IUCrData

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rac-1,1,1,6,6,6-Hexachlorohex-3-yne-2,5-diol hemihydrate

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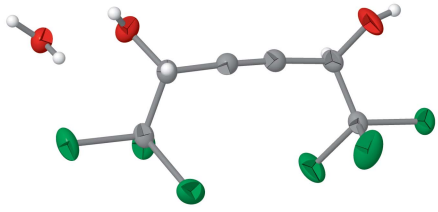
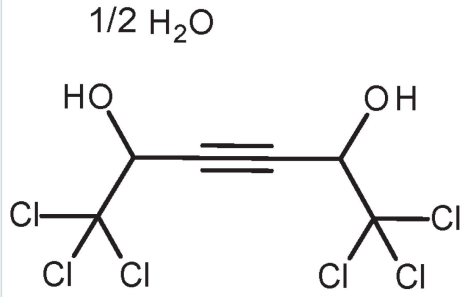
Structural data: full structural data are available from iucrdata.iucr.org

The asymmetric unit of the title compound, $C_6H_4Cl_6O_2\cdot0.5H_2O$, contains one molecule of 1,1,1,6,6,6-hexachlorohex-3-yne-2,5-diol and half a water molecule located on a twofold rotation axis. In the crystal, pairs of hexachlorohexynediol molecules form centrosymmetric dimers connected *via* pairwise O—H···O hydrogen bonds. These dimers are connected by water molecules, resulting in layers parallel to the *ab* plane.

3D view



Chemical scheme



Structure description

Highly chlorinated compounds are of current interest because they are intermediates in the formation of environmental pollutants (Taylor *et al.*, 2000) and they are useful as chemical substrates (Rahimi *et al.*, 2009; Schmidt *et al.*, 2009). Furthermore, their rearrangements (McIntosh *et al.*, 2014; Schollmeyer & Detert, 2017; Detert *et al.*, 2009) are a topic in its own right. The monoclinic unit cell contains four centrosymmetric dimers composed of one molecule with an *R*,*R*-configuration, one with an *S*,*S*-configuration and four water molecules, the latter is located on a twofold rotation axis.

In the monoclinic crystal, the hexachlorohexynediol molecules adopt a *gauche* conformation [C1—C2···C5—C6 = 30.4 (2)°] with a nonperfect *C*2 symmetry (Fig. 1). The C—Cl bonds of the trichloromethyl groups vary between 1.756 (3) (C6—Cl4) and 1.776 (3) Å (C1—Cl2). With bond angles of 176.9 (3) and 175.8 (3)° and a torsion angle of 3 (10)°, the alkyne unit is not perfectly linear. An *R*,*R*- and an *S*,*S*-configured diole are connected *via* short hydrogen bonds [O1—H1*O*···O2^{ii} = 2.725 (3) Å] to a centrosymmetric dimer (Table 1). A C—H···O hydrogen bond [C5—H5···O1^{i} = 3.297 (4) Å] forms a chain parallel to the *b* axis. Hydrogen bonds between atoms O1 and O2 to the water molecule [O2—H2*O*···O3^{i} = 2.773 (3) Å and O3—H3*O*···O1 = 2.999 (3) Å] connect these chains into layers in the *ab* plane (Fig. 2).

Synthesis and crystallization

The title compound was prepared from ethyl magnesium bromide, acetylene and chloral according to Gorgues *et al.* (1986) and Dupont (1910) followed by aqueous work-up. A mixture of three stereoisomers was obtained. Recrystallization from ethanol solution gave the title compound. ^{1}H NMR: ($CDCl_3$/DMSO-d_6, 400 MHz): δ 7.05 (2*H*, OH), 4.79 (2*H*, CH, $^1J_{CH}$ = 154 Hz). Recrystallization from chloroform solution yielded colourless crystals (m.p. 408 K).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were located in difference Fourier maps and were refined with isotropic displacement parameters.

Figure
R,R- and an S,S-configured diole are connected via short hydrogen bonds [O1—H1O···O2^{ii} = 2.725 (3) Å] to a centrosymmetric dimer (Table 1). A C—H···O hydrogen bond [C5—H5···O1^{i} = 3.297 (4) Å] forms a chain parallel to the b axis. Hydrogen bonds between atoms O1 and O2 to the water molecule [O2—H2O···O3^{i} = 2.773 (3) Å and O3—H3O···O1 = 2.999 (3) Å] connect these chains into layers in the ab plane.

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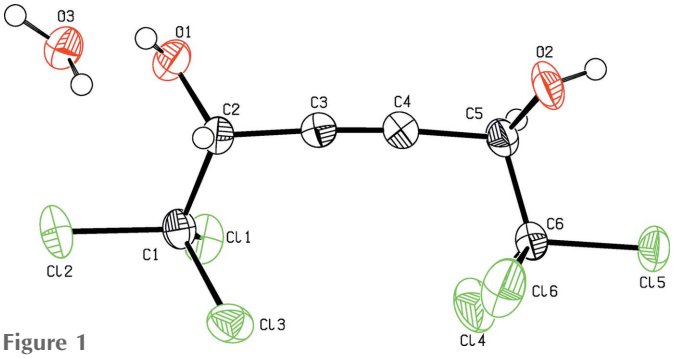

Figure 1
View of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

Table 2
Experimental details.

Crystal data	
Chemical formula	$2C_6H_4Cl_6O_2\cdot H_2O$
M_r	659.60
Crystal system, space group	Monoclinic, *I*2/*a*
Temperature (K)	193
a, *b*, *c* (Å)	19.8354 (11), 5.8480 (2), 21.7082 (13)
β (°)	108.321 (4)
V (Å^3)	2390.5 (2)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	1.41
Crystal size (mm)	0.39 × 0.07 × 0.06
Data collection	
Diffractometer	Stoe IPDS 2T
Absorption correction	Integration (*X-RED32*; Stoe & Cie, 2006*b*)
T_{min}, T_{max}	0.714, 0.933
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6305, 2965, 2202
R_{int}	0.026
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.668
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.039, 0.090, 1.03
No. of reflections	2965
No. of parameters	152
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.59, −0.57

Computer programs: *X-AREA* (Stoe & Cie, 2006*a*), *X-RED32* (Stoe & Cie, 2006*b*), *SIR2004* (Altomare *et al.*, 1999) and *SHELXL2014* (Sheldrick, 2015).

$^1J_{CH}$ = 154 Hz). Recrystallization from chloroform solution yielded colourless crystals (m.p. 408 K).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were located in difference

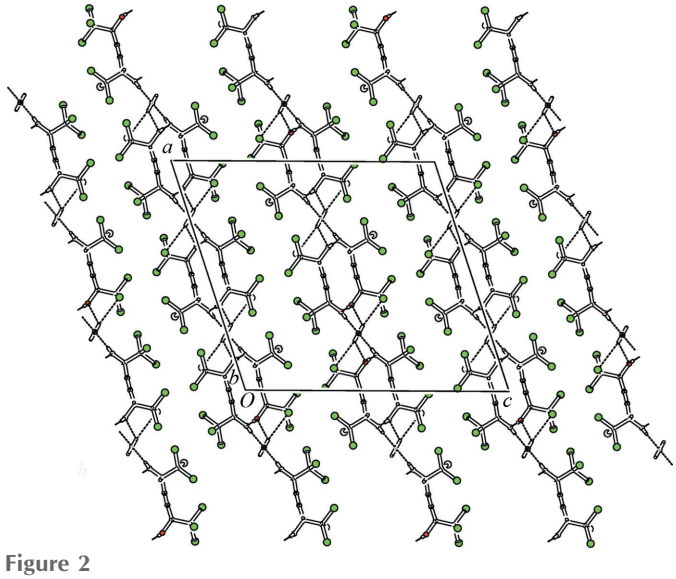

Figure 2
Part of the packing diagram, viewed along the *b* axis. Hydrogen bonds are shown with dashed lines.

full crystallographic data

IUCrData (2017). **2**, x171236 [https://doi.org/10.1107/S2414314617012366]

rac-1,1,1,6,6,6-Hexachlorohex-3-yne-2,5-diol hemihydrate

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Crystal data

$2C_6H_4Cl_6O_2·H_2O$
M_r = 659.60
Monoclinic, *I*2/*a*
a = 19.8354 (11) Å
b = 5.8480 (2) Å
c = 21.7082 (13) Å
β = 108.321 (4)°
V = 2390.5 (2) Å^3
Z = 4
F(000) = 1304
D_x = 1.833 Mg m^{-3}
Melting point: 408 K
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 5782 reflections
θ = 3.4–28.3°
μ = 1.41 mm^{-1}
T = 193 K
Column, colourless
0.39 × 0.07 × 0.06 mm

Data collection

Stoe IPDS 2T diffractometer
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus
Detector resolution: 6.67 pixels mm^{-1}
rotation method scans
Absorption correction: integration (X-RED32; Stoe & Cie, 2006b)
T_{min} = 0.714, T_{max} = 0.933
6305 measured reflections
2965 independent reflections
2202 reflections with $I > 2\sigma(I)$
R_{int} = 0.026
θ_{max} = 28.3°, θ_{min} = 2.4°
h = −26→26
k = −7→6
l = −24→28

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.090
S = 1.03
2965 reflections
152 parameters
0 restraints
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0295P)^2 + 6.4827P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.59 e Å^{-3}
$\Delta\rho_{min}$ = −0.57 e Å^{-3}

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.58326 (13)	0.4054 (5)	0.37414 (13)	0.0269 (5)
C2	0.56624 (13)	0.4444 (5)	0.43828 (13)	0.0268 (5)
H2	0.5573 (14)	0.608 (5)	0.4386 (13)	0.026 (7)*
C3	0.50278 (14)	0.3142 (5)	0.43757 (12)	0.0296 (6)
C4	0.45026 (15)	0.2097 (5)	0.43394 (13)	0.0314 (6)
C5	0.38356 (15)	0.0835 (5)	0.42428 (13)	0.0303 (6)
H5	0.3951 (17)	−0.077 (6)	0.4347 (16)	0.046 (9)*
C6	0.34051 (13)	0.0815 (5)	0.35171 (13)	0.0270 (5)
O1	0.62524 (11)	0.3777 (4)	0.49119 (10)	0.0345 (5)
H1O	0.637 (2)	0.484 (7)	0.5082 (19)	0.051 (12)*
O2	0.34423 (13)	0.1915 (5)	0.46020 (11)	0.0489 (7)
H2O	0.319 (2)	0.114 (7)	0.4692 (19)	0.059 (13)*
O3	0.7500	0.0752 (6)	0.5000	0.0380 (7)
H3O	0.717 (3)	0.171 (10)	0.475 (3)	0.12 (2)*
Cl1	0.59756 (4)	0.11144 (12)	0.36352 (4)	0.03662 (17)
Cl2	0.66181 (4)	0.55802 (13)	0.37759 (4)	0.04003 (19)
Cl3	0.51257 (4)	0.50491 (14)	0.30818 (3)	0.04010 (19)
Cl4	0.38978 (5)	−0.05417 (17)	0.30774 (4)	0.0551 (3)
Cl5	0.26084 (4)	−0.07339 (13)	0.34107 (4)	0.03746 (18)
Cl6	0.31978 (4)	0.36244 (14)	0.32294 (5)	0.0547 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0242 (12)	0.0244 (12)	0.0341 (13)	0.0017 (10)	0.0119 (10)	0.0002 (11)
C2	0.0232 (12)	0.0271 (14)	0.0300 (13)	−0.0016 (10)	0.0083 (10)	0.0002 (11)
C3	0.0268 (13)	0.0357 (15)	0.0257 (12)	−0.0011 (11)	0.0075 (10)	0.0015 (11)
C4	0.0302 (14)	0.0358 (15)	0.0292 (13)	−0.0032 (12)	0.0109 (11)	0.0016 (12)
C5	0.0311 (14)	0.0315 (15)	0.0312 (14)	−0.0084 (12)	0.0138 (11)	−0.0003 (12)
C6	0.0251 (12)	0.0271 (13)	0.0312 (13)	−0.0024 (10)	0.0123 (10)	−0.0012 (11)
O1	0.0297 (10)	0.0338 (12)	0.0349 (11)	−0.0043 (9)	0.0028 (8)	−0.0005 (9)
O2	0.0507 (14)	0.0622 (16)	0.0484 (13)	−0.0332 (13)	0.0367 (11)	−0.0271 (12)
O3	0.0278 (15)	0.0455 (18)	0.0381 (16)	0.000	0.0066 (12)	0.000
Cl1	0.0322 (3)	0.0265 (3)	0.0517 (4)	0.0022 (3)	0.0140 (3)	−0.0071 (3)
Cl2	0.0346 (4)	0.0347 (4)	0.0601 (5)	−0.0071 (3)	0.0282 (3)	−0.0022 (3)
Cl3	0.0384 (4)	0.0489 (4)	0.0334 (3)	0.0119 (3)	0.0118 (3)	0.0097 (3)
Cl4	0.0544 (5)	0.0652 (6)	0.0615 (5)	−0.0178 (4)	0.0408 (4)	−0.0298 (5)
Cl5	0.0301 (3)	0.0397 (4)	0.0436 (4)	−0.0134 (3)	0.0130 (3)	−0.0058 (3)
Cl6	0.0418 (4)	0.0358 (4)	0.0742 (6)	−0.0033 (3)	0.0004 (4)	0.0202 (4)

Geometric parameters (Å, º)

C1—C2	1.549 (4)	C5—O2	1.414 (3)
C1—Cl3	1.758 (3)	C5—C6	1.538 (4)
C1—Cl1	1.769 (3)	C5—H5	0.98 (4)

C1—Cl2	1.776 (3)	C6—Cl4	1.756 (3)
C2—O1	1.413 (3)	C6—Cl6	1.760 (3)
C2—C3	1.467 (4)	C6—Cl5	1.772 (3)
C2—H2	0.97 (3)	O1—H1O	0.72 (4)
C3—C4	1.189 (4)	O2—H2O	0.75 (4)
C4—C5	1.471 (4)	O3—H3O	0.90 (5)
C2—C1—Cl3	109.87 (17)	O2—C5—C4	108.9 (2)
C2—C1—Cl1	110.43 (19)	O2—C5—C6	110.1 (2)
Cl3—C1—Cl1	109.56 (15)	C4—C5—C6	109.5 (2)
C2—C1—Cl2	108.92 (18)	O2—C5—H5	116 (2)
Cl3—C1—Cl2	109.42 (14)	C4—C5—H5	108 (2)
Cl1—C1—Cl2	108.62 (14)	C6—C5—H5	104 (2)
O1—C2—C3	110.7 (2)	C5—C6—Cl4	109.60 (19)
O1—C2—C1	109.4 (2)	C5—C6—Cl6	110.4 (2)
C3—C2—C1	110.1 (2)	Cl4—C6—Cl6	109.69 (15)
O1—C2—H2	111.8 (17)	C5—C6—Cl5	108.81 (18)
C3—C2—H2	110.6 (17)	Cl4—C6—Cl5	108.90 (15)
C1—C2—H2	104.0 (17)	Cl6—C6—Cl5	109.37 (14)
C4—C3—C2	176.9 (3)	C2—O1—H1O	104 (3)
C3—C4—C5	175.8 (3)	C5—O2—H2O	114 (3)
Cl3—C1—C2—O1	−176.19 (18)	O2—C5—C6—Cl4	−179.75 (18)
Cl1—C1—C2—O1	62.8 (2)	C4—C5—C6—Cl4	60.5 (3)
Cl2—C1—C2—O1	−56.3 (3)	O2—C5—C6—Cl6	59.3 (3)
Cl3—C1—C2—C3	62.0 (3)	C4—C5—C6—Cl6	−60.5 (3)
Cl1—C1—C2—C3	−59.0 (3)	O2—C5—C6—Cl5	−60.8 (3)
Cl2—C1—C2—C3	−178.21 (19)	C4—C5—C6—Cl5	179.5 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···O1^{i}	0.98 (4)	2.50 (4)	3.297 (4)	139 (3)
O1—H1*O*···O2^{ii}	0.72 (4)	2.01 (4)	2.725 (3)	168 (4)
O2—H2*O*···O3^{i}	0.75 (4)	2.02 (4)	2.773 (3)	175 (4)
O3—H3*O*···O1	0.90 (5)	2.29 (5)	2.999 (3)	135 (5)
O3—H3*O*···Cl1	0.90 (5)	2.83 (5)	3.5120 (8)	134 (4)
O3—H3*O*···Cl2	0.90 (5)	3.06 (5)	3.895 (3)	155 (5)

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