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Crystal structure of propane-1,3-diaminium squarate dihydrate

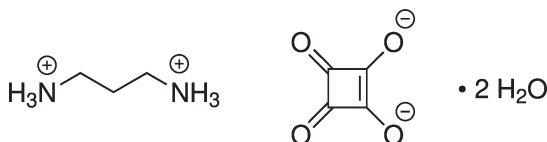
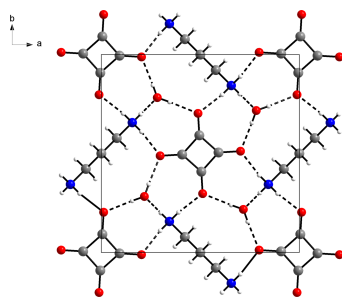
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Propane-1,3-diaminium squarate dihydrate, $C_3H_{12}N_2^{2+} \cdot C_4O_4^{2-} \cdot 2H_2O$, results from the proton-transfer reaction of propane-1,3-diamine with squaric acid and subsequent crystallization from aqueous medium. The title compound crystallizes in the tetragonal crystal system (space group $P4bm$) with $Z = 2$. The squarate dianion belongs to the point group D_{4h} and contains a crystallographic fourfold axis. The propane-1,3-diaminium dication exhibits a C_{2v} -symmetric all-*anti* conformation and resides on a special position with $mm2$ site symmetry. The orientation of the propane-1,3-diaminium ions makes the crystal structure polar in the *c*-axis direction. The solid-state supramolecular structure features a triperiodic network of strong hydrogen bonds of the N—H...O and O—H...O types.

1. Chemical context

Squaric acid ($H_2C_4O_4$; systematic name: 3,4-dihydroxycyclobut-3-ene-1,2-dione) and its derivatives have been widely studied in organic chemistry and materials science (Grus *et al.*, 2021; Laramie *et al.*, 2017; Wurm & Klok, 2013; Xia & Wang, 2017). Squaric acid analogues have also attracted attention in medicinal chemistry (Chasák *et al.*, 2021; Ruseva *et al.*, 2022). In structural chemistry, the interest in squaric acid and its mono- and dianions arises mainly from their planar, symmetrical and strained molecular structures and their diverse hydrogen-bonding patterns in the solid state (Allen *et al.*, 2013; Gilli *et al.*, 2001). As a strong diprotic organic acid with $pK_{a1} = 0.59 \pm 0.09$ and $pK_{a2} = 3.48 \pm 0.023$ at 298 K (as determined by potentiometric titrations; Schwartz & Howard, 1970), squaric acid readily forms proton-transfer compounds with nitrogen bases and a wide variety of structurally characterized examples can be found in the Cambridge Structural Database (CSD; Groom *et al.*, 2016). In the present contribution, we describe the crystal structure of the dihydrate of the proton-transfer compound propane-1,3-diaminium squarate.



2. Structural commentary

Fig. 1 shows the molecular structures of the components of the title compound in the crystal. The squarate dianion exhibits D_{4h} point-group symmetry and contains a crystallographic fourfold rotation axis with the direction $[001]$. The propane-

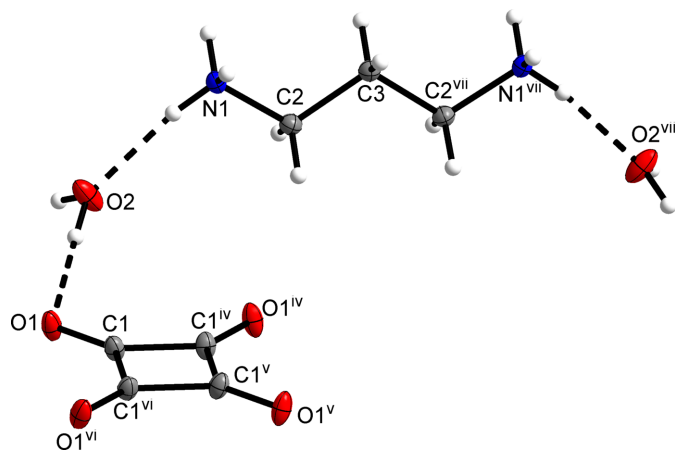


Figure 1
Displacement ellipsoid plot (50% probability level) of the title compound. Hydrogen atoms are shown by small spheres of arbitrary radius. Dashed lines represent hydrogen bonds. Symmetry codes: (iv) $y, -x, z$; (v) $-x, -y, z$; (vi) $-y, x, z$; (vii) $-x + 1, -y, z$;

1,3-diaminium dication adopts a C_{2v} -symmetric all-*anti* conformation and is located on a special position with $mm2$ site symmetry in the crystal structure. The overall orientation of the molecular dications renders the crystal structure polar in the c -axis direction. The water molecule of crystallization sits on a crystallographic mirror plane perpendicular to the $[110]$ direction.

3. Supramolecular features

Apart from ion–ion interactions between propane-1,3-diaminium dications and squarate dianions, hydrogen bonding dominates the solid-state structure of the title compound. The protonated amino group joins two squarate ions *via* $N-H\cdots O$ hydrogen bonds. The remaining hydrogen-bond donor site of the aminium group forms an $N-H\cdots O$ hydrogen bond to a water molecule (Fig. 2). The water mol-

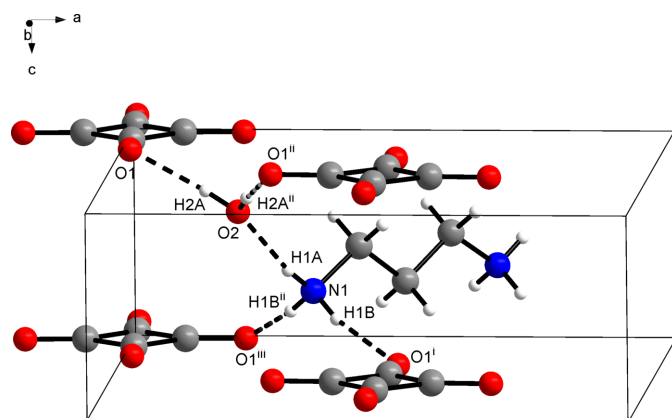


Figure 2
Section of the crystal structure of the title compound, viewed approximately along the $[010]$ direction. Dashed lines illustrate hydrogen bonds. Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, z + 1$; (ii) $-y + \frac{1}{2}, -x + \frac{1}{2}, z$; (iii) $y, -x, z + 1$.

Table 1
Hydrogen-bond geometry ($\text{\AA}, ^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1A\cdots O2$	0.85 (3)	1.92 (3)	2.758 (2)	171 (3)
$N1-H1B\cdots O1^i$	0.896 (19)	1.905 (18)	2.7887 (12)	168.4 (17)
$O2-H2A\cdots O1$	0.84 (2)	1.91 (2)	2.7413 (13)	175 (2)

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

ecule in turn acts as hydrogen-bond acceptor towards two squarate ions, which results in a triperiodic hydrogen-bond network (Fig. 3). Table 1 lists the corresponding hydrogen-bond parameters, which are characteristic of strong hydrogen bonds (Thakuria *et al.*, 2017). The centroid–centroid distance between the squarate ions in the $[001]$ direction corresponds to the c lattice parameter. A packing index of 67.8% (Kitajgorodskij, 1973), as calculated with *PLATON* (Spek, 2020), indicates a relatively open structure. This lends support to the view that strong hydrogen bonding governs the structure rather than van der Waals close packing.

4. Database survey

The CSD (version 5.43 with September 2022 updates; Groom *et al.*, 2016) contains >400 crystal structures with propane-1,3-diaminium cations and >100 crystal structures with squarate dianions. A structure closely related to the title compound is that of the homologous pentane-1,5-diaminium squarate dihydrate (CSD refcode: JARGAN; Ivanova & Spittler, 2014). In contrast to the title compound, the crystal structure of JARGAN is centrosymmetric, although the pentane-1,5-diaminium cation likewise exhibits a polar (approximately) C_{2v} -symmetric all-*anti* conformation. A solvent-free crystal structure of propane-1,3-diaminium bis(hydrogen squarate) has also been published (TURQEC; Mathew *et al.*, 2002). The

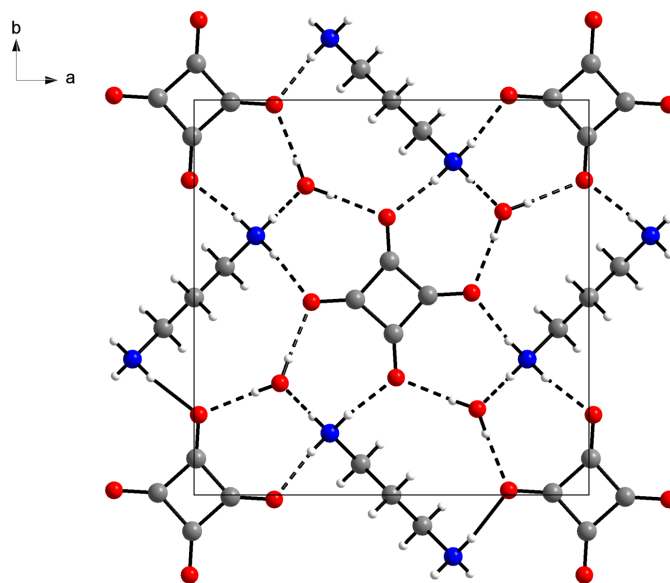


Figure 3
The tetragonal unit cell of the title compound, projected along the c -axis direction. Dashed lines illustrate hydrogen bonds. Colour scheme: C, grey; H, white; N, blue; O, red.

Table 2

Experimental details.

Crystal data	
Chemical formula	$C_3H_{12}N_2^{2+} \cdot C_4O_4^{2-} \cdot 2H_2O$
M_r	224.22
Crystal system, space group	Tetragonal, $P4bm$
Temperature (K)	105
a, c (Å)	11.2716 (2), 4.3310 (1)
V (Å ³)	550.25 (2)
Z	2
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.12
Crystal size (mm)	0.23 × 0.16 × 0.11
Data collection	
Diffractometer	Oxford Diffraction Xcalibur2
Absorption correction	Multi-scan [ABSPACK in <i>CrysAlis PRO</i> (Rigaku OD, 2023)]
T_{min}, T_{max}	0.928, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11463, 745, 721
R_{int}	0.027
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.679
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.027, 0.070, 1.09
No. of reflections	745
No. of parameters	54
No. of restraints	1
H-atom treatment	Only H-atom coordinates refined
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.38, -0.13
Absolute structure	Flack x determined using 298 quotients $[(I^+) - (I^-)] / [(I^+) + (I^-)]$ (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	0.1 (5)

Computer programs: *CrysAlis system* (Oxford Diffraction, 2009), *CrysAlis PRO* (Rigaku OD, 2023), *SHELXS97* (Sheldrick, 2008), *SHELXL2019/3* (Sheldrick, 2015), *DIAMOND* (Brandenburg, 2018) and *publCIF* (Westrip, 2010).

propane-1,3-diaminium cations in TURQEC similarly adopt an all-*anti* conformation with approximate C_{2v} point-group symmetry, but the crystal structure is centrosymmetric. Worthy of note, a low-temperature crystal structure determination of the parent free-base propane-1,3-diamine, which is liquid at room temperature, has also been disclosed (QATVUC; Thalladi *et al.*, 2000).

5. Synthesis and crystallization

Starting materials were obtained from commercial sources and used as received. A solution of propane-1,3-diamine (148 mg, 2 mmol) in 25 mL of ethanol was mixed with a solution of squaric acid (228 mg, 2 mmol) in 40 mL of distilled water. After stirring at 333 K for 4 h, the mixture was left at ambient conditions. After three weeks, colourless crystalline material was collected by filtration and air-dried. Colourless crystals of the title compound suitable for single-crystal X-ray diffraction were grown from methanol/water (1:1) by the slow evaporation method.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Hydrogen-atom positions were

refined freely, and $U_{iso}(H)$ values were set $1.2U_{eq}(C, N, O)$ to improve the data/parameter ratio. The direction of the polar axis was chosen to give a Flack x parameter, as calculated by Parsons' quotient method (Parsons *et al.*, 2013), close to zero. In the absence of significant anomalous scattering, however, the polar axis direction could not be determined reliably in view of the high standard uncertainty of the Flack x parameter (Flack & Bernardinelli, 1999). For this reason, the presence of inversion twinning also cannot be excluded.

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supporting information

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Crystal structure of propane-1,3-diaminium squarate dihydrate

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Computing details

Propane-1,3-diaminium 3,4-dioxocyclobutene-1,2-diolate dihydrate

Crystal data

$C_3H_{12}N_2^{2+} \cdot C_4O_4^{2-} \cdot 2H_2O$

$M_r = 224.22$

Tetragonal, $P4bm$

$a = 11.2716$ (2) Å

$c = 4.3310$ (1) Å

$V = 550.25$ (2) Å³

$Z = 2$

$F(000) = 240$

$D_x = 1.353$ Mg m⁻³

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

Cell parameters from 5992 reflections

$\theta = 3.6$ – 28.7°

$\mu = 0.12$ mm⁻¹

$T = 105$ K

Block, colourless

$0.23 \times 0.16 \times 0.11$ mm

Data collection

Oxford Diffraction Xcalibur2

diffractometer

Radiation source: fine-focus sealed X-ray tube,

Enhance (Mo) X-ray Source

Detector resolution: 8.4171 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

[ABSPACK in CrysAlisPro (Rigaku OD, 2023)]

$T_{\min} = 0.928$, $T_{\max} = 1.000$

11463 measured reflections

745 independent reflections

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

$R_{\text{int}} = 0.027$

$\theta_{\max} = 28.9^\circ$, $\theta_{\min} = 3.6^\circ$

$h = -15 \rightarrow 15$

$k = -15 \rightarrow 14$

$l = -5 \rightarrow 5$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.027$

$wR(F^2) = 0.070$

$S = 1.09$

745 reflections

54 parameters

1 restraint

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier

map

Hydrogen site location: difference Fourier map

Only H-atom coordinates refined

$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.0625P]$

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

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.38$ e Å⁻³

$\Delta\rho_{\min} = -0.13$ e Å⁻³

Absolute structure: Flack x determined using

298 quotients $[(I^+) - (I^-)] / [(I^+) + (I^-)]$ (Parsons *et*

al., 2013)

Absolute structure parameter: 0.1 (5)

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.00512 (11)	0.09200 (10)	0.0161 (4)	0.0143 (3)
C2	0.42195 (10)	0.07805 (10)	0.5294 (5)	0.0137 (4)
H2	0.4703 (15)	0.1281 (16)	0.407 (5)	0.016*
C3	0.500000	0.000000	0.7310 (7)	0.0129 (5)
H3	0.5480 (17)	0.0480 (17)	0.851 (6)	0.015*
N1	0.34377 (9)	0.15623 (9)	0.7173 (4)	0.0126 (3)
H1A	0.3011 (18)	0.1989 (18)	0.601 (7)	0.015*
H1B	0.3902 (15)	0.2026 (15)	0.834 (5)	0.015*
O1	0.01160 (8)	0.20294 (8)	0.0165 (3)	0.0188 (3)
O2	0.21736 (10)	0.28264 (10)	0.2827 (4)	0.0244 (4)
H2A	0.1556 (18)	0.2608 (18)	0.191 (5)	0.029*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0114 (5)	0.0119 (6)	0.0196 (5)	0.0002 (4)	−0.0025 (5)	0.0017 (7)
C2	0.0144 (5)	0.0144 (5)	0.0123 (7)	0.0006 (6)	−0.0005 (6)	0.0005 (6)
C3	0.0132 (7)	0.0132 (7)	0.0124 (11)	0.0005 (9)	0.000	0.000
N1	0.0117 (5)	0.0117 (5)	0.0144 (6)	0.0004 (5)	−0.0013 (5)	0.0013 (5)
O1	0.0149 (4)	0.0098 (4)	0.0316 (5)	−0.0004 (3)	−0.0064 (5)	0.0014 (5)
O2	0.0197 (5)	0.0197 (5)	0.0337 (9)	−0.0071 (6)	−0.0117 (5)	0.0117 (5)

Geometric parameters (\AA , $^\circ$)

C1—O1	1.2527 (14)	C3—H3	0.92 (3)
C1—C1 ⁱ	1.4687 (15)	C3—H3 ^{iv}	0.92 (3)
C1—C1 ⁱⁱ	1.4687 (15)	N1—H1A	0.85 (3)
C2—N1	1.488 (2)	N1—H1B	0.896 (19)
C2—C3	1.520 (3)	N1—H1B ⁱⁱⁱ	0.896 (19)
C2—H2	0.946 (19)	O2—H2A	0.84 (2)
C2—H2 ⁱⁱⁱ	0.946 (19)	O2—H2A ⁱⁱⁱ	0.84 (2)
O1—C1—C1 ⁱ	135.16 (13)	C2 ^{iv} —C3—H3	108.8 (8)
O1—C1—C1 ⁱⁱ	134.84 (13)	C2—C3—H3 ^{iv}	108.8 (8)
C1 ⁱ —C1—C1 ⁱⁱ	89.999 (1)	C2 ^{iv} —C3—H3 ^{iv}	108.8 (8)
N1—C2—C3	111.80 (18)	H3—C3—H3 ^{iv}	112 (3)
N1—C2—H2	107.1 (11)	C2—N1—H1A	110 (2)
C3—C2—H2	109.4 (11)	C2—N1—H1B	108.0 (11)
N1—C2—H2 ⁱⁱⁱ	107.1 (11)	H1A—N1—H1B	109.7 (14)

C3—C2—H2 ⁱⁱⁱ	109.4 (11)	C2—N1—H1B ⁱⁱⁱ	108.0 (11)
H2—C2—H2 ⁱⁱⁱ	112 (2)	H1A—N1—H1B ⁱⁱⁱ	109.7 (14)
C2—C3—C2 ^{iv}	109.9 (2)	H1B—N1—H1B ⁱⁱⁱ	111 (2)
C2—C3—H3	108.8 (8)	H2A—O2—H2A ⁱⁱⁱ	105 (3)
<hr/>			
N1—C2—C3—C2 ^{iv}	180.000 (1)		

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

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
C2—H2...O1 ^v	0.946 (19)	2.590 (19)	3.4712 (18)	155.1 (14)
N1—H1A...O2	0.85 (3)	1.92 (3)	2.758 (2)	171 (3)
N1—H1B...O1 ^{vi}	0.896 (19)	1.905 (18)	2.7887 (12)	168.4 (17)
O2—H2A...O1	0.84 (2)	1.91 (2)	2.7413 (13)	175 (2)

Symmetry codes: (v) $x+1/2, -y+1/2, z$; (vi) $x+1/2, -y+1/2, z+1$.