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Hydrogen Bond Network in Ethylenediammonium Bis(hydrogenmaleate)

J. C. Barnes and **T. J. R. Weakley**

Abstract

In the title compound, $C_2H_{10}N_2^{2+}\cdot 2C_4H_3O_4^-$, ethylene diammonium cations are centred on inversion centres and the mon-hydrogenmaleate anions are in general positions. The components are assembled into double layers by hydrogen bonding. The unique NH_3^+ group connects the planar rings of the intra-molecularly hydrogen-bonded anions into chains and cross-links the chains into centrosymmetric 18-membered rings, with intramolecular O···O 2.452 (2)Å and O···N in the range 2.816 (2)–2.852 (2) Å.

Comment

The ability to form stable hydrogen bond networks (Bernstein, Davis, Shimani & Chang (1995)) decides which of the possible products and solvates will crystallize when polycarboxylic acids reacts with amines. (Barnes and Barnes (1996), Barnes, Longhurst & Weakley (1998).) The monohydrogen anion of maleic acid (*cis* ethenedicarboxylic acid) is stabilized by an intra-molecular hydrogen bond. In solution the stability of this structure is shown by the very wide separation between the pK_A values for maleic acid, 6.22 and 1.92 compared with 4.39 and 3.02 for the corresponding *trans* compound, fumaric acid. (Topp and Davies, 1940.) In the title compound this intra-molecular hydrogen bond O2···H71—O7 (O···O 2.452 (2) Å), gives a 7-membered ring with an r.m.s. deviation from planarity of 0.054 Å. However O1 and O8, which are outside the ring are −0.322 (2) and −0.198 (2) Å out of this plane.

The rings are connected into chains in the c-direction by hydrogen bonds between O2 and O8 and protons of NH_3^+ groups. These chains are crosslinked through the cations to give centrosymmetric 18-membered rings [N11—C12—C12'-N11'-H113'···O1—C3—O2···H112"-]$_2$. (Equivalent symmetry positions are given in the Tables.) These rings are fused in the a-direction to form layers.

Experimental

Ethanolic solutions of 1.0 mmol e thylene diammine hydrate and 2.0 mmol of maleic acid gave an immediate precipitate on mixing. Recrytallized from water.

Computing details

Data collection: Enraf-Nonius *CAD-4 Software*; cell refinement: Enraf-Nonius *CAD-4 Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLUTON* (Spek, 1992); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997).

CIF access

(jcb17)

Crystal data

$C_2H_{10}N_2^{2+}\cdot 2C_4H_3O_4^-$	γ = 105.474 (14)°
M_r = 292.25	V = 315.57 (8) Å^3
Triclinic, $P\overline{1}$	Z = 1
a = 5.7263 (10) Å	Mo $K\alpha$
b = 6.5517 (12) Å	μ = 0.13 mm^{-1}
c = 8.8001 (7) Å	T = 293 (2) K
α = 92.647 (11)°	0.54 × 0.50 × 0.36 mm
β = 95.889 (10)°	

Data collection

Enraf-Nonius CAD-4 diffractometer	R_{int} = 0.014
Absorption correction: none	3 standard reflections
1231 measured reflections	every 300 reflections
1108 independent reflections	intensity decay: none
1019 reflections with $I > 2\sigma(I)$	

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032	123 parameters
$wR(F^2)$ = 0.103	Only H-atom coordinates refined
S = 1.12	$\Delta\rho_{max}$ = 0.23 e Å^{-3}
1108 reflections	$\Delta\rho_{min}$ = −0.14 e Å^{-3}

Table 1
Selected geometric parameters (Å, °)

O1—C3	1.2360 (19)	C6—O8	1.2165 (19)
O2—C3	1.273 (2)	C6—O7	1.298 (2)
C3—C4	1.494 (2)	N11—C12	1.476 (2)
C4—C5	1.325 (2)	C12—C12^{i}	1.511 (3)
C5—C6	1.482 (2)		
O1—C3—O2	123.26 (14)	O8—C6—O7	121.60 (14)
O1—C3—C4	117.79 (14)	O8—C6—C5	118.76 (15)
O2—C3—C4	118.96 (13)	O7—C6—C5	119.64 (13)
C5—C4—C3	130.81 (14)	N11—C12—C12^{i}	110.09 (15)
C4—C5—C6	131.27 (15)		

Symmetry codes: (i) −x, −y−1, −z+1.

Table 2

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O7—H71···O2	1.03 (2)	1.42 (3)	2.4515 (16)	176 (2)
N11—H111···O8^{ii}	0.89 (2)	2.03 (2)	2.8159 (19)	147.0 (18)
N11—H112···O2^{iii}	0.92 (2)	1.97 (2)	2.8516 (18)	159.7 (19)
N11—H113···O1^{iv}	0.94 (2)	1.95 (2)	2.8435 (19)	158.3 (18)

Symmetry codes: (ii) −*x*+1, −*y*, −*z*+2; (iii) −*x*+1, −*y*, −*z*+1; (iv) −*x*, −*y*, −*z*+1.

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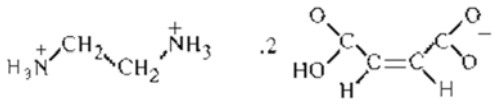
CIF access

Scheme 1



supplementary materials

(jcb17)

Crystal data

$C_2H_{10}N_2^{2+}\cdot 2C_4H_3O_4^-$	$Z = 1$
$M_r = 292.25$	$F_{000} = 154$
Triclinic, $P\overline{1}$	$D_x = 1.538$ Mg m^{-3}
$a = 5.7263$ (10) Å	Mo $K\alpha$ radiation $\lambda = 0.71069$ Å
$b = 6.5517$ (12) Å	Cell parameters from 25 reflections
$c = 8.8001$ (7) Å	$\theta = 14$–15^o
$\alpha = 92.647$ (11)º	$\mu = 0.13$ mm^{-1}
$\beta = 95.889$ (10)º	$T = 293$ (2) K
$\gamma = 105.474$ (14)º	Opaque block, white
$V = 315.57$ (8) Å^3	0.54 × 0.50 × 0.36 mm

Data collection

Enraf-Nonius CAD-4 diffractometer	$R_{int} = 0.014$
Radiation source: fine-focus sealed tube	$\theta_{max} = 25.0^o$
Monochromator: graphite	$\theta_{min} = 2.3^o$
$T = 293$(2) K	$h = 0 \rightarrow 6$
ω–2θ scans	$k = -7 \rightarrow 7$
Absorption correction: none	$l = -10 \rightarrow 10$
1231 measured reflections	3 standard reflections
1108 independent reflections	every 300 reflections
1019 reflections with $I > 2\sigma(I)$	intensity decay: none

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.032$	Only H-atom coordinates refined
$wR(F^2) = 0.103$	Calculated $w = 1/[\sigma^2(F_o^2) + (0.060P)^2 + 0.0745P]$ where $P = (F_o^2 + 2F_c^2)/3$?
$S = 1.12$	$(\Delta/\sigma)_{max} = 0.007$
1108 reflections	$\Delta\rho_{max} = 0.23$ e Å^{-3}
123 parameters	$\Delta\rho_{min} = -0.14$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations

between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 $F^2 > 2\text{sigma}(F^2)$ 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}
O1	0.2533 (2)	0.1517 (2)	0.66433 (12)	0.0473 (4)
O2	0.5827 (2)	0.24353 (18)	0.83351 (13)	0.0425 (3)
C3	0.3534 (3)	0.2044 (2)	0.79683 (17)	0.0326 (4)
C4	0.1955 (3)	0.2231 (2)	0.91874 (17)	0.0349 (4)
C5	0.2429 (3)	0.2391 (2)	1.07008 (17)	0.0346 (4)
C6	0.4681 (3)	0.2446 (2)	1.17147 (17)	0.0340 (4)
O7	0.6714 (2)	0.26329 (19)	1.11316 (14)	0.0433 (3)
O8	0.4575 (2)	0.2327 (2)	1.30826 (13)	0.0531 (4)
N11	0.1914 (3)	−0.2436 (2)	0.44060 (16)	0.0363 (3)
C12	0.0844 (3)	−0.4751 (2)	0.43871 (17)	0.0331 (4)
H41	0.038 (4)	0.211 (3)	0.876 (2)	0.046 (5)*
H51	0.113 (4)	0.235 (3)	1.128 (2)	0.048 (5)*
H71	0.641 (4)	0.257 (3)	0.995 (3)	0.071 (7)*
H111	0.281 (4)	−0.196 (3)	0.531 (3)	0.054 (6)*
H112	0.283 (4)	−0.210 (3)	0.361 (3)	0.056 (6)*
H113	0.064 (4)	−0.179 (3)	0.419 (2)	0.058 (6)*
H121	−0.006 (3)	−0.523 (3)	0.341 (2)	0.043 (5)*
H122	0.218 (4)	−0.539 (3)	0.458 (2)	0.047 (5)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0551 (8)	0.0673 (8)	0.0278 (6)	0.0318 (6)	0.0035 (5)	0.0024 (5)
O2	0.0323 (6)	0.0557 (7)	0.0406 (7)	0.0110 (5)	0.0118 (5)	0.0046 (5)
C3	0.0371 (8)	0.0337 (7)	0.0309 (8)	0.0147 (6)	0.0070 (6)	0.0064 (6)
C4	0.0262 (8)	0.0454 (9)	0.0349 (8)	0.0137 (6)	0.0020 (6)	0.0007 (6)
C5	0.0303 (8)	0.0445 (8)	0.0321 (8)	0.0154 (6)	0.0063 (6)	−0.0005 (6)
C6	0.0361 (8)	0.0345 (8)	0.0322 (8)	0.0140 (6)	−0.0013 (6)	−0.0030 (6)
O7	0.0292 (6)	0.0596 (7)	0.0409 (7)	0.0133 (5)	0.0002 (5)	0.0052 (5)
O8	0.0573 (8)	0.0808 (9)	0.0279 (6)	0.0341 (7)	−0.0014 (5)	−0.0024 (6)
N11	0.0355 (7)	0.0455 (8)	0.0271 (7)	0.0097 (6)	0.0046 (6)	0.0021 (6)
C12	0.0326 (8)	0.0429 (8)	0.0280 (8)	0.0162 (6)	0.0076 (6)	0.0003 (6)

Geometric parameters (Å, °)

O1—C3	1.2360 (19)	C6—O8	1.2165 (19)
O2—C3	1.273 (2)	C6—O7	1.298 (2)
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C4—C5	1.325 (2)	C12—C12^{i}	1.511 (3)
C5—C6	1.482 (2)		
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