, $\sum w\Delta^2$ being minimized. Five water molecules of crystallization were identified from difference syntheses. Anisotropic temperature factors were introduced for all non-hydrogen atoms. With the exception of H(3′) of 2′-GMP molecule *B*, the positions of all 2′-GMP H atoms could be located in difference syntheses and were included in the final refinement cycles, as were the H atoms of the three coordinated water molecules *OW*(1)–*OW*(3). Bond-length constraints d(C–H) = 1·08 ± 0·02, d(N–H) = 1·01 ± 0·02 and d(O–H) = 0·98 ± 0·02 Å were employed. Group isotropic temperature factors were introduced for the H atoms. The H atoms of the non-coordinated water molecules *OW*(4)–*OW*(8) were not included in the refinement. Weights were given by $w = k[\sigma^2(F_o) + 0{\cdot}0002F_o^2]^{-1}$. Complex neutral-atom scattering factors (Cromer & Waber, 1965; Cromer & Liberman, 1970) were employed for the non-hydrogen atoms. Table 2 lists the final coordinates for the non-hydrogen atoms with equivalent isotropic temperature factors $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ (Willis & Pryor, 1975).† Table 3

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36084 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

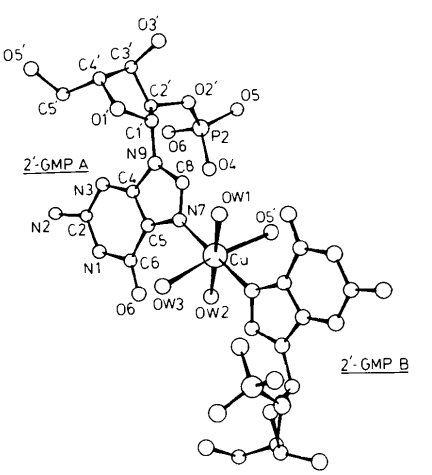

Fig. 1. The structural unit of (1).

Table 2. *Positional parameters* ($\times 10^4$) *and* U_{eq} *values*

[The atoms of the ribose denoted C(1)′ *etc.* in Tables 2–5 are equivalent to C(1′) *etc.*]

	x	y	z	U_{eq} (Å^2)
Cu	10000	0	10000	29 (1)
O*W*(1)	12369 (6)	2186 (6)	11485 (5)	38 (2)
O*W*(2)	7620 (6)	−2190 (6)	8491 (5)	35 (2)
O*W*(3)	9252 (8)	948 (8)	11455 (7)	64 (3)
2′-GMP molecule *A*				
N(1)	5593 (6)	503 (7)	6965 (6)	27 (2)
C(2)	6150 (8)	1758 (8)	6700 (7)	28 (2)
N(2)	5070 (6)	1982 (7)	5962 (6)	38 (2)
N(3)	7665 (6)	2724 (7)	7096 (6)	29 (2)
C(4)	8608 (7)	2367 (8)	7848 (7)	26 (2)
C(5)	8217 (7)	1190 (8)	8236 (7)	24 (2)
C(6)	6545 (7)	109 (8)	7765 (7)	25 (2)
O(6)	5940 (5)	−998 (6)	7987 (6)	39 (2)
N(7)	9607 (6)	1273 (6)	9057 (6)	27 (2)
C(8)	10789 (7)	2490 (8)	9140 (7)	27 (2)
N(9)	10259 (6)	3202 (7)	8430 (6)	26 (2)
C(1)′	11335 (7)	4597 (8)	8368 (7)	27 (2)
O(1)′	11668 (5)	6187 (5)	9225 (5)	33 (1)
C(2)′	10517 (7)	4093 (7)	6762 (7)	24 (2)
O(2)′	10689 (5)	2944 (5)	5911 (5)	31 (2)
C(3)′	11467 (8)	5934 (8)	7075 (7)	32 (2)
O(3)′	13108 (6)	6563 (6)	7578 (6)	43 (2)
C(4)′	11537 (8)	6993 (8)	8374 (7)	31 (2)
C(5)′	9971 (8)	6863 (9)	7821 (7)	38 (2)
O(5)′	10364 (6)	8549 (6)	8208 (5)	43 (2)
P(2)	9079 (2)	951 (2)	4435 (2)	26 (1)
O(4)	8586 (5)	−136 (6)	5077 (5)	33 (2)
O(5)	9739 (6)	385 (6)	3713 (5)	38 (2)
O(6)	7655 (6)	888 (6)	3523 (5)	39 (2)
2′-GMP molecule *B*				
N(1)	14460 (6)	−540 (7)	12792 (6)	29 (2)
C(2)	13883 (8)	−1937 (9)	12937 (8)	33 (2)
N(2)	14991 (8)	−2188 (9)	13583 (9)	59 (3)
N(3)	12375 (6)	−2952 (7)	12540 (6)	31 (2)
C(4)	11431 (7)	−2499 (8)	11924 (6)	22 (2)
C(5)	11879 (7)	−1149 (8)	11728 (7)	25 (2)
C(6)	13528 (8)	−45 (9)	12211 (7)	30 (2)
O(6)	14202 (5)	1247 (6)	12141 (6)	41 (2)
N(7)	10494 (6)	−1224 (6)	11010 (5)	25 (2)
C(8)	9295 (7)	−2557 (8)	10808 (7)	26 (2)
N(9)	9771 (6)	−3394 (6)	11324 (5)	23 (2)
C(1)′	8833 (7)	−4904 (7)	11320 (6)	26 (2)
O(1′)	7135 (5)	−6096 (6)	9949 (5)	32 (1)
C(2)′	8650 (7)	−4525 (7)	12568 (7)	23 (2)
O(2)′	10160 (5)	−3642 (5)	14023 (5)	29 (1)
C(3)′	7207 (7)	−6444 (8)	11902 (7)	27 (2)
O(3)′	7807 (6)	−7406 (6)	12029 (5)	37 (2)
C(4)′	6056 (8)	−7172 (7)	10209 (7)	31 (2)
C(5)′	4598 (8)	−7157 (10)	9678 (9)	39 (2)
O(5)′	5037 (6)	−5548 (6)	10753 (6)	45 (2)
P(2)	1125 (2)	−1624 (2)	5352 (2)	23 (1)
O(4)	11506 (5)	−508 (5)	14702 (5)	31 (1)
O(5)	9944 (5)	−1604 (6)	15652 (5)	31 (1)
O(6)	12704 (5)	−1058 (5)	16627 (5)	32 (1)
Non-coordinated water molecules				
O*W*(4)	6310 (6)	5730 (7)	3814 (6)	50 (2)
O*W*(5)	5770 (7)	4902 (7)	5614 (6)	54 (2)
O*W*(6)	2697 (9)	4840 (8)	3453 (9)	94 (3)
O*W*(7)	5726 (8)	7100 (9)	206 (9)	84 (3)
O*W*(8)	3095 (10)	4120 (11)	5491 (10)	117 (4)

gives the positional parameters for the H atoms, Tables 4 and 5 the bond distances and angles. Calculations were carried out with *SHELX* (Sheldrick, 1976) and local programs. Figs. 1 and 2 were drawn with *RSPLOT* (Sheldrick, 1975).

Table 3. H *atom positional parameters* ($\times 10^3$) *with isotropic temperature factors* ($\times 10^3$)

	x	y	z
2′-GMP molecule *A* [U = 36 (3) Å^2]			
H(1)	466 (5)	12 (8)	704 (7)
H(21)	384 (3)	105 (6)	521 (5)
H(22)	529 (7)	280 (6)	565 (6)
H(8)	1198 (4)	284 (8)	983 (6)
H(1)′	1242 (5)	469 (8)	892 (6)
H(2)′	925 (3)	362 (7)	617 (6)
H(3)′	1090 (7)	591 (8)	607 (4)
H(31)	1364 (7)	748 (6)	746 (7)
H(4)′	1263 (5)	840 (3)	910 (6)
H(4)	903 (7)	−69 (7)	538 (6)
H(51)	958 (7)	675 (8)	850 (6)
H(52)	899 (5)	603 (7)	661 (2)
H(5)′	1027 (7)	877 (7)	746 (5)
2′-GMP molecule *B* [U = 36 (3) Å^2]			
H(1)	1569 (3)	21 (7)	1334 (6)
H(21)	1470 (7)	−318 (6)	1374 (7)
H(22)	1605 (5)	−178 (8)	1376 (7)
H(8)	803 (3)	−310 (7)	1029 (6)
H(1)′	934 (7)	−560 (7)	1128 (7)
H(2)′	809 (7)	−390 (7)	1238 (6)
H(31)	769 (7)	−787 (7)	1260 (6)
H(4)′	549 (7)	−856 (3)	947 (5)
H(4)	1259 (4)	15 (7)	1493 (7)
H(51)	420 (7)	−707 (8)	873 (5)
H(52)	392 (7)	−813 (6)	981 (7)
H(5)′	558 (6)	−459 (5)	1067 (6)
Coordinated water molecules [U = 58 (9) Å^2]			
H(11)	1301 (8)	174 (10)	1165 (8)
H(12)	1296 (8)	333 (5)	1243 (5)
H(21)	692 (8)	−193 (10)	801 (8)
H(22)	718 (9)	−299 (8)	747 (4)
H(31)	879 (8)	153 (8)	1160 (8)
H(32)	871 (8)	8 (7)	1161 (8)

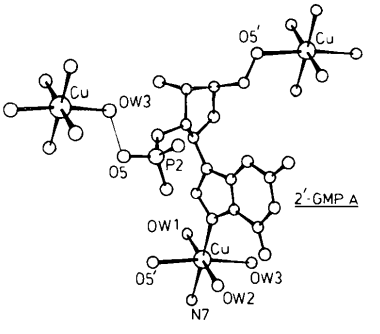

Fig. 2. Direct and indirect binding of Cu atoms by 2′-GMP molecule *A*. The O*W*(3)–H···O(5′) hydrogen bond is indicated by a single line.

Table 4. *Bond lengths* (Å)

$OW(1)$–Cu	1·962 (4)	$OW(2)$–Cu	1·969 (4)
$OW(3)$–Cu	2·336 (10)	N(7)–Cu	2·012 (7)
O(5)′–Cu	2·474 (8)	N(7)–Cu	2·052 (7)
2′-GMP molecule *A*			
C(2)–N(1)	1·355 (11)	C(6)–N(1)	1·400 (11)
N(2)–C(2)	1·333 (12)	N(3)–C(2)	1·320 (10)
C(4)–N(3)	1·339 (12)	C(5)–C(4)	1·370 (13)
N(9)–C(4)	1·383 (10)	C(6)–C(5)	1·443 (10)
N(7)–C(5)	1·412 (11)	O(6)–C(6)	1·212 (11)
C(8)–N(7)	1·316 (10)	N(9)–C(8)	1·379 (12)
C(1)′–N(9)	1·469 (11)	O(1)′–C(1)′	1·384 (10)
C(2)′–C(1)′	1·509 (11)	C(4)′–O(1)′	1·477 (11)
O(2)′–C(2)′	1·423 (11)	C(3)′–C(2)′	1·518 (11)
P(2)–O(2)′	1·588 (3)	O(3)′–C(3)′	1·433 (11)
C(4)′–C(3)′	1·525 (13)	C(5)′–C(4)′	1·538 (14)
O(5)′–C(5)′	1·421 (11)	O(4)–P(2)	1·561 (7)
O(5)–P(2)	1·481 (8)	O(6)–P(2)	1·480 (7)
2′-GMP molecule *B*			
C(2)–N(1)	1·381 (12)	C(6)–N(1)	1·374 (12)
N(2)–C(2)	1·345 (14)	N(3)–C(2)	1·319 (10)
C(4)–N(3)	1·360 (12)	C(5)–C(4)	1·370 (12)
N(9)–C(4)	1·382 (9)	C(6)–C(5)	1·418 (11)
N(7)–C(5)	1·391 (11)	O(6)–C(6)	1·251 (11)
C(8)–N(7)	1·303 (10)	N(9)–C(8)	1·345 (12)
C(1)′–N(9)	1·440 (10)	O(1)′–C(1)′	1·425 (6)
C(2)′–C(1)′	1·529 (12)	C(4)′–O(1)′	1·468 (11)
O(2)′–C(2)′	1·417 (7)	C(3)′–C(2)′	1·536 (9)
O(3)′–C(3)′	1·408 (12)	C(4)′–C(3)′	1·541 (10)
C(5)′–C(4)′	1·510 (14)	O(5)′–C(5)′	1·422 (11)
O(2)′–P(2)	1·594 (5)	O(4)–P(2)	1·563 (7)
O(5)–P(2)	1·521 (7)	O(6)–P(2)	1·472 (5)

Discussion

The principal features of the structure are displayed in Figs. 1 and 2. It consists of structural units of the type $[Cu(2'\text{-GMP})_2(H_2O)_3]$, which are linked into a polymeric chain by O–Cu bonds involving the ribose O(5′) of one of the two 2′-GMP molecules. There are five non-coordinated water molecules of crystallization which take part in a complex network of hydrogen bonds.

The coordination of the Cu atom is distorted [4 + 2]-octahedral. It is bound to three different 2′-GMP molecules *A*, *B* and *A′ via* two mutually *trans* equatorial Cu–N(7) bonds and one axial Cu–O(5′) bond. This Cu–ribose oxygen bond involves a 2′-GMP molecule *A′* which is symmetry-related to molecule *A* by a translation of $-b$. The coordination sphere of the Cu atom is completed by three coordinated water molecules, two of which are equatorial and one axial.

This is the first time that Cu–ribose oxygen binding has been observed in the solid state for a nucleotide complex. ^{13}C NMR studies have indicated an absence of direct metal-ion–ribose interaction in aqueous solutions of nucleoside and mononucleotide complexes of Mn^{2+} and Cu^{2+} (Martin & Mariam, 1979). Chelation of Cu^{2+} by the ribose ring in ATP has, however, been

Table 5. *Bond angles* (°)

$OW(2)$–Cu–$OW(1)$	179·3 (3)	$OW(3)$–Cu–$OW(1)$	95·0 (2)
$OW(3)$–Cu–$OW(2)$	85·4 (2)	N(7)–Cu–$OW(1)$	86·1 (2)
N(7)–Cu–$OW(2)$	93·4 (2)	N(7)–Cu–$OW(3)$	91·3 (3)
O(5)′–Cu–$OW(1)$	93·6 (2)	O(5)′–Cu–$OW(2)$	86·0 (2)
O(5)′–Cu–$OW(3)$	171·3 (2)	O(5)′–Cu–N(7)	90·7 (3)
N(7)–Cu–$OW(1)$	91·8 (2)	N(7)–Cu–$OW(2)$	88·7 (2)
N(7)–Cu–$OW(3)$	89·3 (3)	N(7)–Cu–N(7)	177·9 (2)
N(7)–Cu–O(5)′	89·1 (3)		
2′-GMP molecule *A*			
N(2)–C(2)–N(1)	116·9 (7)	C(6)–N(1)–C(2)	125·8 (6)
N(3)–C(2)–N(2)	119·0 (8)	N(3)–C(2)–N(1)	124·0 (8)
C(5)–C(4)–N(3)	129·7 (7)	C(4)–N(3)–C(2)	111·8 (8)
N(9)–C(4)–C(5)	105·6 (7)	N(9)–C(4)–N(3)	124·7 (8)
N(7)–C(5)–C(4)	110·6 (6)	C(6)–C(5)–C(4)	118·0 (8)
C(5)–C(6)–N(1)	110·6 (7)	N(7)–C(5)–C(6)	131·3 (8)
O(6)–C(6)–C(5)	129·0 (8)	O(6)–C(6)–N(1)	120·4 (7)
C(8)–N(7)–Cu	122·0 (6)	C(5)–N(7)–Cu	133·7 (5)
N(9)–C(8)–N(7)	112·4 (7)	C(8)–N(7)–C(5)	104·3 (7)
C(1)′–N(9)–C(4)	129·5 (7)	C(8)–N(9)–C(4)	107·0 (7)
O(1)′–C(1)′–N(9)	110·0 (8)	C(1)′–N(9)–C(8)	123·5 (6)
C(2)′–C(1)′–O(1)′	106·7 (7)	C(2)′–C(1)′–N(9)	112·6 (4)
O(2)′–C(2)′–C(1)′	113·1 (7)	C(4)′–O(1)′–C(1)′	108·9 (6)
C(3)′–C(2)′–O(2)′	112·2 (7)	C(3)′–C(2)′–C(1)′	101·2 (4)
O(3)′–C(3)′–C(2)′	108·4 (7)	P(2)–O(2)′–C(2)′	120·5 (4)
C(4)′–C(3)′–O(3)′	111·8 (4)	C(4)′–C(3)′–C(2)′	99·8 (7)
C(5)′–C(4)′–O(1)′	109·6 (7)	C(3)′–C(4)′–O(1)′	104·8 (7)
O(5)′–C(5)′–C(4)′	111·6 (5)	C(5)′–C(4)′–C(3)′	113·6 (6)
O(4)–P(2)–O(2)′	104·6 (3)	C(5)′–O(5)′–Cu	118·4 (6)
O(5)–P(2)–O(4)	110·6 (4)	O(5)–P(2)–O(2)′	103·3 (3)
O(6)–P(2)–O(4)	107·8 (4)	O(6)–P(2)–O(2)′	111·1 (3)
		O(6)–P(2)–O(5)	118·6 (4)
2′-GMP molecule *B*			
C(6)–N(1)–C(2)	124·1 (7)	N(2)–C(2)–N(1)	115·9 (7)
N(3)–C(2)–N(1)	124·1 (8)	N(3)–C(2)–N(2)	119·9 (9)
C(4)–N(3)–C(2)	112·0 (7)	C(5)–C(4)–N(3)	128·4 (7)
N(9)–C(4)–N(3)	124·9 (7)	N(9)–C(4)–C(5)	106·6 (7)
C(6)–C(5)–C(4)	118·2 (8)	N(7)–C(5)–C(4)	108·3 (6)
N(7)–C(5)–C(6)	133·5 (8)	C(5)–C(6)–N(1)	113·1 (8)
O(6)–C(6)–N(1)	117·6 (7)	O(6)–C(6)–C(5)	129·2 (9)
C(5)–N(7)–Cu	132·3 (5)	C(8)–N(7)–Cu	120·6 (5)
C(8)–N(7)–C(5)	106·1 (7)	N(9)–C(8)–N(7)	112·5 (7)
C(8)–N(9)–C(4)	106·4 (6)	C(1)′–N(9)–C(4)	123·8 (7)
C(1)′–N(9)–C(8)	129·7 (6)	O(1)′–C(1)′–N(9)	107·6 (6)
C(2)′–C(1)′–N(9)	117·3 (6)	C(2)′–C(1)′–O(1)′	102·8 (6)
C(4)′–O(1)′–C(1)′	107·8 (6)	O(2)′–C(2)′–C(1)′	112·5 (6)
C(3)′–C(2)′–C(1)′	100·5 (5)	C(3)′–C(2)′–O(2)′	114·2 (7)
C(2)′–O(2)′–P(2)	119·3 (5)	O(3)′–C(3)′–C(2)′	109·5 (6)
C(4)′–C(3)′–C(2)′	99·8 (6)	C(4)′–C(3)′–O(3)′	109·2 (6)
C(3)′–C(4)′–O(1)′	106·8 (5)	C(5)′–C(4)′–O(1)′	109·2 (7)
C(5)′–C(4)′–C(3)′	116·9 (8)	O(5)′–C(5)′–C(4)′	113·0 (4)
O(4)–P(2)–O(2)′	105·6 (3)	O(5)–P(2)–O(2)′	108·2 (3)
O(5)–P(2)–O(4)	109·6 (4)	O(6)–P(2)–O(2)′	105·3 (3)
O(6)–P(2)–O(4)	110·1 (3)	O(6)–P(2)–O(5)	117·3 (3)

Table 6. *Conformation of the* 2′*-GMP molecules*

	Molecule *A*	Molecule *B*
Glycosidic torsion angle	*syn*	*anti*
χ_{CN}[O(1′)–C(1′)–N(9)–C(8)]	−112·8 (6)°	35·8 (6)°
Conformation of C(5′)–O(5′)		*gauche–gauche*
ψ_{OO}[O(5′)–C(5′)–C(4′)–O(1′)]	129·9 (6)	−79·4 (5)
ψ_{OC}[O(5′)–C(5′)–C(4′)–C(3′)]	−113·2 (6)	41·9 (6)
Ribose conformation	C(2′)-*endo*–C(3′)-*exo*	C(2′)-*endo*

observed for pH > 10 (Gabriel, Larcher, Thirion, Torreilles & Crastes de Paulet, 1977; Gabriel, Larcher, Boubel, Peguy & Torreilles, 1978). It is significant that direct Cu–phosphate oxygen binding is not observed for (1). Furthermore, it is revealing that (1) was synthesized under conditions (acid solution with a pH = 4·5) which would not *a priori* be expected to be conducive to metal–ribose binding. It may be that steric factors prevent the observation of such binding in metal complexes of 5′-nucleotides. The endocyclic O(2′)–*M*–O(3′) (*M* = metal) angle would indeed be very small in metal chelates. It is, therefore, possible that metal–ribose binding may be more important in complexes of 2′- and 3′-nucleotides, which present O(5′) as a potential binding site. Unfortunately, no X-ray structural studies of binary metal complexes of 3′-nucleotides are, at present, available.

The axial Cu–O(5′) bond is 0·138 Å longer than the opposite Cu–O bond to a coordinated water molecule. It appears, therefore, that the Cu–ribose interaction is not unduly strong. The equatorial Cu–N(7) bonds are similar in length to the average distance of 2·016 (3) Å previously observed for complexes of purine base containing nucleic acid components with octahedrally coordinated Cu (Swaminathan & Sundaralingam, 1979). As typically observed for transition-metal complexes of guanosine derivatives (Gellert & Bau, 1979; Swaminathan & Sundaralingam, 1979), the structure is stabilized by intramolecular O(6)···H–O*W* hydrogen bonds between the 2′-GMP molecules and equatorially coordinated water molecules. O*W*(1) is hydrogen bonded to O(6) of molecule *B* and O*W*(2) to O(6) of molecule *A* in this way. Distances are O*W*(1)···O(6*B*) 2·56 (1) and O*W*(2)···O(6*A*) 2·61 (1) Å.

As mentioned in the *Introduction*, this is the first X-ray structural characterization of a purine 2′-nucleotide. The molecular-conformation characteristics of 2′-GMP molecules *A* and *B* are summarized in Table 6. Cu–ribose bonding to O(5′) of molecule *A* leads to drastic changes in the nucleotide conformation of molecule *A* in comparison to *B*. The values of χ_{CN}, ψ_{OO} and ψ_{OC} for 2′-GMP molecule *B* are similar to those observed for purine 3′- and 5′-mononucleotides (Sundaralingam, 1969, 1975). The molecular conformation of *B* may be described as C(2′)-*endo*,*anti*, *gauche*$^+$, which is one of the two major families of conformations observed for 5′-nucleotides, the other, C(3′)-*endo*,*anti*,*gauche*$^+$, differing essentially in the sugar pucker. In contrast to *B*, the conformation at the glycosidic bond N(9)–C(1′) in molecule *A* is unusual being *syn*, $\chi_{CN} = -112{\cdot}8\ (6)°$. The involvement of O(5′) in metal binding leads to the adoption of non-preferred torsion angles of 129·9 (6) and −113·2 (6)° for ψ_{OO} and ψ_{OC} about C(5′)–C(4′). In previous studies of transition-metal complexes of 3′- and 5′-nucleotides, which display metal–base and metal–phosphate binding, nucleotide conformations similar to those preferred by free nucleotides have been found. The non-preferred molecular conformations found for molecule *A* in (1) indicate a possible energetic explanation for the non-observation of metal–ribose binding in previous studies of metal–nucleotide complexes.

The crystal structure of (1) is stabilized by a wide variety of hydrogen bonds. Although the Cu is not directly bonded to the phosphate O atoms of 2′-GMP molecules *A* and *B*, it is connected *via* a hydrogen-bonded linkage of the type Cu–O–H···O–P, involving the axially coordinated water molecule O*W*(3) and the phosphate O(5) of a symmetry-related 2′-GMP molecule *A*″ at a translation of +*c*. Thus the 2′-GMP molecule *A* is directly bonded to two different Cu atoms *via* N(7)–Cu and O(5′)–Cu bonds and indirectly bonded to a third Cu atom *via* an O(5)···H–O*W*(3) hydrogen bond of length 2·78 (1) Å (Fig. 2).

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