Crystal structure of betainium perchlorate hydrate, [(CH₃)₃NCH₂COOH]ClO₄ · H₂O

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Abstract

C₅H₁₄ClNO₇, monoclinic, *P*12₁/*c*1 (No. 14), *a* = 9.867(4) Å, *b* = 9.246(3) Å, *c* = 12.200(5) Å, β = 110.93(3)°, *V* = 1039.6 Å³, *Z* = 8, *R*_{gt}(*F*) = 0.040, *wR*_{ref}(*F*²) = 0.120, *T* = 293 K.

Source of material

The compound was synthesised by neutralizing an aqueous solution of betaine (*N,N,N*-trimethylaminoacetic acid) monohydrate (Aldrich, 99% purity) with perchloric acid. After a few weeks of slow evaporation small single crystals grew from the solution.

Experimental details

The H-atoms of the organic moiety were placed at calculated positions and refined as riding using the SHELXL-97 [1] defaults, except for those of the water molecule which were located from a difference Fourier synthesis and refined isotropically with *U*_{eq} = 1.5(O7) and a restrained O—H distance of 0.86 Å. The anisotropic refinement converged to a relatively large value of *wR*(*F*²) = 0.18. At this stage, examination of the crystal structure with PLATON [2] showed that there were no solvent-accessible voids in the crystal lattice but residual density peaks appeared on a difference Fourier synthesis close to the anion tetrahedron. Also, inspection of the atomic displacement parameters of the perchlorate O atoms showed a large anisotropy which was interpreted to possibly indicate disorder of the anion. Therefore, the positions of the O atoms were split in two sets with a refinable occupancy constrained to add up to unity. The Cl—O bond lengths and O—Cl—O angles were restrained to be equal using a set of appropriate DFIX instructions and a DELU instruction was used to regularize the anisotropic displacement parameters of the O at-

oms. The restrained refinement converged to give an occupancy of the two alternate positions of the anion tetrahedron of 52.1(13)% and 47.9(13)%, with significant decrease of the *wR*-factor by 6 units. The refined common values of the Cl—O bond length and O—Cl—O angles were 1.383(2) Å and 109.5(1)°, respectively.

Discussion

The *N*-methylated α-amino acid betaine (*N,N,N*-trimethylaminoacetic acid) is commonly found in plant and animal tissues as a biological oxidation product of choline. It acts in amino acid synthesis as a transmethylation agent. Betaine exists in free form as an inner salt (zwitterion) which has a basic character due to the proton affinity of the carboxylate group. It forms numerous salts and adducts with both organic and inorganic acids. It is also well known as a chelating agent for both transition metal and lanthanide atoms [3, 4]. From the point of view of the physical properties, betaine compounds are interesting because ferroelectric or antiferroelectric ordering is found for many such compounds [5–7]. However, many compounds are centrosymmetric at room temperature and polar properties are only observed at low temperature. A few compounds also exhibit ferroelasticity, which induces structural phase transitions to both commensurate and incommensurate modulated superstructures [8–10]. Undoubtedly, the most famous betaine compound is betaine calcium chloride dihydrate (BCCD) which shows an unusual series of commensurate and incommensurate phases developing at low temperature, chained in a sequence known as the ‘devil’s staircase’ [11]. The large asymmetry between the two carboxy C—O bond lengths clearly shows that the O1 atom is protonated. Although it is usually found that the betaine skeleton is practically planar [7, 12, 13], a significant deviation from planarity is observed in the present case. The atoms C4, C5, O1 and O2 lie in one plane within 0.007(4) Å but this plane defines a dihedral angle of 18.8(3)° with that defined by atoms N, C1 and C4. Inspection of the torsion angles C1–N–C4–C5 and N–C4–C5–O1 shows that the deviation from planarity of the betaine skeleton is due to a combined twist of the trimethylamino group of –7.2° around the single N—C4 bond and a rotation of 21.74° of the carboxylic group around the C4—C5 bond. The betaine cation establishes a hydrogen bond with the water molecule via the carboxyl group. The water molecule bridges two perchlorate anions related by the glide plane in chains running parallel to the *c*-axis.

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Table 1. Data collection and handling.

Crystal:	translucent block, size $0.08 \times 0.10 \times 0.20$ mm
Wavelength:	Mo K_{α} radiation (0.71073 Å)
μ :	3.81 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD-4, $\omega/2\theta$
$2\theta_{\text{max}}$:	50.16°
$N(hkl)_{\text{measured}}, N(hkl)_{\text{unique}}$:	1929, 1837
Criterion for $I_{\text{obs}}, N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1246
$N(\text{param})_{\text{refined}}$:	178
Programs:	SHELXS-97 [14], SHELXL-97 [1], PLATON [3], ORTEPII [15]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
H(1A)	4e	0.9045	0.2765	0.4188	0.100
H(1B)	4e	0.7864	0.1894	0.4494	0.100
H(1C)	4e	0.8689	0.3172	0.5303	0.100
H(2A)	4e	0.7096	0.6003	0.3414	0.096
H(2B)	4e	0.8589	0.5280	0.3562	0.096
H(2C)	4e	0.8197	0.5630	0.4670	0.096
H(3A)	4e	0.6371	0.4159	0.5104	0.105
H(3B)	4e	0.5510	0.2980	0.4199	0.105
H(3C)	4e	0.5259	0.4624	0.3876	0.105
H(4A)	4e	0.6326	0.2300	0.2581	0.057
H(4B)	4e	0.7368	0.3348	0.2255	0.057
H(1)	4e	0.398(3)	0.349(5)	0.036(3)	0.102
H(7A)	4e	0.199(4)	0.360(4)	-0.121(3)	0.123
H(7B)	4e	0.167(3)	0.404(6)	-0.044(3)	0.123

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	4e		0.8289(4)	0.2831(4)	0.4508(3)	0.063(2)	0.062(2)	0.062(2)	0.015(2)	0.008(2)	0.011(2)
C(2)	4e		0.7816(4)	0.5325(3)	0.3865(3)	0.057(2)	0.046(2)	0.079(2)	-0.011(2)	0.011(2)	-0.004(2)
C(3)	4e		0.5966(3)	0.3912(5)	0.4286(3)	0.051(2)	0.109(3)	0.056(2)	0.000(2)	0.026(2)	0.000(2)
C(4)	4e		0.6587(3)	0.3308(3)	0.2562(2)	0.053(2)	0.040(2)	0.048(2)	0.004(1)	0.015(1)	-0.003(1)
C(5)	4e		0.5293(3)	0.4100(3)	0.1722(2)	0.047(2)	0.046(2)	0.045(2)	0.000(2)	0.018(1)	0.002(1)
N	4e		0.7145(2)	0.3868(2)	0.3789(2)	0.040(1)	0.041(1)	0.046(1)	0.000(1)	0.015(1)	0.000(1)
O(1)	4e		0.4641(3)	0.3259(3)	0.0831(2)	0.070(2)	0.066(2)	0.052(1)	0.011(1)	0.003(1)	-0.013(1)
O(2)	4e		0.4929(2)	0.5306(2)	0.1832(2)	0.063(1)	0.048(1)	0.069(2)	0.012(1)	0.013(1)	-0.002(1)
Cl	4e		0.12911(7)	0.08913(8)	0.73853(6)	0.0463(4)	0.0494(4)	0.0463(4)	0.0028(4)	0.0134(3)	0.0001(4)
O(3A)	4e	0.52(1)	0.060(1)	0.0752(9)	0.6185(2)	0.064(4)	0.19(1)	0.049(5)	0.021(5)	-0.009(3)	0.001(5)
O(4A)	4e	0.52	0.196(1)	-0.0400(5)	0.7846(7)	0.22(1)	0.051(3)	0.110(6)	0.048(4)	0.073(6)	0.027(4)
O(5A)	4e	0.52	0.2322(9)	0.1976(8)	0.7617(9)	0.127(6)	0.068(4)	0.158(8)	-0.045(5)	0.058(6)	-0.016(5)
O(6A)	4e	0.52	0.0287(8)	0.124(1)	0.7896(8)	0.083(5)	0.24(1)	0.130(7)	0.006(6)	0.079(5)	-0.033(7)
O(3B)	4e	0.48	0.097(1)	0.069(1)	0.6196(2)	0.132(9)	0.21(1)	0.046(5)	0.070(8)	0.037(5)	-0.008(6)
O(4B)	4e	0.48	0.115(1)	-0.0406(7)	0.7899(8)	0.24(1)	0.102(6)	0.137(8)	-0.024(6)	0.079(9)	0.049(6)
O(5B)	4e	0.48	0.2699(5)	0.139(1)	0.790(1)	0.030(3)	0.165(8)	0.153(8)	-0.010(4)	-0.008(4)	-0.002(7)
O(6B)	4e	0.48	0.0343(9)	0.190(1)	0.755(1)	0.098(6)	0.135(7)	0.140(8)	0.034(5)	0.042(5)	-0.053(6)
O(7)	4e	0.48	0.2281(3)	0.4263(3)	-0.0731(3)	0.067(2)	0.081(2)	0.079(2)	0.004(2)	0.002(1)	-0.013(2)

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