

# Potassium sodium (2*R*,3*R*)-tartrate tetrahydrate: the paraelectric phase of Rochelle salt at 105 K

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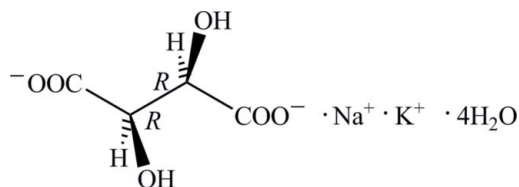
Received 7 February 2008; accepted 25 February 2008

 Key indicators: single-crystal X-ray study;  $T = 105$  K; mean  $\sigma(\text{C}-\text{C}) = 0.001$  Å;  $R$  factor = 0.030;  $wR$  factor = 0.069; data-to-parameter ratio = 51.5.

Rochelle salt,  $\text{K}^+\cdot\text{Na}^+\cdot\text{C}_4\text{H}_4\text{O}_6^{2-}\cdot 4\text{H}_2\text{O}$ , is known for its remarkable ferroelectric state between 255 and 297 K. The current investigation, based on data collected at 105 K, provides very accurate structural information for the low-temperature paraelectric form. Unlike the ferroelectric form, there is only one tartrate molecule in the asymmetric unit, and the structure displays no disorder to large anisotropic atomic displacements.

## Related literature

For previous and related structures, see: Beevers & Hughes (1941); Iwata *et al.* (1989); Solans *et al.* (1997); Ottenz *et al.* (1998); Hinazumi & Mitsui (1972); Kay (1978); Kuroda & Mason (1981); Brožek & Stadnicka (1994); Suzuki *et al.* (1996*a,b*); Ambady & Kartha (1968); Boese *et al.* (1995). For irradiation studies, see: Suzuki (1974); Treeck, van & Windsch (1977). For a description of the Cambridge Structural Database, see: Allen (2002).



## Experimental

### Crystal data

 $\text{K}^+\cdot\text{Na}^+\cdot\text{C}_4\text{H}_4\text{O}_6^{2-}\cdot 4\text{H}_2\text{O}$   
 $M_r = 282.23$   
 Orthorhombic,  $P2_12_12$   
 $a = 11.7859$  (6) Å  
 $b = 14.1972$  (7) Å  
 $c = 6.1875$  (3) Å

 $V = 1035.33$  (9) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.60$  mm<sup>-1</sup>  
 $T = 105$  (2) K  
 0.5 mm (radius)

### Data collection

 Siemens SMART CCD diffractometer  
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)  
 $T_{\min} = 0.398$ ,  $T_{\max} = 0.551$   
 (expected range = 0.722–1.000)

 33523 measured reflections  
 10040 independent reflections  
 8947 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.037$ 

### Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.029$   
 $wR(F^2) = 0.069$   
 $S = 1.06$   
 10040 reflections  
 195 parameters  
 12 restraints

 All H-atom parameters refined  
 $\Delta\rho_{\text{max}} = 0.50$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.73$  e Å<sup>-3</sup>  
 Absolute structure: Flack, 1983,  
 4266 Friedel pairs  
 Flack parameter: 0.044 (14)

**Table 1**

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O5—H5...O2	0.789 (17)	2.031 (16)	2.5946 (6)	128.2 (14)
O6—H6...O4W <sup>i</sup>	0.861 (16)	1.968 (16)	2.8119 (7)	166.5 (16)
O1W—H11W...O6	0.824 (8)	1.960 (8)	2.7832 (6)	176.8 (15)
O1W—H12W...O4 <sup>ii</sup>	0.843 (9)	2.010 (9)	2.8500 (7)	174.8 (18)
O2W—H21W...O3 <sup>iii</sup>	0.868 (9)	1.830 (9)	2.6941 (7)	173.4 (19)
O2W—H22W...O2 <sup>iv</sup>	0.862 (9)	1.890 (9)	2.7505 (7)	175.5 (19)
O3W—H31W...O6 <sup>v</sup>	0.843 (9)	2.391 (15)	3.1029 (7)	142.5 (19)
O3W—H31W...O2 <sup>vi</sup>	0.843 (9)	2.499 (17)	3.1181 (7)	131.0 (17)
O3W—H31W...O3 <sup>v</sup>	0.843 (9)	2.584 (14)	3.1569 (8)	126.2 (15)
O3W—H32W...O4 <sup>vii</sup>	0.862 (8)	1.926 (8)	2.7842 (8)	173.8 (16)
O4W—H41W...O1 <sup>viii</sup>	0.858 (9)	1.888 (10)	2.7124 (6)	160.4 (19)
O4W—H42W...O3W <sup>iv</sup>	0.836 (8)	1.939 (9)	2.7532 (8)	164.4 (16)

 Symmetry codes: (i)  $-x + \frac{1}{2}, y + \frac{1}{2}, -z + 1$ ; (ii)  $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$ ; (iii)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + 2$ ; (iv)  $x, y, z + 1$ ; (v)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + 1$ ; (vi)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z$ ; (vii)  $-x, -y, z - 1$ ; (viii)  $-x, -y, z$ .

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINTE-Plus* (Bruker, 2001); data reduction: *SAINTE-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

The purchase of the Siemens SMART CCD diffractometer was made possible through support from the Research Council of Norway (NFR)

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BG2163).

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# metal-organic compounds

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## supporting information

*Acta Cryst.* (2008). E64, m507–m508 [doi:10.1107/S1600536808005266]

## Potassium sodium (2*R*,3*R*)-tartrate tetrahydrate: the paraelectric phase of Rochelle salt at 105 K

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### S1. Comment

The radiation-induced free radical chemistry of dicarboxylic acids and their salts has received attention for several decades. The Rochelle salt, is of particular interest as it exhibits a ferroelectric phase between 255 and 297 K, where the structure is monoclinic, space group  $P2_1$ ; outside this temperature range the compound is paraelectric and presents orthorhombic phases in space group  $P2_12_12$ . The nature of the radicals formed in Rochelle salt is currently investigated in order to understand the mechanisms producing changes in the ferroelectric properties of this compound upon irradiation (Suzuki, 1974; Treeck, van & Windsch, 1977). For the analysis of the electron magnetic resonance data, precise knowledge of the low-temperature orthorhombic form is necessary. Structural data for the high-temperature orthorhombic form were first provided by Beevers & Hughes (1941). Iwata *et al.* (1989) carried out a neutron diffraction study for both orthorhombic forms; more accurate X-ray diffraction studies were later presented by Solans *et al.* (1997), who concluded that differences between the two  $P2_12_12$  states are "small but significant". None of these structures are, however, available in the Cambridge Structural Database (Version 5.29 of November 2007; Allen, 2002). A high-precision redetermination of Rochelle salt at low temperature has therefore been executed.

The molecular structure of (I) is shown in Fig. 1. The crystal packing arrangement, illustrated in Fig. 2, is very similar to those found in the  $P2_12_12$  structures of other salts of tartaric acid in which  $\text{Na}^+$  is replaced by  $\text{Li}^+$  and/or  $\text{K}^+$  by  $\text{NH}_4^+$  or  $\text{Tl}^+$  [ $\text{Li}^+/\text{K}^+$ : Ottenz *et al.*, 1998;  $\text{Li}^+/\text{NH}_4^+$ : Hinazumi & Mitsui, 1972;  $\text{Li}^+/\text{Tl}^+$ : Kay, 1978;  $\text{Na}^+/\text{NH}_4^+$  (II): Kuroda & Mason, 1981; Brożek & Stadnicka, 1994; Suzuki *et al.*, 1996*a*] as well as in salts where  $\text{K}^+$  has been only partly replaced by  $\text{NH}_4^+$  (Suzuki *et al.*, 1996*a*; Suzuki *et al.*, 1996*b*). The pure sodium (Ambady & Kartha, 1968) or potassium salts (Boese *et al.*, 1995) on the other hand, have completely different structures.

Hydrogen bonds are listed in Table 1, the most unusual feature is the almost symmetric four-center interaction involving H31W.

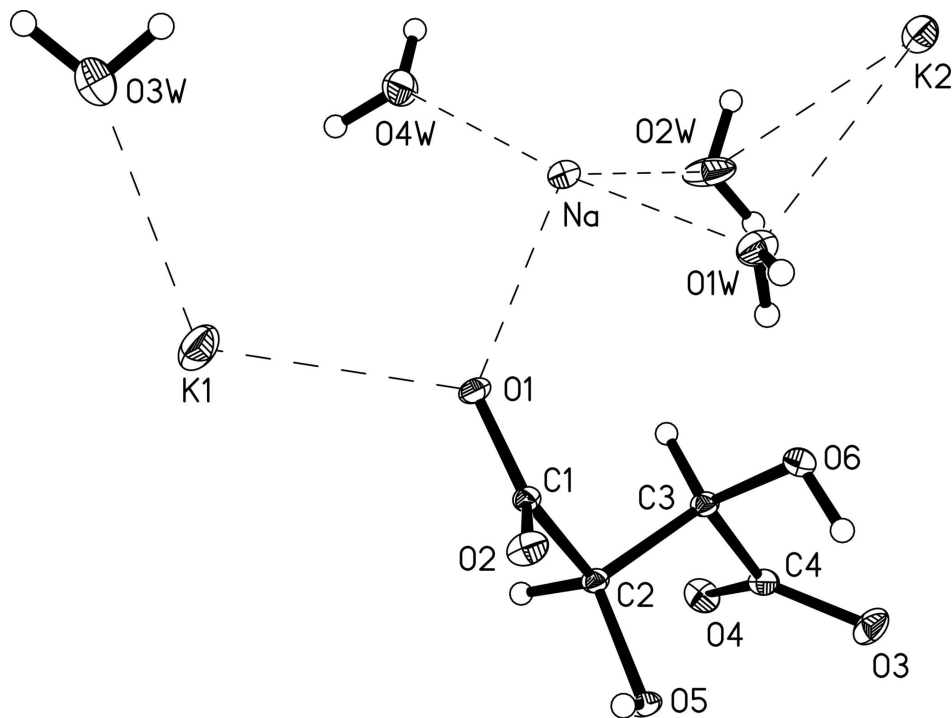
When  $\text{K}^+$  is replaced by  $\text{NH}_4^+$  [as, for instance, in II] the four shortest  $\text{K2}\cdots\text{O}$  contacts are converted into hydrogen bonds, while only the two  $\text{K1}\cdots\text{O4}$  interactions are transformed into short hydrogen bonds, the  $\text{K1}\cdots\text{O1W}$  and  $\text{K1}\cdots\text{O2W}$  contacts being replaced by a three-center hydrogen bond.

### S2. Experimental

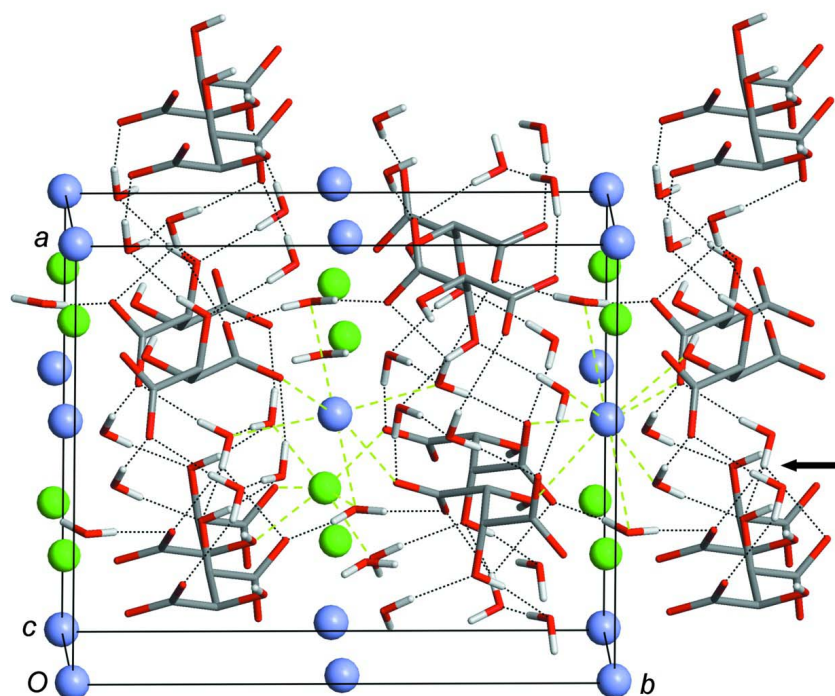
Rochelle salt was obtained from Sigma-Aldrich and tetrahydrate crystals were grown from saturated aqueous solutions. A large block-shaped specimen was ground into a sphere in a mill and used for data collection.

### S3. Refinement

Full isotropic refinement was carried out for all H atoms.

**Figure 1**

The molecular structure of (I). Displacement ellipsoids are shown at the 50% probability level. Metal coordination has been indicated by dashed lines.

**Figure 2**

Crystal packing arrangement viewed approximately along the  $c$  axis. H atoms bonded to C have been left out for clarity.  $\text{Na}^+$  is yellow,  $\text{K}^+$  is light blue with K1 at the centre of the unit cell and K2 at the cell edge. Hydrogen bonds are shown as black dotted lines while ligand coordination is indicated in orange for three selected metal ions. The arrow points to H31W, which is involved in a four-center hydrogen bond.

### Potassium sodium (2*R*,3*R*)-tartrate tetrahydrate

#### Crystal data

$\text{K}^+\cdot\text{Na}^+\cdot\text{C}_4\text{H}_4\text{O}_6^{2-}\cdot 4\text{H}_2\text{O}$

$M_r = 282.23$

Orthorhombic,  $P2_12_12$

$a = 11.7859$  (6) Å

$b = 14.1972$  (7) Å

$c = 6.1875$  (3) Å

$V = 1035.33$  (9) Å<sup>3</sup>

$Z = 4$

$F(000) = 584$

$D_x = 1.811$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 10000 reflections

$\theta = 2.9\text{--}49.7^\circ$

$\mu = 0.60$  mm<sup>-1</sup>

$T = 105$  K

Sphere, colourless

0.5 mm (radius)

#### Data collection

Siemens SMART CCD  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 8.3 pixels mm<sup>-1</sup>

sets of exposures each taken over  $0.3^\circ$   $\omega$   
rotation scans

Absorption correction: multi-scan  
(*SADABS*; Sheldrick, 1996)

$T_{\min} = 0.398$ ,  $T_{\max} = 0.551$

33523 measured reflections

10040 independent reflections

8947 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.037$

$\theta_{\max} = 49.7^\circ$ ,  $\theta_{\min} = 2.9^\circ$   
 $h = -25 \rightarrow 25$

$k = -28 \rightarrow 30$   
 $l = -12 \rightarrow 12$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.029$

$wR(F^2) = 0.069$

$S = 1.06$

10040 reflections

195 parameters

12 restraints

Primary atom site location: structure-invariant  
 direct methods

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0324P)^2 + 0.0088P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 0.50 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.73 \text{ e } \text{\AA}^{-3}$

Extinction correction: *SHELXTL* (Bruker,  
 2000),  $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.132 (3)

Absolute structure: Flack, 1983, 4266 Friedel  
 pairs

Absolute structure parameter: 0.044 (14)

*Special details*

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Data were collected by measuring six sets of exposures with the detector set at  $2\theta = 29^\circ$  and  $65^\circ$ , crystal-to-detector distance 5.00 cm. Refinement of  $F^2$  against ALL reflections.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
K1	0.0000	0.0000	0.04255 (4)	0.02054 (4)
K2	0.5000	0.0000	0.83902 (3)	0.01318 (3)
Na	0.23248 (2)	-0.007143 (18)	0.51526 (4)	0.01041 (4)
O1	0.12000 (3)	0.10859 (3)	0.34799 (7)	0.01016 (5)
O2	0.21269 (4)	0.20379 (3)	0.11755 (7)	0.01211 (6)
O3	0.22830 (4)	0.40729 (3)	0.82011 (8)	0.01585 (7)
O4	0.04765 (4)	0.35891 (3)	0.84893 (8)	0.01439 (7)
O5	0.16547 (4)	0.35790 (3)	0.32421 (7)	0.01060 (5)
H5	0.1932 (12)	0.3393 (11)	0.216 (3)	0.021 (3)*
O6	0.29638 (3)	0.24888 (3)	0.63394 (7)	0.01132 (6)
H6	0.3284 (13)	0.2989 (11)	0.584 (3)	0.025 (3)*
C1	0.15538 (4)	0.18798 (3)	0.28320 (8)	0.00798 (6)
C2	0.12505 (4)	0.27375 (3)	0.42269 (8)	0.00802 (6)
H2	0.0351 (13)	0.2714 (11)	0.429 (3)	0.024 (3)*
C3	0.17752 (4)	0.26353 (3)	0.64784 (8)	0.00867 (6)
H3	0.1368 (13)	0.2117 (11)	0.726 (3)	0.027 (4)*
C4	0.14865 (5)	0.35032 (4)	0.78496 (9)	0.01035 (6)
O1W	0.39615 (4)	0.08350 (3)	0.48487 (8)	0.01405 (7)
H11W	0.3642 (12)	0.1317 (8)	0.527 (2)	0.023 (3)*
H12W	0.4433 (14)	0.0974 (13)	0.388 (3)	0.058 (6)*
O2W	0.23689 (6)	0.04149 (3)	0.87925 (8)	0.02083 (10)
H21W	0.2524 (16)	0.0009 (10)	0.980 (2)	0.045 (5)*
H22W	0.2331 (16)	0.0930 (8)	0.953 (3)	0.044 (5)*

O3W	0.05896 (4)	-0.19201 (4)	-0.03036 (10)	0.01860 (8)
H31W	0.1210 (11)	-0.2072 (13)	0.028 (3)	0.051 (6)*
H32W	0.0307 (13)	-0.2458 (8)	-0.066 (3)	0.037 (5)*
O4W	0.07835 (4)	-0.10799 (4)	0.57031 (9)	0.01684 (8)
H41W	0.0099 (9)	-0.1009 (14)	0.526 (3)	0.054 (6)*
H42W	0.0734 (12)	-0.1431 (10)	0.6784 (19)	0.026 (4)*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
K1	0.02786 (8)	0.01565 (7)	0.01810 (8)	-0.00967 (7)	0.000	0.000
K2	0.01563 (5)	0.01227 (5)	0.01164 (6)	-0.00229 (5)	0.000	0.000
Na	0.01174 (8)	0.00770 (8)	0.01179 (9)	-0.00031 (6)	-0.00041 (6)	0.00065 (7)
O1	0.01294 (12)	0.00587 (11)	0.01166 (15)	-0.00070 (9)	-0.00034 (11)	0.00031 (10)
O2	0.01710 (14)	0.00966 (13)	0.00956 (15)	-0.00019 (11)	0.00367 (11)	-0.00079 (10)
O3	0.02292 (18)	0.01090 (15)	0.01373 (18)	-0.00454 (13)	-0.00006 (14)	-0.00398 (12)
O4	0.01600 (14)	0.01549 (16)	0.01168 (16)	0.00482 (12)	0.00046 (12)	-0.00285 (13)
O5	0.01694 (14)	0.00605 (12)	0.00880 (14)	-0.00054 (10)	-0.00024 (11)	0.00062 (9)
O6	0.01094 (12)	0.00955 (13)	0.01345 (16)	0.00182 (10)	-0.00145 (10)	0.00072 (11)
C1	0.01007 (13)	0.00605 (13)	0.00782 (15)	0.00050 (11)	-0.00097 (11)	-0.00050 (10)
C2	0.01034 (13)	0.00591 (13)	0.00780 (16)	0.00042 (11)	-0.00044 (11)	-0.00038 (10)
C3	0.01152 (13)	0.00669 (14)	0.00780 (16)	0.00042 (11)	-0.00063 (12)	-0.00042 (11)
C4	0.01571 (16)	0.00818 (15)	0.00715 (16)	0.00110 (13)	-0.00097 (13)	-0.00082 (11)
O1W	0.01351 (14)	0.01088 (14)	0.01774 (19)	-0.00051 (11)	0.00272 (12)	0.00068 (12)
O2W	0.0434 (3)	0.00952 (15)	0.00958 (18)	0.00494 (17)	0.00155 (17)	-0.00014 (11)
O3W	0.01445 (15)	0.0230 (2)	0.0183 (2)	0.00034 (14)	-0.00277 (14)	0.00046 (16)
O4W	0.01251 (14)	0.01583 (17)	0.0222 (2)	-0.00316 (12)	-0.00284 (13)	0.00420 (15)

*Geometric parameters (Å, °)*

K1—O1	2.8194 (4)	O2—C1	1.2479 (6)
K1—O1 <sup>i</sup>	2.8194 (4)	O3—C4	1.2581 (7)
K1—O3W <sup>i</sup>	2.8491 (6)	O4—C4	1.2604 (7)
K1—O3W	2.8491 (6)	O5—C2	1.4232 (6)
K1—O2W <sup>ii</sup>	3.0271 (7)	O5—H5	0.789 (17)
K1—O2W <sup>iii</sup>	3.0270 (7)	O6—C3	1.4188 (6)
K2—O1W	2.7758 (5)	O6—H6	0.861 (16)
K2—O1W <sup>iv</sup>	2.7758 (5)	C1—C2	1.5348 (7)
K2—O4 <sup>v</sup>	2.8383 (5)	C2—C3	1.5311 (7)
K2—O4 <sup>vi</sup>	2.8383 (5)	C2—H2	1.062 (15)
K2—O5 <sup>vii</sup>	2.9822 (4)	C3—C4	1.5342 (7)
K2—O5 <sup>viii</sup>	2.9822 (4)	C3—H3	1.004 (17)
K2—O2W	3.1662 (7)	O1W—H11W	0.824 (8)
K2—O2W <sup>iv</sup>	3.1662 (7)	O1W—H12W	0.843 (9)
Na—O1W	2.3264 (5)	O2W—H21W	0.868 (9)
Na—O4W	2.3379 (5)	O2W—H22W	0.862 (9)
Na—O1	2.3512 (5)	O3W—H31W	0.843 (9)
Na—O2W	2.3562 (6)	O3W—H32W	0.862 (8)

Na—O3 <sup>vii</sup>	2.4485 (6)	O4W—H41W	0.858 (9)
Na—O5 <sup>vii</sup>	2.4707 (5)	O4W—H42W	0.836 (8)
O1—C1	1.2668 (6)		
O2—C1—O1	126.74 (5)	C2—C3—C4	109.72 (4)
O2—C1—C2	116.44 (4)	O6—C3—H3	113.2 (9)
O1—C1—C2	116.82 (4)	C2—C3—H3	108.4 (10)
O5—C2—C3	109.50 (4)	C4—C3—H3	102.5 (10)
O5—C2—C1	110.32 (4)	O3—C4—O4	126.03 (5)
C3—C2—C1	110.02 (4)	O3—C4—C3	116.52 (5)
O5—C2—H2	112.1 (8)	O4—C4—C3	117.44 (5)
C3—C2—H2	111.5 (9)	H11W—O1W—H12W	109.6 (12)
C1—C2—H2	103.2 (9)	H21W—O2W—H22W	101.2 (11)
O6—C3—C2	110.95 (4)	H31W—O3W—H32W	102.7 (11)
O6—C3—C4	111.73 (4)	H41W—O4W—H42W	105.2 (11)
O2—C1—C2—O5	3.05 (6)	O5—C2—C3—C4	57.57 (5)
O1—C1—C2—O5	-177.09 (4)	C1—C2—C3—C4	178.98 (4)
O2—C1—C2—C3	-117.87 (5)	O6—C3—C4—O3	16.43 (7)
O1—C1—C2—C3	61.98 (5)	C2—C3—C4—O3	-107.06 (5)
O5—C2—C3—O6	-66.37 (5)	O6—C3—C4—O4	-164.68 (5)
C1—C2—C3—O6	55.04 (5)	C2—C3—C4—O4	71.84 (6)

Symmetry codes: (i)  $-x, -y, z$ ; (ii)  $-x, -y, z-1$ ; (iii)  $x, y, z-1$ ; (iv)  $-x+1, -y, z$ ; (v)  $x+1/2, -y+1/2, -z+2$ ; (vi)  $-x+1/2, y-1/2, -z+2$ ; (vii)  $-x+1/2, y-1/2, -z+1$ ; (viii)  $x+1/2, -y+1/2, -z+1$ .

#### Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O5—H5 $\cdots$ O2	0.789 (17)	2.031 (16)	2.5946 (6)	128.2 (14)
O6—H6 $\cdots$ O4W <sup>x</sup>	0.861 (16)	1.968 (16)	2.8119 (7)	166.5 (16)
O1W—H11W $\cdots$ O6	0.82 (1)	1.96 (1)	2.7832 (6)	177 (2)
O1W—H12W $\cdots$ O4 <sup>viii</sup>	0.84 (1)	2.01 (1)	2.8500 (7)	175 (2)
O2W—H21W $\cdots$ O3 <sup>vi</sup>	0.87 (1)	1.83 (1)	2.6941 (7)	173 (2)
O2W—H22W $\cdots$ O2 <sup>x</sup>	0.86 (1)	1.89 (1)	2.7505 (7)	176 (2)
O3W—H31W $\cdots$ O6 <sup>vii</sup>	0.84 (1)	2.39 (2)	3.1029 (7)	143 (2)
O3W—H31W $\cdots$ O2 <sup>xi</sup>	0.84 (1)	2.50 (2)	3.1181 (7)	131 (2)
O3W—H31W $\cdots$ O3 <sup>vii</sup>	0.84 (1)	2.58 (1)	3.1569 (8)	126 (2)
O3W—H32W $\cdots$ O4 <sup>ii</sup>	0.86 (1)	1.93 (1)	2.7842 (8)	174 (2)
O4W—H41W $\cdots$ O1 <sup>i</sup>	0.86 (1)	1.89 (1)	2.7124 (6)	160 (2)
O4W—H42W $\cdots$ O3W <sup>x</sup>	0.84 (1)	1.94 (1)	2.7532 (8)	164 (2)

Symmetry codes: (i)  $-x, -y, z$ ; (ii)  $-x, -y, z-1$ ; (vi)  $-x+1/2, y-1/2, -z+2$ ; (vii)  $-x+1/2, y-1/2, -z+1$ ; (viii)  $x+1/2, -y+1/2, -z+1$ ; (ix)  $-x+1/2, y+1/2, -z+1$ ; (x)  $x, y, z+1$ ; (xi)  $-x+1/2, y-1/2, -z$ .