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Structure of the Disodium Salt of Glucose 1-Phosphate Hydrate, $2Na^+.C_6H_{11}O_9P^{2-}.3\cdot5H_2O$

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Abstract. $M_r = 367\cdot2$, monoclinic, $C2$, $a = 8\cdot429$ (1), $b = 10\cdot184$ (2), $c = 16\cdot570$ (2) Å, $\beta = 99\cdot18$ (1)°, $U = 1404\cdot2$ Å^3, $Z = 4$, $D_m = 1\cdot73$, $D_x = 1\cdot74$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1\cdot5418$ Å, $\mu = 2\cdot99$ mm^{-1}, $F(000) = 764$, $T = 300$ K, final R for 1524 observed reflections is 0·069. The endocyclic C—O bonds in the glucose ring are nearly equal with C(5)—O(5) = 1·445 (10) and C(1)—O(5) = 1·424 (10). The pyranose sugar ring adopts a $^4C_1$ chair conformation. The conformation about the exocyclic C(5)—C(6) bond is *gauche–gauche*, in contrast to *gauche–trans* observed in the structure of the dipotassium salt of glucose 1-phosphate. The phosphate ester bond, P—O(1), is 1·641 (6) Å, slightly longer than the 'high-energy' P$\sim$O bond in the monopotassium salt of phosphoenolpyruvate [1·612 (6) Å]. Two sodium ions are six coordinated while the third has only five neighbours.

Introduction. Glucose 1-phosphate (G1P) is an intermediate in glycogen metabolism. Its free energy of hydrolysis is small, −20·9 kJ mol^{-1}, compared to that of 'high-energy' phosphates such as phosphoenolpyruvate (−58·5 kJ mol^{-1}) (Lehninger, 1973). We report here the structure of Na_2G1P obtained from X-ray diffraction studies. This investigation follows our earlier studies on the phosphoenolpyruvate and glucose 6-phosphate anions (Katti, Hosur & Viswamitra, 1981; Katti, Seshadri & Viswamitra, 1982).

Experimental. Crystals from aqueous solutions of the compound by diffusion of acetone, D_m by flotation in acetone/bromoform, preliminary examination by rotation and Weissenberg photographs; cell parameters from 25 high-angle reflections collected on an Enraf–Nonius CAD-4 diffractometer; Cu $K\alpha$ intensity data up to $\sin\theta/\lambda = 0\cdot63$ Å^{-1}, crystal 0·13 × 0·25 × 0·5 mm, ω–2θ scan mode, 1524 of 1735 reflections considered observed [$F > 3\sigma(F)$]; index range $h \pm 10$, k 0–12, l 0–20; backgrounds measured for 1/6 total scan angle on either side of Bragg peak; two strong reflections monitored periodically during data collection showed crystal stable to X-rays; $R_{\rm int} = 0\cdot044$; Lorentz and polarization corrections applied; structure solved by direct methods (Main, Woolfson & Germain, 1971) and successive difference Fourier maps; full-matrix least-squares refinement using *SHELX*76 (Sheldrick, 1976); with anisotropic refinement, temperature factors of some non-H atoms negative; this was eliminated on correction of data for secondary extinction effects ($g = 7 \times 10^{-6}$); difference Fourier maps revealed all molecular H atoms except for hydroxyl H atoms; refinement with H atoms reduced R to 0·069; function minimized $\sum w(|F_o| - |F_c|)^2$, $w = 1\cdot0$; $S = 3\cdot242$. Scattering factors for non-H atoms from Cromer & Waber (1965), for H atoms from Stewart, Davidson & Simpson (1965). Max. Δ/σ for non-H atoms 0·005; residual electron density in final difference Fourier map within −0·83 and 1·12 e Å^{-3}.

Discussion. Positional parameters for the atoms are given in Table 1.* Bond lengths and angles are listed in Table 2. The molecular structure and the numbering scheme are shown in Fig. 1. The packing arrangement is shown in Fig. 2.

The glucose ring. The two endocyclic C—O bonds are nearly equal in this compound although they are significantly different in the structure of the Ba salt of glucose 6-phosphate [1·463 (23), 1·395 (23) Å] (Katti *et al.*, 1982). These bonds are also found to be nearly equal in other glucose structures such as β-D-glucose (Chu & Jeffrey, 1968), methyl tetra-*O*-acetyl-β-D-glucoside (Zugenmaier & Rappenecker, 1978) and α-D-glucose (Brown & Levy, 1979).

The C(1)—O(1) distance (Table 2) follows the usual trend of being shorter than the other exocyclic C—O(H) distances. The pyranose ring has the $^4C_1$ chair conformation (Fig. 1) with C(4) and C(1) displaced from the C(2)–C(3)–C(5)–O(5) plane by −0·672 (8) and 0·703 (8) Å, respectively. The Cremer & Pople

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* Lists of structure amplitudes, anisotropic thermal parameters, torsion angles, sodium coordination distances, H-bond interactions and mean-plane calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39391 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional coordinates* ($\times 10^4$; *for* H $\times 10^3$) *with equivalent isotropic temperature factors for non-hydrogen atoms,* $U_{\rm iso}$ *for* H *atoms* ($Å^2 \times 10^2$)

E.s.d.'s are given in parentheses.

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}/U_{\rm iso}$
P	4358 (2)	−248	1856 (1)	0·7 (1)
O(7)	4802 (8)	−1336 (7)	2477 (4)	1·4 (2)
O(8)	5364 (6)	−232 (8)	1182 (3)	1·5 (1)
O(9)	2565 (6)	−154 (8)	1549 (3)	1·5 (1)
O(1)	4854 (7)	1149 (6)	2323 (3)	1·0 (2)
C(1)	4364 (10)	1416 (9)	3071 (5)	1·2 (2)
C(2)	4172 (9)	2911 (9)	3169 (5)	0·9 (2)
C(3)	5797 (9)	3588 (9)	3226 (5)	1·0 (2)
C(4)	6999 (9)	2975 (9)	3903 (5)	1·0 (2)
C(5)	7068 (9)	1496 (9)	3782 (5)	1·0 (2)
O(5)	5479 (6)	944 (6)	3746 (3)	1·0 (2)
O(2)	3101 (7)	3454 (7)	2502 (4)	1·7 (2)
O(3)	5636 (7)	4952 (7)	3431 (3)	1·4 (2)
O(4)	8584 (6)	3517 (7)	3942 (4)	1·5 (2)
C(6)	8084 (11)	817 (10)	4487 (5)	1·7 (2)
O(6)	7471 (7)	1086 (7)	5222 (3)	1·8 (2)
Na(1)	5000	−112 (6)	5000	1·8 (1)
Na(2)	5000	1372 (6)	0	2·0 (1)
Na(3)	8116 (4)	−387 (5)	1234 (2)	2·4 (1)
W(1)	0	2878 (11)	0	2·8 (3)
W(2)	7796 (8)	839 (8)	21 (4)	2·3 (2)
W(3)	9937 (7)	1127 (7)	1953 (4)	2·1 (2)
W(4)	10183 (8)	−1956 (7)	1044 (4)	2·1 (2)
H(1)	345 (10)	90 (9)	316 (7)	1·2 (4)
H(2)	389 (9)	303 (9)	357 (6)	0·6 (4)
H(3)	612 (9)	339 (9)	274 (6)	0·6 (4)
H(4)	675 (9)	331 (9)	438 (6)	0·8 (4)
H(5)	721 (9)	139 (9)	325 (6)	1·1 (4)
H(6)	925 (9)	129 (9)	448 (6)	1·1 (4)
H′(6)	811 (9)	−26 (10)	442 (7)	2·0 (4)
H*W*(3)	1040 (1)	117 (1)	266 (1)	1·6 (4)
H′*W*(3)	1086 (1)	95 (1)	178 (1)	1·7 (4)

Table 2. *Bond lengths* (Å) *and angles* (°)

P–O(7)	1·518 (7)	C(2)–O(2)	1·423 (10)
P–O(8)	1·506 (5)	C(3)–C(4)	1·521 (12)
P–O(9)	1·519 (5)	C(3)–O(3)	1·442 (11)
P–O(1)	1·641 (6)	C(4)–C(5)	1·521 (13)
C(1)–O(1)	1·394 (10)	C(4)–O(4)	1·438 (10)
C(1)–C(2)	1·542 (14)	C(5)–O(5)	1·445 (10)
C(1)–O(5)	1·424 (10)	C(5)–C(6)	1·502 (12)
C(2)–C(3)	1·522 (12)	C(6)–O(6)	1·424 (10)
O(7)–P–O(8)	113·8 (4)	C(3)–C(2)–O(2)	109·0 (7)
O(7)–P–O(9)	113·4 (4)	C(2)–C(3)–C(4)	110·3 (7)
O(7)–P–O(1)	107·2 (3)	C(2)–C(3)–O(3)	109·4 (7)
O(8)–P–O(9)	113·5 (3)	C(4)–C(3)–O(3)	107·4 (7)
O(8)–P–O(1)	102·1 (3)	C(3)–C(4)–C(5)	110·1 (7)
O(9)–P–O(1)	105·6 (3)	C(3)–C(4)–O(4)	112·3 (7)
P–O(1)–C(1)	120·0 (5)	C(5)–C(4)–O(4)	109·4 (7)
O(1)–C(1)–C(2)	109·7 (7)	C(4)–C(5)–O(5)	109·7 (7)
O(1)–C(1)–O(5)	112·3 (7)	C(4)–C(5)–C(6)	112·5 (7)
C(2)–C(1)–O(5)	108·5 (7)	O(5)–C(5)–C(6)	105·3 (7)
C(1)–C(2)–C(3)	110·2 (7)	C(1)–O(5)–C(5)	113·1 (6)
C(1)–C(2)–O(2)	111·5 (7)	C(5)–C(6)–O(6)	109·6 (7)

(1975) puckering parameters are $Q = 0{\cdot}584\ (2)$ Å, $\theta = 2{\cdot}62\ (22)°$ and $\varphi = 20{\cdot}7\ (44)°$. The distortion from the perfect chair form is towards the $^{O,3}B$ boat geometry.

Conformation about the exocyclic C(5)–C(6) *bond.* The torsion angles O(6)–C(6)–C(5)–O(5) and O(6)–C(6)–C(5)–C(4) are −61·2 (8) and 58·2 (9)°. The conformation about the C(5)–C(6) bond is therefore *gauche–gauche.* It is significantly different from the *gauche–trans* geometry (52·0, 174·7°) observed in K_2G1P (Beevers & Maconochie, 1965).

Phosphate group. The phosphate group exists as a dianion as the compound is a disodium salt. As the three terminal P–O bonds are nearly equal (Table 2), presumably the negative charges are distributed between O(7), O(8) and O(9).

Na^+ *coordination.* There are three crystallographically independent sodium ions in the structure. Na(1) and Na(2) are situated on the twofold axis. Only O(8) of the three phosphate O atoms is involved in the sodium coordination. The presence of both six and five coordinations for Na^+ ions has also been observed in the nucleotide structures Na_25'-dGMP.$4H_2O$ (Viswamitra & Seshadri, 1974; Young, Tollin & Wilson, 1974) and Na_25'-dUMP.$5H_2O$ (Viswamitra, Seshadri & Post, 1980). The sodium coordination distances have been deposited.*

Hydrogen bonding. A list of hydrogen-bonding interactions has been deposited.* The hydroxyl groups take part in hydrogen bonds as both acceptors and donors. There is no intramolecular hydrogen bonding

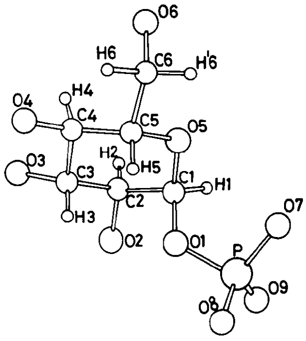

Fig. 1. The structure of the G1P dianion, showing the numbering of the atoms. Further H atoms (not located in the analysis) are linked to O(2), O(3), O(4) and O(6).

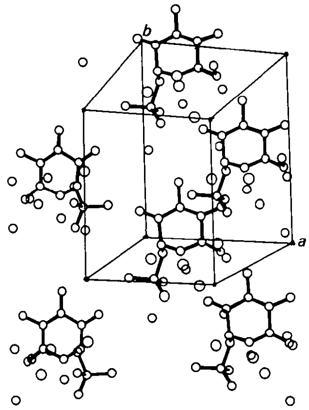

Fig. 2. The packing arrangement in the unit cell approximately along **c**.

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* See deposition footnote.

similar to that found in K_2G1P (Beevers & Maconochie, 1965). The ring oxygen O(5) accepts a hydrogen bond from the hydroxyl O(4) of a symmetry-related molecule. The distance between O(1) and the water molecule $W(4)$ is 2·915 (10) Å. Since the H atoms of $W(4)$ have not been located, it is uncertain whether hydrogen bonding is involved.

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Structure de l'Aqua(aza-4 azonia-1 bicyclo[2.2.2]octane)trinitratocobalt(II), $[Co(C_6H_{13}N_2)(NO_3)_3(H_2O)]$

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Abstract. $M_r = 376{\cdot}2$, monoclinic, $P2_1$, $a = 6{\cdot}961$ (6), $b = 6{\cdot}982$ (5), $c = 13{\cdot}68$ (1) Å, $\gamma = 95{\cdot}4$ (1)°, $V = 662$ (2) Å^3, $Z = 2$, $D_m = 1{\cdot}85$ (3), $D_x = 1{\cdot}89$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 1{\cdot}35$ mm^{-1}, $F(000) = 386$, $T = 294$ (1) K, $R = 0{\cdot}039$ for 1958 independent reflections. The crystal used contains two twin components. The structure consists of layers of molecules parallel to (001). The molecules are linked together by O—H···O, N—H···O and C—H···O hydrogen bonds. This structure is closely related to that of $[Cd(C_6H_{13}N_2)(NO_3)_3(H_2O)]$. However, the coordination polyhedron of the Co atom is a bipyramid with a trigonal base instead of a bipyramid with a hexagonal base for the Cd atom.

Introduction. La détermination de la structure de l'aqua(aza-4 azonia-1 bicyclo[2.2.2]octane)trinitratocobalt(II) s'inscrit dans le cadre de l'étude des composés de coordination formés par les polyamines tertiaires. Elle fait suite à celle de la structure de $[Cd(C_6H_{13}N_2)(NO_3)_3(H_2O)]$ (Viossat, Khodadad & Rodier, 1984). Le produit utilisé a été préparé par une méthode voisine de celle déjà décrite à propos du dérivé du cadmium. On neutralise par l'acide nitrique l'une des fonctions amine du diaza-1,4 bicyclo[2.2.2]-octane, puis ajoute du nitrate de cobalt en quantité équimoléculaire. Les trois réactifs sont utilisés en solution dans le méthanol. L'addition d'éther-oxyde

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