Acta Crystallographica Section C
**Crystal Structure Communications**
ISSN 0108-2701

# Ammonium hydrogen squarate–water (3/2)

**Tsonko Kolev,[a] Zornitza Glavcheva,[a]* Rosica Petrova[b] and Olyana Angelova[b]**

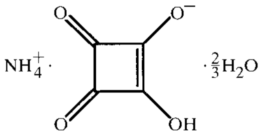
[a]Bulgarian Academy of Sciences, Institute of Organic Chemistry, Acad. G. Bonchev. str. 9, 1113 Sofia, Bulgaria, and [b]Bulgarian Academy of Sciences, CL of Mineralogy and Crystallography, Rakovski str. 92, 1000 Sofia, Bulgaria
Correspondence e-mail: zornitza@orgchm.bas.bg

Received 17 February 1999
Accepted 19 October 1999

In the title compound, $NH_4^+\cdot C_4HO_4^-\cdot\frac{2}{3}H_2O$, the hydrogen squarate anions and water molecules are arranged to form planes almost parallel to *bc*. The ammonium cations are located between these planes and cross-link them in the *a* direction by means of an extensive network of hydrogen bonds. There are two symmetry-independent sets of cations and anions. One of the hydrogen squarate anions and one of the ammonium cations are situated on a twofold axis and the H atoms of these moieties are disordered over the symmetry-related sites.

## Comment

The structure determination of ammonium hydrogen squarate–water (3/2), (I), was carried out as part of a project investigating the non-linear optical properties of new classes of organic compounds. The crystal structures of L-argininium hydrogen squarate (Angelova, Velikova *et al.*, 1996), *R*-(–)-1-phenylglycinium hydrogen squarate (Angelova, Petrova *et al.*, 1996), guanidinium hydrogen squarate (Kolev, Preut *et al.*, 1997), 1-phenylethylammonium hydrogen squarate monohydrate (Kolev, Stahl *et al.*, 1997), bis[L-(–)-asparaginum hydrogen squarate] monohydrate (Kolev, Stahl, Preut, Koniczek *et al.*, 1998) and L-(+)-serinium hydrogen squarate (Kolev, Stahl, Preut, Bleckmann & Radomirska *et al.*, 1998) have already been published. A search of the chemical literature (Chemical Abstracts and Beilstein) has shown no entry for (I). The crystal structures of hydrogen squarates of $[H_2NMe_2]^+$ (Wang & Stucky, 1974), some alkali metals (Bull *et al.*, 1973; Semmingsen, 1976) and 3*d* metals such as Co and Ni (Brach *et al.*, 1987) are already known.



(I)

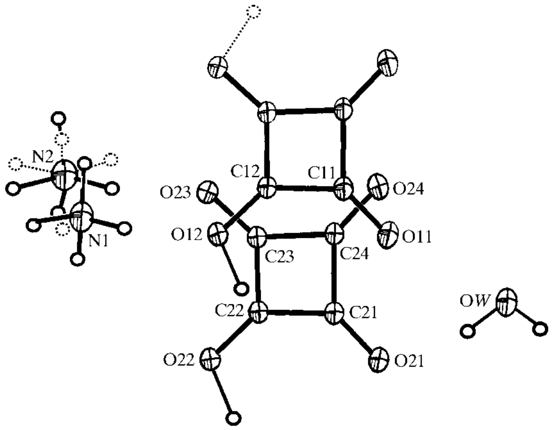


**Figure 1**
The independent entities in the structure of (I), with atom labels and 50% probability ellipsoids for non-H atoms. The disordered H atoms are indicated by dotted lines.

The title compound exhibits a structure in which hydrogen squarate anions and water molecules are hydrogen-bonded and arranged to form planes almost parallel to the *bc* plane. The ammonium ions are located between these planes and connect them by an extensive network of hydrogen bonds. The structures of the individual moieties and the atomic numbering scheme are shown in Fig. 1, while the packing of the structure along the *a* axis is shown in Fig. 2.

There are two symmetry-independent squarate anions in the asymmetric unit. One of them has $C_2$ symmetry and is situated on the twofold axis at $(0, y, \frac{1}{4})$. The set of symmetrically equivalent anions of this type are hydrogen-bonded to

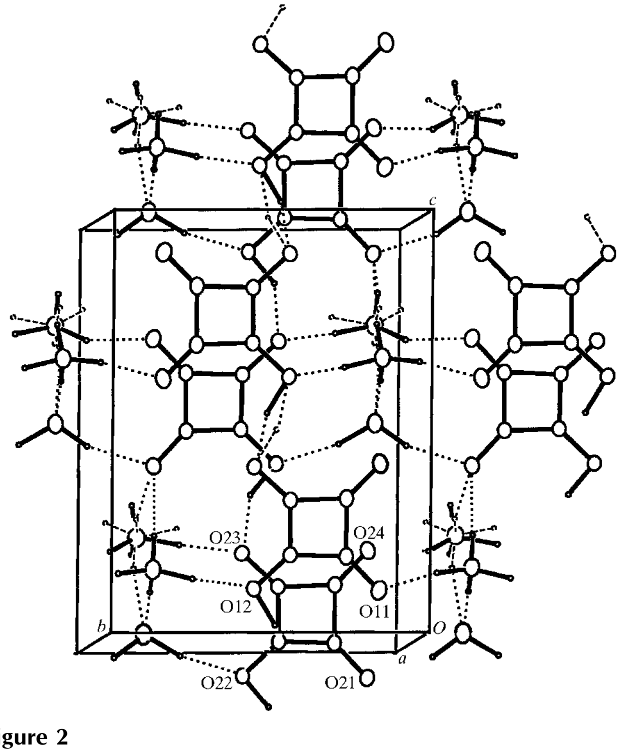


**Figure 2**
The packing of the molecules in (I) down the *a* axis. The hydrogen bonds are indicated by dotted lines and the disordered H atoms are indicated by dashed lines.

each other and build zigzag chains which run parallel to the *c* axis. These chains are arranged to form squarate planes (*S*) which are virtually coincident with the (100) plane. The hydrogen squarate anions of the second type do not possess crystallographic $C_2$ symmetry, but still form similar hydrogen-bonded chains which are, in addition, hydrogen-bonded to the water molecules. The water molecules thereby cross-link this latter type of anionic chains and the thus-constituted squarate–water planes (*S*/*W*) lie parallel to (100) but are located at approximately $\frac{1}{4}$ and $\frac{3}{4}$ along the *a* axis. The two ammonium ions have different structural roles. The cation involving N1 is in a general position and the ammonium ions of this type cross-link one *S* plane to its neighbouring *S*/*W* planes situated on either side along the *a* direction. In addition, these cations cross-link adjacent anionic chains within each *S* plane. The cation involving N2 is situated on a twofold axis at $(\frac{1}{2}, y, \frac{1}{4})$. The ammonium ions of this type couple adjacent *S*/*W* planes *via* N—H···O hydrogen bonds and, together with the water molecules, also help to cross-link adjacent anionic chains within each *S*/*W* plane. Thus, the structure can be described as a set of alternating layers of anions and cations arranged in the sequence *S*–N1–*S*/*W*–N2–*S*/*W*–N1–*S*··· along the *a* axis.

In most of the reported structures of organic compounds containing hydrogen squarate moieties, the anions are hydrogen-bonded to each other to create similar chains. The only known exception is the structure of L-argininium hydrogen squarate, where the squarate anions are dimerized through double cyclic O—H···O bonds (Angelova, Velikova *et al.*, 1996).

Full details of the hydrogen-bonding geometry are given in Table 2. The O···O contacts within the hydrogen squarate chains of 2.4510 (13) and 2.464 (2) Å indicate very strong hydrogen bonding (Emsley, 1980). The hydrogen bonds formed between hydrogen squarate chains and water molecules within the *S*/*W* plane can be described as normal, with O···O distances of 2.7534 (18) and 2.7840 (18) Å. Significantly weaker are the N—H···O hydrogen bonds, which connect the ammonium cations to the squarate anions and the water molecules. The N···O distances vary between 2.8312 (14) and 3.109 (2) Å.

## Experimental

The title compound was prepared by addition of an aqueous solution of ammonium carbonate to a water solution of squaric acid in a 2:1 molar ratio with continuous stirring for 30 min. The product was purified by multiple recrystallization from double-distilled water. Colourless crystals of (I) suitable for X-ray analysis were grown by slow evaporation from an aqueous solution at room temperature.

*Crystal data*

$NH_4^+ \cdot C_4HO_4^- \cdot \frac{2}{3}H_2O$
$M_r = 143.10$
Monoclinic, *P*2/*c*
$a = 10.031$ (3) Å
$b = 8.2799$ (17) Å
$c = 10.968$ (2) Å
$\beta = 99.274$ (2)°
$V = 899.02$ (16) Å$^3$
$Z = 6$

$D_x = 1.586$ Mg m$^{-3}$
Mo *Kα* radiation
Cell parameters from 22 reflections
$\theta = 20.03$–21.66°
$\mu = 0.148$ mm$^{-1}$
$T = 293$ (2) K
Prismatic, colourless
0.40 × 0.33 × 0.26 mm

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\omega$–2$\theta$ scans
4406 measured reflections
2166 independent reflections
1343 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.106$

$\theta_{\max} = 27.91°$
$h = 0 \rightarrow 13$
$k = -10 \rightarrow 10$
$l = -14 \rightarrow 14$
3 standard reflections every 500 reflections intensity decay: 0.7%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.146$
$S = 1.009$
2166 reflections
181 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0811P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.51$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.33$ e Å$^{-3}$
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.014 (3)

All H atoms were placed in positions found from difference Fourier syntheses and allowed to refine freely. Due to the local $C_2$ symmetry of one of the hydrogen squarate anions, the position of the H atom of this anion has been refined with a site occupancy of 0.5. Positional disorder of this type is known in L-(+)-serinium hydrogen squarate. Atom N2 of one ammonium group is situated on a twofold axis. Four non-equivalent H atoms were located around this N atom and their positions were similarly refined with site occupancies of 0.5.

Data collection: *CAD*-4 *Manual* (Enraf–Nonius, 1988); data reduction: *SDP*/*PDP* (Enraf–Nonius, 1985); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics:

**Table 1**
Selected geometric parameters (Å).

| | | | |
|---|---|---|---|
| C12—O12 | 1.2820 (17) | C21—C24 | 1.5048 (17) |
| C12—C12$^{\rm i}$ | 1.420 (2) | C22—O22 | 1.2859 (17) |
| C12—C11 | 1.465 (2) | C22—C23 | 1.4217 (17) |
| C11—O11 | 1.2241 (17) | C23—O23 | 1.2710 (17) |
| C11—C11$^{\rm i}$ | 1.501 (3) | C23—C24 | 1.481 (2) |
| C21—O21 | 1.2365 (18) | C24—O24 | 1.2210 (17) |
| C21—C22 | 1.447 (2) | | |

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

**Table 2**
Hydrogen-bonding geometry (Å, °).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O12—H1···O12$^{\rm i}$ | 0.96 (8) | 1.52 (7) | 2.464 (2) | 167 (8) |
| O22—H2···O23$^{\rm ii}$ | 1.12 (3) | 1.33 (3) | 2.4510 (13) | 177 (4) |
| N1—H11···O11$^{\rm iii}$ | 0.92 (2) | 1.93 (3) | 2.856 (2) | 176.0 (18) |
| N1—H12···O21$^{\rm iv}$ | 0.91 (2) | 2.05 (2) | 2.953 (2) | 172.2 (19) |
| N1—H13···O*W*$^{\rm iii}$ | 1.00 (3) | 1.84 (3) | 2.838 (2) | 171 (2) |
| N1—H14···O12 | 0.89 (3) | 2.05 (3) | 2.916 (2) | 166 (2) |
| N2—H21···O24$^{\rm iii}$ | 1.07 (5) | 1.93 (5) | 2.981 (2) | 167 (4) |
| N2—H22···O*W*$^{\rm v}$ | 0.92 (4) | 1.95 (4) | 2.8312 (14) | 160 (4) |
| N2—H23···O23 | 0.89 (5) | 2.24 (5) | 3.109 (2) | 165 (5) |
| N2—H24···O21$^{\rm vi}$ | 0.92 (6) | 2.04 (6) | 2.9481 (13) | 167 (4) |
| O*W*—H*W*1···O22$^{\rm vii}$ | 0.79 (3) | 2.05 (3) | 2.7840 (18) | 153 (2) |
| O*W*—H*W*2···O21 | 0.86 (3) | 1.92 (3) | 2.7534 (18) | 163 (2) |

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

*Acta Cryst.* (2000). C**56**, 110–112 Tsonko Kolev *et al.* • $NH_4^+ \cdot C_4HO_4^- \cdot \frac{2}{3}H_2O$ **111**

*ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

This work was supported by the Bulgarian Academy of Sciences and the Bulgarian National Science Fund (Project ch-605).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1082). Services for accessing these data are described at the back of the journal.

## References

Angelova, O., Petrova, R., Radomirska, V. & Kolev, Ts. (1996). *Acta Cryst.* C**52**, 2218–2220.

Angelova, O., Velikova, V., Kolev, Ts. & Radomirska, V. (1996). *Acta Cryst.* C**52**, 3252–3256.

Brach, L., Rozière, J., Anselment, B. & Peters, K. (1987). *Acta Cryst.* C**43**, 458–460.

Bull, R., Ladd, M. F. C., Povey, D. C. & Shirley, R. (1973). *Cryst. Struct. Commun.* **2**, 625–628.

Emsley, J. (1980). *Chem. Soc. Rev.* **9**, 91–124.

Enraf–Nonius (1985). *Structure Determination Package. SDP/PDP User's Guide*. Version 3.0. Enraf–Nonius, Delft, The Netherlands.

Enraf–Nonius (1988). *CAD-4 Manual.* Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennesse, USA.

Kolev, Ts., Preut, H., Bleckmann, P. & Radomirska, V. (1997). *Acta Cryst.* C**53**, 805–807.

Kolev, Ts., Stahl, R., Preut, H., Bleckmann, P. & Radomirska, V. (1998). *Z. Kristallogr.* **213**, 169–170.

Kolev, Ts., Stahl, R., Preut, H., Koniczek, L., Bleckmann, P. & Radomirska, V. (1997). *Z. Kristallogr. New Cryst. Struct.* **212**, 417–418.

Kolev, Ts., Stahl, R., Preut, H., Koniczek, L., Bleckmann, P. & Radomirska, V. (1998). *Z. Kristallogr. New Cryst. Struct.* **213**, 167–168.

Semmingsen, D. (1976). *Acta Chem. Scand. Ser. A*, **30**, 808–812.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL*97. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Wang, Y. & Stucky, G. D. (1974). *J. Chem. Soc. Perkin Trans.* 2, pp. 925–928.