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Crystal engineering with heteroboranes. II. 1,2-Dicarboxy-1,2-dicarba-*closo*-dodecaborane(12) ethanol hemisolvate

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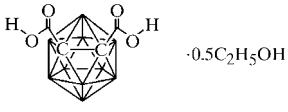
The title compound, 1,2-$(COOH)_2$-1,2-*closo*-$C_2B_{10}H_{10}\cdot 0.5C_2H_6O$ or $C_4H_{12}B_{10}O_4\cdot 0.5C_2H_6O$, forms a tetramer by incorporating ethanol (solvent) molecules through hydrogen bonding. Two eight-membered rings [graph set $R_2^2(8)$] are formed by hydrogen bonding between two carboxylic acid groups, whereas two ten-membered rings [$R_3^3(10)$] are formed by hydrogen bonding between two carboxylic acid groups and the OH group of an ethanol molecule (solvent). Two crystallographically independent tetramers are present in the crystal structure.

Comment

Crystal engineering is an emerging interdisciplinary research area which has many applications in pure and applied chemistry. The use of heteroboranes in studies of crystal engineering has only recently begun to be exploited (Centore *et al.*, 1994; Hosmane *et al.*, 1998; Lee *et al.*, 2000; Hardie *et al.*, 2000; Hardie & Raston, 2000, 2001; Welch *et al.*, 2001; O'Dowd *et al.*, 2002), yet such compounds have a number of potential advantages in this respect. Within the field of crystal engineering, the carboxylic acid group is frequently used to afford supramolecular assemblies through intermolecular H···O bonding (Leiserowitz, 1976). Accordingly, we have begun a



(I)

systematic study of the crystal structures of carborane carboxylic acids. The monocarboxylic acid 1-COOH-1,2-*closo*-$C_2B_{10}H_{11}$ forms discrete dimers (Welch *et al.*, 2001) and the 1,12-dicarboxylic acid 1,12-$(COOH)_2$-1,12-*closo*-$C_2B_{10}H_{10}$ forms infinite chains (Centore *et al.*, 1994) *via* intermolecular

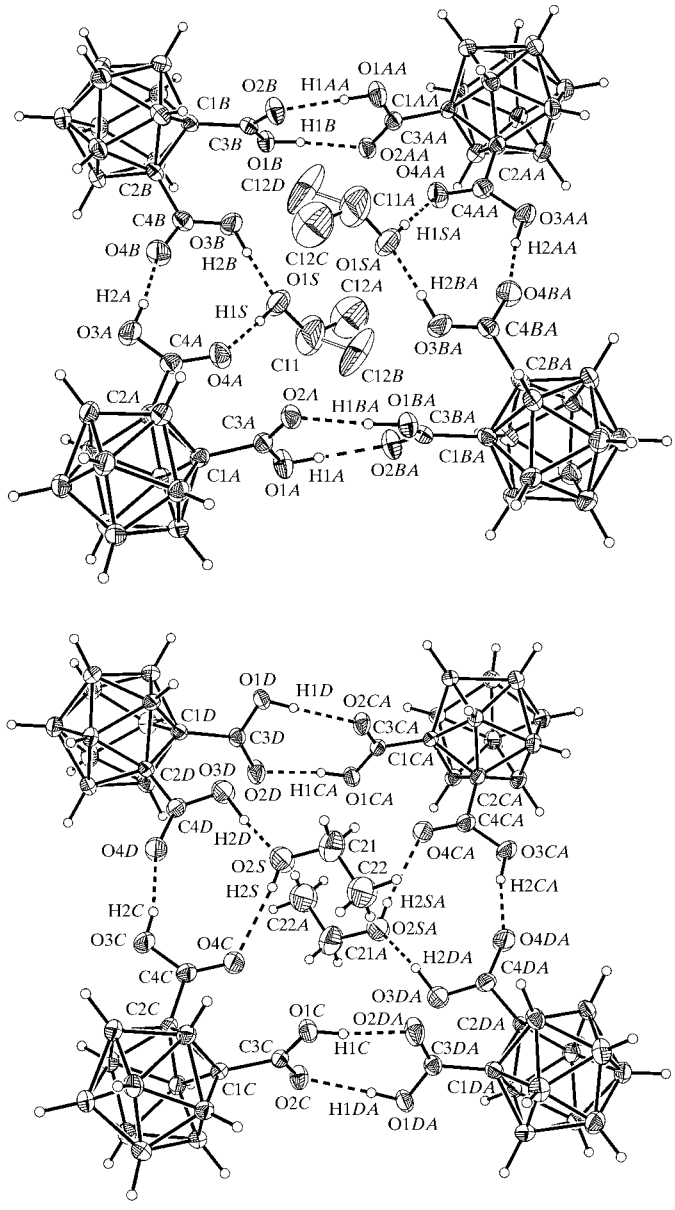


Figure 1
Perspective views of the two tetramers of (I), with displacement ellipsoids at the 50% probability level for non-H atoms. H atoms are drawn as small circles of arbitrary radii and the ethyl H atoms in the ethanol molecule of the upper tetramer are not depicted for clarity. The *AA*/*BA* labels are related to *A*/*B* by the symmetry code $(1-x, 1-y, -z)$, and *CA*/*DA* labels are related to *C*/*D* by the code $(2-x, -y, 1-z)$.

eight-membered hydrogen-bonded rings. In this paper, we report the crystal and molecular structure of 1,2-$(COOH)_2$-1,2-*closo*-$C_2B_{10}H_{10}$, (I).

Compound (I) crystallizes from ethanol with half a molecule of ethanol of solvation. There are four different carborane molecules in the asymmetric unit. The crystal structure reveals two crystallographically independent tetramer units, each arranged about an inversion centre. The tetramers are constructed from two sorts of hydrogen-bonding interactions, *viz*. two conventional eight-membered-ring carboxylic acid dimers and two ten-membered rings involving two

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carboxylic acid groups and an ethanol molecule. In graph-set terminology (Etter, 1990; Etter & MacDonald, 1990), the former is denoted as $R_2^2(8)$ and the latter is represented as $R_3^3(10)$; in each of the four crystallographically independent cages, the two carboxylic acid groups lie perpendicular to each other, preventing the formation of the cyclic trimer that might have been expected if the carboxylic acid groups were in the same plane. Thus, within each cage, one pair of $C_{cage}-C_{cage}-C-O$ torsion angles has values close to +90 and −90°, with the other pair having values close to 0 and 180°. For the second kind of carboxylic acid group, the OH group is *syn* to the first kind of carboxylic acid group in half the cages in each tetrameric unit, and *anti* to it in the other half.

Hydrogen-bond dimensions are H···O = 1.46 (4)–2.08 (4) Å, O···O = 2.476 (2)–2.806 (3) Å and O—H···O = 167 (3)–178 (3)°. The hydrogen bonds formed between the carboxylic acid H atom and the solvent molecule O atom (O3*B*—H2*B*···O1*S* and O3*D*—H2*D*···O2*S*) are the strongest of all the hydrogen bonds [H···O = 1.58 (4) and 1.46 (4) Å]. They are classified as 'very strong' hydrogen bonds, while all the other hydrogen bonds are classified as strong hydrogen bonds (Desiraju & Steiner, 1999). The hydrogen bonds involving the H atoms of the solvent molecule and the O atoms of the carboxylic acid groups are the weakest hydrogen bonds.

The C1—C2 bond distances [1.651 (3)–1.660 (2) Å] are somewhat longer than in the parent compound 1,2-*closo*-$C_2B_{10}H_{12}$ [1.629 (6) and 1.630 (6) Å; Davidson *et al.*, 1996] and the monocarboxylic acid 1-COOH-1,2-*closo*-$C_2B_{10}H_{11}$ [1.631 (2) Å; Welch *et al.*, 2001]. The B—C distances lie between 1.701 (3) and 1.749 (3) Å, while the B—B distances range from 1.763 (3) to 1.799 (4) Å. There appears to be a correlation between the C—COOH distance and the orientation of the COOH group, with lengths of 1.510 (3)–1.516 (3) Å when the C—C—C—O torsion angle is 0 or 180°, and 1.522 (3)–1.527 (3) Å when C—C—C—O is 90 or −90°.

Experimental

Compound (I) was prepared in 85% yield according to a local variation of the literature method of Heying *et al.* (1963) and crystals were grown by evaporation of an ethanol solution. Analysis calculated for $C_4H_{12}B_{10}O_4$: C 20.68, H 5.22%; found: C 19.33, H 5.64%. $^{11}B\{^1H\}$ FT–NMR (128.4 MHz): δ (p.p.m.) 0.298 (2B), −6.499 (2B), −8.024 (6B). The carboxylic acid H atoms were not observed in the ^1H NMR spectrum due to fast intermolecular exchange. The NMR spectra were recorded from a CD_3CN solution at 293 K on a Bruker DPX400 spectrometer.

Crystal data

$C_4H_{12}B_{10}O_4\cdot0.5C_2H_6O$
M_r = 255.27
Triclinic, $P\overline{1}$
a = 12.133 (5) Å
b = 12.658 (5) Å
c = 19.104 (5) Å
α = 76.390 (5)°
β = 73.260 (5)°
γ = 76.620 (5)°
V = 2688.2 (17) Å^3
Z = 8
D_x = 1.250 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 40 reflections
θ = 9.2–24.9°
μ = 0.08 mm^{-1}
T = 160 K
Multifaceted block, colourless
0.5 × 0.5 × 0.5 mm

Data collection

Bruker *P*4 diffractometer
ω scans
10 856 measured reflections
9408 independent reflections
7890 reflections with $I > 2\sigma(I)$
R_{int} = 0.079
θ_{max} = 25.0°
$h = -14 \rightarrow 1$
$k = -14 \rightarrow 14$
$l = -22 \rightarrow 22$
3 standard reflections
every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.144
S = 1.03
9408 reflections
755 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0661P)^2 + 1.6557P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.55 e Å^{-3}
$\Delta\rho_{min}$ = −0.47 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1*A*—C2*A*	1.651 (3)	C1*C*—C2*C*	1.652 (2)
C1*A*—C3*A*	1.523 (3)	C1*C*—C3*C*	1.525 (2)
C3*A*—O1*A*	1.301 (2)	C3*C*—O1*C*	1.306 (2)
C3*A*—O2*A*	1.212 (2)	C3*C*—O2*C*	1.212 (2)
C2*A*—C4*A*	1.510 (3)	C2*C*—C4*C*	1.510 (3)
C4*A*—O3*A*	1.304 (3)	C4*C*—O3*C*	1.300 (2)
C4*A*—O4*A*	1.205 (3)	C4*C*—O4*C*	1.209 (2)
C1*B*—C2*B*	1.660 (2)	C1*D*—C2*D*	1.653 (2)
C1*B*—C3*B*	1.527 (3)	C1*D*—C3*D*	1.522 (3)
C3*B*—O1*B*	1.298 (2)	C1*D*—B6*D*	1.745 (3)
C3*B*—O2*B*	1.214 (2)	C3*D*—O1*D*	1.304 (2)
C2*B*—C4*B*	1.516 (3)	C2*D*—C4*D*	1.514 (3)
C4*B*—O3*B*	1.283 (3)	C4*D*—O3*D*	1.286 (3)
C4*B*—O4*B*	1.204 (2)	C4*D*—O4*D*	1.201 (3)
C3*A*—C1*A*—C2*A*	121.07 (15)	C3*C*—C1*C*—C2*C*	122.21 (15)
C4*A*—C2*A*—C1*A*	115.75 (15)	C4*C*—C2*C*—C1*C*	116.56 (15)
O2*A*—C3*A*—O1*A*	125.80 (18)	O2*C*—C3*C*—O1*C*	125.83 (17)
O4*A*—C4*A*—O3*A*	126.73 (19)	O4*C*—C4*C*—O3*C*	127.21 (19)
C3*B*—C1*B*—C2*B*	120.41 (15)	C3*D*—C1*D*—C2*D*	118.93 (15)
C4*B*—C2*B*—C1*B*	119.17 (15)	C4*D*—C2*D*—C1*D*	117.91 (15)
O2*B*—C3*B*—O1*B*	126.20 (18)	O2*D*—C3*D*—O1*D*	125.75 (18)
O4*B*—C4*B*—O3*B*	126.8 (2)	O4*D*—C4*D*—O3*D*	126.7 (2)
C3*A*—C1*A*—C2*A*—C4*A*	1.9 (2)	C4*C*—C2*C*—C1*C*—C3*C*	−3.3 (2)
C2*A*—C1*A*—C3*A*—O1*A*	−92.0 (2)	C2*C*—C1*C*—C3*C*—O1*C*	88.1 (2)
C2*A*—C1*A*—C3*A*—O2*A*	93.2 (2)	C2*C*—C1*C*—C3*C*—O2*C*	−98.0 (2)
C1*A*—C2*A*—C4*A*—O3*A*	−178.63 (16)	C1*C*—C2*C*—C4*C*—O3*C*	−178.84 (16)
C1*A*—C2*A*—C4*A*—O4*A*	2.9 (3)	C1*C*—C2*C*—C4*C*—O4*C*	0.5 (3)
C3*B*—C1*B*—C2*B*—C4*B*	1.4 (2)	C3*D*—C1*D*—C2*D*—C4*D*	1.2 (2)
C2*B*—C1*B*—C3*B*—O1*B*	−97.6 (2)	C2*D*—C1*D*—C3*D*—O1*D*	−105.25 (19)
C2*B*—C1*B*—C3*B*—O2*B*	87.0 (2)	C2*D*—C1*D*—C3*D*—O2*D*	77.0 (2)
C1*B*—C2*B*—C4*B*—O3*B*	15.8 (2)	C1*D*—C2*D*—C4*D*—O3*D*	29.7 (2)
C1*B*—C2*B*—C4*B*—O4*B*	−164.77 (19)	C1*D*—C2*D*—C4*D*—O4*D*	−150.0 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*A*—H1*A*···O2*B*^{i}	0.87 (3)	1.78 (3)	2.647 (2)	175 (3)
O1*B*—H1*B*···O2*A*^{ii}	0.91 (3)	1.78 (3)	2.687 (2)	175 (3)
O1*S*—H1*S*···O4*A*^{iii}	0.90 (4)	1.89 (4)	2.790 (3)	175 (4)
O3*A*—H2*A*···O4*B*^{iii}	0.93 (3)	1.70 (3)	2.624 (2)	172 (3)
O3*B*—H2*B*···O1*S*	0.90 (4)	1.58 (4)	2.478 (2)	175 (3)
O1*C*—H1*C*···O2*D*^{iv}	0.89 (4)	1.79 (4)	2.677 (2)	172 (4)
O1*D*—H1*D*···O2*C*^{iv}	0.85 (3)	1.83 (3)	2.689 (2)	178 (3)
O2*S*—H2*S*···O4*C*^{v}	0.73 (4)	2.08 (4)	2.806 (3)	172 (4)
O3*C*—H2*C*···O4*D*^{vi}	0.85 (3)	1.79 (3)	2.628 (2)	167 (3)
O3*D*—H2*D*···O2*S*^{vii}	1.03 (4)	1.46 (4)	2.476 (2)	169 (4)

Symmetry codes: (i) $x, y, z-1$; (ii) $x, y, 1+z$; (iii) $1-x, 1-y, 1-z$; (iv) $2-x, 1-y, 1-z$; (v) $x-1, y, z$; (vi) $x, y-1, z$; (vii) $1+x, 1+y, z$.

Methyl atom C12 of one of the solvent molecules is disordered. Two positions were located (C12*A*/C12*B*) and the distances to the more ordered adjacent C atom (C11) were restrained to 1.45 (5) Å. The carboxylic acid H atoms and the hydroxy H atoms of the solvent molecules were located from a difference Fourier map. Their U_{iso} values were allowed to refine freely in subsequent refinement cycles. The positions of the cage H atoms and the ethyl H atoms of the solvent molecules were calculated using appropriate HFIX options in *SHELXL*97 (Sheldrick, 1997).

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1173). Services for accessing these data are described at the back of the journal.

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