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Sodium hydrogensquarate monohydrate

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Key indicators

Single-crystal X-ray study
T = 290 K
Mean σ(C–C) = 0.009 Å
R factor = 0.058
wR factor = 0.145
Data-to-parameter ratio = 8.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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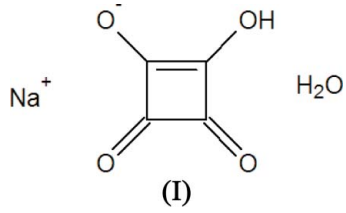
In the title compound, sodium 2-hydroxy-3,4-dioxocyclobut-1-en-1-olate monohydrate, $Na^+\cdot C_4HO_4^-\cdot H_2O$, the Na atom is six-coordinated by the O atoms from four hydrogensquarate anions and two water molecules. The three-dimensional packing is stabilized by a system of hydrogen bonds.

Comment

The structure determination of the title compound, $NaHC_4O_4\cdot H_2O$, (I), was carried out in the course of our study of squaric acid derivatives (Kolev *et al.*, 2000, 2004, 2006), in which sodium hydrogensquarate was used in the syntheses of new phases. Peters *et al.* (1978) discussed the influence of hydrogen bonding on squarate anion configuration based on the crystal structures of nine squarate salts. They reported the space-group symmetry and unit-cell parameters of (I), although atomic parameters were not published. For the related compound $Na_2C_4O_4\cdot 3H_2O$, (II), crystal structures of triclinic (Ranganathan *et al.*, 2002) and monoclinic (Busetti *et al.*, 1997) polymorphs have been reported.



(I)

In (I), the Na atom is six-coordinated by four organic and two water molecules, forming an octahedron (Fig. 1) with Na—O distances (Table 1) similar to those observed in the polymorphs of (II). Neighboring sodium polyhedra share edges, forming infinite chains along the *a* axis. A similar arrangement of the sodium polyhedra is found in the poly-

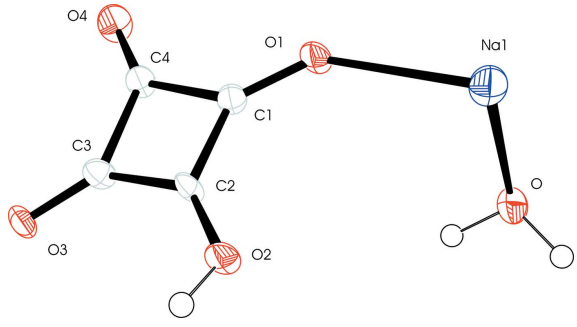


Figure 1
View of the asymmetric unit of (I), with the atom-numbering scheme, showing 50% probability displacement ellipsoids.

morphs of (II). The hydrogensquarate anions are hydrogen-bonded to each other and build zigzag chains running parallel to the *c* axis. The water molecule supplements sodium coordination polyhedra formation and takes part in the stabilization of the three-dimensional packing though the formation of a hydrogen-bonded network (Fig. 2).

The presence of one water molecule and its strong bonding in the structure were confirmed by differential thermal analysis (DTA) and thermogravimetry (TG) (Fig. 3). The endothermal effect at 441 K on the DTA curve corresponds to a weight lose of 10.8% on the TG curve. This amount indicates the release of exactly one water molecule from the asymmetric unit of the structure.

Experimental

The title compound was prepared by addition of an aqueous solution of sodium carbonate to an aqueous solution of squaric acid in a 1:2 molar ratio at 338 K. Colorless crystals were obtained by slow evaporation of the solution. DTA–TG analyses were performed on Stantan Redcroft STA 780 apparatus under the following conditions: temperature heating rate 10 K min^{-1}, argon atmosphere and Al_2O_3 as a reference material.

Crystal data

$Na^+\cdot C_4HO_4^-\cdot H_2O$
M_r = 154.05
Monoclinic, *Pc*
a = 3.6239 (10) Å
b = 8.1320 (11) Å
c = 9.392 (4) Å
β = 97.97 (3)°
V = 274.10 (14) Å^3
Z = 2
D_x = 1.867 Mg m^{-3}
Mo *K*α radiation
μ = 0.24 mm^{-1}
T = 290 (2) K
Prism, colorless
0.26 × 0.25 × 0.24 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1413 measured reflections
760 independent reflections
543 reflections with $I > 2\sigma(I)$
R_{int} = 0.077
θ_{max} = 29.9°
3 standard reflections
frequency: 120 min
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.145
S = 1.20
760 reflections
91 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0298P)^2 + 0.6752P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.43 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Na1—O^{i}	2.343 (6)	Na1—O4^{iii}	2.405 (6)
Na1—O	2.367 (6)	Na1—O1	2.474 (6)
Na1—O3^{ii}	2.393 (7)	Na1—O3^{iv}	2.691 (7)
O^{i}—Na1—O3^{ii}	171.3 (2)	Na1^{v}—O—Na1	100.6 (2)
O4^{iii}—Na1—O1	176.3 (3)	Na1^{vi}—O3—Na1^{vii}	90.7 (2)
O—Na1—O3^{iv}	176.3 (2)		

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

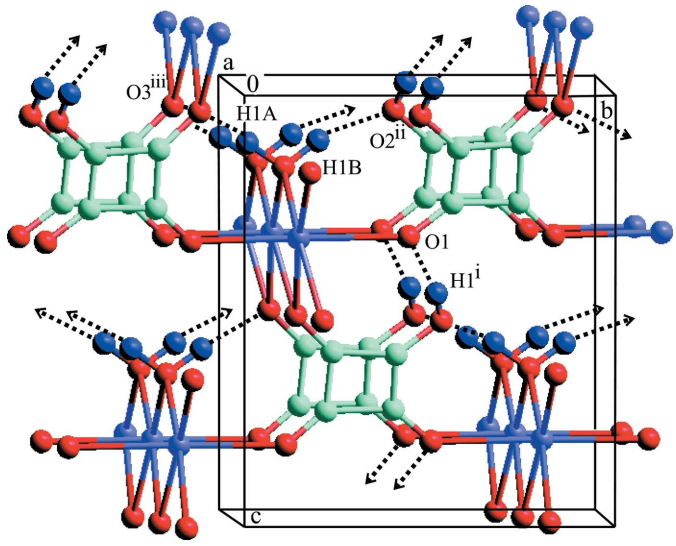


Figure 2
The packing in (I), with hydrogen bonds represented by dotted lines. [Symmetry codes: (i) $1+x, 1-y, \frac{1}{2}+z$; (ii) $1+x, y, z$; (iii) $1+x, -1+y, z$.]

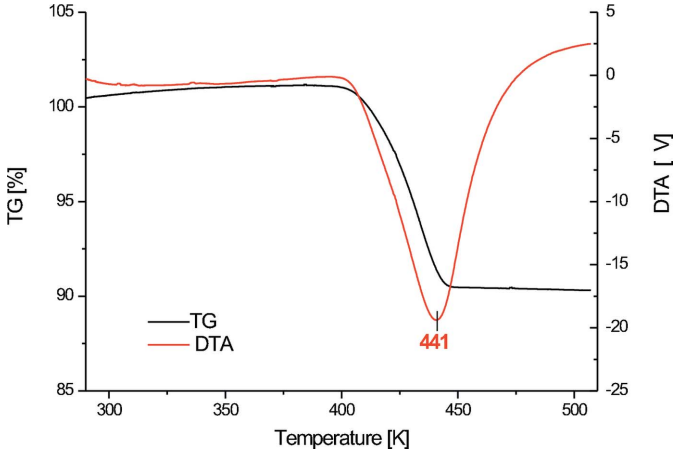


Figure 3
T G and DTA profiles of (I), showing the weight loss of 10.8 wt% in one step due to dehydration between 394 and 480 K.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H1···O1^{vi}	0.82	1.71	2.522 (7)	166
O—H1*B*···O2^{v}	0.97	1.86	2.803 (7)	163
O—H1*A*···O3^{viii}	0.97	1.84	2.794 (7)	165

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

The hydroxy H atom was located in a difference map. Water H atoms were placed in idealized positions (O—H = 0.97 Å). All H atoms were constrained to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(O).

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97*

(Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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