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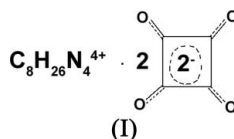
Key indicators

Single-crystal X-ray study
 $T = 296$ K
Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.034
 wR factor = 0.091
Data-to-parameter ratio = 14.9For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Bis(3-ammoniopropyl)ethylenediaminium
bis(squarate)

In the crystal structure of the title compound, $\text{C}_8\text{H}_{26}\text{N}_4^{4+} \cdot 2\text{C}_4\text{O}_4^{2-}$, the bis(3-ammoniopropyl)ethylenediaminium (PAED) cation lies on an inversion centre and the squarate anion (Sq^{2-}) is in a general position. Salt formation occurs by donation of four H atoms from two squaric acid molecules to the bis(3-aminopropyl)ethylenediamine base. In the crystal structure, the strongest interactions are between H atoms of NH_2^+ groups and squarate O atoms. All the H atoms of NH_3^+ groups of the PAED cation also participate in hydrogen bonding with the O atoms of the Sq^{2-} anion, contributing to the crystal packing.

Comment

Squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione, H_2Sq) is a very strong dibasic acid and has been used to synthesize new types of organic compounds having potential applications in non-linear optics (Kolev *et al.*, 1997; Bulut *et al.*, 2003; Uçar *et al.*, 2004; Körođlu *et al.*, 2005). It can crystallize as uncharged H_2Sq , and also as HSq^- or Sq^{2-} anions on deprotonation by amine groups. These three forms of squaric acid have been observed to crystallize with various types of hydrogen bonding, as summarized by Bertolasi *et al.* (2001). The present study reports the Sq^{2-} form of squaric acid.



The asymmetric unit of (I) contains one squarate anion (Sq^{2-}) and one half of a centrosymmetric bis(3-ammoniopropyl)ethylenediaminium cation. A view of the hydrogen-bonded structure of (I) is shown in Fig. 1. This structure is formed such that each of two squaric acid molecules donates two H atoms, one to an NH group and another to an NH_2 group. The bond lengths and angles of the squarate anion (Table 1) are similar to those previously reported (Bertolasi *et al.*, 2001; Bulut *et al.*, 2003; Körođlu *et al.*, 2005).

Each O atom of the Sq^{2-} anion makes a hydrogen-bonding contribution to the crystal packing. The hydrogen bonds between squarate atoms O1 and O4 and the protonated NH_2^+ part of the PAED cation are quite strong (Table 2) and are also the reasons for the longer N—H bond distances. These strong hydrogen bonds connect the cations and anions into layers parallel to (101). Atoms O2 and O3 of the Sq^{2-} anions interact with all the H atoms of the NH_3^+ group (Table 2), forming a three-dimensional network (Fig. 2).

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Experimental

Bis(3-aminopropyl)ethylenediamine and squaric acid in a 1:2 molar ratio were dissolved in a mixture of methanol (50%) and water (50%) and stirred at 333 K for 12 h. Crystals of (I) were obtained by slow evaporation of the resulting solution. The crystals formed were filtered, washed in water and methanol, and dried in a vacuum.

Crystal data

$C_8H_{26}N_4^{4+} \cdot 2C_4O_4^{2-}$
 $M_r = 402.41$
 Monoclinic, $P2_1/n$
 $a = 10.0027$ (10) Å
 $b = 8.3325$ (12) Å
 $c = 12.0951$ (12) Å
 $\beta = 112.340$ (7)°
 $V = 932.43$ (19) Å³
 $Z = 2$

$D_x = 1.433$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 4300 reflections
 $\theta = 2.2$ – 28.0 °
 $\mu = 0.12$ mm⁻¹
 $T = 296$ (2) K
 Block, colourless
 $0.44 \times 0.42 \times 0.27$ mm

Data collection

Stoe IPDS-II diffractometer
 ω scans
 Absorption correction: integration
 (*X-RED32*; Stoe & Cie, 2002)
 $T_{\min} = 0.946$, $T_{\max} = 0.975$
 6003 measured reflections
 2185 independent reflections

1749 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$
 $\theta_{\text{max}} = 27.9$ °
 $h = -13 \rightarrow 13$
 $k = -10 \rightarrow 9$
 $l = -15 \rightarrow 15$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.091$
 $S = 1.09$
 2184 reflections
 147 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0405P)^2 + 0.1497P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.17$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.16$ e Å⁻³

Table 1

Selected bond lengths (Å).

C1–O1	1.2570 (15)	C2–C3	1.4629 (17)
C1–C2	1.4514 (17)	C3–O3	1.2441 (15)
C1–C4	1.4591 (18)	C3–C4	1.4712 (16)
C2–O2	1.2541 (15)	C4–O4	1.2475 (15)

Table 2

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>
N1–H1A...O2 ⁱ	0.910 (19)	1.94 (2)	2.8390 (17)	171.2 (16)
N1–H1B...O3 ⁱⁱ	0.88 (2)	1.98 (2)	2.7905 (17)	152.4 (16)
N1–H1C...O2 ⁱⁱⁱ	0.868 (19)	1.956 (19)	2.7912 (16)	161.2 (16)
N2–H2A...O1 ⁱ	0.977 (17)	1.777 (17)	2.7355 (15)	166.0 (13)
N2–H2B...O4	0.969 (18)	1.783 (18)	2.7195 (14)	161.4 (15)

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

The methylene H atoms were placed in calculated positions ($C-H = 0.97$ Å), and were allowed to ride on their parent atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The remaining H atoms were found in a difference map and their parameters were freely refined. The badly fitting reflection (103) was omitted during the final cycles of refinement.

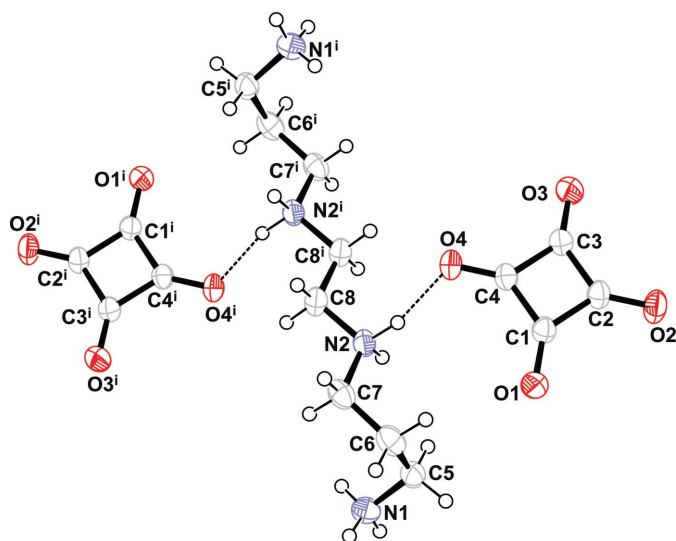


Figure 1

ORTEP^{III} (Burnett & Johnson, 1996) plot of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are shown as small spheres of arbitrary radii and hydrogen bonds are indicated by dashed lines [Symmetry code: (i) $-x, -y, -z$].

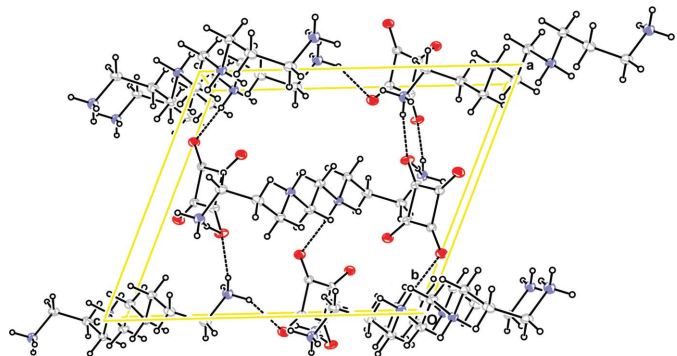


Figure 2

The crystal packing of (I), viewed along the *b* axis. Displacement ellipsoids are drawn at the 10% probability level. Dashed lines indicate hydrogen bonds.

Data collection: *X-Area* (Stoe & Cie, 2002); cell refinement: *X-Area*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP^{III}* (Burnett & Johnson, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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