

trans-Diaquabis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato- κ^2O,O')cobalt(II) dihydrate

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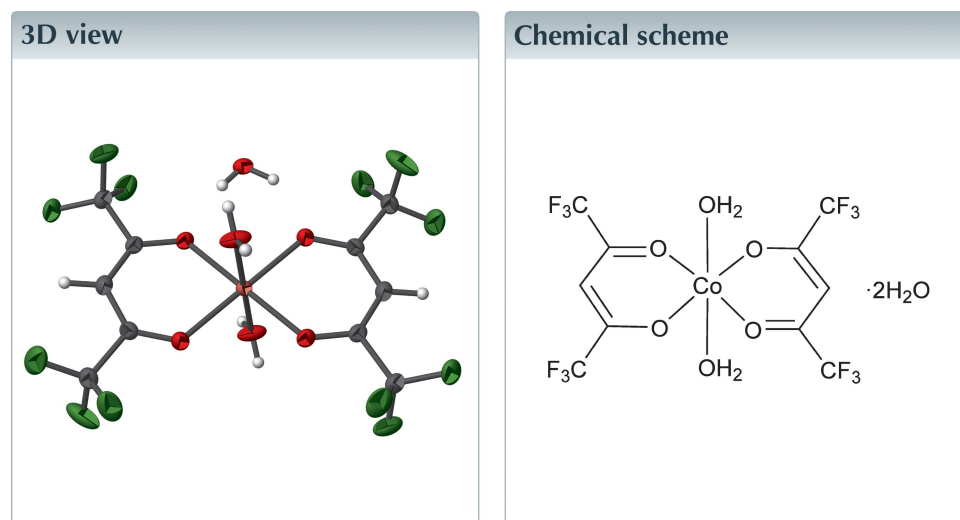
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Keywords: crystal structure; Co^{II} complex; 1,1,1,5,5,5-hexafluoropentane-2,4-dionate; hydrogen bonding; hydrate compounds..

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

The Co^{II} atom in the mononuclear title compound, [Co(C₅HF₆O₂)₂(H₂O)₂] \cdot 2H₂O, is situated on an inversion centre and exhibits a slightly distorted octahedral coordination sphere. In the crystal, molecules are arranged in layers parallel to (100), held together by O—H \cdots O and O—H \cdots F hydrogen bonds.



Structure description

Metal complexes with hfac⁻ ligands (hfac⁻ = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate, C₅HF₆O₂) can occur with various numbers of aqua ligands [M(hfac)₂(H₂O)_{*n*}] (Maverick *et al.*, 2002). These compounds are useful precursors of numerous complexes used in supramolecular chemistry (Horikoshi *et al.*, 2005).

An isomer of the molecular entity *cis*-[Co(hfac)₂(H₂O)₂] (Petrukhina *et al.*, 2005) was now obtained as a dihydrate with a *trans*-configuration about the Co^{II} atom, representing the title compound [Co(hfac)₂(H₂O)₂] \cdot 2H₂O (Fig. 1). The metal cation is situated on an inversion centre, hence only half of the complex is present in the asymmetric unit. The symmetry-related hfac⁻ ligands chelate the Co^{II} atom in the equatorial plane, the slightly distorted coordination sphere being completed by two axially bound water molecules. The hydrogen atoms of the two solvate water molecules hydrogen-bond to the two O atom pairs of the hfac⁻ ligands, whereas the hydrogen atoms of the aqua ligands hydrogen-bond to the oxygen atoms of the solvate water molecules which leads to the formation of a two-dimensional network structure extending parallel to (100) (Table 1, Fig. 2). Additional intralayer O—H \cdots F hydrogen bonds between the solvate water molecules and the F atoms of the hfac⁻ ligands are present (Table 1).

A search of the Cambridge Structural Database (Groom *et al.*, 2016) revealed no other examples of structurally characterized dihydrate crystals with formula [M(hfac)₂(H₂O)_{*n*}] \cdot 2H₂O. In the monohydrate crystals of *trans*-[M(hfac)₂(H₂O)₂] \cdot H₂O [M

Table 1
Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O4—H5···O2	0.88 (3)	2.13 (3)	2.853 (2)	140 (3)
O4—H5···F6	0.88 (3)	2.32 (3)	3.105 (3)	148 (3)
O4—H4···O1 ⁱ	0.77 (3)	2.03 (3)	2.766 (2)	160 (3)
O4—H4···F3 ⁱ	0.77 (3)	2.55 (3)	3.086 (3)	129 (3)
O3—H2···O4 ⁱⁱ	0.76 (3)	2.00 (3)	2.756 (3)	175 (3)
O3—H1···O4 ⁱⁱⁱ	0.84 (3)	1.85 (3)	2.687 (3)	175 (3)

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

= Zn (Adams *et al.*, 1986), Mn (Dickman *et al.*, 1997), and Cu (Maverick *et al.*, 2002)], of which the Zn and Mn compounds are isotopic with each other, the solvate water molecule forms hydrogen bonds with two of the four oxygen atoms of the hfac⁻ ligands in the complex, whereas the other two oxygen atoms form hydrogen bonds with the aqua ligands of an

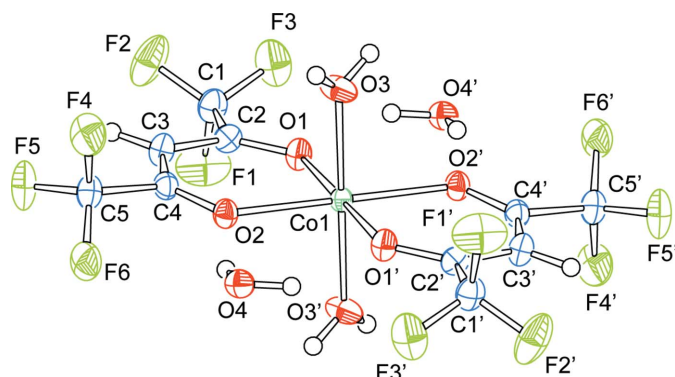


Figure 1
The molecular components in the title structure, with displacement ellipsoids drawn at the 50% probability level. Primed atoms are related to the non-primed atoms by the symmetry operation $-x + 1, -y + 1, -z + 1$.

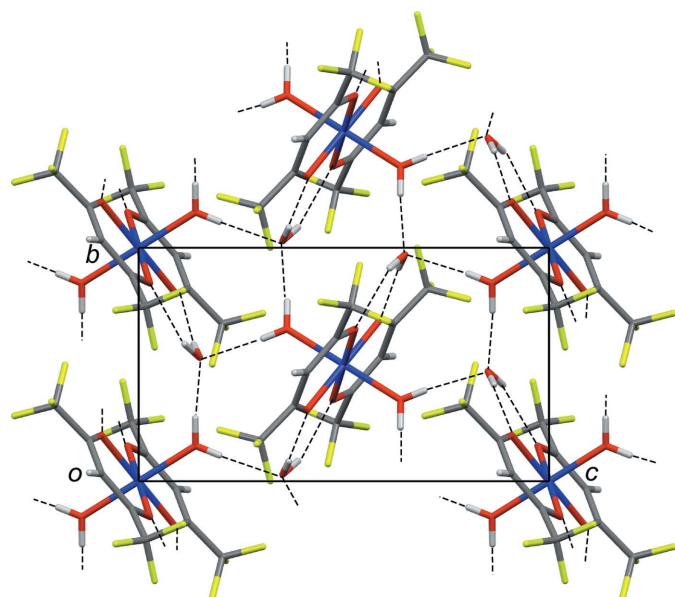


Figure 2
Packing diagram of the title structure in a view along [100]. O—H···O interactions are illustrated as dashed lines.

Table 2
Experimental details.

Crystal data	
Chemical formula	[Co(C ₅ HF ₆ O ₂) ₂ (H ₂ O)]·2H ₂ O
<i>M_r</i>	545.11
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.139 (7), 6.979 (4), 12.546 (8)
β (°)	102.221 (7)
<i>V</i> (Å ³)	953.2 (10)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	1.05
Crystal size (mm)	0.15 × 0.14 × 0.10
Data collection	
Diffractometer	Bruker APEXII CCD area detector
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2015)
<i>T_{min}</i> , <i>T_{max}</i>	0.83, 0.90
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	4980, 2085, 1897
<i>R_{int}</i>	0.033
($\sin \theta/\lambda$) _{max} (Å ⁻¹)	0.641
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.030, 0.080, 1.09
No. of reflections	2085
No. of parameters	158
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.46, -0.33

Computer programs: *APEX2* and *SAINT* (Bruker, 2015), *SHELXT* (Sheldrick, 2015a), *SHELXL2014/7* (Sheldrick, 2015b), *ORTEP* for Windows (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2008) and *pubCIF* (Westrip, 2010).

adjacent complex. In contrast, *cis*-[*M*(hfac)₂(H₂O)₂] [*M* = Co (Petrukhina *et al.*, 2005), Zn (Adams & Allen, 1986), Ni (Romero *et al.*, 1992) and Mn (Trojanov *et al.*, 1999)] form no crystals with additional solvate water molecules, and the crystals obtained are isotopic with each other. Thus, the *cis*- and *trans*-[*M*(hfac)₂(H₂O)₂] isomers occur as anhydrate and dihydrate crystals, respectively, for the Co, Zn, and Mn complexes.

Synthesis and crystallization

Slow evaporation of a dichloromethane solution of commercially available Co(hfac)₂·*n*H₂O (12 mg) and a tetranuclear ruthenium complex produced pale orange platy crystals of the title compound (7 mg).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

IUCrData (2017). 2, x170002 [https://doi.org/10.1107/S2414314617000025]

***trans*-Diaquabis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato- κ^2O,O')cobalt(II) dihydrate**

Takumi Tominaga and Tomoyuki Mochida

trans-Diaquabis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato- κ^2O,O')cobalt(II) dihydrate

Crystal data

[Co(C₅HF₆O₂)₂(H₂O)]·2H₂O

$M_r = 545.11$

Monoclinic, $P2_1/c$

$a = 11.139$ (7) Å

$b = 6.979$ (4) Å

$c = 12.546$ (8) Å

$\beta = 102.221$ (7)°

$V = 953.2$ (10) Å³

$Z = 2$

$F(000) = 538$

$D_x = 1.899$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3472 reflections

$\theta = 3.3$ – 28.7 °

$\mu = 1.05$ mm⁻¹

$T = 100$ K

Plate, clear light orange

0.15 × 0.14 × 0.10 mm

Data collection

Bruker APEXII CCD area detector
diffractometer

Bruker Helios multilayer confocal mirror
monochromator

Detector resolution: 8.3333 pixels mm⁻¹

phi an_diffn_radiation_type scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2015)

$T_{\min} = 0.83$, $T_{\max} = 0.90$

4980 measured reflections

2085 independent reflections

1897 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.033$

$\theta_{\max} = 27.1$ °, $\theta_{\min} = 1.9$ °

$h = -13$ → 14

$k = -8$ → 6

$l = -15$ → 16

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.030$

$wR(F^2) = 0.080$

$S = 1.09$

2085 reflections

158 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0286P)^2 + 0.6401P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.46$ e Å⁻³

$\Delta\rho_{\min} = -0.33$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.79557 (17)	0.8251 (3)	0.70389 (15)	0.0275 (4)
C2	0.73400 (16)	0.6744 (3)	0.62063 (14)	0.0215 (4)
C3	0.80755 (17)	0.5324 (3)	0.59026 (16)	0.0259 (4)
H3	0.8933	0.5359	0.6201	0.031*
C4	0.76128 (16)	0.3842 (3)	0.51766 (14)	0.0224 (4)
C5	0.85596 (17)	0.2501 (3)	0.48259 (16)	0.0280 (4)
Co1	0.5	0.5	0.5	0.01650 (11)
F1	0.77683 (13)	0.7802 (2)	0.80271 (10)	0.0447 (3)
F2	0.91612 (11)	0.8405 (2)	0.71227 (11)	0.0430 (3)
F3	0.74684 (13)	0.99850 (17)	0.67922 (12)	0.0421 (3)
F4	0.88486 (14)	0.3160 (2)	0.39182 (12)	0.0557 (4)
F5	0.95906 (12)	0.2319 (2)	0.55607 (13)	0.0543 (4)
F6	0.81060 (12)	0.0745 (2)	0.46112 (13)	0.0465 (4)
H1	0.508 (2)	0.769 (4)	0.362 (2)	0.038 (7)*
H2	0.484 (3)	0.612 (5)	0.304 (2)	0.047 (8)*
H4	0.481 (3)	0.085 (4)	0.366 (2)	0.042 (7)*
H5	0.601 (3)	0.087 (5)	0.388 (2)	0.051 (8)*
O1	0.61928 (11)	0.69704 (18)	0.59076 (10)	0.0219 (3)
O2	0.65242 (11)	0.34813 (19)	0.47266 (10)	0.0234 (3)
O3	0.49099 (16)	0.6521 (2)	0.36142 (12)	0.0318 (3)
O4	0.53489 (14)	0.02958 (19)	0.35107 (11)	0.0238 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0239 (9)	0.0314 (10)	0.0260 (9)	-0.0047 (8)	0.0026 (7)	-0.0066 (8)
C2	0.0218 (8)	0.0226 (9)	0.0197 (8)	-0.0037 (7)	0.0035 (6)	-0.0016 (7)
C3	0.0197 (8)	0.0304 (10)	0.0260 (9)	-0.0010 (7)	0.0018 (7)	-0.0044 (8)
C4	0.0212 (8)	0.0244 (9)	0.0221 (8)	0.0024 (7)	0.0054 (7)	-0.0007 (7)
C5	0.0217 (9)	0.0298 (10)	0.0322 (10)	0.0035 (8)	0.0052 (7)	-0.0047 (8)
Co1	0.01709 (18)	0.01662 (18)	0.01582 (17)	-0.00037 (11)	0.00357 (12)	-0.00182 (11)
F1	0.0567 (8)	0.0541 (9)	0.0234 (6)	-0.0155 (7)	0.0089 (6)	-0.0115 (6)
F2	0.0248 (6)	0.0510 (8)	0.0512 (8)	-0.0109 (6)	0.0037 (5)	-0.0231 (6)
F3	0.0424 (8)	0.0254 (7)	0.0518 (9)	-0.0030 (5)	-0.0048 (6)	-0.0113 (5)
F4	0.0596 (9)	0.0653 (10)	0.0540 (9)	0.0242 (8)	0.0388 (8)	0.0114 (8)
F5	0.0313 (7)	0.0642 (10)	0.0592 (9)	0.0217 (7)	-0.0089 (6)	-0.0226 (8)
F6	0.0346 (7)	0.0317 (7)	0.0748 (10)	0.0046 (6)	0.0148 (6)	-0.0181 (7)
O1	0.0214 (6)	0.0209 (6)	0.0226 (6)	-0.0017 (5)	0.0028 (5)	-0.0047 (5)
O2	0.0199 (6)	0.0241 (7)	0.0261 (6)	0.0006 (5)	0.0044 (5)	-0.0065 (5)
O3	0.0598 (10)	0.0190 (7)	0.0172 (7)	-0.0053 (7)	0.0099 (6)	-0.0018 (5)
O4	0.0297 (7)	0.0202 (6)	0.0214 (6)	0.0008 (6)	0.0056 (6)	-0.0034 (5)

Geometric parameters (Å, °)

C1—F2	1.329 (2)	C5—F6	1.331 (3)
C1—F3	1.336 (3)	Co1—O3 ⁱ	2.0215 (17)
C1—F1	1.337 (2)	Co1—O3	2.0215 (17)
C1—C2	1.538 (3)	Co1—O1	2.0766 (14)
C2—O1	1.263 (2)	Co1—O1 ⁱ	2.0766 (14)
C2—C3	1.389 (3)	Co1—O2	2.0904 (15)
C3—C4	1.402 (3)	Co1—O2 ⁱ	2.0904 (15)
C3—H3	0.95	O3—H1	0.84 (3)
C4—O2	1.250 (2)	O3—H2	0.76 (3)
C4—C5	1.542 (3)	O4—H4	0.77 (3)
C5—F5	1.318 (2)	O4—H5	0.88 (3)
C5—F4	1.330 (3)		
F2—C1—F3	107.40 (17)	O3 ⁱ —Co1—O3	180.0
F2—C1—F1	107.40 (16)	O3 ⁱ —Co1—O1	88.09 (7)
F3—C1—F1	106.94 (16)	O3—Co1—O1	91.91 (7)
F2—C1—C2	114.03 (16)	O3 ⁱ —Co1—O1 ⁱ	91.91 (7)
F3—C1—C2	111.18 (16)	O3—Co1—O1 ⁱ	88.09 (7)
F1—C1—C2	109.57 (16)	O1—Co1—O1 ⁱ	180.00 (5)
O1—C2—C3	128.77 (17)	O3 ⁱ —Co1—O2	88.89 (6)
O1—C2—C1	113.18 (16)	O3—Co1—O2	91.11 (6)
C3—C2—C1	118.03 (16)	O1—Co1—O2	88.74 (6)
C2—C3—C4	123.17 (17)	O1 ⁱ —Co1—O2	91.26 (6)
C2—C3—H3	118.4	O3 ⁱ —Co1—O2 ⁱ	91.11 (6)
C4—C3—H3	118.4	O3—Co1—O2 ⁱ	88.89 (6)
O2—C4—C3	129.04 (17)	O1—Co1—O2 ⁱ	91.26 (6)
O2—C4—C5	113.93 (16)	O1 ⁱ —Co1—O2 ⁱ	88.74 (6)
C3—C4—C5	116.96 (16)	O2—Co1—O2 ⁱ	180.00 (7)
F5—C5—F4	107.42 (18)	C2—O1—Co1	124.71 (12)
F5—C5—F6	106.87 (17)	C4—O2—Co1	124.59 (12)
F4—C5—F6	107.21 (17)	Co1—O3—H1	122.6 (18)
F5—C5—C4	113.96 (17)	Co1—O3—H2	127 (2)
F4—C5—C4	109.78 (17)	H1—O3—H2	110 (3)
F6—C5—C4	111.30 (16)	H4—O4—H5	105 (3)

Symmetry code: (i) $-x+1, -y+1, -z+1$.

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O4—H5 \cdots O2	0.88 (3)	2.13 (3)	2.853 (2)	140 (3)
O4—H5 \cdots F6	0.88 (3)	2.32 (3)	3.105 (3)	148 (3)
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Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+1, y+1/2, -z+1/2$; (iii) $x, y+1, z$.