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Ethylenediammonium bis(2-carboxylato-3,4,5,6-tetrahydro-2,6,6-trimethyl-2*H*-pyran-5-carboxylic acid) dihydrate [ethylenediammonium bis(hydrogen cineolate) dihydrate]

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In the title compound, $2C_{10}H_{15}O_5 \cdot C_2H_{10}N_2 \cdot 2H_2O$, the asymmetric unit is one anion, half a cation and one water molecule. The hydrogen cineolate anion has virtually the same conformation as in racemic cineolic acid. The ethylenediammonium cation has a *gauche* conformation and possesses twofold crystallographic rotation symmetry. The anions form hydrogen-bonded layers parallel to the *bc* plane. Extensive hydrogen bonding to cations and water molecules connects pairs of these layers to form double layers half a unit cell thick.

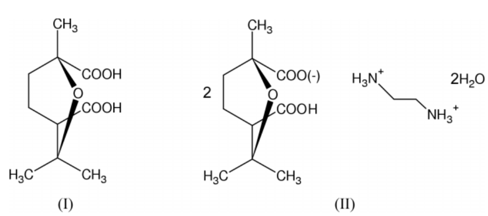
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.002 Å
R factor = 0.049
wR factor = 0.113
Data-to-parameter ratio = 15.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Salts of polycarboxylic acids with protonated cations, such as the ammonium and ethylenediammonium, $(NH_3CH_2)_2^{2+}$, ions, often contain extended hydrogen-bonded arrays. The importance of these arrays has been reviewed by Jeffrey & Saenger (1994). Examples from this laboratory include di-, tri- and tetracarboxylates in which the groups linking the acid functions may be rigid (Barnes *et al.*, 1991; Barnes, 1997) or rotationally unrestricted (Barnes & Barnes, 1996; Barnes *et al.*, 1998; Barnes & Weakley, 2000).



The structure of cineolic acid, (I), was reported in the previous paper (Barnes & Weakley, 2003). Reaction of (I) with 1,2-diaminoethane in various proportions gave only one product, (II), in which the asymmetric unit is one anion, one water molecule and half a cation. The formation of the acid salt rather than full neutralization is typical of reactions of this type. Frequently, only one of the range of likely salts can be obtained as a solid product regardless of the proportions of components in the solution (Barnes & Barnes, 1996; Barnes, 1997; Barnes *et al.*, 1998; Barnes & Weakley, 2000).

Fig. 1 shows that the conformation of the anion in (II) is very similar to that in the free acid, (I). The deprotonated carboxylate group on C2 is axial, whereas the group on C5 is equatorial with the hydrogen on O13 in (II), whereas (I) has this H atom on O12. The torsion angles O9—C8—C2—O1 and C6—C5—C11—O13 are 141.0 (1) and 87.0 (2)° in (II) compared with 142.26 (7) and 82.90 (7)° in (I). This similarity between acid and anion is unusual. It suggests that the carboxylate groups are not free to rotate about the bonds to C2 and C5 because of intramolecular crowding by the methyl groups. More often, the relative orientation of carboxylate

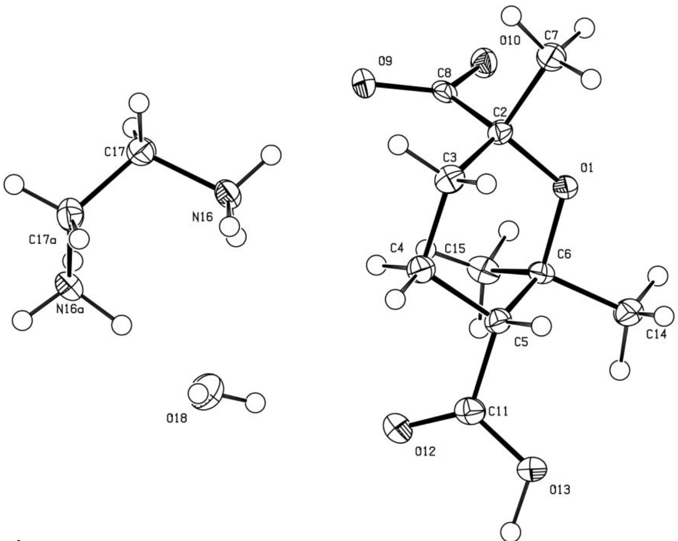


Figure 1
The components of (II), showing ellipsoids at the 50% probability level. The anion is shown in a similar orientation to the free acid (Barnes & Weakley, 2003, Fig. 1)

groups is controlled by optimization of the intermolecular hydrogen bonding for each structure. Relatively free rotation in the cation allows the *gauche* conformation in (II) [N16—C15—C15′–N16′ −62.3 (3)°], rather than the staggered conformation seen in, for example, ethyenediammonium bis(hydrogenmalonate) (Barnes & Weakley, 2000). The structure shows no unusual interatomic distances or angles.

The extensive intermolecular hydrogen bonding is shown in Fig. 2. Two layers of anions lying parallel to the *bc* plane are crosslinked by cations and water molecules to form a double layer half a unit cell thick in the *a* direction. Network analysis of this hydrogen bonding by the techniques of Etter (1990), as extended by Bernstein *et al.* (1995), are unprofitable, since the double layer contains many linked pathways including a 32-membered ring. There are only van der Waals contacts between these double layers.

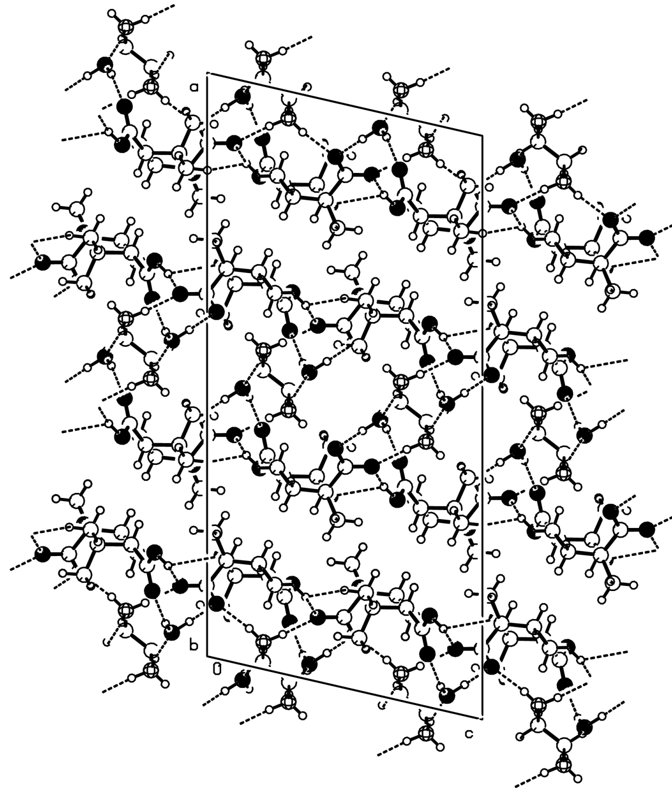


Figure 2
View down *b*, edge on to the hydrogen-bonded double layers which are parallel to the *bc* plane.

Experimental

Crystals were grown by slow evaporation of an aqueous mixture of 1,2-diaminoethane and racemic cineolic acid (1:1).

Crystal data

$C_2H_{10}N_2^{2+}\cdot 2C_{10}H_{15}O_5^{-}\cdot 2H_2O$
$M_r = 528.60$
Monoclinic, $C2/c$
$a = 26.5948$ (14) Å
$b = 7.9327$ (4) Å
$c = 12.8480$ (9) Å
$\beta = 102.938$ (2)°
$V = 2641.7$ (3) Å^3
$Z = 4$
$D_x = 1.329$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5796 reflections
$\theta = 2.9$–27.5°
$\mu = 0.11$ mm^{-1}
$T = 150$ (2) K
Lath, colourless
0.30 × 0.15 × 0.06 mm

Data collection

Enraf–Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.848$, $T_{max} = 0.997$
7946 measured reflections
2939 independent reflections
1936 reflections with $I > 2\sigma(I)$
$R_{int} = 0.070$
$\theta_{max} = 27.5°$
$h = -34 \rightarrow 33$
$k = -8 \rightarrow 9$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.114$
$S = 0.98$
2939 reflections
190 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0487P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C8—O10	1.263 (2)	C11—O12	1.223 (2)
C8—O9	1.265 (2)	C11—O13	1.325 (2)
O10—C8—O9	123.15 (16)	O12—C11—O13	123.33 (16)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O13—H13*A*···O10^{i}	1.04 (3)	1.61 (3)	2.6202 (17)	163 (2)
N16—H16*A*···O10^{i}	0.95 (2)	1.87 (2)	2.770 (2)	156.8 (17)
N16—H16*B*···O18^{ii}	1.02 (2)	1.85 (2)	2.826 (2)	160.6 (18)
N16—H16*C*···O9^{iii}	0.91 (2)	1.87 (2)	2.768 (2)	170 (2)
O18—H18*A*···O9^{iv}	1.05 (3)	1.71 (3)	2.7533 (19)	175 (2)
O18—H18*B*···O12	0.80 (3)	2.25 (3)	3.039 (2)	170 (3)

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

H atoms attached to C atoms were placed in calculated positions and allowed to ride during the refinement. Isotropic displacement parameters were constrained to be $1.3U_{eq}$ of the parent C atom. H atoms attached to O or N atoms were located on a difference synthesis. The positional and isotropic displacement parameters of these H atoms were allowed to refine.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL*97.

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