Zwitterionic 2-guanidinium-1-aminocarboxylate monohydrate

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It is found that the commercial product with formula $C_2H_8N_4O_3$, supposedly aminoguanidinium hydrogen carbonate, is actually a monohydrate of aminoguanidinium betaine. In the zwitterion, the guanidinium and $NHCO_2$ groups are planar and nearly perpendicular to each other, with a dihedral angle of 83.26 (5)°. The crystal structure can be thought of as composed of layers of organic molecules alternating with layers of water molecules. The structural units are held together by an extensive hydrogen-bonding network.

Comment

The two protonated forms of the strong base aminoguanidine have been described: monoprotonated (Adams, 1977) and diprotonated (Ross *et al.*, 1999). In the course of our study of guanidinium derivatives, several salts with squaric acid have been investigated by means of vibrational (IR and Raman) spectroscopy and single-crystal analysis (Kolev, Glavcheva *et al.*, 1997; Kolev, Preut, Bleckmann & Radomirska, 1997; Kolev *et al.*, 1997*a,b*). One of these compounds, aminoguanidinium squarate, has been synthesized using the commercial products aminoguanidinium hydrogen carbonate (AGHC) (Fluka, EGA Chemie, Aldrich) and squaric acid (Huels–Marl, Germany).

(I)
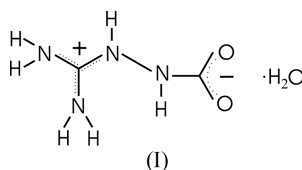
The vibrational spectra of AGHC differ significantly from the expected ones, although that compound contains the aminoguanidinium cation, confirmed by the crystal structure of aminoguanidinium squarate (Kolev, Glavcheva *et al.*, 1997). In the IR spectrum of AGHC, there are no characteristic bands for the hydrogen carbonate anion and, in addition, two strong bands appear at 1688 and 1634 cm^{-1}. We have compared our spectrum with that of aminoguanidinium chloride, which can be used as a model system for the IR study of the aminoguanidinium cation. There are seven ν(N—H) bands in the IR spectrum of aminoguanidinium chloride and only five in the spectrum of AGHC. These discrepancies motivated us to calculate the theoretical spectrum of aminoguanidinium cation on *ab initio RHF* 6-31G^* and *DFT B3LYP* 6-31G^* levels. The resulting theoretical frequencies proved our assumption that the commercial product is not AGHC. The assignment of the bands in the IR and RAMAN spectra
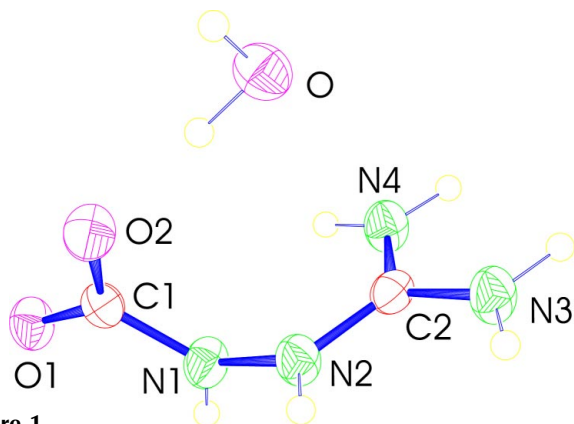
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Figure 1
The structural units of (I), with labelling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level.
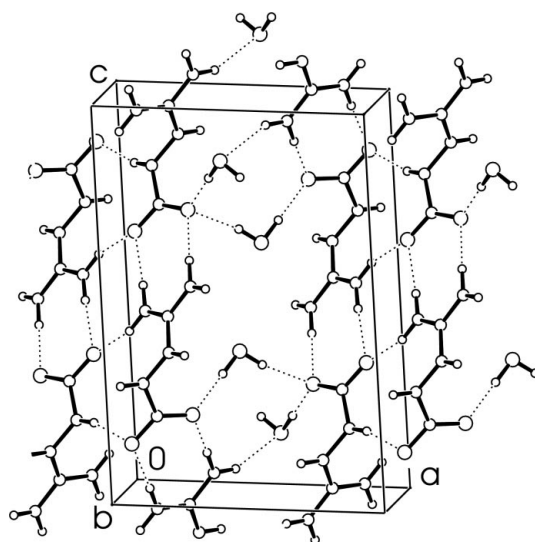

Figure 2
The three-dimensional packing of the structural units in (I). Hydrogen bonds are shown as dotted lines.

of the products under study is more in accordance with the literature data for different betaines (Szafran & Koput, 1996; Viertorinne *et al.*, 1999). The detailed vibrational and quantum chemical investigation is in progress and will be published later.

The reason for the present determination of the molecular and crystal structure of AGHC, (I), is that we could find no literature references to it, in Chemical Abstracts, in Beilstein, or in the Cambridge Structural Database.

The structure of (I) can be regarded as a derivative of aminoguanidinium, where the positive charge is delocalized over the guanidinium moiety and the negative charge over the $-NHCO_2$ group (Fig. 1). This is corroborated by the solid-state IR spectrum (KBr pellet). The guanidinium and $-NHCO_2$ groups are planar and nearly perpendicular to each other, with a dihedral angle of 83.26 (5)°. An extensive hydrogen-bonding network holds the structural units together (Fig. 2). H32 and H42, attached respectively to N3 and N4, form N—H⋯O bonds through which the organic molecules are connected to form zigzag chains parallel to the *c* axis. The

chains are linked along the *b* axis and thus a layer perpendicular to the *a* axis is formed. The water molecule is a donor of two and an acceptor of two hydrogen bonds, which hold the layers along the *a* axis. The crystal structure can be thought as a layered one, where layers of organic molecules alternate with those formed by water molecules only.

Experimental

The commercial product is a gray powder. It was recrystallized four times, first from water–ethanol and three times from doubly distilled water. The IR and Raman spectra of the compound were measured after each recrystallization and they show that the compound remained unchanged. Prismatic colorless single crystals suitable for X-ray analysis were grown from doubly distilled water at room temperature.

Crystal data

$C_2H_6N_4O_2 \cdot H_2O$	$D_x = 1.537$ Mg m^{-3}
$M_r = 136.12$	Mo Kα radiation
Monoclinic, $P2_1/c$	Cell parameters from 22
$a = 9.1929$ (8) Å	reflections
$b = 4.8380$ (5) Å	$\theta = 20.0–21.9°$
$c = 13.2467$ (11) Å	$\mu = 0.14$ mm^{-1}
$\beta = 93.073$ (7)°	$T = 293$ (2) K
$V = 588.30$ (9) Å^3	Plate, colorless
$Z = 4$	$0.26 \times 0.26 \times 0.13$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	$\theta_{max} = 29.9°$
ω–2θ scans	$h = 0 \rightarrow 12$
Absorption correction: none	$k = -6 \rightarrow 6$
3408 measured reflections	$l = -18 \rightarrow 18$
1708 independent reflections	3 standard reflections
1230 reflections with $I > 2\sigma(I)$	every 500 reflections
$R_{int} = 0.029$	frequency: 120 min
	intensity decay: 1.0%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0625P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.040$	$+ 0.0484P]$
$wR(F^2) = 0.115$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} = 0.001$
1708 reflections	$\Delta\rho_{max} = 0.21$ e Å^{-3}
114 parameters	$\Delta\rho_{min} = -0.32$ e Å^{-3}
All H-atom parameters refined	

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H11⋯O1^i	0.85 (1)	2.08 (2)	2.926 (2)	166 (2)
N3—H31⋯O	0.87 (1)	2.15 (2)	2.974 (2)	155 (1)
N3—H32⋯O2^{ii}	0.95 (1)	1.94 (2)	2.892 (2)	176 (2)
N2—H21⋯O^{iii}	0.89 (2)	1.98 (2)	2.842 (2)	166 (2)
O—H1⋯O2^{iv}	0.89 (2)	1.89 (2)	2.777 (2)	170 (2)
O—H2⋯O2^v	0.98 (2)	1.75 (2)	2.733 (1)	179 (2)
N4—H41⋯O1^{ii}	0.93 (2)	1.92 (2)	2.846 (2)	175 (2)
N4—H42⋯O1^{vi}	0.91 (2)	2.09 (2)	2.916 (2)	151 (2)

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

All of the H atoms were found in a difference Fourier map and their positions refined freely.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *DATARED* (P. Vasilev, unpublished); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97

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