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3,5-Dihydroxy-3,5-bis(trifluoromethyl)-1,2-dioxolane–1,4-dioxane (1/1) at 173 K

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Key indicators

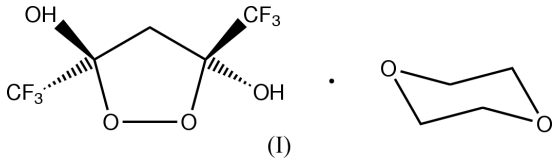
Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.003 Å
R factor = 0.053
wR factor = 0.105
Data-to-parameter ratio = 13.3

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

The 1,2-dioxolane of the title adduct, $C_5H_4F_6O_4\cdot C_4H_8O_2$, is produced slowly by air oxidation of diaquabis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)manganese(II) in the presence of 1,4-dioxane. This dioxolane is formally derived from the addition of H_2O_2 to 1,1,1,5,5,5-hexafluoropentane-2,4-dione. The hydroxy groups of the dioxolane are hydrogen bonded to dioxane to form an alternating chain structure.

Comment

An attempt to synthesize bis(1,4-dioxane)bis(hfac)-manganese(II) (hfac = 1,1,1,5,5,5-hexafluoropentane-2,4-dionato) resulted in the isolation of diaquabis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)manganese(II) 1.5-(1,4-dioxane) solvate, identified by an X-ray crystal structure analysis. A sample of this solvate kept in a sealed glass vial was observed, after several months, to deposit colourless crystals near the top of the vial, apparently by sublimation. Structure analysis of these crystals revealed the title 1,2-dioxolane, (I), hydrogen bonded to 1,4-dioxane (Fig. 1). The two hydroxy groups are hydrogen bonded to different dioxane molecules to form a chain in which dioxane and dioxolane alternate.



(I)

Presumably autoxidation of 1,4-dioxane forms peroxide which then reacts with $Mn(hfac)_2(H_2O)_2$ to produce 1,2-dioxolane. Fluorinated organic peroxides have been found useful as synthetic reagents (Sawada, 1996).

O1 and O2 are out of the C2—C3—C4 plane by −0.295 (5) and 0.361 (5) Å, respectively. Structure reports of 1,2-dioxolanes in which the dioxolane ring is not fused to other rings are relatively uncommon. Among these are 3,3′-vinylidene-di-(5-phenyl-1,2-dioxolane) and 4-(5′-phenyl-1′,2′-dioxolan-3′-yl)-3-vinyl-1,2-dioxolane (Feldman *et al.*, 1986); bis(3,5,5-trimethyl-1,2-dioxolan-3-yl) peroxide (Ramm, 1996); and two steroid derivatives (Hernández *et al.*, 1996; Boto *et al.*, 1998).

Experimental

$Mn(hfac)_2(H_2O)_3$ was made by a standard procedure (Morris *et al.*, 1968). $Mn(hfac)_2(H_2O)_3$ (0.5 g) was added to a mixture of *n*-heptane (50 ml) and 1,4-dioxane (5 ml). This mixture was distilled until nearly 5 ml of the solution had evaporated. The remaining yellow solution was allowed to cool at room temperature in a loosely covered beaker. After about a day, yellow crystals formed. These were identified as $Mn(hfac)_2(H_2O)_2$ 1.5-(1,4-dioxane) solvate. This compound was isolated by filtration and stored in a sealed glass vial. Colourless crystals of the title formula formed slowly over a period of months.

Crystal data

$C_5H_4F_6O_4{\cdot}C_4H_8O_2$	D_x = 1.658 Mg m^{-3}
M_r = 330.19	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 5471 reflections
a = 8.1997 (3) Å	θ = 2.2–28.3°
b = 18.2477 (6) Å	μ = 0.19 mm^{-1}
c = 8.8871 (3) Å	T = 173 (2) K
β = 95.798 (1)°	Rod, colourless
V = 1322.94 (8) Å^3	0.36 × 0.15 × 0.15 mm
Z = 4	

Data collection

CCD area-detector diffractometer	R_{int} = 0.059
ω scans	θ_{max} = 28.3°
14 324 measured reflections	$h = -10 \rightarrow 10$
3163 independent reflections	$k = -23 \rightarrow 23$
1972 reflections with $I > 2\sigma(I)$	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.026P)^2 + 0.85P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.053	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2)$ = 0.105	$\Delta\rho_{max}$ = 0.21 e Å^{-3}
S = 1.04	$\Delta\rho_{min}$ = −0.27 e Å^{-3}
3163 reflections	
238 parameters	
All H-atom parameters refined	

Table 1
Selected geometric parameters (Å, °).

C1—F3	1.330 (3)	C5—F4	1.329 (3)
C1—F1	1.336 (3)	C5—F6	1.331 (3)
C1—F2	1.338 (3)	C5—F5	1.335 (3)
C1—C2	1.530 (3)	C6—O5	1.433 (3)
C2—O3	1.384 (3)	C6—C7	1.494 (4)
C2—O1	1.431 (2)	C7—O6	1.442 (3)
C2—C3	1.522 (3)	C8—O6	1.440 (3)
C3—C4	1.523 (3)	C8—C9	1.493 (4)
C4—O4	1.381 (2)	C9—O5	1.438 (3)
C4—O2	1.429 (2)	O1—O2	1.472 (2)
C4—C5	1.529 (3)		
O1—C2—C3	105.85 (17)	C2—O1—O2	103.30 (13)
C2—C3—C4	102.91 (17)	C4—O2—O1	103.40 (14)
O2—C4—C3	105.40 (16)		
O1—C2—C3—C4	−12.4 (2)	C3—C4—O2—O1	36.48 (19)
C2—C3—C4—O2	−15.2 (2)	C2—O1—O2—C4	−44.83 (18)
C3—C2—O1—O2	34.6 (2)		

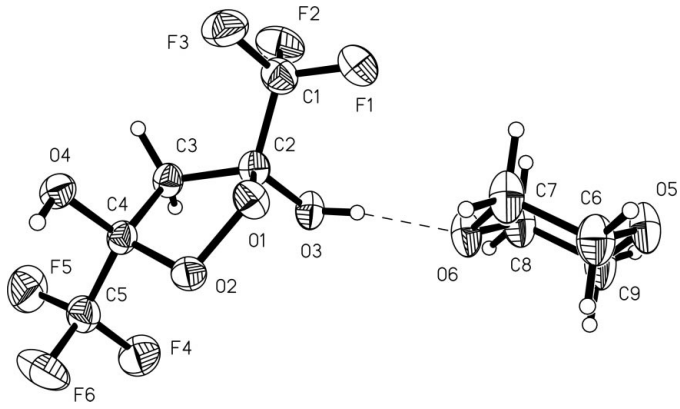


Figure 1
A view of the title structure. Displacement ellipsoids are drawn at the 50% probability level.

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H1O3···O6	0.85 (3)	1.85 (3)	2.688 (2)	170 (3)
O4—H1O4···O5^{i}	0.86 (3)	1.81 (3)	2.663 (2)	173 (3)

Symmetry codes: (i) $x-1, \frac{3}{2}-y, \frac{1}{2}+z$.

H atoms were refined isotropically in observed positions. C—H distances ranged from 0.94 (2) to 1.06 (3) Å and O—H distances were 0.85 (3) and 0.86 (3) Å.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SHELXTL* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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