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# The Crystal Structures of the *A* and *B* Forms of Potassium D-Gluconate Monohydrate by Neutron Diffraction

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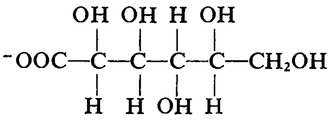
Neutron diffraction data have been used to refine the crystal structure of the *A* form of potassium D-gluconate monohydrate, $KC_6H_{11}O_7.H_2O$, $P2_12_12_1$, $a=8{\cdot}220$ (4), $b=17{\cdot}840$ (8), $c=6{\cdot}717$ (3) Å, $Z=4$, and to determine by direct methods and refine the structure of the *B* form, $P2_1$, $a=9{\cdot}353$ (7), $b=7{\cdot}357$ (5), $c=7{\cdot}229$ (5) Å, $\beta=109{\cdot}39$ (2)°, $Z=2$. These structures are an example of conformational dimorphism, in that the gluconate ion is a straight-chain conformer in *A* and a bent-chain conformer in *B*. The new atomic coordinates for form *A* differ from the previous X-ray results by a mean of $1{\cdot}5\sigma$, except for the hydrogen atoms. The more accurate hydrogen positions confirm the existence of an intramolecular hydrogen bond, which is associated with a *syn*-axial orientation of alternate hydroxyls in the straight-chain conformation. In the *B* form, there is no intramolecular hydrogen bond. The gluconate ion has one of the two most probable bent-chain conformations predicted for the DDLD configuration of the $-(CHOH)_4-$ sequence in a polyhydroxyl alkyl chain. In both structures, there is extensive intermolecular hydrogen bonding involving all the hydroxy and water hydrogens.

## Introduction

The primary objective of this work was to study the conformation of the D-gluconate ion (I).



$$^{-}OOC-\overset{OH}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}-\overset{OH}{\underset{H}{C}}-CH_2OH$$

(I)

Earlier crystal-structure studies of D-glucitol (Park, Jeffrey & Hamilton, 1971) and other hexitols and pentitols (Jeffrey & Kim, 1970) and of related alditol derivatives by n.m.r. measurements (El Khadem, Horton & Page, 1968; Horton & Wander, 1969, 1970) led to the expectation that, because of its DDLD configuration, the D-gluconate ion should be the bent, or 'sickle-shaped' conformer, both in the crystalline state and predominantly in solution. This conformational preference has its origin in the repulsion of *syn*-axially related hydroxyl groups in the straight-chain conformer. An early crystal structure analysis by Littleton (1953) contradicted this prediction by showing that the gluconate ion is the straight-chain conformer in the crystal structure of anhydrous potassium D-gluconate. Jeffrey & Fasiska (1972) determined the structure of the orthorhombic *A* form of potassium D-gluconate monohydrate by X-rays and also found a straight-chain conformation for the ion. This conformation appeared to be stabilized by an intramolecular hydrogen bond between the two *syn*-axially related hydroxyls, a feature which is not generally observed either in crys-

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* Deceased.

tal structures or hydrolytic solution studies of carbohydrates, where *syn*-axial hydroxyls are generally associated with repulsion terms favoring those conformations where they are avoided (*cf.* Stoddart, 1971). Such *syn*-axial intramolecular hydrogen bonding is not observed, for example, in any of the 11 alditol structures which have been studied (Jeffrey & Kim, 1970), nor in epi-inositol where *syn*-axial interactions cannot be avoided (Jeffrey & Kim, 1971). Since there were some unusual features in the hydrogen bonding of the monohydrate deduced from the X-ray data, a refinement of the structure was undertaken using neutron diffraction. During the recrystallization of the potassium gluconate from aqueous solutions, a second, monoclinic (*B*) form, was obtained and this structure was determined entirely from neutron diffraction data.

Table 1. *Crystal data*

| | *A* form, $KC_6H_{11}O_7.H_2O$* | *B* form, $KC_6H_{11}O_7.H_2O$ |
|---|---|---|
| Space group | $P2_12_12_1$ | $P2_1$ |
| $a$ | 8·220 (4) Å | 9·353 (7) Å |
| $b$ | 17·840 (8) | 7·357 (5) |
| $c$ | 6·717 (3) | 7·229 (5) |
| $\beta$ | | 109·39 (2)° |
| $V$ | 985 (2) Å$^2$ | 469·3 Å$^3$ |
| Z | 4 | 2 |
| $D_x$ | 1·701 (7) g cm$^{-3}$ | 1·786 g cm$^{-3}$ |
| $D_B$ | 1·695 (7) | 1·783 |
| $\lambda_{\text{neution}}$ | 1·0142 Å | 1·0142 Å |
| $\mu_{\text{neutron}}$ | 2·12 cm$^{-1}$ | 2·22 cm$^{-1}$ |

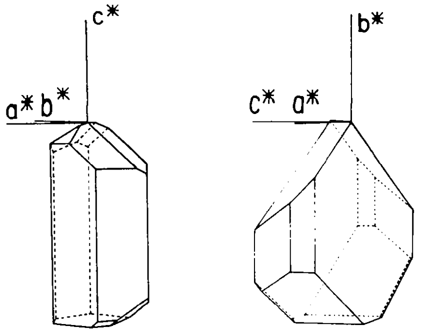
* from Jeffrey & Fasiska (1972).

## Experimental

Both forms of potassium gluconate monohydrate were obtained by slow evaporation of an aqueous solution of the salt supplied by Fisher Scientific Company. Large crystals were grown with well developed faces, as illustrated in Fig. 1. The crystal data, given in Table 1, are verified values of those reported by Jeffrey & Fasiska (1972) for *A*, and new values measured by X-rays with a small crystal on a CAD-4 diffractometer for *B*. The crystals used for the neutron measurements had volumes of 13·7 mm$^3$ for *A*, 50·1 mm$^3$ for *B*. The intensities were measured at the Brookhaven National Laboratory high-flux beam reactor using a four-circle diffractometer and a crystal-monochromated beam ($\lambda$=1·014 Å). A $\theta$–$2\theta$ step-scan technique was used in the measurement of the profiles of 2821 $hkl$ and $\bar{h}kl$ reflections for *A* and 2704 $hkl$, $\bar{h}kl$, $\bar{h}k\bar{l}$, $hk\bar{l}$ reflections for *B* with $\sin\theta/\lambda \leq 0{\cdot}76$ Å$^{-1}$. The profiles were processed with the Brookhaven data processing programs, described by Schlemper, Hamilton & La Placa (1971). The integrated intensity, $I$, was obtained with a background correction method which divides peak and background in such a way that $\sigma(I)/I$ is minimized, where $\sigma(I)$ is based on counting statistics (Lehmann, Hamilton & Larsen, 1972). The intensities were corrected for the Lorentz kinematic factor and for absorption with a Gaussian numerical integration. The transmission coefficient varied between 0·75 and 0·64 for *A*, and 0·65 and 0·39 for *B*. The symmetry related reflections were averaged giving 1444 unique reflections for *A* with an agreement factor $R_c = \sum|F_o^2 - \bar{F}^2|/\sum F_o^2 = 0{\cdot}034$, where $\bar{F}$ is the mean of the symmetry-related reflections. For *B*, 1266 unique reflections were obtained with an agreement factor of 0·017.

## Refinement of structure *A*

The final coordinates of Jeffrey & Fasiska (1972) were used as input parameters for the refinement. The neutron scattering lengths in $10^{-12}$ cm units were taken as $b_O = 0{\cdot}575$, $b_C = 0{\cdot}6626$, $b_K = 0{\cdot}370$ and $b_H = -0{\cdot}3723$. The weights for $F$ were chosen as $w = 1/(\sigma F_o)^2$, with $\sigma F_o$ calculated from $\sigma^2(F_o^2) = \sigma^2_{\text{count}}(F_o^2) + (0{\cdot}034F_o^2)^2$ where $\sigma^2_{\text{count}}$ is that of the counting statistics. In the final cycle of refinement, 1173 reflections with $F_o^2 > 3\sigma_{\text{count}}(F_o^2)$ were included. In the initial cycles of refinement, some of the hydrogen-atom parameters misbehaved and more reliable positions for all the hydrogen atoms were determined from a difference synthesis. The crystal showed severe extinction and the Zachariasen isotropic extinction parameter was refined by the method of Coppens & Hamilton (1970). The ratio $|F_{o\text{uncorrected}}|^2/|F_{o\text{corrected}}|^2$ ranged from 1·00 to 0·50, with the exception of the 200 reflection for which the ratio had the value of 0·32. The final value of the extinction parameter was $g = 4{\cdot}1\ (1) \times 10^4$. In the final cycles of refinement, a full-matrix least-squares program was used and all 254 parameters were varied concurrently. The final unweighted agreement index was $R(F) = 0{\cdot}034$ and the weighted $R_w = 0{\cdot}037$, where $R(F) = \sum|F_o - |F_c||/\sum F_o$ and $R_w = (\sum_w|F_o - |F_c||^2/\sum_w F_o^2)^{1/2}$. The final atomic and thermal parameters are given in Table 2(*a*) and the observed and calculated structure factors are available.*



(*a*) (*b*)

Fig. 1. Morphology of crystals of potassium D-gluconate monohydrate used in the neutron diffraction study. (*a*) Form *A*. (*b*) Form *B*.

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* These have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30365 (15pp., 1 microfiche). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

### Solution and refinement of structure *B*

It has been suggested by Sikka (1969) that the direct methods should be applicable to neutron diffraction data when the amount of scattering from the hydrogen atoms, $Q_H=\sum b_H^2/\sum b_i^2$, $i$ over all atoms, is less than about 0·30 and the number of atoms per unit cell is less than 100. Though the present structure, with $Q_H=$

Table 2. *Atomic parameters of potassium* D-*gluconate monohydrate*

The thermal parameters are of the form $\exp\,[-10^{-4}(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$. Estimated standard deviations given in parentheses refer to the least significant digit in the parameter value.

(*a*) Form *A*

| | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| K | 0·6439 (5) | 0·2784 (2) | 0·0545 (7) | 80 (6) | 14 (1) | 149 (9) | 2 (2) | −9 (6) | 12 (3) |
| C(1) | 1·0505 (2) | −0·0537 (1) | −0·0489 (3) | 61 (3) | 13·6 (5) | 110 (4) | 2 (1) | 18 (3) | −9 (1) |
| C(2) | 0·9320 (2) | 0·0016 (1) | 0·0487 (3) | 46 (3) | 11·4 (5) | 101 (4) | −2 (1) | 16 (3) | −8 (1) |
| C(3) | 1·0171 (2) | 0·0518 (1) | 0·2034 (3) | 54 (2) | 8·5 (5) | 92 (4) | 1 (1) | 1 (3) | 2 (1) |
| C(4) | 0·8977 (2) | 0·1095 (1) | 0·2901 (3) | 54 (3) | 9·5 (5) | 95 (4) | 0 (1) | 2 (3) | −2 (1) |
| C(5) | 0·9696 (2) | 0·1604 (1) | 0·4511 (3) | 66 (3) | 10·7 (5) | 88 (4) | −1 (1) | −8 (3) | 0 (1) |
| C(6) | 0·8339 (3) | 0·2053 (1) | 0·5478 (4) | 90 (3) | 16·6 (6) | 142 (5) | 13 (1) | −25 (4) | −18 (2) |
| O(0) | 1·1186 (3) | −0·1015 (1) | 0·0609 (4) | 102 (4) | 18·8 (8) | 161 (6) | 16 (1) | 30 (4) | 6 (2) |
| O(1) | 1·0701 (3) | −0·0477 (2) | −0·2321 (4) | 102 (4) | 29·4 (9) | 110 (6) | 20 (2) | 24 (4) | −9 (2) |
| O(2) | 0·8541 (3) | 0·0448 (1) | −0·1010 (4) | 64 (4) | 18·6 (7) | 116 (6) | 8 (1) | −19 (4) | −11 (2) |
| O(3) | 1·1491 (3) | 0·0895 (1) | 0·1133 (4) | 48 (3) | 14·2 (7) | 138 (6) | −3 (1) | −6 (4) | 11 (2) |
| O(4) | 0·8407 (3) | 0·1596 (1) | 0·1394 (4) | 99 (4) | 13·9 (7) | 124 (6) | 12 (1) | −36 (4) | −9 (2) |
| O(5) | 1·0480 (3) | 0·1200 (2) | 0·6047 (4) | 83 (4) | 24·8 (8) | 98 (5) | 13 (2) | −13 (4) | 3 (2) |
| O(6) | 0·8903 (4) | 0·2613 (2) | 0·6809 (4) | 160 (5) | 15·2 (8) | 119 (6) | 9 (2) | −34 (5) | −17 (2) |
| H(2) | 0·8370 (5) | −0·0306 (2) | 0·1253 (8) | 92 (6) | 23 (1) | 209 (12) | −16 (2) | 47 (7) | −14 (3) |
| H(3) | 1·0590 (6) | 0·0155 (2) | 0·3250 (7) | 137 (7) | 13 (1) | 154 (10) | 5 (2) | −1 (7) | 12 (3) |
| H(4) | 0·7957 (5) | 0·0779 (3) | 0·3534 (8) | 90 (6) | 22 (1) | 233 (13) | −16 (3) | 44 (7) | −18 (4) |
| H(5) | 1·0563 (6) | 0·1986 (3) | 0·3799 (7) | 121 (7) | 27 (1) | 151 (10) | −24 (3) | 6 (7) | 0 (3) |
| H(6) | 0·7589 (6) | 0·1667 (3) | 0·6333 (10) | 129 (8) | 37 (2) | 312 (17) | −9 (3) | 77 (10) | −42 (5) |
| H′(6) | 0·7579 (8) | 0·2297 (3) | 0·4332 (9) | 218 (12) | 47 (2) | 241 (15) | 63 (5) | −98 (12) | −44 (5) |
| H(O2) | 0·9327 (6) | 0·0526 (3) | −0·2081 (8) | 121 (7) | 38 (2) | 142 (11) | 14 (3) | 8 (8) | −1 (4) |
| H(O3) | 1·2509 (5) | 0·0732 (3) | 0·1733 (7) | 61 (6) | 25 (1) | 178 (11) | 0 (2) | −12 (6) | 3 (3) |
| H(O4) | 0·8155 (6) | 0·1279 (3) | 0·0252 (8) | 142 (8) | 23 (1) | 153 (11) | 10 (3) | −44 (8) | −8 (4) |
| H(O5) | 1·1589 (6) | 0·1084 (3) | 0·5704 (8) | 100 (7) | 31 (2) | 195 (12) | 23 (3) | −21 (7) | −9 (4) |
| H(O6) | 0·8904 (6) | 0·3082 (3) | 0·6157 (9) | 157 (9) | 21 (2) | 264 (16) | −2 (3) | −6 (9) | −17 (4) |
| O(*W*) | 0·9865 (4) | 0·3471 (2) | 0·0792 (6) | 156 (5) | 25 (1) | 171 (8) | 12 (2) | 15 (6) | −17 (3) |
| H(*W*) | 0·9834 (8) | 0·3832 (4) | −0·0232 (9) | 201 (12) | 36 (2) | 234 (15) | 16 (4) | 5 (11) | 2 (5) |
| H′(*W*) | 0·9561 (7) | 0·3715 (3) | 0·2004 (9) | 139 (8) | 30 (2) | 213 (14) | 2 (3) | −5 (9) | −16 (4) |

(*b*) Form *B*

| | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| K | 0·4605 (5) | 1·1814 (7) | 0·0614 (6) | 60 (5) | 51 (7) | 97 (8) | 0 (5) | 28 (5) | 3 (6) |
| C(1) | 0·2428 (2) | 0·5946* | 0·1343 (3) | 48 (2) | 34 (4) | 72 (4) | −5 (3) | 21 (2) | −11 (3) |
| C(2) | 0·2712 (3) | 0·7861 (4) | 0·2234 (3) | 45 (2) | 26 (3) | 59 (4) | 1 (2) | 16 (2) | −2 (3) |
| C(3) | 0·2620 (2) | 0·7767 (4) | 0·4307 (3) | 44 (2) | 34 (4) | 63 (4) | 0 (2) | 18 (2) | −2 (3) |
| C(4) | 0·3096 (2) | 0·9512 (4) | 0·5501 (3) | 36 (2) | 34 (4) | 65 (4) | 0 (2) | 15 (2) | −8 (3) |
| C(5) | 0·2269 (2) | 1·1254 (4) | 0·4534 (3) | 46 (2) | 38 (4) | 77 (4) | 2 (2) | 21 (2) | −1 (3) |
| C(6) | 0·0552 (2) | 1·1123 (5) | 0·3773 (3) | 46 (2) | 45 (4) | 102 (4) | 5 (3) | 15 (3) | 0 (4) |
| O(0) | 0·1170 (3) | 0·5233 (5) | 0·1215 (4) | 57 (3) | 48 (5) | 122 (5) | −15 (3) | 34 (3) | −15 (4) |
| O(1) | 0·3435 (3) | 0·5205 (6) | 0·0866 (5) | 76 (4) | 59 (5) | 193 (7) | −1 (4) | 74 (4) | −35 (5) |
| O(2) | 0·4102 (3) | 0·8587 (5) | 0·2222 (4) | 56 (3) | 51 (5) | 82 (5) | −12 (3) | 28 (3) | 3 (4) |
| O(3) | 0·3638 (3) | 0·6399 (5) | 0·5386 (4) | 80 (4) | 34 (5) | 82 (5) | 16 (3) | 14 (4) | 10 (4) |
| O(4) | 0·2978 (3) | 0·9274 (5) | 0·7391 (3) | 53 (3) | 65 (5) | 60 (4) | 2 (3) | 18 (3) | −8 (4) |
| O(5) | 0·2751 (3) | 1·2716 (5) | 0·5900 (4) | 61 (3) | 35 (4) | 121 (6) | −9 (3) | 25 (4) | −17 (4) |
| O(6) | −0·0145 (3) | 1·2800 (6) | 0·3040 (5) | 60 (3) | 74 (5) | 155 (6) | 32 (4) | 46 (4) | 45 (5) |
| H(2) | 0·1819 (6) | 0·8753 (8) | 0·1308 (7) | 83 (6) | 74 (8) | 113 (9) | 25 (6) | 13 (6) | 17 (8) |
| H(3) | 0·1453 (5) | 0·7417 (8) | 0·4193 (7) | 76 (6) | 104 (10) | 144 (10) | −24 (6) | 48 (6) | −11 (8) |
| H(4) | 0·4306 (5) | 0·9744 (8) | 0·5743 (7) | 54 (5) | 95 (9) | 150 (10) | −6 (5) | 33 (5) | −9 (8) |
| H(5) | 0·2665 (6) | 1·1611 (9) | 0·3308 (8) | 99 (6) | 115 (11) | 147 (11) | 8 (7) | 65 (7) | 27 (8) |
| H(6) | 0·0142 (7) | 1·0710 (10) | 0·4960 (10) | 86 (6) | 150 (13) | 220 (12) | 6 (7) | 65 (7) | 69 (11) |
| H′(6) | 0·0199 (7) | 1·0088 (10) | 0·2642 (10) | 100 (7) | 122 (12) | 236 (15) | 7 (8) | −9 (8) | −77 (12) |
| H(O2) | 0·4930 (6) | 0·7908 (9) | 0·3059 (8) | 71 (6) | 125 (11) | 165 (11) | 14 (7) | 34 (7) | 36 (10) |
| H(O3) | 0·3137 (7) | 0·5240 (8) | 0·5270 (9) | 145 (8) | 48 (9) | 178 (12) | −3 (7) | 40 (8) | 11 (8) |
| H(O4) | 0·1995 (6) | 0·8748 (9) | 0·7271 (7) | 84 (7) | 129 (10) | 128 (10) | −16 (7) | 47 (6) | −1 (9) |
| H(O5) | 0·2259 (6) | 1·2558 (9) | 0·6879 (8) | 104 (7) | 115 (10) | 135 (10) | −11 (7) | 43 (7) | −41 (9) |
| H(O6) | 0·0458 (6) | 1·3492 (9) | 0·2438 (8) | 93 (6) | 101 (10) | 183 (12) | 9 (7) | 56 (7) | 39 (10) |
| O(*W*) | 0·1413 (4) | 1·2181 (6) | 0·8924 (5) | 68 (4) | 86 (6) | 175 (7) | −12 (4) | 45 (4) | −66 (6) |
| H(*W*) | 0·1386 (6) | 1·3262 (8) | 0·9658 (8) | 106 (7) | 90 (10) | 172 (11) | −1 (7) | 33 (7) | −49 (9) |
| H′(*W*) | 0·0509 (7) | 1·1504 (9) | 0·8843 (9) | 94 (7) | 112 (11) | 194 (12) | −20 (7) | 42 (7) | −27 (9) |

* Fixed parameter.

0·25 and 56 atoms in the unit cell, is well within the theoretical limits, the application of a direct method revealed only eight of the 14 carbon and oxygen atoms. Nevertheless, it was possible to proceed from this information to the complete structure.

The $E$ values were calculated for all the reflections and the statistical test confirmed the noncentrosymmetric structure. 240 reflections with $E \geq 1{\cdot}30$ were used as input to the program of Germain, Main & Woolfson (1971). The best solution, with a figure of merit of 1·71, gave an $E$ map which showed eight peaks which could be linked to form part of the gluconate ion; these were later identified as carbon atoms (1) to (5) and oxygen atoms (1), (3) and (4). A lower peak was identified later as O(6). Difference syntheses failed to reveal the positions of the missing atoms, which were obtained from model structures based on the observed fragment. A difference synthesis calculated with phases derived from one of these models gave reasonable positions for the remaining atoms, *i.e.* one carbon, four oxygens, potassium and 13 hydrogens. This model was then refined satisfactorily with the full-matrix least-squares program *ORFLS*, as modified by Coppens & Hamilton (1970). 253 parameters were varied simultaneously, including one scale factor and a Zachariasen extinction parameter. The reflections were weighted with $w = 1/\sigma F_o^2$, where $\sigma F_o$ was calculated from the standard deviation of $F_o^2$, $\sigma^2(F_o^2) = \sigma^2_{\text{count}}(F_o^2) + (0{\cdot}071F_o^2)^2$. In the final cycle, 1266 reflections with $F_o^2 > 3\sigma_{\text{count}}(F_o^2)$ were included. The final unweighted agreement index $R(F) = 0{\cdot}033$ and the weighted index $R_w = 0{\cdot}045$. The final value of the extinction parameter was $3{\cdot}1\ (1) \times 10^{-4}$. The minimum ratio of $|F_{o\text{uncorrected}}|^2/|F_{o\text{corrected}}|^2$ for the extinction-corrected reflections was 0·29. The atomic parameters are given in Table 2(*b*) and the observed and calculated structure factors are available.*

## The structure of the gluconate ions

The gluconate ions as they occur in the two forms are shown in Fig. 2, which also gives the thermal ellipsoids (Johnson, 1965) and the atomic notation. The ions in *A* have the straight-chain conformation with a well-defined intramolecular hydrogen bond, O(4)–H···O(2), and a weaker intramolecular interaction, O(2)–H···O(1). The ions in *B* have a bent-chain conformation with no intramolecular hydrogen bonds. This conformation can be derived from the planar conformation of *A*, by first rotating 120° about C(3)–C(4) so that H(4) moves into the *syn*-axial position relative to O(2) that was previously occupied by O(4), then rotating by 120° about C(4)–C(5), so as to bring H(5) *syn*-axial with C(2). This bent-chain conformation is one of the two predicted for the polyhydroxyalkyl chain of D-glucitol by Jeffrey & Kim (1970), from the previous work on the crystal structures of the sugar

Table 3. *Deviations from least-squares planes in the potassium* D-*gluconate monohydrates*

Atoms marked * were excluded from the least-squares plane, $Ax + By + Cz = D$.

*A*-form

| | *P*1 | *P*2 | *P*3 | *P*4 |
|---|---|---|---|---|
| C(1) | −0·032 Å | 0·018 Å | 0·064* Å | 0·007 Å |
| C(2) | 0·001 | −0·025 | −0·012 | −0·001 |
| C(3) | −0·019 | −0·011 | 0·011 | −0·012 |
| C(4) | 0·094 | 0·025 | 0·013 | 0·060* |
| C(5) | 0·036 | −0·007 | −0·013 | 0·006 |
| C(6) | −0·078 | −0·202* | −0·243* | −0·150* |
| *A* | 1·403 | 1·923 | 2·126 | 1·639 |
| *B* | 12·076 | 11·792 | 11·628 | 11·886 |
| *C* | −4·809 | −4·789 | −4·789 | −4·827 |
| *D* | 1·093 | 1·603 | 1·780 | 1·321 |

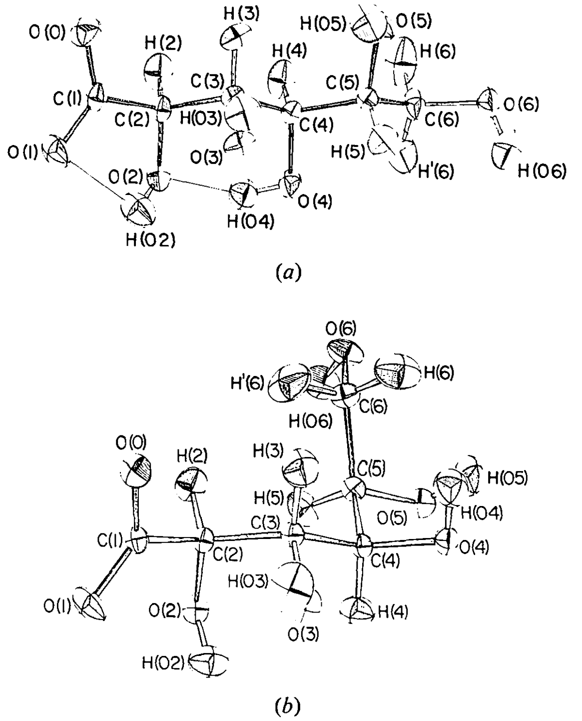
Interplanar angles

| | | | | | |
|---|---|---|---|---|---|
| *P*1, *P*2 | 3·7° | *P*1, *P*4 | 1·8 | *P*2, *P*4 | 2·0° |
| *P*1, *P*3 | 5·2 | *P*2, *P*3 | 1·5 | *P*3, *P*4 | 3·5 |

*B*-form

| | *P*1 | | | *P*2 | |
|---|---|---|---|---|---|
| C(1) | 0·049 Å | *A* = −5·025 | C(1) | −3·460* Å | *A* = −3·206 |
| | | *B* = −1·312 | | | *B* = 2·299 |
| C(2) | −0·043 | *C* = 6·911 | C(2) | −2·499* | *C* = 6·864 |
| | | *D* = 0·757 | | | *D* = 4·970 |
| C(3) | −0·057 | | C(3) | −1·068* | |
| C(4) | 0·051 | | C(4) | 0·000 | |
| C(5) | −0·988* | | C(5) | 0·000 | |
| C(6) | −2·431* | | C(6) | 0·000 | |
| O(4) | 0·037* | | O(6) | 0·106* | |

Interplanar angle *P*1, *P*2 30·8°



(*a*)

(*b*)

Fig. 2. *ORTEP* plots of gluconate ion in potassium D-gluconate monohydrate. The thermal ellipsoids are at 50 % probability. (*a*) Form *A*. (*b*) Form *B*.

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* SUP 30365. See previous footnote.

alcohols. It has also been observed in the D-gluconate moiety of calcium lactobionate bromide tetrahydrate (Cook & Bugg, 1973). The other conformation, which avoids the *syn*-axial O(2) to O(4) interaction by rotating about C(2)–C(3), is that actually observed in the *A* form of D-glucitol (Park, Jeffrey & Hamilton, 1971).

The ideal straight-chain conformation of an isolated gluconate ion has the six carbon atoms lying in one plane. In the crystal structure of the *A* form of potassium D-gluconate monohydrate, there are small but significant deviations from this ideal conformation, as shown by the data on the least-squares planes given in Table 3. There are corresponding variations in the C–C torsion angles of ± 5° from the ideal 60°. Such variations are commonly observed in the crystal structures of the alditols and reflect the flexibility of the polyhydroxyalkyl chains in adjusting to the environment of the crystal field (Jeffrey, 1973*a*). In the *B* form, the carbon atoms lie in two planes, C(1)···C(4) which also includes O(4), and C(4)···C(6), which includes O(6), see Table 3. The variations from 60° torsion angles are larger, lying in the range of ± 10°. It is reasonable to assume that this is because the packing of the bent conformers incurs more departure from the ideal staggered conformation than for the straight molecule-ions.

In both structures, the conformation of the carboxylate group is such that the torsion angle O(1)–C(1)–C(2)–O(2) is very small, 5° in *A* and 6° in *B*. This almost planar conformation for the –C(OH)–COO moiety is a conformational characteristic of α-hydroxy carboxylic acids or carboxylate ions which has been observed in more than 20 structures (*e.g.* Jeffrey & Parry, 1952; Nordman, Weldon & Patterson, 1960; Okaya, Stemple & Kay, 1966; Kroon, Peerdeman & Bijvoet, 1965; Ellison, Johnson & Levy, 1971). With the exceptions discussed below, the bond distances and angles in the two ions, given in Table 4, show very close agreement. The terminal carbon bonds, C(5)–C(6), are 0·016 Å shorter than the mean of the other four in both structures. Similar observations have been made in some, but not all, of the alditol structures. In D-glucitol, for example, the terminal C–C bond lengths are the shorter, but the difference from the mean of the other C–C bonds is only 0·008 Å. While this may be a reflection of the difference in electronic structure between a primary and secondary alcohol group, uncertainty in the magnitude of the thermal-motion corrections for the terminal atoms makes the significance of this difference uncertain. There is no significant variation in the C–OH bond lengths (including the terminal bonds) from the overall mean value of 1·419 Å. The carboxylate group appears to be unsymmetrical in both forms in a way which relates to the hydrogen bonding and is discussed later. The C–C–C valence angles at C(3), C(4), C(5) are close to 115° in *B*, whereas in *A* only that at C(4) is greater than 110°. In the straight-chain conformer, the normal tetrahedral angle at C(3) will be retained because of the intramolecular hydrogen bond. The distinction between the C(4) and C(5) angles can be explained by strain arising from the two O(3)···H(5), O(5)···H(3) interactions at 2·75 and 2·65 Å, whereas across C(5), the corresponding interactions are O(4)···H′(6) and H(4)···H(6). In the bent conformer, the overcrowding must arise primarily from the H(2)···H′(6) interaction at 2·27 Å, and to a lesser

Table 4. *Interatomic distances* (Å) *and angles* (°) *in the A and B forms of potassium* D-*gluconate monohydrate*

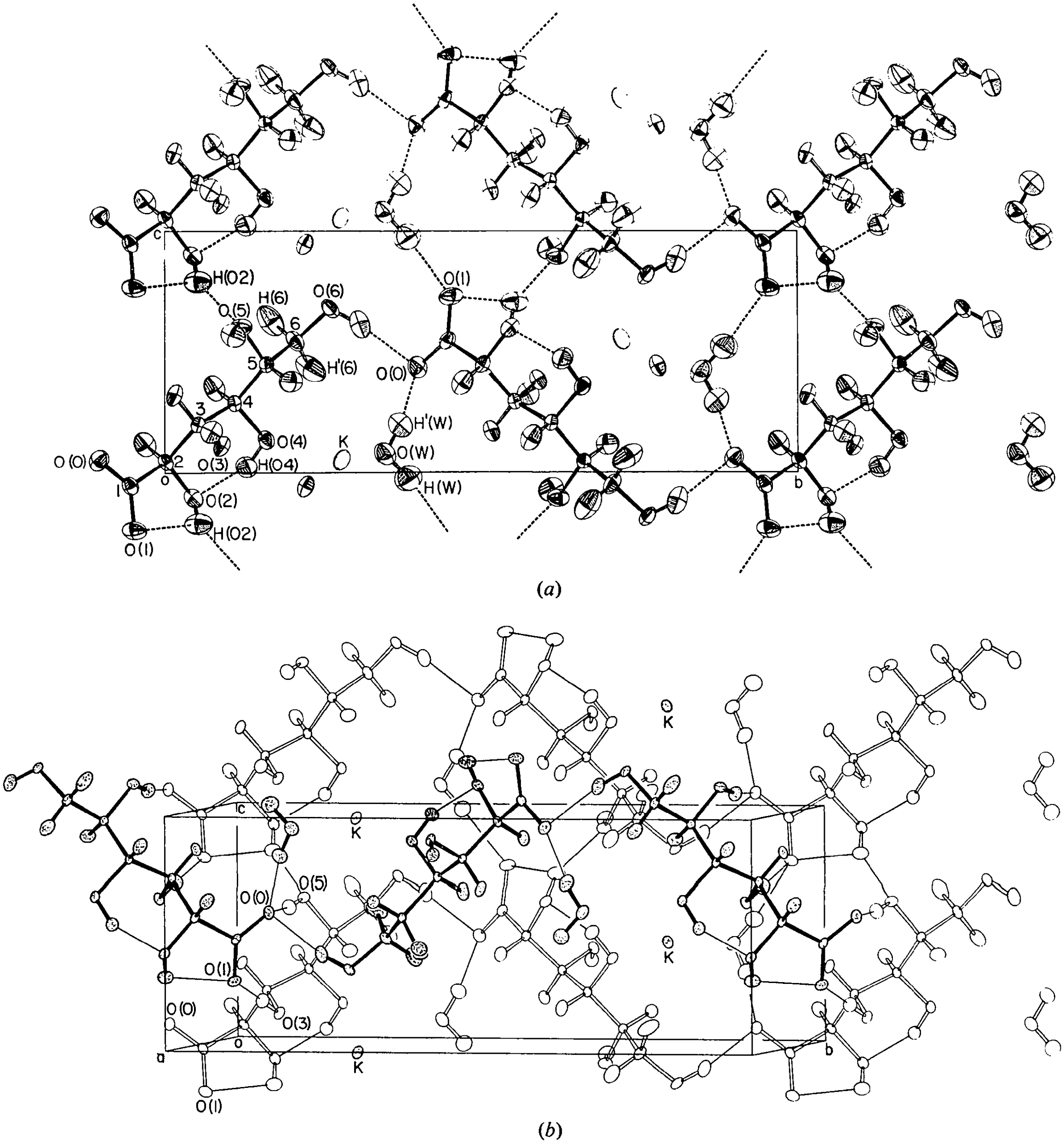
The O–H distances are given in Table 5.

| | *A* | *B* |
|---|---|---|
| C(1)–C(2) | 1·534 (3) | 1·535 (3) |
| C(2)–C(3) | 1·539 (3) | 1·531 (4) |
| C(3)–C(4) | 1·537 (3) | 1·529 (4) |
| C(4)–C(5) | 1·531 (3) | 1·540 (4) |
| C(5)–C(6) | 1·519 (3) | 1·518 (4) |
| C(1)–O(0) | 1·259 (3) | 1·263 (4) |
| C(1)–O(1) | 1·246 (4) | 1·232 (4) |
| C(2)–O(2) | 1·420 (3) | 1·409 (4) |
| C(3)–O(3) | 1·413 (3) | 1·426 (4) |
| C(4)–O(4) | 1·429 (3) | 1·418 (4) |
| C(5)–O(5) | 1·414 (3) | 1·429 (4) |
| C(6)–O(6) | 1·418 (4) | 1·414 (5) |
| C(2)–H(2) | 1·098 (5) | 1·098 (6) |
| C(3)–H(3) | 1·098 (5) | 1·097 (6) |
| C(4)–H(4) | 1·096 (5) | 1·100 (6) |
| C(5)–H(5) | 1·095 (5) | 1·098 (6) |
| C(6)–H(6) | 1·088 (7) | 1·092 (7) |
| C(6)–H′(6) | 1·083 (7) | 1·085 (8) |
| O(0)—C(1)—O(1) | 125·4 (2) | 125·2 (3) |
| C(2)—C(1)—O(0) | 117·9 (2) | 116·0 (2) |
| C(2)—C(1)—O(1) | 116·7 (2) | 118·8 (2) |
| C(1)—C(2)—C(3) | 112·0 (2) | 108·2 (2) |
| C(1)—C(2)—O(2) | 109·5 (2) | 112·2 (2) |
| C(1)—C(2)—H(2) | 108·4 (3) | 107·6 (3) |
| H(2)—C(2)—O(2) | 107·2 (3) | 106·6 (4) |
| H(2)—C(2)—C(3) | 108·1 (3) | 110·2 (3) |
| O(2)—C(2)—C(3) | 111·6 (2) | 112·2 (2) |
| C(2)—C(3)—C(4) | 110·8 (2) | 114·5 (2) |
| C(2)—C(3)—O(3) | 109·7 (2) | 108·8 (2) |
| C(2)—C(3)—H(3) | 107·6 (3) | 108·3 (4) |
| H(3)—C(3)—O(3) | 110·0 (3) | 110·0 (4) |
| H(3)—C(3)—C(4) | 108·3 (3) | 109·6 (4) |
| O(3)—C(3)—C(4) | 109·5 (2) | 105·5 (2) |
| C(3)—C(4)—C(5) | 114·8 (2) | 115·7 (2) |
| C(3)—C(4)—O(4) | 111·1 (2) | 109·8 (2) |
| C(3)—C(4)—H(4) | 106·9 (3) | 108·2 (3) |
| H(4)—C(4)—O(4) | 110·2 (3) | 105·7 (4) |
| H(4)—C(4)—C(5) | 109·0 (3) | 106·2 (3) |
| O(4)—C(4)—C(5) | 104·8 (2) | 110·7 (2) |
| C(4)—C(5)—C(6) | 109·4 (2) | 115·0 (2) |
| C(4)—C(5)—O(5) | 112·8 (2) | 108·4 (2) |
| C(4)—C(5)—H(5) | 108·1 (3) | 108·2 (4) |
| H(5)—C(5)—O(5) | 109·8 (3) | 105·3 (4) |
| H(5)—C(5)—C(6) | 109·7 (3) | 108·9 (4) |
| O(5)—C(5)—C(6) | 106·9 (2) | 110·5 (2) |
| C(5)—C(6)—O(6) | 113·6 (2) | 112·4 (3) |
| C(5)—C(6)—H(6) | 108·0 (4) | 109·8 (4) |
| C(5)—C(6)—H′(6) | 109·4 (4) | 109·7 (4) |
| H(6)—C(6)—H′(6) | 107·6 (5) | 107·4 (6) |
| H(6)—C(6)—O(6) | 107·3 (4) | 107·4 (4) |
| H′(6)—C(6)—O(6) | 110·7 (4) | 110·0 (5) |
| C(2)—O(2)—H(O2) | 107·4 (4) | 110·8 (5) |
| C(3)—O(3)—H(O3) | 109·9 (3) | 111·1 (5) |
| C(4)—O(4)—H(O4) | 105·3 (4) | 109·7 (4) |
| C(5)—O(5)—H(O5) | 111·5 (4) | 107·3 (5) |
| C(6)—O(6)—H(O6) | 109·4 (4) | 111·3 (6) |
| H′(*W*)–O(*W*)–H(*W*) | 107·7 (6) | 106·1 (6) |

degree H(2)···H(5) at 2·52 and H(2)–C(5) at 2·89 Å. It is surprising that the terminal primary alcohol group does not twist about C(5)–C(6) to increase this H(2)···H′(6) separation; such a twist would also displace O(6)H and is presumably resisted by the intermolecular hydrogen bonds to that hydroxyl.

## The crystal environment of the gluconate ion

These two structures provide an example of *conformational dimorphism*, which can be directly correlated to hydrogen bonding. In the absence of intramolecular hydrogen bonding, the gluconate ions in form *B* have the bent-chain conformation, which is consistent with previous studies of 11 related alditol structures (Jeffrey & Kim, 1970; Azarnia, Jeffrey & Shen, 1972). In the *A* form, the ions have the straight-chain conformation, with an intramolecular hydrogen bond between two *syn*-axially related hydroxyls, a structural feature which has not hitherto been observed in the crystal structure of any of the acylic or cyclic sugars with the exception of some thioribopyranosides (Jeffrey, 1973*b*).



(*a*)

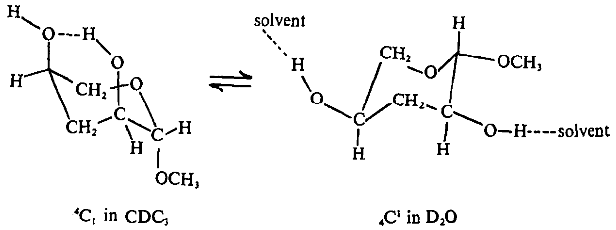
(*b*)

Fig. 3. View of the crystal structure of the *A* form of potassium D-gluconate monohydrate. (*a*) Projection down **a**, showing single row of ions. (*b*) Projection down a in perspective, showing whole unit cell.

A similar intramolecular hydrogen bond can be anticipated with the straight-chain conformation observed in the anhydrous potassium gluconate (Littleton, 1953).

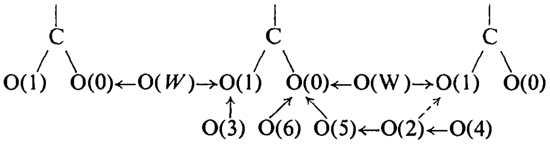
Since the *A* and *B* forms of the monohydrate cocrystallize from the same aqueous solution, the populations of the straight and bent-chain rotamers of the gluconate ions are likely to be comparable. This is also in contrast to the alditols, where n.m.r. studies on triazole derivatives in chloroform solution indicate that conformers with *syn*-axially related hydroxyls are not favored, and have an unobservably low rotameric population (Durette, Horton & Wander, 1973).

Although rare in the solid state, the association of a conformational difference with the stabilization of a *syn*-axial interaction by the presence of an O–H···O intramolecular hydrogen bond is a familiar concept in carbohydrate solution studies. It is exemplified by the effect of solvent on the $^4C_1 \rightleftharpoons {}^1C_4$ pyranoside equilibrium shown below, as postulated by Lemieux (1971) from optical and n.m.r. studies.



By analogy, the suggestion is made that the presence of the cations in the gluconate salt structure disturbs the typical intermolecular hydrogen bonding of the polyhydroxyalkyl system observed in the sugar alcohol structures and permits coexistence of conformers consistent with the geometrically less favorable intramolecular hydrogen bonding (see Jeffrey, 1973*b*). These two structures are described and contrasted from this point of view.

In the *A* form, the linear ions are arranged parallel in rows as shown in Fig. 3. When viewed along the *c* axis direction, these rows form corrugated or puckered sheets, as shown in Fig. 5 of the X-ray determination (Jeffrey & Fasiska, 1972). The carboxylate ions and water molecules are hydrogen bonded into infinite chains which extend in the *c* axis direction, as shown most clearly in Fig. 3(*a*). This general description of the structure was correctly deduced from the X-ray study by Jeffrey & Fasiska (1972), although some of the details of the hydrogen bonding were incorrect. The other hydrogen bonds form single links or short chains, which are attached to this main carboxylate-water 'backbone', as shown schematically below; (arrows indicate donor directions of hydrogen bonds).

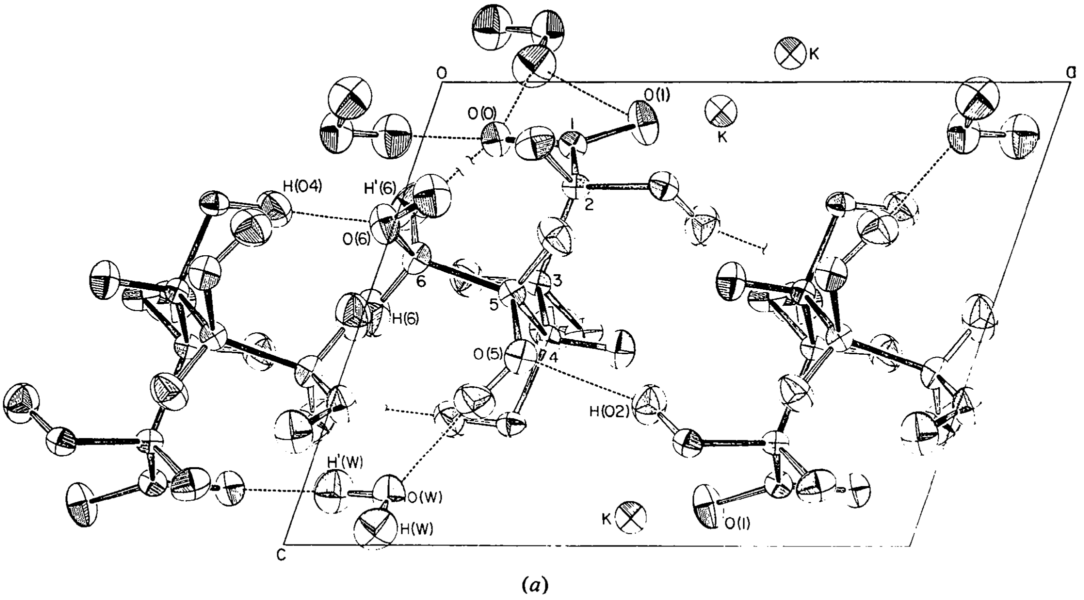


The data on these hydrogen bonds are given in Table 5. All the hydroxylic hydrogens participate in the hydrogen bonding; O(4)–H···O(2) is intramolecular and there is a weak intramolecular interaction from O(2)H to O(1), with a H···O distance of 2·12 Å and a rather acute O–H···O angle of 107°. The carboxylate O(0) accepts three hydrogen bonds [see Fig. 3(*b*)], and O(1) two (excluding the weak intramolecular interaction). This may account for the small difference in bond lengths [0·013 Å; a similar systematic increase of C=O bond lengths with the number of hydrogen bonds accepted by the oxygen has been noted in a series of barbiturate structures by Craven, Cusatis, Gartland & Vizzini (1973)]. In addition to the hydrogen bonds from the water molecules, the carboxylate oxygens, O(0) and O(1), accept hydrogen bonds from O(3)H and O(5)H of a gluconate ion in an adjacent layer, as shown

Table 5. *Hydrogen bonding in potassium* D-*gluconate monohydrate*

| | $i$ | $j$ | $k$ | $d_{ij}$ (Å) | $d_{jk}$ (Å) | $d_{ik}$ (Å) | $\angle_{ijk}$ (°) |
|---|---|---|---|---|---|---|---|
| *A* Form | | | | | | | |
| | Intramolecular | | | | | | |
| | O(2) | H(O4) | O(4) | 1·737 (6) | 0·975 (6) | 2·610 (4) | 147·1 (5) |
| | O(1) | H(O2) | O(2) | 2·121 (6) | 0·977 (6) | 2·579 (4) | 106·8 (4) |
| | Intermolecular | | | | | | |
| | O(0) | H′(*W*) | O(*W*) | 1·783 (6) | 0·956 (7) | 2·726 (5) | 168·1 (6) |
| | O(0) | H(O5) | O(5) | 1·834 (6) | 0·963 (6) | 2·776 (4) | 165·3 (5) |
| | O(0) | H(O6) | O(6) | 2·001 (6) | 0·946 (6) | 2·938 (4) | 171·0 (5) |
| | O(1) | H(O3) | O(3) | 1·666 (5) | 0·973 (5) | 2·639 (4) | 177·3 (5) |
| | O(1) | H(*W*) | O(*W*) | 2·102 (7) | 0·942 (7) | 3·029 (5) | 167·8 (6) |
| | O(5) | H(O2) | O(2) | 1·982 (6) | 0·977 (6) | 2·872 (4) | 150·4 (5) |
| *B* Form | | | | | | | |
| | Intermolecular | | | | | | |
| | O(0) | H(O6) | O(6) | 1·805 (7) | 0·965 (7) | 2·745 (5) | 164·2 (6) |
| | O(0) | H′(*W*) | O(*W*) | 1·817 (7) | 0·966 (7) | 2·784 (5) | 178·0 (6) |
| | O(0) | H(*W*) | O(*W*) | 1·887 (7) | 0·961 (7) | 2·844 (5) | 173·2 (6) |
| | O(5) | H(O3) | O(3) | 1·974 (7) | 0·963 (7) | 2·894 (5) | 159·1 (6) |
| | O(5) | H(O2) | O(2) | 2·051 (7) | 0·951 (7) | 2·874 (5) | 143·9 (5) |
| | O(6) | H(O4) | O(4) | 1·809 (7) | 0·975 (7) | 2·783 (5) | 178·0 (6) |
| | O(*W*) | H(O5) | O(5) | 1·915 (7) | 0·972 (7) | 2·885 (5) | 176·2 (6) |

in Fig. 3(*b*). These are two of the three strongest hydrogen bonds in the structure; H···O, 1·67, 1·83 Å, with angles 177, 165°; and they must also be important factors contributing to the stabilization of the straight-chain conformation. A third hydrogen bond from O(6)H, which is somewhat weaker, H···O, 2·00 Å, completes the cross-linking of the gluconate ions in the lattice. In summary, a strong hydrogen-bond system forms the framework by which the gluconate ions cohere. The cations are in voids between the puckered sheets of hydrogen-bonded anions, and appear to have a somewhat secondary role in determining the structure. The details of the cation coordination are given in Table 6. Interestingly, the cations are as far removed as possible from the carboxylate oxygens, which are not included in the first cationic coordination shell. The eight nearest K···O distances include O(3), O(4) twice, O(5), O(6) and two water oxygens, at distances ranging from 2·61 to 3·24 Å. The fact that the charge on the gluconate ions is, at least formally, located on the carboxylate group would not be deduced from observing this structure.



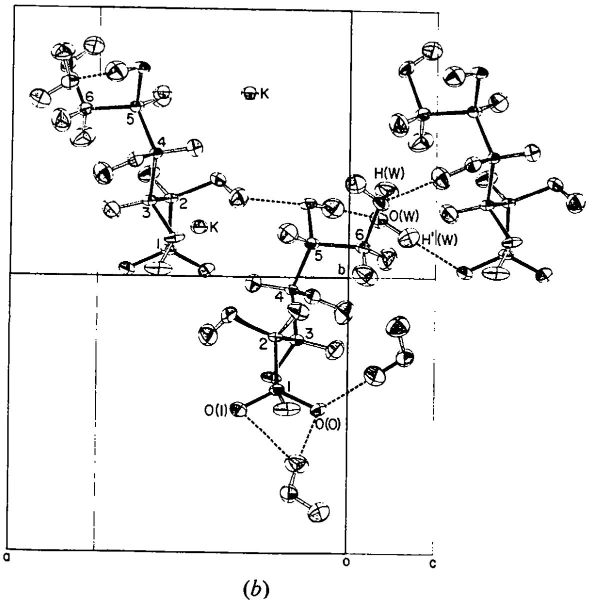


Fig. 4. View of the crystal structure of the *B* form of potassium D-gluconate monohydrate. (*a*) Projection down **b**. (*b*) Projection down **c***.

Table 6. *Cation coordination in potassium* D-*gluconate monohydrate*

The Roman numerals are a key to Fig. 5. The first number in square brackets indicates the symmetry operation given below followed by three numbers for the lattice translation.

*A*-form

1: $x,\ y,\ z$
2: $\frac{1}{2}-x,\ -y,\ \frac{1}{2}+z$
3: $\frac{1}{2}+x,\ \frac{1}{2}-y,\ -z$

*B*-form

1: $x,\ y,\ z$
2: $-x,\ \frac{1}{2}+y,\ -z$

| *A*-form | | *B*-form | |
|---|---|---|---|
| K–O(3)I[3·$\bar{1}$00] | 2·612 (5) Å | K–O(1)I[2·100] | 2·685 (6) Å |
| K–O(4)I[1·000] | 2·727 (5) | K–O(2)I[1·000] | 2·751 (6) |
| K–O(*W*)I[3·$\bar{1}$00] | 2·738 (5) | K–O(1)II[1·010] | 2·754 (6) |
| K–O(6)I[3·$\bar{1}$01] | 2·830 (5) | K–O(3)[2·101] | 2·829 (6) |
| K–O(4)II[3·$\bar{1}$00] | 3·022 (5) | K–O(*W*)[1·00$\bar{1}$] | 2·838 (6) |
| K–O(5)II[3·$\bar{1}$01] | 3·025 (5) | K–O(4)I[2·101] | 2·881 (6) |
| K–O(*W*)II[1·000] | 3·076 (5) | K–O(4)II[1·00$\bar{1}$] | 2·980 (6) |
| K–O(6)II[1·00$\bar{1}$] | 3·239 (5) | K–O(2)II[2·100] | 3·003 (6) |
| | | K–O(5)[1·00$\bar{1}$] | 3·338 (6) |

The crystal structure of the *B* form is shown in Fig. 4. Because of the bent conformation of the anions it appears to be more complex, but in fact it conforms more closely to what might be expected for an organic salt structure. Again the water molecules form part of an infinite chain of hydrogen bonds which, in this case, includes only one of the carboxylate oxygens, O(0). This hydrogen-bond chain forms a spiral in the *b* axis direction, to which the gluconate hydroxyls are linked by short segments of hydrogen bonds, as shown schematically below.

$$\begin{tikzcd}
& & O(2) \arrow[r] & O(5) \arrow[d] & O(3) \arrow[l] & & \\
{} & O(W) \arrow[l] \arrow[r] & O(0) & O(W) \arrow[l] \arrow[r] & O(0) & O(W) \arrow[l] \arrow[r] & {} \\
& & & & O(6) \arrow[u] & O(4) \arrow[l] &
\end{tikzcd}$$

The cations form a zigzag linear array close to the twofold screw axis at $x=\frac{1}{2}$ [see Fig. 4(*a*)]. The water oxygens, O(1) of the carboxylate group and four of the hydroxyls, O(2)H, O(3)H, O(4)H and O(5)H, form an irregular channel around these rows of cations. The eightfold coordination of each K$^+$ consists of O(*W*), O(1) twice, O(2) twice, O(4) twice, with K$^+\cdots$O distances ranging from 2·68 to 3·00 Å. There is a ninth nearest neighbor, O(5) at 3·34 Å. In contrast to the *A* form, one carboxylate oxygen O(1) is the closest atom to the K$^+$ and is not involved in the hydrogen bonding. [The nearest hydrogen to O(1) is a water hydrogen at 2·32 Å, which might be regarded as a weak interaction, except for the O(1)–H(*W*)–O(*W*) angle of 123°.] The C–O(1) distance is 0·031 Å shorter than C–O(0), the oxygen of which accepts three hydrogen bonds. This is consistent with the trend noted above for form *A*. The coordination polyhedra of the K$^+$ ions are shown in Fig. 5; they are distorted dodecahedra of type number 14 in the catalogue of Britton & Dunitz (1973).

The ionic coordination in *B* is stronger than that in *A*; 8 *versus* 7 with a cut-off at 3·1 Å, or 9 *versus* 8 with a cut-off at 3·3 Å, as shown in Table 6. The mean value for the eight nearest neighbors is 2·85 Å in *B* compared with 2·91 Å in *A*.

It is pertinent to ask why such conformational dimorphism, involving the presence or absence of intramolecular hydrogen bonding, has not been observed in any of the 11 alditol structures that have been studied, which included three polymorphic forms of mannitol (Kim, Jeffrey & Rosenstein, 1968; Berman, Jeffrey & Rosenstein, 1968). The explanation may lie in the observation that the sugar alcohols are hydrogen bonded intermolecularly so that, in general, each hydroxyl both donates and accepts hydrogen bonds. In the aldonate salts, this is not possible because of competition from the K$^+\cdots$O interactions. As many as possible of the hydrogen-bond acceptor directions, *i.e.* the lone pairs, of the hydroxyls are directed toward the cations, thereby pointing towards regions of the structure where hydrogens tend to be excluded. In addition, the carboxylate groups compete with the hydroxyls as hydrogen-bond acceptors. In form *A*, for example, the hydrogen bonding to the carboxylate group further stabilizes the extended conformation by 'chelating' across O(3) and O(5) of the same molecule, as shown most clearly in Fig. 3(*b*). In consequence, only two of the five hydroxyls accept hydrogen bonds in these gluconate structures. It can be argued, therefore, that the presence of both the cations and the carboxylate oxygens inhibits the formation of the most energetically favorable system of donor–acceptor intermolecular

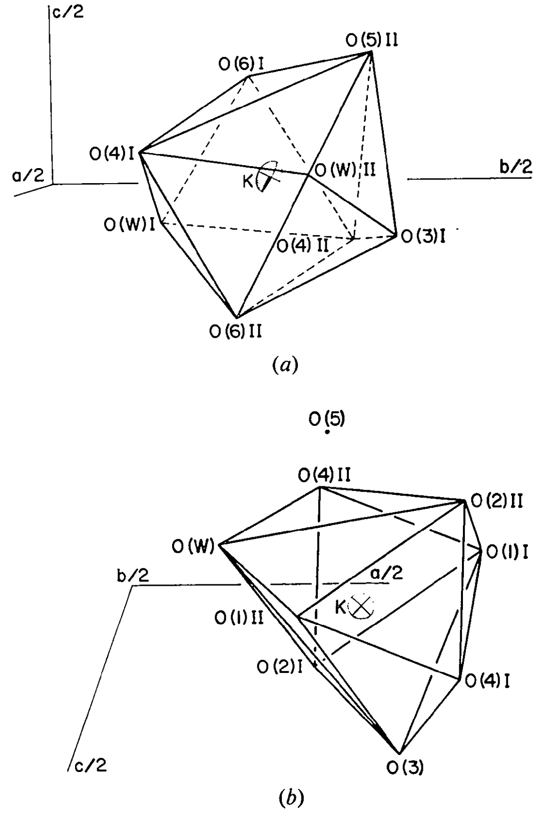


Fig. 5. The coordination polyhedra of the K$^+$ ions in potassium D-gluconate monohydrate. (*a*) Form *A*. (*b*) Form *B*.

hydrogen bonds between hydroxyls, as observed in the alditols, thereby permitting other alternatives which may involve conformational changes as in this pair of structures.

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# Aza Analogs of Nucleic Acid Constituents.
# IV. The Crystal and Molecular Structure of 6-Azauracil

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The crystal and molecular structure of 6-azauracil, $C_3N_3O_2H_3$, has been determined from three-dimensional X-ray data obtained on an automatic four-circle diffractometer equipped with a graphite monochromator and Mo $K\alpha$ radiation. The material crystallizes in space group $P2_12_12_1$ of the orthorhombic system with four molecules in a cell of dimensions $a=4{\cdot}875$ (4), $b=17{\cdot}611$ (15), and $c=5{\cdot}022$ (3) Å; the observed and calculated densities are 1·73 (2) and 1·74 g cm$^{-3}$, respectively. The structure has been refined by full-matrix least-squares techniques using 714 independent data to a conventional $R$ index of 0·037. The azapyrimidine ring is roughly planar, with all possible donor and acceptor atoms except N(6) participating in intermolecular hydrogen bonding. This latter feature is in contrast to the structure of uracil, in which only one of the oxygen atoms participates in hydrogen bonding. Consequently, in 6-azauracil the C–O bond lengths are equal (1·224 Å) while in uracil they are markedly unequal. The effect on the ring geometry of the substitution of N(6) for C(6)–H is discussed.

## Introduction

Many aza analogs of purines, pyrimidines and their nucleosides are anti-neoplastic and fungistatic agents (Skoda, 1963; Roblin, Lampen, English, Cole & Vaughan, 1945). Biological effects of 6-azauracil have been investigated extensively. It has been shown to inhibit animal tumors (Schindler & Welch, 1957) and