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Crystal structure of diglycine hydroxylammonium chloride, $(C_2H_5NO_2)_2[NH_3(OH)]Cl$

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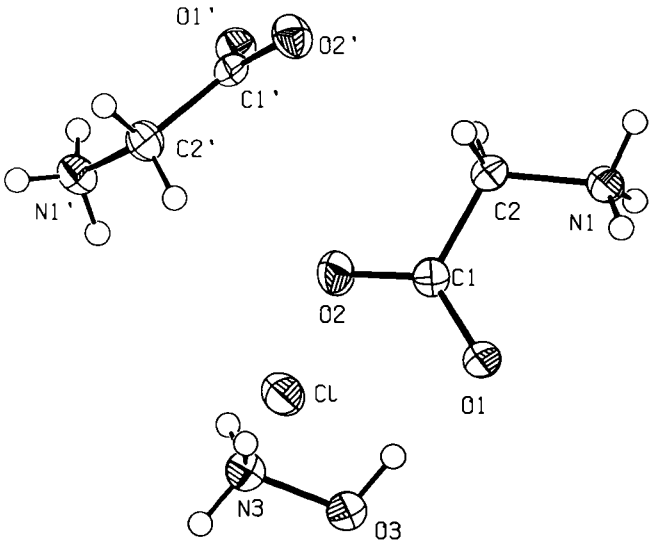

Abstract

$C_4H_{14}ClN_3O_5$, monoclinic, $P12_1/n1$ (No. 14), $a = 5.3043(7)$ Å, $b = 23.320(2)$ Å, $c = 7.490(1)$ Å, $\beta = 99.29(1)°$, $V = 914.3$ Å^3, $Z = 4$, $R_{gt}(F) = 0.031$, $wR_{ref}(F^2) = 0.093$, $T = 293$ K.

Source of material

The compound was synthesized by controlled evaporation, at 313 K, of an aqueous solution of glycine and hydroxylammonium chloride in the molar ratio 1:1. The small single crystal used for the X-ray data collection was cut from a larger specimen of good quality.

Experimental details

Hydrogen atoms from the hydroxylammomium ion were located on a difference Fourier synthesis and refined isotropically; all hydrogen atoms involved in C—H bonds were refined as riding using appropriate AFIX instructions with SHELXL-97 [1] defaults. The final structure was examined with PLATON [2] showing that there are no solvent-accessible voids in the crystal structure.

Discussion

Many glycine salts and adducts exhibit interesting dielectric properties, the most well known compound of this family being TGS (triglycine sulfate) which orders ferroelectrically below 322 K [3]. The present compound is a result from the search for new dielectric materials and their thorough structural characterization carried out in our laboratories. The asymmetric unit cell of title compound contains two neutral glycine molecules in addition to one hydroxyalammonium and chlorine ions. The glycine molecules have the inner dipolar, zwitterionic form, as determined by the localization of the three H-atoms bonded to the N atom in a Fourier difference map and confirmed from an inspection of the carboxylic C—O bond distances [1.238(2) Å – 1.262(2) Å]. Examination of the crystal structure shows layers of Cl^- ions running parallel to '*ac*' planes, intercalated between triple layers of hydrogen-bonded glycine and hydroxylammonium ions. The two glycine molecules have slightly different conformations: although their carboxy skeletons are both planar within 0.003(1) Å, in one of them the N atom is displaced from this plane by 0.235(3) Å, whereas in the other the corresponding displacement is 0.010(3) Å. The angle between these two glycine molecules is 69.54(6)°. The relevant torsion angles describing the conformation of the glycine molecules are ∠N1—C2—C1—O1 = 10.6 ° and ∠N1′—C2′—C1′—O1′ = 0.2(2)°. These can be compared with the equivalent angles, 18.2°, 22.6° and 12.6° in the α, β and γ forms of pure glycine [4-6]. The moieties are linked together by an intricate network of hydrogen bond interactions. The strongest of these bonds involves the O3 atom of the hydroxilammonium ion as a donor and a bare oxygen atom of one of the glycine molecules (O1) as an acceptor [d(O3–H31···O1) = 2.581(2) Å]. In fact, the shared proton may be considered to participate in a bifurcated bond, the much weaker second bond being directed towards the carboxylic O2 atom [d(O3–H31···O2) = 3.057(2) Å]. The H2 atom of the $NH_3(OH)^+$ ion establishes also a bifurcated hydrogen bond with two carboxylic O atoms of neighbouring glycine molecules [d(N3–H2···O2) = 2.848(2) Å and d(N3–H2···O2′) = 3.122(2) Å], the H1 and H3 atoms are each involved in hydrogen bonds towards Cl^- ions [d(N3–H1···Cl) = 3.1621(16) Å, d(N3–H3···Cl) = 3.1683(18) Å]. The NH_3 groups of both glycine molecules are also involved in several hydrogen bonds towards the oxygen atoms of the carboxylic groups of neighbouring molecules. The N1 atom, establishes hydrogen bonds with three other glycine molecules, the bond lengths varying between 2.805(2) Å and 2.928(2) Å. The N1′ atom participates as a donor in two hydrogen bonds towards the carboxylic groups of neighbour glycine molecules [d(N1′–H1C′···O2′) = 2.883(2) Å, d(N1′–H1A′···O1) = 2.879(2) Å] and another bond with a Cl^- ion [d(N1′–H1B′···Cl) = 3.265(2) Å].

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Table 1. Data collection and handling.

Crystal:	colourless square prism, size 0.2 x 0.3 x 0.3 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	4.17 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD4, $\omega/2\theta$
$2\theta_{max}$:	55°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3705, 2075
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1632
$N(param)_{refined}$:	174
Programs:	SHELXS-97 [7], SHELXL-97 [1], PLATON [2], ORTEPII [8]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(2A)	4e	0.872(4)	0.2465(9)	0.496(3)	0.029(5)
H(2B)	4e	1.026(4)	0.1952(8)	0.443(3)	0.023(5)
H(1A)	4e	0.914(4)	0.230(1)	0.150(3)	0.036(6)
H(1B)	4e	1.093(4)	0.2643(9)	0.258(3)	0.031(5)
H(1C)	4e	0.832(4)	0.282(1)	0.222(3)	0.032(5)
H(2A')	4e	0.786(4)	0.078(1)	0.725(3)	0.036(6)
H(2B')	4e	0.955(4)	0.064(1)	0.900(3)	0.035(5)
H(1A')	4e	0.653(5)	0.125(1)	1.011(4)	0.051(7)
H(1B')	4e	0.621(5)	0.067(1)	0.995(4)	0.061(8)
H(1C')	4e	0.488(6)	0.104(1)	0.868(4)	0.052(7)
H(1)	4e	0.063(4)	0.055(1)	0.394(3)	0.033(5)
H(2)	4e	0.222(4)	0.098(1)	0.483(3)	0.039(6)
H(3)	4e	0.343(5)	0.055(1)	0.376(3)	0.043(6)
H(31)	4e	0.285(6)	0.133(1)	0.225(4)	0.08(1)

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	4e	0.5297(2)	0.17712(5)	0.2106(2)	0.0295(6)	0.0337(7)	0.0204(6)	-0.0082(5)	0.0022(5)	-0.0003(4)
O(2)	4e	0.5685(3)	0.16319(6)	0.5072(2)	0.0421(7)	0.0422(8)	0.0219(6)	-0.0134(6)	0.0104(5)	-0.0004(5)
C(1)	4e	0.6400(3)	0.18387(7)	0.3715(2)	0.0272(8)	0.0196(8)	0.0215(8)	0.0002(6)	0.0062(6)	-0.0024(5)
C(2)	4e	0.8822(3)	0.21940(7)	0.4035(2)	0.0250(8)	0.0262(8)	0.0196(7)	-0.0017(6)	0.0022(6)	-0.0007(6)
N(1)	4e	0.9315(3)	0.25046(6)	0.2409(2)	0.0240(7)	0.0248(7)	0.0233(7)	-0.0033(6)	0.0045(5)	-0.0007(5)
O(1')	4e	0.9014(2)	0.19070(5)	0.8943(2)	0.0286(6)	0.0247(6)	0.0260(6)	-0.0005(4)	0.0051(4)	-0.0033(4)
O(2')	4e	1.1685(2)	0.14518(5)	0.7406(2)	0.0233(6)	0.0320(7)	0.0336(6)	0.0004(4)	0.0109(5)	0.0028(5)
C(1')	4e	0.9805(3)	0.14721(7)	0.8235(2)	0.0195(7)	0.0242(8)	0.0192(7)	0.0009(5)	-0.0004(5)	0.0029(5)
C(2')	4e	0.8451(3)	0.09041(7)	0.8383(2)	0.0246(8)	0.0255(8)	0.0282(8)	-0.0002(6)	0.0070(6)	-0.0005(6)
N(1')	4e	0.6299(3)	0.09663(7)	0.9392(2)	0.0242(7)	0.0274(8)	0.0303(7)	-0.0037(6)	0.0078(6)	-0.0001(6)
N(3)	4e	0.2004(3)	0.07692(7)	0.3864(2)	0.0291(8)	0.0293(8)	0.0299(8)	-0.0038(6)	0.0013(6)	0.0026(6)
O(3)	4e	0.1448(3)	0.11096(6)	0.2297(2)	0.0302(6)	0.0420(8)	0.0335(7)	-0.0089(5)	-0.0039(5)	0.0117(5)
Cl	4e	0.67813(8)	0.01009(2)	0.28560(6)	0.0279(2)	0.0302(2)	0.0381(3)	-0.0026(2)	0.0056(2)	0.0026(2)

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