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

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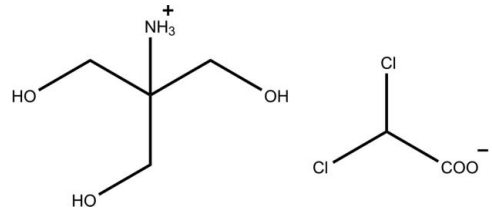
Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.003 Å; $R$ factor = 0.031; $wR$ factor = 0.069; data-to-parameter ratio = 15.7.

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

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

### Data collection

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

### Refinement

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

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1$A$···O3$^{i}$ | 0.89 | 2.00 | 2.881 (2) | 169 |
| N1—H1$B$···O2$^{ii}$ | 0.89 | 1.97 | 2.858 (2) | 172 |
| N1—H1$C$···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*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2442).

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# supporting information

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

**Yan-Hong Yu and Kun Qian**

### S1. 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.

### S2. 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.

### S3. 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 *U*iso(H) = 1.2*U*eq(C) and *U*iso(H) = 1.5*U*eq(N,O).

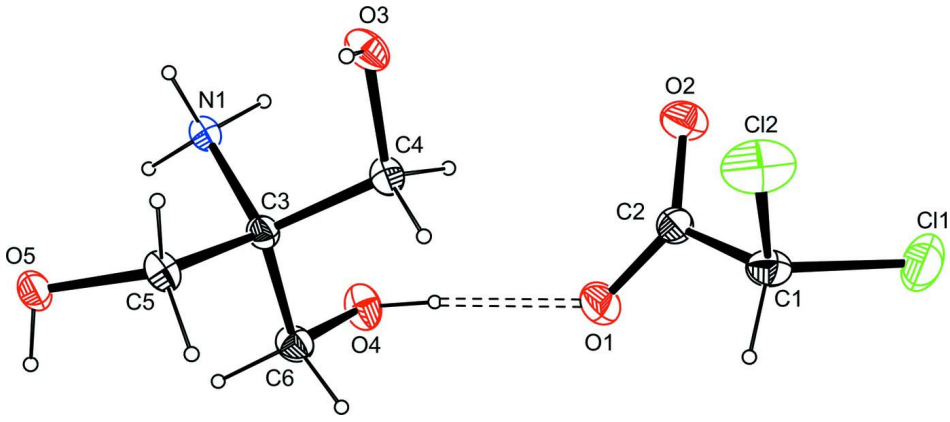


**Figure 1**

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.

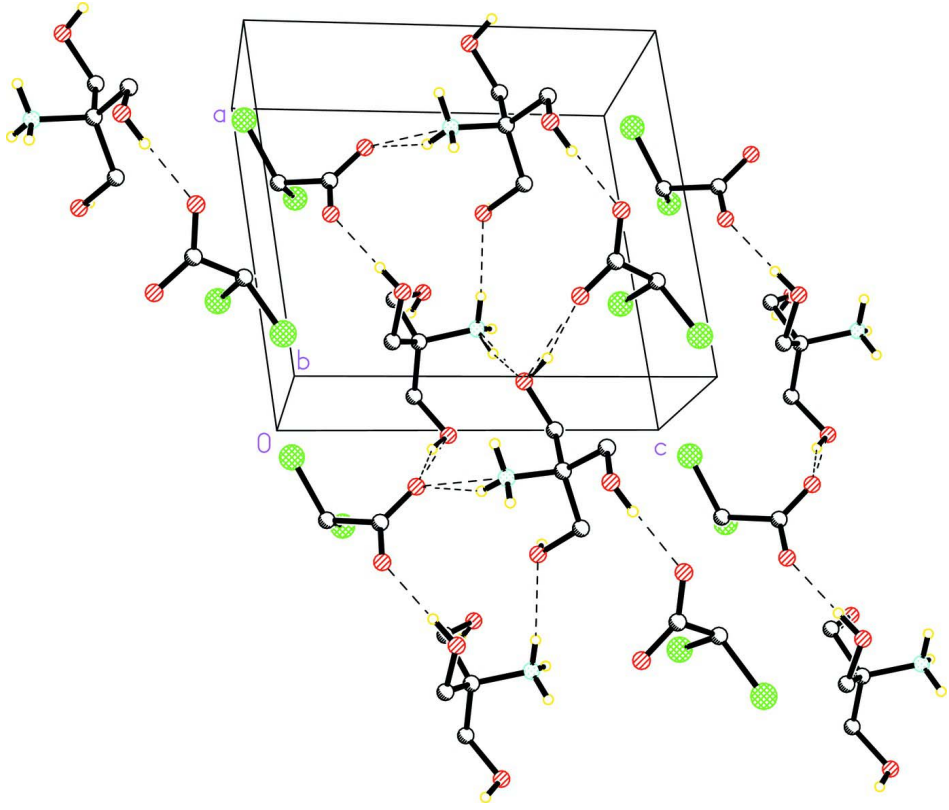


**Figure 2**

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.]

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

*Crystal data*

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

*Data collection*

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

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.069$
$S = 1.10$
2044 reflections
130 parameters
3 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0218P)^2 + 0.166P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.23$ e Å$^{-3}$
$\Delta\rho_{min} = -0.25$ e Å$^{-3}$
Absolute structure: Flack (1983), 920 Friedel pairs
Absolute structure parameter: 0.67 (6)

*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 (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| 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, º)*

| | | | |
|---|---|---|---|
| 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, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1*A*···O3$^{i}$ | 0.89 | 2.00 | 2.881 (2) | 169 |
| N1—H1*B*···O2$^{ii}$ | 0.89 | 1.97 | 2.858 (2) | 172 |
| N1—H1*C*···O5$^{iii}$ | 0.89 | 2.03 | 2.909 (2) | 169 |
| O3—H3···O4$^{iv}$ | 0.81 | 1.85 | 2.654 (2) | 169 |
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Symmetry codes: (i) −*x*+1, *y*+1/2, −*z*+1; (ii) −*x*+1, *y*−1/2, −*z*+1; (iii) −*x*, *y*+1/2, −*z*+1; (iv) *x*, *y*−1, *z*; (v) *x*−1, *y*, *z*.