

of the glycosidic bond is 0.026 Å shorter than that of thymidine. This may be due to the change in the sugar puckering and/or in the glycosidic bond rotation (Lo, Shefter & Cochran, 1975).

The packing scheme in the crystal is shown in Fig. 2. The ionic groups and the water molecules are located close to each other, and form a layer parallel to the *bc* plane, as frequently observed in nucleotide crystals. In the present structure, no appreciable base stacking is observed. All available hydrogens participate in hydrogen bonding, *i.e.* N(3)—H...O(2P) [2.895 (4) Å], O(3')—H...O(W2) [2.669 (4) Å], O(W1)—H(1)...O(3P) [2.700 (4) Å], O(W1)—H(2)...O(1P) [2.692 (4) Å], O(W2)—H(1)...O(2P) [2.801 (4) Å], and O(W2)—H(2)...O(2) [2.788 (5) Å]. The Ca²⁺ ion is surrounded by seven oxygen atoms [O(4), O(3'), O(5'), O(1P), O(2P), O(3P) and O(W1)] at distances ranging from 2.291 (3) to 2.555 (2) Å. Apart from those stated above, there are no notable intermolecular short contacts.

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Structure of Calcium 2'-Deoxyadenosine 5'-Phosphate Pentahydrate, Ca²⁺.C₁₀H₁₂N₅O₆P²⁻.5H₂O

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Abstract. $M_r = 459.4$, orthorhombic, $P2_12_12_1$, $a = 6.882$ (1), $b = 39.761$ (3), $c = 6.569$ (1) Å, $V = 1797.6$ (2) Å³, $Z = 4$, $D_x = 1.697$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu(\text{Cu } K\alpha) = 4.40$ mm⁻¹, $F(000) = 960$, room temperature, final $R = 0.024$ for 1884 observed reflections. The molecule has a C(4)-*exo*-O(4')-*endo* (^o T_4) sugar associated with an *anti* glycosidic bond rotation [torsion angle O(4')—C(1')—N(9)—C(8) = 60.9 (3)°]. The conformations about the C(4')—C(5') and C(5')—O(5') bonds are *trans-gauche* [C(3')—C(4')—C(5')—O(5') = -71.3 (2)°] and *trans* [C(4')—C(5')—O(5')—P = 169.1 (1)°], respectively. All available H atoms participate in intermolecular hydrogen bonds.

Introduction. The crystal structure of the Na salt of 2'-deoxyadenosine 5'-phosphate has been reported (Reddy & Viswamitra, 1975). We have crystallized the Ca salt of the same nucleotide and subjected it to X-ray analysis. This study is part of a series of crystallographic investigations of nucleic acid constituents.

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Experimental. Crystals grown from a water/2-methyl-2,4-pentanediol solution by vapor diffusion, colorless plates, D_m not determined, crystal 0.15 × 0.20 × 0.20 mm. Rigaku AFC-5 diffractometer, graphite monochromator, Cu $K\alpha$ radiation. Lattice parameters refined by least-squares method (25 reflections, $29 < 2\theta < 50^\circ$), $2\theta \leq 140^\circ$ ($\sin\theta/\lambda \leq 0.609$ Å⁻¹), ω scan ($2\theta \leq 30^\circ$), ω - 2θ scan ($2\theta > 30^\circ$); h 0 to 8, k 0 to 48, l 0 to 8. 1976 independent reflections. No absorption correction. Structure solved by *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). H atoms from difference Fourier. Structure refined by block-diagonal least-squares method, anisotropic temperature factors for non-H atoms, isotropic for H atoms; $\sum w\Delta^2$ minimized, $\Delta = |F_o| - |F_c|$, $w = 1/\sigma^2(F_o)$ for $|F_c| \geq 3\sigma(F_o)$, $w = 0$ for $|F_c| < 3\sigma(F_o)$ or $|\Delta| \geq 3\sigma(F_o)$, $\sigma(F_o) = \{\sigma_1^2(F_o) + 0.00080|F_o|^2\}^{1/2}$, $\sigma_1(F_o)$ is the e.s.d. based on counting errors (Grant, Killean & Lawrence, 1969). $R = 0.024$ for 1884 reflections ($w \neq 0$), $R_w = 0.032$, $S = 1.06$. Atomic scattering factors from *International Tables for X-ray*

Crystallography (1974). $(\Delta/\sigma)_{\max} = 0.4$. Final $\Delta\rho$ excursions $< |0.8| e \text{ \AA}^{-3}$. No correction for secondary extinction.

Table 1. *Fractional atomic coordinates and isotropic thermal parameters*

$$B_{\text{eq}} = \frac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}(\text{\AA}^2)$
N(1)	0.7263 (3)	-0.04642 (4)	0.8226 (3)	1.86 (3)
C(2)	0.5386 (3)	-0.03789 (5)	0.8220 (4)	2.20 (4)
N(3)	0.4571 (3)	-0.00755 (4)	0.8154 (3)	2.00 (4)
C(4)	0.5934 (3)	0.01669 (4)	0.8104 (3)	1.49 (4)
C(5)	0.7942 (3)	0.01195 (4)	0.8109 (3)	1.63 (4)
C(6)	0.8606 (3)	-0.02148 (4)	0.8185 (3)	1.59 (4)
N(7)	0.8896 (3)	0.04269 (4)	0.8116 (3)	2.01 (4)
C(8)	0.7482 (3)	0.06474 (4)	0.8077 (4)	2.10 (4)
N(9)	0.5660 (2)	0.05072 (4)	0.8068 (3)	1.71 (3)
N(6)	1.0485 (3)	-0.03004 (4)	0.8214 (3)	2.08 (4)
O(4')	0.3702 (2)	0.08622 (3)	0.6143 (2)	1.86 (3)
C(1')	0.3788 (3)	0.06734 (5)	0.7998 (3)	2.06 (4)
C(2')	0.3426 (4)	0.0928 (1)	0.9697 (4)	3.52 (6)
C(3')	0.2662 (3)	0.12444 (4)	0.8651 (3)	1.67 (4)
C(4')	0.2340 (3)	0.11307 (4)	0.6442 (3)	1.47 (4)
O(3')	0.0894 (2)	0.13607 (3)	0.9552 (2)	1.87 (3)
C(5')	0.2800 (3)	0.13932 (5)	0.4845 (3)	2.07 (4)
O(5')	0.1335 (2)	0.16448 (3)	0.4942 (2)	1.74 (3)
P	0.1665 (1)	0.19889 (1)	0.3691 (1)	1.04 (1)
O(1P)	-0.0183 (2)	0.21840 (3)	0.3991 (2)	1.52 (3)
O(2P)	0.3333 (2)	0.21793 (3)	0.4665 (2)	1.47 (3)
O(3P)	0.2126 (2)	0.18932 (3)	0.1501 (2)	1.64 (3)
Ca	0.1582 (1)	0.26731 (1)	0.5794 (1)	1.26 (1)
O(W1)	0.0689 (2)	0.23873 (4)	0.8881 (3)	2.32 (3)
O(W2)	0.1194 (2)	0.31602 (3)	0.8073 (3)	2.33 (3)
O(W3)	0.1930 (2)	0.28446 (4)	0.2261 (2)	2.51 (3)
O(W4)	0.7118 (3)	-0.11887 (4)	0.7734 (4)	3.87 (5)
O(W5)	-0.2430 (2)	0.14797 (4)	0.7147 (3)	3.43 (4)

Table 2. *Molecular dimensions*

Bond distances (Å)			
N(1)–C(2)	1.336 (3)	O(4')–C(1')	1.432 (2)
N(1)–C(6)	1.356 (3)	O(4')–C(4')	1.434 (2)
C(2)–N(3)	1.331 (3)	C(1')–C(2')	1.527 (4)
N(3)–C(4)	1.345 (3)	C(2')–C(3')	1.527 (4)
C(4)–C(5)	1.395 (3)	C(3')–C(4')	1.536 (3)
C(4)–N(9)	1.366 (3)	C(3')–O(3')	1.430 (2)
C(5)–C(6)	1.406 (3)	C(4')–C(5')	1.513 (3)
C(5)–N(7)	1.387 (3)	C(5')–O(5')	1.422 (2)
C(6)–N(6)	1.337 (3)	O(5')–P	1.612 (2)
N(7)–C(8)	1.310 (3)	P–O(1P)	1.503 (2)
C(8)–N(9)	1.372 (3)	P–O(2P)	1.517 (2)
N(9)–C(1')	1.449 (3)	P–O(3P)	1.522 (2)
Bond angles (°)			
C(2)–N(1)–C(6)	118.3 (2)	N(9)–C(1')–O(4')	107.6 (2)
N(1)–C(2)–N(3)	129.6 (2)	N(9)–C(1')–C(2')	115.1 (2)
C(2)–N(3)–C(4)	110.9 (2)	O(4')–C(1')–C(2')	105.5 (2)
N(3)–C(4)–C(5)	126.4 (2)	C(1')–C(2')–C(3')	105.9 (3)
N(3)–C(4)–N(9)	127.9 (2)	C(2')–C(3')–C(4')	103.4 (2)
C(5)–C(4)–N(9)	105.7 (2)	C(2')–C(3')–O(3')	111.9 (2)
C(4)–C(5)–C(6)	116.7 (2)	C(4')–C(3')–O(3')	111.3 (2)
C(4)–C(5)–N(7)	110.5 (2)	O(4')–C(4')–C(3')	104.7 (2)
C(6)–C(5)–N(7)	132.7 (2)	O(4')–C(4')–C(5')	106.4 (2)
N(1)–C(6)–C(5)	118.1 (2)	C(3')–C(4')–C(5')	114.9 (2)
N(1)–C(6)–N(6)	118.2 (2)	C(4')–C(5')–O(5')	107.8 (2)
C(5)–C(6)–N(6)	123.7 (2)	C(5')–O(5')–P	118.3 (1)
C(5)–N(7)–C(8)	103.8 (2)	O(5')–P–O(1P)	104.6 (1)
N(7)–C(8)–N(9)	114.0 (2)	O(5')–P–O(2P)	108.4 (1)
C(4)–N(9)–C(8)	106.0 (2)	O(5')–P–O(3P)	107.4 (1)
C(4)–N(9)–C(1')	125.1 (2)	O(1P)–P–O(2P)	109.1 (1)
C(8)–N(9)–C(1')	128.9 (2)	O(1P)–P–O(3P)	115.4 (1)
C(1')–O(4')–C(4')	107.5 (1)	O(2P)–P–O(3P)	111.5 (1)

Discussion. The refined atomic parameters are in Table 1.* A perspective view of the molecule is shown in Fig. 1. Bond distances and angles are listed in Table 2.

The deoxyribose ring adopts a C(4')-*exo*-O(4')-*endo* twist form. The pseudorotation coordinates of the five-membered ring (Sato, 1983) are $\Pi = 34.9 (2)$ and $\Phi = 165.8 (5)^\circ$. This is probably the first example of deoxyribose showing the C(4')-*exo*-O(4')-*endo* puckering, but similar sugar conformations ranging from C(4')-*exo* to O(4')-*endo* puckering have been found in nucleoside and nucleotide structures (Olson, 1981). The stability of O(4')-*endo*-like puckers is of current interest in relation to the B-type structures of DNA, which probably incorporate these puckers (Levitt, 1978; Wing, Drew, Takano, Broka, Itakura & Dickerson, 1980). An energy calculation performed by Levitt & Warshel (1978) shows that the potential barrier to the pseudorotation path at O(4')-*endo* is extremely small and, therefore, O(4')-*endo*-like puckers, which were previously thought as unusual, are also eligible to the DNA structures. However, the validity of this calculation has been questioned by Olson (1982) on the basis of the so-called 'gauche effect', which was neglected in the calculation. This affects the torsional potentials about O–C–C–O and O–C–C–C sequences, so that the puckers from C(3')-*endo* to O(4')-*endo* are appreciably destabilized in the case of deoxyribose. Although this explains qualitatively the predominance of C(2')-*endo*-like sugars observed in deoxynucleoside and nucleotide crystals (Olson & Sussman, 1982), the observation of the C(4')-*exo*-O(4')-*endo* pucker in the present study, as well as those of two examples of C(4')-*exo* pucker (Barr, Chananont, Hamor, Jones, O'Leary & Walker, 1980; Sato, 1984a), indicates that the destabilization, if it exists, is not prohibitive. According to Olson's calculation, these puckers are most unstable and their potential energies are 6.3 kJ mol⁻¹ or more higher than that of the stable C(2')-*endo* pucker.

* Lists of structure factors, anisotropic temperature factors and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39148 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

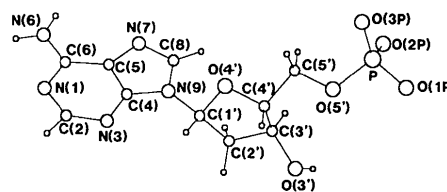


Fig. 1. A perspective view of the molecule, showing the atom numbering.

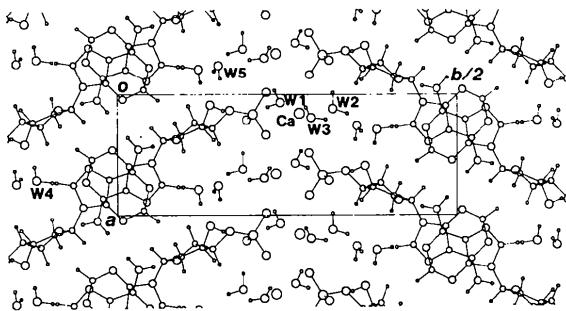


Fig. 2. A projection of the structure viewed along the *c* axis.

The sugar is associated with an *anti* glycosidic bond rotation. This conformation does not involve notable sugar–base atomic contacts. This is in contrast to the crowded atomic arrangement around the glycosidic bond found in a pyrimidine nucleotide of similar conformation (Sato, 1984*a*). The conformations about the C(4′)–C(5′) and C(5′)–O(5′) bonds are *trans-gauche* and *trans*, respectively.

The bond distances of the adenine base are in agreement (within 0.013 Å) with the ‘standard’ values derived for the neutral form (Taylor & Kennard, 1982). The atoms in the purine ring are coplanar to within 0.019 Å. The glycosidic bond is 0.025 Å shorter than that of 2′-deoxyadenosine (Sato, 1984*b*). This may be due to changes in the sugar puckering and/or in the glycosidic bond rotation (Lo, Shefter & Cochran, 1975). The bond shrinkage seems to be correlated with an elongation (0.020 Å) of the O(4′)–C(1′) bond.

The packing scheme in the crystal is shown in Fig. 2. The ionic groups and the water molecules are arranged close to each other, and form a layer parallel to the *ac* plane, each layer separated from the other by another layer consisting mainly of stacked adenine bases. All

available H atoms participate in intermolecular hydrogen bonds. Among them, N(6)–H(2)⋯O(4′) [N⋯O 3.001 (2), H⋯O 2.27 (3) Å] is noticeable, because, for most cases, the ring oxygen O(4′) does not participate in hydrogen-bond formation. The Ca²⁺ ion is surrounded by seven O atoms [O(1P), O(1P′), O(2P), O(2P′′), O(W1), O(W2) and O(W3)] at distances ranging from 2.302 (2) to 2.581 (2) Å. Apart from those stated above, there are no notable short intermolecular contacts.

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Dipotassium Salt of 3-Hydroxy-4-mercapto-2-thioxo-3-cyclobuten-1-one Dihydrate (Potassium 1,3-Dithiosquarate Dihydrate), K₂[C₄O₂S₂].2H₂O, at 140 K

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Abstract. *M_r* = 258.4, monoclinic, *P*2₁/*c*, *a* = 7.309 (2), *b* = 8.404 (3), *c* = 8.120 (3) Å, β = 112.6 (3)°, *V* = 460.6 Å³, *Z* = 2, *D_m* = 1.82, *D_x* = 1.86 Mg m⁻³, λ(Mo Kα) = 0.71069 Å, μ = 1.43 mm⁻¹,

F(000) = 240. Final *R* = 0.026 for 945 independent observed reflections. The planar 1,3-dithiosquarate dianion is situated on an inversion center; the lengths of the C–C bonds are 1.463 (2) and 1.467 (2) Å. The