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Cyclohexylammonium hydrogensquarate hemihydrate

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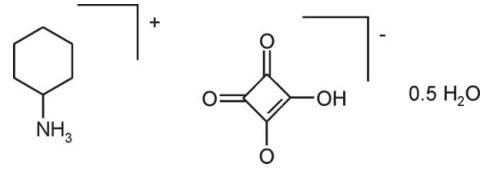
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.004 Å; R factor = 0.051; wR factor = 0.141; data-to-parameter ratio = 13.8.

The components of the title compound, $C_6H_{14}N^+\cdot C_4HO_4^-\cdot 0.5H_2O$, are connected by moderate intermolecular N—H···O hydrogen bonds between the anions and cations into infinite three-dimensional networks. The cyclohexylammonium cation interacts with the solvent molecule by means of an N—H···O hydrogen bond. The hydrogensquarate anions form α chains through strong O—H···O interactions.

Related literature

For related literature, see: Kolev *et al.* (1998, 2006); Koleva *et al.* (2007).



Experimental

Crystal data

$C_6H_{14}N^+\cdot C_4HO_4^-\cdot 0.5H_2O$
M_r = 222.24
Orthorhombic, *Pbcn*
a = 9.3553 (8) Å
b = 11.087 (4) Å
c = 22.1880 (19) Å
V = 2301.4 (9) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 294 (2) K
0.53 × 0.51 × 0.48 mm

Data collection

Siemens P4 diffractometer
Absorption correction: ψ scan (*ABSPsiScan*; Spek, 2003)
T_{min} = 0.948, T_{max} = 0.953
2655 measured reflections
2015 independent reflections
1272 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
3 standard reflections
every 97 reflections
intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.142
S = 1.02
2015 reflections
146 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O8—H8···O9^{i}	0.82	1.67	2.485 (2)	171
N1—H11···O10^{ii}	0.89	1.93	2.811 (3)	169
N1—H12···O20^{iii}	0.89	1.98	2.859 (2)	171
N1—H13···O7	0.89	1.99	2.864 (2)	166
O20—H20···O9	0.86 (2)	1.93 (2)	2.7358 (18)	156 (2)

Symmetry codes: (i) $-x+\frac{1}{2}, y+\frac{1}{2}, z$; (ii) $-x+\frac{3}{2}, y+\frac{1}{2}, z$; (iii) $x+1, y, z$.

Data collection: *R3m/V* (Siemens, 1989); cell refinement: *R3m/V*; data reduction: *XDISK* (Siemens, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2617).

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supplementary materials

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Cyclohexylammonium hydrogensquarate hemihydrate

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Comment

In the course of our spectroscopic and structural studies on hydrogensquarates (Kolev *et al.*, 1998, 2006; Koleva *et al.*, 2007), the crystal structure of cyclohexyammonium hydrogensquarate semihydrate (I) is reported. The molecular structure of (I) is depicted in Fig. 1. The crystal structure consists of three-dimensional networks of cations and anions connected by moderate intermolecular N—H···O [N···O = 2.811 (3), and 2.864 (2) Å] hydrogen bonds. The cations interact with solvent molecule by means of N—H···O [N···O = 2.859 (2) Å] hydrogen bonds and the hydrogensquarate anions form alpha chains through strong O—H···O [O···O = 2.485 (2) Å] interactions (Fig. 2).

Experimental

Cyclohexylammonium hydrogensquarate hemihydrate was prepared by mixing an equimolar ratio of cyclohexylamine (Merck) and squaric acid (Sigma-Aldrich) in 10 ml water. Suitable crystals for X-ray analysis, were grown by allowing the solution to slowly evaporate for a week, and were filtered off, washed with methanol and dried under air.

Refinement

H atoms were constrained to idealized positions and refined using a riding model, with C—H distances of 0.98 Å (CH) and 0.97 Å (CH_2); [U_{iso}(H) = 1.2 U_{iso}(C)], N—H distances of 0.86 Å; [U_{iso}(H) = 1.5 U_{iso}(N)] and an O—H distance of 0.82 Å, [U_{iso}(H) = 1.5 U_{iso}(O)].

Figures

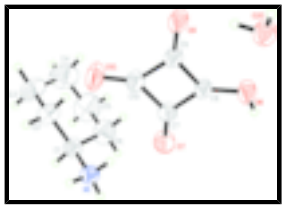

Fig. 1. The molecular structure of the title compound, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

Cyclohexylammonium hydrogensquarate hemihydrate

Crystal data

$C_6H_{14}N^+·C_4HO_4^-·0.5(H_2O)$	D_x = 1.283 Mg m^{-3}
M_r = 222.24	Melting point: not measured K
Orthorhombic, *Pbcn*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -P 2n 2ab	Cell parameters from 50 reflections

a = 9.3553 (8) Å	θ = 4.8–12.4º
b = 11.087 (4) Å	μ = 0.10 mm^{-1}
c = 22.1880 (19) Å	T = 294 (2) K
V = 2301.4 (9) $Å^3$	Prism, colourless
Z = 8	0.53 × 0.51 × 0.48 mm
F_{000} = 952	

Data collection

Siemens P4 4-circle diffractometer	R_{int} = 0.037
Radiation source: fine-focus sealed tube	θ_{max} = 25.0º
Monochromator: graphite	θ_{min} = 2.9º
T = 294(2) K	h = −1→11
ω–scans	k = −1→13
Absorption correction: ψ scan (ABSPsiScan; Spek, 2003)	l = −1→26
T_{min} = 0.948, T_{max} = 0.953	3 standard reflections
2655 measured reflections	every 97 reflections
2015 independent reflections	intensity decay: 1%
1272 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)]$ = 0.051	$w = 1/[\sigma^2(F_o^2) + (0.0675P)^2 + 0.3613P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.142	$(\Delta/\sigma)_{max} < 0.001$
S = 1.02	$\Delta\rho_{max}$ = 0.20 e $Å^{-3}$
2015 reflections	$\Delta\rho_{min}$ = −0.14 e $Å^{-3}$
146 parameters	Extinction correction: SHELXL, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.021 (3)
Secondary atom site location: difference Fourier map	

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. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2sigma(F^2)$ is used only for calculat-

ing *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.86327 (19)	0.35921 (16)	0.16649 (8)	0.0419 (5)
H11	0.8933	0.4346	0.1719	0.063*
H12	0.8987	0.3124	0.1954	0.063*
H13	0.7682	0.3573	0.1679	0.063*
C1	0.9127 (2)	0.3146 (2)	0.10672 (10)	0.0426 (6)
H1	1.0160	0.3282	0.1039	0.051*
C2	0.8854 (3)	0.1809 (2)	0.10055 (12)	0.0555 (7)
H21	0.7838	0.1649	0.1041	0.067*
H22	0.9342	0.1378	0.1325	0.067*
C3	0.9391 (3)	0.1371 (3)	0.03954 (13)	0.0698 (9)
H31	1.0422	0.1461	0.0378	0.084*
H32	0.9169	0.0522	0.0350	0.084*
C4	0.8725 (4)	0.2066 (3)	−0.01147 (14)	0.0895 (11)
H41	0.9145	0.1805	−0.0492	0.107*
H42	0.7709	0.1890	−0.0130	0.107*
C5	0.8934 (4)	0.3396 (3)	−0.00458 (14)	0.0875 (11)
H51	0.8415	0.3813	−0.0362	0.105*
H52	0.9941	0.3586	−0.0091	0.105*
C6	0.8415 (3)	0.3845 (2)	0.05702 (12)	0.0638 (8)
H61	0.8635	0.4696	0.0613	0.077*
H62	0.7386	0.3749	0.0598	0.077*
O7	0.56071 (16)	0.39632 (13)	0.17312 (8)	0.0507 (5)
O8	0.21107 (16)	0.38561 (12)	0.18896 (8)	0.0538 (5)
H8	0.2417	0.4547	0.1860	0.081*
O9	0.21940 (16)	0.10179 (12)	0.18503 (8)	0.0537 (5)
O10	0.56638 (18)	0.10553 (14)	0.17129 (9)	0.0619 (6)
C7	0.4700 (2)	0.31678 (19)	0.17684 (10)	0.0352 (5)
C8	0.3163 (2)	0.30963 (18)	0.18360 (10)	0.0349 (5)
C9	0.3157 (2)	0.18191 (19)	0.18237 (10)	0.0368 (6)
C10	0.4724 (2)	0.18142 (19)	0.17581 (10)	0.0379 (6)
O20	0.0000	0.2003 (2)	0.2500	0.0474 (6)
H20	0.060 (3)	0.150 (2)	0.2342 (13)	0.071*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0394 (11)	0.0340 (10)	0.0524 (12)	−0.0024 (9)	−0.0006 (9)	−0.0033 (9)
C1	0.0386 (13)	0.0418 (13)	0.0475 (14)	−0.0004 (11)	0.0045 (11)	−0.0008 (11)
C2	0.0688 (18)	0.0414 (14)	0.0564 (16)	−0.0031 (13)	0.0067 (14)	−0.0052 (12)
C3	0.083 (2)	0.0600 (18)	0.066 (2)	−0.0056 (17)	0.0209 (16)	−0.0195 (15)
C4	0.108 (3)	0.108 (3)	0.0526 (19)	−0.002 (2)	0.0044 (19)	−0.0177 (19)
C5	0.119 (3)	0.090 (3)	0.0529 (18)	0.007 (2)	0.0053 (19)	0.0152 (18)

C6	0.079 (2)	0.0553 (17)	0.0574 (17)	0.0053 (15)	0.0030 (15)	0.0104 (13)
O7	0.0368 (9)	0.0352 (9)	0.0801 (13)	−0.0081 (7)	0.0038 (9)	0.0050 (9)
O8	0.0329 (9)	0.0232 (8)	0.1054 (15)	0.0006 (7)	0.0017 (9)	−0.0016 (8)
O9	0.0350 (9)	0.0232 (8)	0.1029 (15)	−0.0022 (7)	0.0070 (9)	−0.0036 (9)
O10	0.0422 (10)	0.0394 (10)	0.1042 (16)	0.0125 (8)	0.0161 (10)	−0.0014 (10)
C7	0.0334 (12)	0.0311 (11)	0.0411 (13)	−0.0017 (10)	0.0013 (10)	0.0020 (10)
C8	0.0327 (12)	0.0236 (11)	0.0485 (13)	0.0019 (10)	−0.0007 (10)	−0.0003 (10)
C9	0.0354 (12)	0.0237 (11)	0.0513 (14)	0.0004 (10)	0.0023 (11)	−0.0018 (10)
C10	0.0367 (13)	0.0311 (11)	0.0461 (14)	0.0026 (10)	0.0053 (11)	0.0014 (10)
O20	0.0435 (14)	0.0400 (13)	0.0585 (16)	0.000	0.0070 (12)	0.000

Geometric parameters (Å, °)

N1—C1	1.489 (3)	C5—C6	1.534 (4)
N1—H11	0.8900	C5—H51	0.9700
N1—H12	0.8900	C5—H52	0.9700
N1—H13	0.8900	C6—H61	0.9700
C1—C6	1.503 (3)	C6—H62	0.9700
C1—C2	1.511 (3)	O7—C7	1.226 (2)
C1—H1	0.9800	O8—C8	1.301 (2)
C2—C3	1.523 (3)	O8—H8	0.8200
C2—H21	0.9700	O9—C9	1.267 (2)
C2—H22	0.9700	O10—C10	1.221 (2)
C3—C4	1.504 (4)	C7—C8	1.449 (3)
C3—H31	0.9700	C7—C10	1.501 (3)
C3—H32	0.9700	C8—C9	1.416 (3)
C4—C5	1.496 (5)	C9—C10	1.473 (3)
C4—H41	0.9700	O20—H20	0.86 (2)
C4—H42	0.9700		
C1—N1—H11	109.5	C3—C4—H42	109.2
C1—N1—H12	109.5	H41—C4—H42	107.9
H11—N1—H12	109.5	C4—C5—C6	111.7 (3)
C1—N1—H13	109.5	C4—C5—H51	109.3
H11—N1—H13	109.5	C6—C5—H51	109.3
H12—N1—H13	109.5	C4—C5—H52	109.3
N1—C1—C6	110.16 (19)	C6—C5—H52	109.3
N1—C1—C2	110.74 (19)	H51—C5—H52	107.9
C6—C1—C2	111.4 (2)	C1—C6—C5	110.2 (2)
N1—C1—H1	108.1	C1—C6—H61	109.6
C6—C1—H1	108.1	C5—C6—H61	109.6
C2—C1—H1	108.1	C1—C6—H62	109.6
C1—C2—C3	109.7 (2)	C5—C6—H62	109.6
C1—C2—H21	109.7	H61—C6—H62	108.1
C3—C2—H21	109.7	C8—O8—H8	109.5
C1—C2—H22	109.7	O7—C7—C8	137.1 (2)
C3—C2—H22	109.7	O7—C7—C10	135.1 (2)
H21—C2—H22	108.2	C8—C7—C10	87.78 (17)
C4—C3—C2	111.6 (3)	O8—C8—C9	130.3 (2)
C4—C3—H31	109.3	O8—C8—C7	136.50 (19)

C2—C3—H31	109.3	C9—C8—C7	93.22 (18)
C4—C3—H32	109.3	O9—C9—C8	134.6 (2)
C2—C3—H32	109.3	O9—C9—C10	135.23 (19)
H31—C3—H32	108.0	C8—C9—C10	90.12 (18)
C5—C4—C3	111.9 (3)	O10—C10—C9	136.7 (2)
C5—C4—H41	109.2	O10—C10—C7	134.5 (2)
C3—C4—H41	109.2	C9—C10—C7	88.88 (17)
C5—C4—H42	109.2		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O8—H8···O9^{i}	0.82	1.67	2.485 (2)	171
N1—H11···O10^{ii}	0.89	1.93	2.811 (3)	169
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O20—H20···O9	0.86 (2)	1.93 (2)	2.7358 (18)	156 (2)

Symmetry codes: (i) −*x*+1/2, *y*+1/2, *z*; (ii) −*x*+3/2, *y*+1/2, *z*; (iii) *x*+1, *y*, *z*.

Fig. 1