organic compounds

1,3-Dihydroxy-2-(hydroxymethyl)-propan-2-aminium 2,2-dichloroacetate

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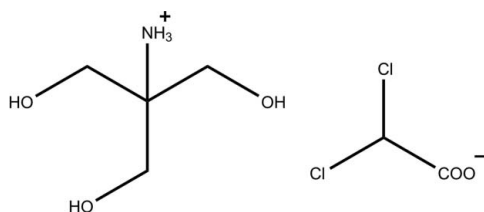Correspondence e-mail: yuyanhong001@yahoo.com.cn

The title compound, $C_4H_{12}NO_3^+ \cdot C_2HCl_2O_2^-$, was obtained from dichloroacetic acid and 2-amino-2-(hydroxymethyl)-propane-1,3-diol. In the crystal structure, the cations and anions are connected by intermolecular N—H···O and O—H···O hydrogen bonding, forming a two-dimensional array parallel to (001). The crystal used for analysis was a merohedral twin, as indicated by the Flack parameter of 0.67 (6).

Related literature

For the engineering of organic crystals for quadratic non-linear optics, see: Etter & Frankenbach (1989); Yaghi *et al.* (1997). For hydrogen-bond networks, see: Etter (1990).

Experimental

Crystal data

$C_4H_{12}NO_3^+ \cdot C_2HCl_2O_2^-$	a = 8.6231 (17) Å
M_r = 250.07	b = 6.1376 (12) Å
Monoclinic, $P2_1$	c = 9.898 (2) Å
β = 97.03 (3)°	μ = 0.62 mm^{-1}
V = 519.92 (18) Å^3	T = 293 K
Z = 2	0.22 × 0.18 × 0.12 mm
Mo $K\alpha$ radiation	

Data collection

Rigaku SCXmini diffractometer	4914 measured reflections
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)	2044 independent reflections
T_{min} = 0.875, T_{max} = 0.929	1951 reflections with $I > 2\sigma(I)$
	R_{int} = 0.025

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031	H-atom parameters constrained
$wR(F^2)$ = 0.069	$\Delta\rho_{max}$ = 0.23 e Å^{-3}
S = 1.10	$\Delta\rho_{min}$ = −0.25 e Å^{-3}
2044 reflections	Absolute structure: Flack (1983), 920 Friedel pairs
130 parameters	Flack parameter: 0.67 (6)
3 restraints	

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O3^i	0.89	2.00	2.881 (2)	169
N1—H1B···O2^{ii}	0.89	1.97	2.858 (2)	172
N1—H1C···O5^{iii}	0.89	2.03	2.909 (2)	169
O3—H3···O4^{iv}	0.81	1.85	2.654 (2)	169
O4—H4···O1	0.82	1.84	2.655 (2)	173
O5—H5···O2^v	0.82	1.88	2.691 (2)	168

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996), *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

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supplementary materials

1,3-Dihydroxy-2-(hydroxymethyl)propan-2-aminium 2,2-dichloroacetate

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Comment

During the past 15 years, organic crystals for quadratic nonlinear optics have been intensely engineered (Etter & Frankenbach, 1989; Yaghi *et al.*, 1997). Arising from the complexation of organic and inorganic molecules based on acid–base interactions, highly polarisable cations, responsible for NLO properties, are linked to inorganic anions through hydrogen bond networks which generate a noncentrosymmetric structural organization (Etter, 1990). In this paper, a novel nonlinear hybrid molecular crystal, $NH_2C(CH_2OH)_3$, has been prepared by complexation between dichloroacetic and tris(hydroxymethyl)amino methane.

The structure is built up from cations and anions (Fig. 1) connected through strong intermolecular hydrogen bonds (Table 1, Fig. 2) to form a two-dimensional layer developing parallel to the (001) plane. As suggested by the value of the Flack parameter (Flack, 1983), 0.67 (6), based on 920 Friedel's pairs, the particular crystal is twinned by inversion.

Experimental

The crystals were grown by slow evaporation at ambient temperature of the solution prepared by adding dichloroacetic acid to the aqueous solution of tris(hydroxymethyl)aminomethane in a stoichiometric ratio. For the X-ray diffraction analysis, suitable single crystals of compound (I) were obtained after one night by slow evaporation from an filtration water solution.

Refinement

All H atoms were found from a difference Fourier map but they were treated as riding on their parent atoms with C—H = 0.97 Å (methylene) or 0.98 Å (methine), N—H = 0.89 Å and O—H = 0.82 Å with Uiso(H) = $1.2U$eq(C) and Uiso(H) = $1.5U$eq(N,O).

Figures

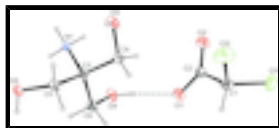Fig. 1. The molecular structure of the title compound with the atom labeling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii. H bond is drawn as dashed line.
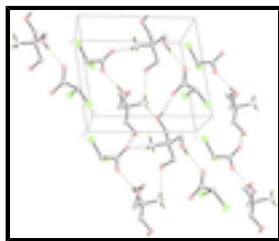

Fig. 2. Partial packing view showing the intricated hydrogen bond framework. H atoms not involved in hydrogen bondings were omitted. [Symmetry code: (i) -x + 1, y + 1/2, -z + 1.]

supplementary materials

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Crystal data

$C_4H_{12}NO_3^+ \cdot C_2HCl_2O_2^-$	$F_{000} = 260$
$M_r = 250.07$	$D_x = 1.597$ Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: P 2yb	Cell parameters from 735 reflections
$a = 8.6231$ (17) Å	$\theta = 2.8–27.5°$
$b = 6.1376$ (12) Å	$\mu = 0.62$ mm^{-1}
$c = 9.898$ (2) Å	$T = 293$ K
$\beta = 97.03$ (3)°	Prism, colourless
$V = 519.92$ (18) Å^3	$0.22 \times 0.18 \times 0.12$ mm
$Z = 2$	

Data collection

Rigaku SCXmini diffractometer	2044 independent reflections
Radiation source: fine-focus sealed tube	1951 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.025$
Detector resolution: 13.6612 pixels mm^{-1}	$\theta_{max} = 26.0°$
$T = 293$ K	$\theta_{min} = 3.3°$
ω scans	$h = -10 \rightarrow 10$
Absorption correction: multi-scan (CrystalClear; Rigaku, 2005)	$k = -7 \rightarrow 7$
$T_{min} = 0.875$, $T_{max} = 0.929$	$l = -12 \rightarrow 12$
4914 measured reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.031$	$w = 1/[\sigma^2(F_o^2) + (0.0218P)^2 + 0.166P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.069$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.10$	$\Delta\rho_{max} = 0.23$ e Å^{-3}
2044 reflections	$\Delta\rho_{min} = -0.25$ e Å^{-3}
130 parameters	Extinction correction: none
3 restraints	Absolute structure: Flack (1983), 920 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.67 (6)
Secondary atom site location: difference Fourier map	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.86491 (9)	0.39154 (15)	0.00483 (7)	0.0630 (2)
Cl2	0.70850 (10)	0.03942 (11)	0.13016 (8)	0.0598 (2)
C1	0.6938 (3)	0.3135 (4)	0.0737 (2)	0.0342 (5)
H1	0.6046	0.3263	0.0026	0.041*
C2	0.6675 (2)	0.4656 (4)	0.1919 (2)	0.0282 (5)
C3	0.2265 (2)	0.2569 (3)	0.3756 (2)	0.0215 (4)
C4	0.3748 (2)	0.1471 (3)	0.3394 (2)	0.0248 (4)
H4A	0.3540	0.0827	0.2496	0.030*
H4B	0.4558	0.2562	0.3365	0.030*
C5	0.0883 (2)	0.0986 (3)	0.3577 (2)	0.0249 (4)
H5A	0.0543	0.0801	0.2613	0.030*
H5B	0.1226	−0.0423	0.3944	0.030*
C6	0.1911 (2)	0.4607 (3)	0.2892 (2)	0.0270 (4)
H6A	0.1841	0.4215	0.1937	0.032*
H6B	0.0905	0.5188	0.3058	0.032*
N1	0.25465 (19)	0.3243 (3)	0.52217 (16)	0.0221 (3)
H1A	0.3470	0.3903	0.5382	0.033*
H1B	0.2540	0.2070	0.5750	0.033*
H1C	0.1797	0.4156	0.5403	0.033*
O1	0.54454 (19)	0.5709 (3)	0.17435 (18)	0.0444 (4)
O2	0.76863 (19)	0.4708 (3)	0.29336 (16)	0.0403 (4)
O3	0.42905 (16)	−0.0160 (2)	0.43407 (15)	0.0306 (4)
H3	0.3857	−0.1281	0.4071	0.046*
O4	0.30642 (17)	0.6233 (2)	0.31776 (17)	0.0336 (4)
H4	0.3805	0.5959	0.2759	0.050*
O5	−0.04042 (15)	0.1704 (3)	0.42311 (15)	0.0274 (3)
H5	−0.0931	0.2564	0.3735	0.041*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0535 (4)	0.0984 (7)	0.0405 (4)	−0.0075 (4)	0.0196 (3)	−0.0042 (4)

Cl2	0.0872 (5)	0.0321 (3)	0.0549 (4)	−0.0001 (4)	−0.0123 (4)	−0.0081 (3)
C1	0.0339 (12)	0.0377 (13)	0.0292 (11)	0.0008 (10)	−0.0040 (9)	−0.0007 (10)
C2	0.0274 (11)	0.0271 (10)	0.0304 (11)	−0.0002 (10)	0.0048 (9)	0.0064 (9)
C3	0.0185 (9)	0.0225 (10)	0.0233 (10)	−0.0014 (8)	0.0018 (8)	0.0011 (8)
C4	0.0213 (10)	0.0248 (11)	0.0288 (11)	0.0005 (9)	0.0052 (9)	0.0000 (9)
C5	0.0191 (9)	0.0233 (11)	0.0324 (11)	−0.0007 (8)	0.0029 (8)	−0.0030 (9)
C6	0.0247 (10)	0.0227 (10)	0.0332 (11)	0.0007 (9)	0.0017 (9)	0.0044 (9)
N1	0.0180 (7)	0.0224 (8)	0.0259 (9)	0.0000 (7)	0.0031 (7)	−0.0006 (7)
O1	0.0347 (9)	0.0503 (11)	0.0494 (10)	0.0142 (8)	0.0097 (8)	0.0129 (9)
O2	0.0424 (9)	0.0425 (10)	0.0337 (9)	0.0120 (8)	−0.0048 (7)	−0.0105 (7)
O3	0.0238 (7)	0.0236 (8)	0.0433 (9)	0.0036 (6)	−0.0002 (7)	0.0001 (7)
O4	0.0293 (8)	0.0219 (7)	0.0510 (10)	−0.0038 (6)	0.0105 (7)	0.0024 (7)
O5	0.0179 (7)	0.0308 (8)	0.0337 (8)	−0.0002 (6)	0.0043 (6)	0.0027 (6)

Geometric parameters (Å, °)

Cl1—C1	1.765 (2)	C5—O5	1.421 (2)
Cl2—C1	1.773 (3)	C5—H5A	0.9700
C1—C2	1.536 (3)	C5—H5B	0.9700
C1—H1	0.9800	C6—O4	1.413 (3)
C2—O1	1.236 (3)	C6—H6A	0.9700
C2—O2	1.247 (3)	C6—H6B	0.9700
C3—N1	1.499 (3)	N1—H1A	0.8900
C3—C6	1.525 (3)	N1—H1B	0.8900
C3—C4	1.527 (3)	N1—H1C	0.8900
C3—C5	1.531 (3)	O3—H3	0.8119
C4—O3	1.411 (2)	O4—H4	0.8205
C4—H4A	0.9700	O5—H5	0.8200
C4—H4B	0.9700		
C2—C1—Cl1	109.75 (16)	O5—C5—C3	112.99 (16)
C2—C1—Cl2	110.36 (16)	O5—C5—H5A	109.0
Cl1—C1—Cl2	110.39 (14)	C3—C5—H5A	109.0
C2—C1—H1	108.8	O5—C5—H5B	109.0
Cl1—C1—H1	108.8	C3—C5—H5B	109.0
Cl2—C1—H1	108.8	H5A—C5—H5B	107.8
O1—C2—O2	127.1 (2)	O4—C6—C3	112.27 (17)
O1—C2—C1	114.5 (2)	O4—C6—H6A	109.2
O2—C2—C1	118.38 (19)	C3—C6—H6A	109.2
N1—C3—C6	108.33 (17)	O4—C6—H6B	109.2
N1—C3—C4	107.93 (16)	C3—C6—H6B	109.2
C6—C3—C4	110.28 (16)	H6A—C6—H6B	107.9
N1—C3—C5	108.57 (16)	C3—N1—H1A	109.5
C6—C3—C5	110.83 (16)	C3—N1—H1B	109.5
C4—C3—C5	110.81 (17)	H1A—N1—H1B	109.5
O3—C4—C3	112.12 (16)	C3—N1—H1C	109.5
O3—C4—H4A	109.2	H1A—N1—H1C	109.5
C3—C4—H4A	109.2	H1B—N1—H1C	109.5
O3—C4—H4B	109.2	C4—O3—H3	106.3
C3—C4—H4B	109.2	C6—O4—H4	109.1

H4A—C4—H4B	107.9	C5—O5—H5	109.5

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O3[i]	0.89	2.00	2.881 (2)	169
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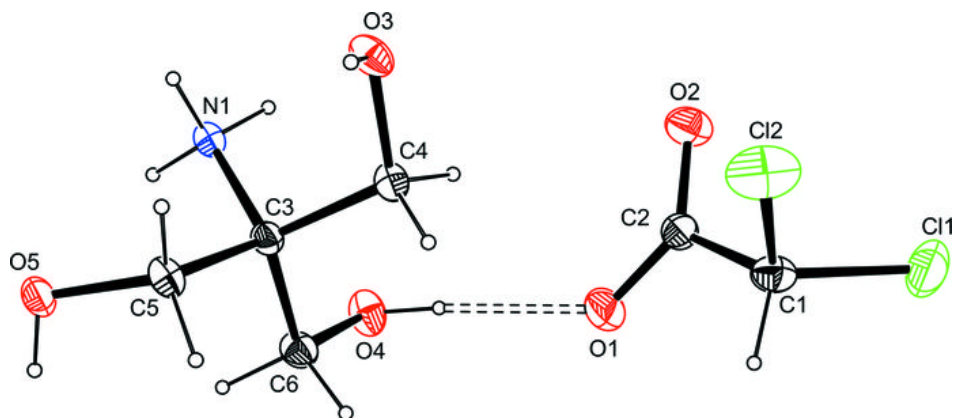
Fig. 1

Fig. 2