

Tableau 3. *Liaisons hydrogène* (Å, °)

O(6)...O(1 <sup>vi</sup> )	2,899 (6)	O(6)—H[1O(6)]...O(1 <sup>vi</sup> )	159 (28)
O(9)...O(8)	2,836 (9)	O(9)—H[1O(9)]...O(8)	169 (19)
O(7)...O(9)	2,782 (6)	O(7)—H[2O(7)]...O(9)	170 (21)
O(7)...O(6)	2,696 (6)	O(7)—H[1O(7)]...O(6)	168 (28)
O(6)...O(8 <sup>vii</sup> )	2,830 (9)	O(8 <sup>vii</sup> )—H[1O(8 <sup>vii</sup> )]...O(6)	152 (25)

Code de symétrie: (tableaux et figures) (i)  $x - 1, y, z$ ; (ii)  $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$ ; (iii)  $-x, -y, -z$ ; (iv)  $x - 1, \frac{1}{2} - y, z - \frac{1}{2}$ ; (v)  $1 - x, -y, -z$ ; (vi)  $x - 2, \frac{1}{2} - y, z - \frac{1}{2}$ ; (vii)  $-x, 1 - y, -z$ ; (viii)  $x, y - 1, z$ ; (ix)  $1 - x, 1 - y, -z$ ; (x)  $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$ ; (xi)  $2 - x, y - \frac{1}{2}, \frac{1}{2} - z$ ; (xii)  $x + 1, y, z$ .

Les deux atomes d'hydrogène de cette molécule sont impliqués dans deux liaisons respectivement avec les molécules H<sub>2</sub>O(6) et H<sub>2</sub>O(9). La dernière molécule, H<sub>2</sub>O(8), est maintenue par une liaison O(8)...H[1O(9)]—O(9). Deux liaisons supplémentaires accroissent la stabilité de l'édifice par l'intermédiaire d'H<sub>2</sub>O(6): O(8<sup>vii</sup>)—H[1O(8<sup>vii</sup>)]...O(6) et O(6)—H[1O(6)]...O(1). Les oxygènes des quatre molécules d'eau [O(6), O(7), O(8) et O(9)] forment un réseau plan d'équation:  $0,48228x - 0,56788y - 0,66702z - 4,74513 = 0$ . Les distances (Å) des différents atomes au plan moyen valent respectivement: O(6): 0,005 (5); O(8): 0,005 (5); O(7): -0,005 (4); O(9): -0,005 (7) Å. Les plans sont reliés par deux liaisons hydrogène: O(6)—H...O(8<sup>vii</sup>) et son équivalente se déduisant par l'opération de symétrie  $\bar{1}$ .

La présente étude structurale n'a pas permis de mettre en évidence de formation de chélate dans la forme cristallisée du complexe cuivrique neutre de l'acide phosphono-3 propionique.

Contrairement au cas de l'hydroxyméthylphosphonate de cuivre ce n'est donc pas à l'effet stabilisant d'une tel enchaînement que peut être attribuée la stabilité particulière du complexe formé. Nous avons cependant noté l'existence de liaisons cuivre-oxygène phosphonique particulièrement courtes.

La comparaison avec le complexe acide correspondant dont l'étude structurale est en cours devrait nous apporter des éléments d'interprétation, ce dernier ne présentant pas à l'image du complexe neutre une stabilité supérieure à celle déterminée par la prise en compte des seuls effets induits par la chaîne carbonée.

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## Structure of the Dipotassium Salt of Fructose 6-Phosphate Hexahydrate

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**Abstract.** K<sub>2</sub>[C<sub>6</sub>H<sub>11</sub>O<sub>9</sub>P].6H<sub>2</sub>O,  $M_r = 444.4$ , orthorhombic,  $P2_12_12_1$ ,  $a = 9.855$  (3),  $b = 10.593$  (2),  $c = 17.057$  (3) Å,  $Z = 4$ ,  $U = 1780.6$  Å<sup>3</sup>,  $D_m = 1.7$ ,  $D_x = 1.66$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu K}\alpha) = 1.5418$  Å,  $\mu = 6.17$  mm<sup>-1</sup>,  $F(000) = 928$ ,  $T = 300$  K, final  $R = 0.080$  for 1358 observed reflections. The phosphate ester bond length, P—O(6) [1.609 (7) Å], corresponds to a high-energy P~O bond. The conformation about the C(5)—C(6) bond is *gauche-trans*. The furanose ring adopts the <sup>3</sup>E envelope conformation. The two endocyclic C—O bonds C(2)—O(5) and C(5)—O(5) are nearly equal [1.400 (12), 1.441 (12) Å]. The K<sup>+</sup> ions

bind to the phosphate group only indirectly through water bridges and exocyclic hydroxyls O(2), O(3) and O(4). The ring O is a binding site for K<sup>+</sup>. The crystal structure is stabilized by hydrogen bonds between the molecular O atoms and the water.

**Introduction.** Fructose 6-phosphate (F6P) is an intermediate in glycolysis. It is classified as a 'low-energy' phosphate as its free energy of hydrolysis is small, -15.9 kJ mol<sup>-1</sup>, compared to that of a 'high-energy' phosphate such as phosphoenolpyruvate (-61.9 kJ mol<sup>-1</sup>) (Lehninger, 1973). We report here

the structure of the title compound as obtained from X-ray diffraction studies. This investigation follows our earlier studies on the monobarium salt of glucose 6-phosphate heptahydrate, the disodium salt of glucose 1-phosphate hydrate and the trisodium salt of fructose 1,6-diphosphate octahydrate (Katti, Seshadri & Viswamitra, 1982; Narendra, Seshadri & Viswamitra, 1984, 1985).

**Experimental.** Crystals were grown from aqueous solutions of the compound by diffusion of acetone.  $D_m$  by flotation in acetone/bromoforn. Preliminary examination by rotation and Weissenberg photographs. Cell parameters refined by least-squares calculations from 25 high-angle reflections. CAD-4 diffractometer. Cu  $K\alpha$  intensity data up to  $\sin\theta/\lambda = 0.56 \text{ \AA}^{-1}$ . Crystal  $0.1 \times 0.05 \times 0.5 \text{ mm}$ .  $\omega$ - $2\theta$  scan mode. 1358 reflections out of 1658 considered observed [ $F > 3\sigma(F)$ ]; Min. and max.  $h, k, l$  values 0, 11; 0, 11 and 0, 19, respectively. Two strong reflections monitored periodically during data collection showed the crystal stable to X-rays, but instrumental instability caused intensities of the two standard reflections to vary from the average by 6.4 and 8.5%. Lorentz and polarization corrections were applied. Structure solved by direct methods with *MULTAN80* (Main *et al.*, 1980) and *SHELX76* (Sheldrick, 1976). The phosphate group was located in the  $E$  map with highest combined figure of merit of 2.48. The water O atoms and then the furanose ring and exocyclic O atoms and finally all the H atoms were located from subsequent difference Fourier maps. Full-matrix least-squares refinement using *SHELX76* with anisotropic temperature factors for non-hydrogen atoms and isotropic temperature factors for H converged at  $R = 0.080$ . The function minimized was  $\sum w(|F_o| - |F_c|)^2$ ;  $w = 1/\sigma^2(F)$ .  $wR = 0.086$ ,  $S = 8.35$ . Scattering factors for non-H atoms were taken from Cromer & Waber (1965), for H atoms from Stewart, Davidson & Simpson (1965). Max.  $\Delta/\sigma$  for non-H atoms 0.07, and 0.3 including H atoms. Residual electron density in final difference Fourier map  $-0.95$  to  $0.83 \text{ e \AA}^{-3}$ . No correction for secondary extinction. The application of an absorption correction using the method of Palm (1964) did not improve the  $R$  factor. The parameters reported here are based on the uncorrected data.

**Discussion.** Positional parameters for the atoms are given in Table 1.\* Bond lengths and bond angles are listed in Table 2. An *ORTEP* (Johnson, 1965) diagram

\* Lists of structure amplitudes, anisotropic thermal parameters, torsion angles, hydrogen-bond distances and details of least-squares-plane calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42399 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

of the molecule and the numbering scheme are shown in Fig. 1. The environment of the phosphate group viewed along  $b$  is shown in Fig. 2.

**Phosphate group.** As the compound is a dipotassium salt, the phosphate group carries two negative charges. The bond length P—O(6) is  $1.609(7) \text{ \AA}$  which is comparable to the high-energy P~O bond of  $1.612(6) \text{ \AA}$  in phosphoenolpyruvate monopotassium salt (Hosur & Viswamitra, 1981). The O—P—O angles have a mean value of  $109.3^\circ$ . The three terminal P—O bonds are nearly equal (Table 2); presumably the two negative charges are distributed over O(7), O(8) and O(9).

**Furanose ring.** The sugar moiety exists in the furanose form similar to that found in fructose 1,6-diphosphate (Narendra, Seshadri & Viswamitra, 1985). The sugar adopts the  ${}^3E$  envelope conformation, with C(3) displaced from the O(5)—C(2)—C(4)—C(5)

Table 1. Fractional coordinates ( $\times 10^4$ , for H  $\times 10^3$ ) with equivalent isotropic temperature factors ( $\text{\AA}^2 \times 10^2$ )

For H atoms the temperature factors are the refined isotropic values. E.s.d.'s are given in parentheses.  $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$ .

	$x$	$y$	$z$	$U_{eq}$ or $U_{iso}$
P	9645 (3)	-2516 (2)	1412 (1)	2.3 (0.1)
O(7)	10340 (8)	-1268 (6)	1219 (4)	3.3 (0.2)
O(8)	9329 (8)	-2628 (8)	2280 (4)	3.7 (0.2)
O(9)	10363 (9)	-3656 (7)	1085 (4)	3.5 (0.2)
C(1)	3395 (12)	-3759 (11)	1905 (7)	4.3 (0.2)
C(2)	4322 (10)	-2603 (9)	1761 (6)	2.9 (0.2)
C(3)	3652 (10)	-1538 (10)	1272 (6)	2.6 (0.2)
C(4)	4849 (9)	-849 (9)	944 (5)	2.1 (0.2)
C(5)	5940 (11)	-1920 (10)	836 (5)	2.6 (0.2)
C(6)	7275 (11)	-1494 (10)	1073 (6)	3.2 (0.2)
O(1)	2948 (8)	-4279 (8)	1195 (5)	4.5 (0.2)
O(2)	4725 (8)	-2101 (8)	2485 (4)	4.0 (0.2)
O(3)	2771 (7)	-768 (7)	1723 (4)	3.4 (0.2)
O(4)	4576 (8)	-165 (7)	245 (4)	3.6 (0.2)
O(5)	5451 (8)	-2949 (7)	1311 (4)	3.3 (0.2)
O(6)	8228 (7)	-2546 (7)	944 (4)	3.5 (0.2)
K(1)	4710 (4)	-2649 (2)	5262 (1)	6.1 (0.1)
K(2)	3092 (4)	-244 (3)	3472 (2)	6.5 (0.1)
O1W(1)	423 (10)	-978 (8)	3384 (5)	5.0 (0.2)
O1W(2)	656 (9)	-3916 (8)	3453 (5)	4.7 (0.2)
O1W(3)	2050 (8)	-1751 (8)	7012 (5)	4.7 (0.2)
O1W(4)	3119 (13)	-2867 (11)	3919 (6)	7.9 (0.3)
O1W(5)	-1570 (13)	-4743 (10)	4964 (6)	7.7 (0.2)
O1W(6)	1846 (15)	-3232 (10)	5691 (6)	8.9 (0.3)
H(1)	250 (5)	-352 (5)	226 (4)	3.1 (0.6)
H <sup>+</sup> (1)	380 (5)	-447 (5)	209 (4)	4.1 (0.6)
H(3)	310 (5)	190 (5)	84 (4)	2.2 (0.6)
H(4)	525 (5)	10 (5)	130 (4)	2.8 (0.6)
H(5)	555 (5)	230 (5)	24 (4)	4.7 (0.6)
H(6)	744 (5)	-49 (5)	92 (4)	3.3 (0.6)
H <sup>+</sup> (6)	743 (5)	-118 (5)	172 (4)	1.3 (0.6)
O1(H)	219 (5)	-417 (5)	106 (5)	7.5 (0.6)
O2(H)	549 (5)	-232 (5)	274 (4)	5.0 (0.5)
O3(H)	252 (5)	-80 (5)	144 (4)	5.3 (0.6)
O4(H)	483 (5)	-9 (5)	-24 (5)	11.3 (0.6)
W(1)H	29 (5)	-36 (5)	346 (5)	3.8 (0.6)
W <sup>+</sup> (1)H	48 (5)	-147 (5)	297 (4)	4.2 (0.6)
W(2)H	50 (5)	-476 (5)	342 (4)	2.7 (0.6)
W <sup>+</sup> (2)H	24 (5)	-342 (5)	308 (5)	4.9 (0.6)
W(3)H	229 (5)	-86 (5)	689 (4)	4.3 (0.6)
W <sup>+</sup> (3)H	254 (5)	-201 (5)	735 (5)	4.8 (0.6)
W(4)H	255 (5)	-285 (5)	441 (4)	5.0 (0.6)
W <sup>+</sup> (4)H	244 (5)	-209 (5)	383 (4)	11.2 (0.5)
W(5)H	26 (4)	-502 (4)	515 (3)	1.8 (0.6)
W <sup>+</sup> (5)H	-129 (5)	-537 (5)	458 (4)	5.2 (0.5)
W(6)H	108 (4)	-368 (4)	575 (3)	1.1 (0.5)
W <sup>+</sup> (6)H	198 (5)	-277 (5)	625 (4)	5.7 (0.5)

Table 2. Distances (Å) and angles (°)

P—O(7)	1.525 (7)	C(2)—C(3)	1.551 (14)
P—O(8)	1.518 (7)	C(3)—O(3)	1.418 (12)
P—O(9)	1.507 (8)	C(3)—C(4)	1.496 (13)
P—O(6)	1.609 (7)	C(4)—O(4)	1.421 (11)
C(1)—O(1)	1.401 (15)	C(4)—C(5)	1.574 (14)
C(1)—C(2)	1.547 (15)	C(5)—O(5)	1.441 (12)
C(2)—O(2)	1.402 (12)	C(5)—C(6)	1.448 (15)
C(2)—O(5)	1.400 (12)	C(6)—O(6)	1.474 (13)
O(7)—P—O(8)	111.7 (4)	O(3)—C(3)—C(4)	113.9 (8)
O(7)—P—O(9)	113.8 (4)	O(3)—C(3)—C(2)	112.8 (8)
O(8)—P—O(9)	113.3 (4)	C(4)—C(3)—C(2)	102.7 (8)
O(6)—P—O(7)	107.4 (4)	O(4)—C(4)—C(3)	114.4 (8)
O(6)—P—O(8)	107.7 (4)	O(4)—C(4)—C(5)	113.5 (7)
O(6)—P—O(9)	102.0 (4)	C(3)—C(4)—C(5)	103.3 (7)
O(1)—C(1)—C(2)	111.1 (9)	O(5)—C(5)—C(6)	112.5 (8)
C(1)—C(2)—C(3)	114.2 (8)	O(5)—C(5)—C(4)	104.5 (7)
C(1)—C(2)—O(5)	109.1 (8)	C(6)—C(5)—C(4)	111.3 (8)
C(1)—C(2)—O(2)	110.4 (8)	C(5)—C(6)—O(6)	107.5 (8)
C(3)—C(2)—O(2)	108.6 (8)	C(2)—O(5)—C(5)	112.1 (7)
C(3)—C(2)—O(5)	103.5 (8)	C(6)—O(6)—P	117.6 (6)
O(2)—C(2)—O(5)	110.9 (8)		
Potassium coordination distances (average e.s.d. 0.01 Å)			
K(1) OW(4)	2.79	K(2) OW(5 <sup>ii</sup> )	2.69
OW(1)	2.82	OW(1)	2.75
OW(6 <sup>i</sup> )	2.82	O(5 <sup>iii</sup> )	2.85
OW(5 <sup>i</sup> )	2.86	OW(4)	2.88
O(4 <sup>ii</sup> )	2.89	O(2)	3.05
OW(2 <sup>i</sup> )	2.90	O(3)	3.05
OW(6)	2.98		

Symmetry code: (i)  $\frac{1}{2} + x, -\frac{1}{2} - y, 1 - z$ ; (ii)  $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$ ; (iii)  $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$ .

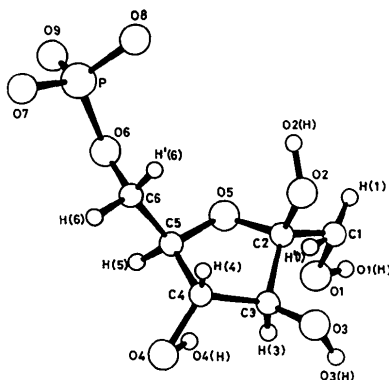


Fig. 1. Molecular structure and atomic numbering scheme of the dianion.

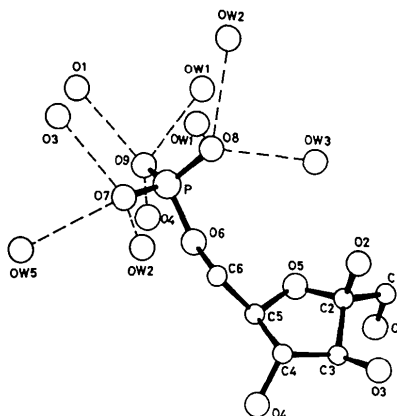


Fig. 2. The environment of the phosphate group. Broken lines indicate hydrogen bonds.

plane by 0.549 (10) Å. The two endocyclic C—O bonds C(2)—O(5) and C(5)—O(5) are nearly equal [1.400 (12), 1.441 (12) Å]. The Cremer & Pople (1975) puckering parameters are  $Q_2 = 0.359 (2)$  Å and  $\varphi_2 = 244.1 (3)^\circ$ .

The torsion angles O(6)—C(6)—C(5)—O(5) and O(6)—C(6)—C(5)—C(4) are 63.7 (10) and  $-179.4 (7)^\circ$ , respectively. The conformation about the C(5)—C(6) bond is therefore *gauche-trans* (gt) similar to that found in Na<sub>3</sub>(F1,6-dp) (Narendra *et al.*, 1985).

*Potassium coordination and hydrogen bonding.\** There are two crystallographically independent K<sup>+</sup> ions in the structure. They do not interact directly with the phosphate O atoms, which are involved in hydrogen bonding with water molecules and the exocyclic hydroxyls as shown in Fig. 2. K(1) is seven coordinated and K(2) has six neighbours within a distance of 3.2 Å (Table 2). Their interaction with phosphate is through water O and exocyclic hydroxyls O(2), O(3) and O(4).

There is no intramolecular hydrogen bonding similar to that found in F1,6-dp (Narendra *et al.*, 1985). The ring O(5) and phosphate ester O(6) are not involved in hydrogen bonding. The exocyclic hydroxyls O(1) and O(3) act as both donors and acceptors of hydrogen bonds, whereas hydroxyls O(2) and O(4) are donors.

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\* See deposition footnote.

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