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Diaquabis(5-fluoro-2-hydroxybenzoato- κ O¹)zinc(II)

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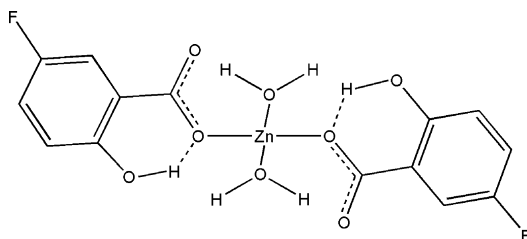
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 Key indicators: single-crystal X-ray study; $T = 150$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.035; wR factor = 0.081; data-to-parameter ratio = 12.1.

The title compound, $[\text{Zn}(\text{C}_7\text{H}_4\text{FO}_3)_2(\text{H}_2\text{O})_2]$, is a monomeric Zn^{II} complex. The Zn^{II} atom, which lies on a twofold rotation axis, is situated in a distorted tetrahedral environment composed of two monodentate carboxylate O atoms and two water O atoms. $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds link these units, forming sheets that are stacked along the c axis.

Related literature

For general background, see: Ellsworth & zur Loye (2008); Janiak (2003); Mehrotra & Bohra (1983); Wasuke *et al.* (2005). For related structures, see: Brownless *et al.* (1999); Wang *et al.* (2006).



Experimental

Crystal data

$[\text{Zn}(\text{C}_7\text{H}_4\text{FO}_3)_2(\text{H}_2\text{O})_2]$
 $M_r = 411.61$
 Monoclinic, $C2/c$
 $a = 15.3096$ (10) Å
 $b = 5.4706$ (4) Å
 $c = 17.7741$ (12) Å
 $\beta = 91.674$ (1)°

$V = 1487.99$ (18) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 1.72$ mm⁻¹
 $T = 150$ K
 $0.16 \times 0.12 \times 0.05$ mm

Data collection

Bruker SMART APEX CCD diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2001)
 $T_{\text{min}} = 0.893$, $T_{\text{max}} = 1.000$
 (expected range = 0.820–0.918)

8435 measured reflections
 1520 independent reflections
 1341 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.053$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.081$
 $S = 1.09$
 1520 reflections
 126 parameters
 3 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.43$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.27$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Zn1—O4	1.966 (2)	Zn1—O1	1.9716 (17)
O4—Zn1—O4 ⁱ	100.61 (13)	O4—Zn1—O1 ⁱ	94.50 (8)
O4—Zn1—O1	121.01 (8)	O1—Zn1—O1 ⁱ	124.62 (11)

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
O3—H3 ^{..} ·O1	0.803 (18)	1.84 (2)	2.564 (3)	149 (3)
O4—H4A ^{..} ·O2 ⁱⁱ	0.834 (18)	1.83 (2)	2.641 (3)	162 (3)
O4—H4B ^{..} ·O3 ⁱⁱⁱ	0.834 (19)	1.89 (2)	2.711 (3)	170 (4)

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

Data collection: SMART (Bruker, 2007); cell refinement: SAINT-Plus (Bruker, 2007); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: DIAMOND (Brandenburg, 1999); software used to prepare material for publication: SHELXTL (Sheldrick, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2183).

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supporting information

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Diaquabis(5-fluoro-2-hydroxybenzoato- κ O¹)zinc(II)

Diana Rishmawi, Jennifer Kelley, Mark D. Smith, LeRoy Peterson and Hans-Conrad zur Loye

S1. Comment

Metal carboxylate complexes have long been an extensively studied class of compounds (Mehrotra & Bohra, 1983), and in recent years they have become a major focus of study due to their potentially useful properties (Janiak, 2003; Wasuke *et al.*, 2005). As a continuation of our own studies (Ellsworth & zur Loye, 2008), we report here the crystal structure of the title compound.

The structure of the title compound is built from the monomeric complex of formula $\text{Zn}(5\text{-fsalicyl})_2(\text{H}_2\text{O})_2$ (Fig. 1) (5-fsalicyl = 5-fluorosalicylate). The asymmetric unit consists of one Zn^{II} atom that lies on a twofold rotation axis, one 5-fsalicyl ligand, and one water molecule. The coordination environment of the Zn^{II} atom is that of a distorted tetrahedron consisting of two equivalent O atoms from two monodentate carboxylates, and two equivalent O atoms from two water molecules. All four Zn—O bond distances fall within the normal range, with an average length of 1.969 (2) Å. It is worth noting that for the carboxylate O2 atom, the Zn \cdots O2 distance of 2.692 (2) Å falls outside the range considered normal for a Zn—O coordination bond (Wang *et al.*, 2006).

Due to its monodentate binding mode, the 5-fsalicyl carboxylate group adopts a highly asymmetrical configuration. This is manifested in a C1—O1 distance [1.289 (3) Å] for the coordinating O atom that is noticeably longer than the C1—O2 distance [1.246 (3) Å] corresponding to the noncoordinating O atom. In addition, the carboxylate group of the 5-fsalicyl ligand is twisted with a dihedral angle of 9.7 (2) ° with respect to the phenyl ring. As is typical for salicylates, the hydroxyl group of 5-fsalicyl is internally hydrogen bonded to its carboxylate O1 that is located on the same side of the ligand (Brownless *et al.*, 1999).

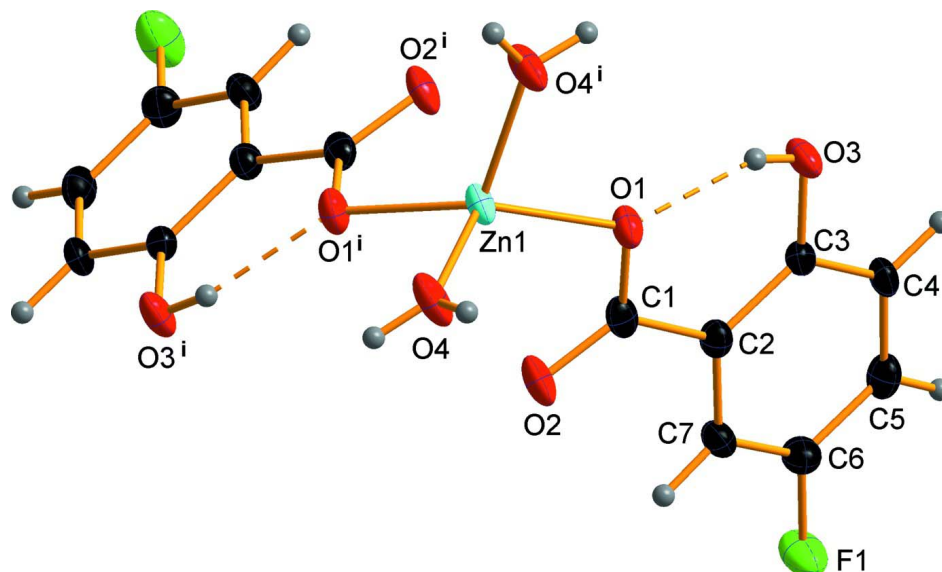
The monomeric units are hydrogen bonded into chains that are themselves hydrogen bonded into sheets that are stacked along the *c* axis (Fig. 2).

S2. Experimental

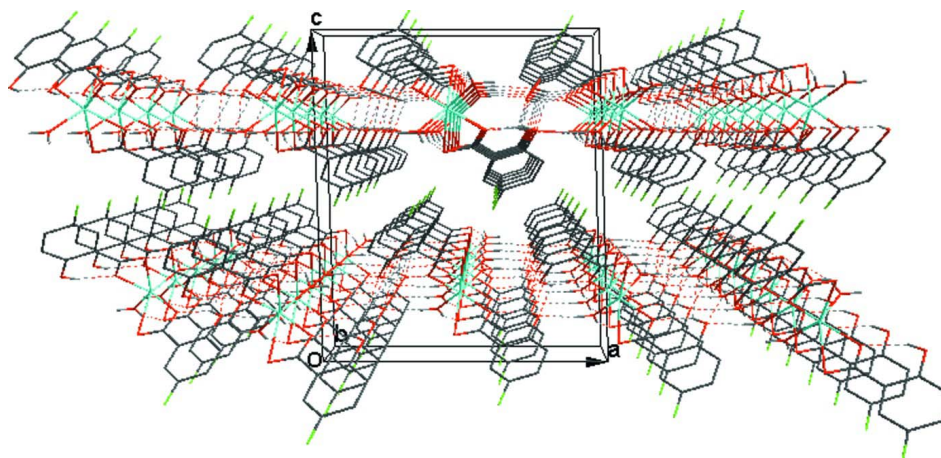
All chemicals and solvents were purchased from commercial sources and used without further purification. 5-Fluoro-salicylic acid (3 mmol) was added to 100 ml of water and subsequently brought to pH 6.5 by the addition of 3M NaOH with constant stirring. To this solution was added 10 ml of a 0.10 M solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Single crystals of the title compound were formed in four weeks after complete evaporation of the solution under ambient conditions.

S3. Refinement

H atoms bonded to C atoms were positioned geometrically and refined as riding atoms. O-bound H atoms were located in a difference Fourier map and refined isotropically, with their O—H distances restrained to 0.84 (2) Å.

**Figure 1**

Molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are represented by dashed lines. [Symmetry code: (i) $-x+1, y, -z+3/2$.]

**Figure 2**

View of the crystal packing in the title compound. All H atoms except for those of water and the hydroxyl group are omitted for clarity. Hydrogen bonds are represented by dashed lines.

Diaquabis(5-fluoro-2-hydroxybenzoato- κO^1)zinc(II)

Crystal data

$[\text{Zn}(\text{C}_7\text{H}_4\text{FO}_3)_2(\text{H}_2\text{O})_2]$

$M_r = 411.61$

Monoclinic, $C2/c$

Hall symbol: $-C 2yc$

$a = 15.3096 (10) \text{ \AA}$

$b = 5.4706 (4) \text{ \AA}$

$c = 17.7741 (12) \text{ \AA}$

$\beta = 91.674 (1)^\circ$

$V = 1487.99 (18) \text{ \AA}^3$

$Z = 4$

$F(000) = 832$

$D_x = 1.837 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 2066 reflections

$\theta = 2.7\text{--}24.1^\circ$

$\mu = 1.72 \text{ mm}^{-1}$

$T = 150$ K $0.16 \times 0.12 \times 0.05$ mm
 Plate, colorless

Data collection

Bruker SMART APEX CCD diffractometer	8435 measured reflections
Radiation source: fine-focus sealed tube	1520 independent reflections
Graphite monochromator	1341 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.053$
Absorption correction: multi-scan (SADABS; Bruker, 2001)	$\theta_{\text{max}} = 26.4^\circ$, $\theta_{\text{min}} = 2.3^\circ$
$T_{\text{min}} = 0.893$, $T_{\text{max}} = 1.000$	$h = -18 \rightarrow 18$
	$k = -6 \rightarrow 6$
	$l = -22 \rightarrow 22$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.035$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.081$	$w = 1/[\sigma^2(F_o^2) + (0.0397P)^2 + 0.7409P]$
$S = 1.09$	where $P = (F_o^2 + 2F_c^2)/3$
1520 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
126 parameters	$\Delta\rho_{\text{max}} = 0.43 \text{ e } \text{\AA}^{-3}$
3 restraints	$\Delta\rho_{\text{min}} = -0.27 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.5000	0.08063 (8)	0.7500	0.01954 (15)
C1	0.56321 (16)	0.4151 (5)	0.65619 (14)	0.0204 (5)
C2	0.62447 (16)	0.5945 (5)	0.62352 (14)	0.0199 (5)
C3	0.71316 (16)	0.6031 (5)	0.64632 (14)	0.0191 (5)
C4	0.76803 (16)	0.7820 (5)	0.61874 (14)	0.0221 (6)
H4	0.8278	0.7864	0.6346	0.026*
C5	0.73553 (18)	0.9533 (5)	0.56829 (15)	0.0246 (6)
H5	0.7724	1.0775	0.5495	0.029*
C6	0.64862 (18)	0.9416 (5)	0.54547 (15)	0.0248 (6)
C7	0.59321 (16)	0.7666 (5)	0.57150 (14)	0.0223 (6)
H7	0.5339	0.7624	0.5543	0.027*
O1	0.59620 (11)	0.2481 (3)	0.69963 (10)	0.0233 (4)
O2	0.48283 (11)	0.4310 (3)	0.64435 (11)	0.0265 (4)
F1	0.61747 (11)	1.1088 (3)	0.49488 (10)	0.0391 (5)
O3	0.74885 (12)	0.4400 (4)	0.69676 (11)	0.0266 (4)
H3	0.7120 (18)	0.341 (5)	0.7060 (18)	0.044 (10)*
O4	0.42296 (13)	-0.1489 (4)	0.69475 (13)	0.0305 (5)
H4A	0.437 (2)	-0.271 (5)	0.6700 (16)	0.039 (10)*
H4B	0.3689 (13)	-0.132 (8)	0.691 (2)	0.068 (14)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0113 (2)	0.0184 (2)	0.0290 (3)	0.000	0.00249 (16)	0.000

C1	0.0169 (13)	0.0199 (13)	0.0245 (14)	0.0015 (10)	0.0036 (10)	-0.0063 (11)
C2	0.0174 (12)	0.0209 (13)	0.0214 (13)	-0.0025 (11)	0.0021 (10)	-0.0012 (11)
C3	0.0149 (12)	0.0239 (14)	0.0186 (13)	0.0015 (10)	0.0019 (10)	-0.0007 (11)
C4	0.0118 (12)	0.0293 (15)	0.0252 (14)	-0.0026 (11)	0.0016 (10)	-0.0009 (12)
C5	0.0224 (14)	0.0238 (15)	0.0277 (14)	-0.0068 (11)	0.0065 (11)	0.0003 (12)
C6	0.0233 (14)	0.0255 (15)	0.0256 (14)	0.0021 (12)	0.0000 (11)	0.0056 (12)
C7	0.0151 (13)	0.0263 (14)	0.0253 (14)	-0.0005 (11)	-0.0013 (10)	0.0008 (12)
O1	0.0150 (9)	0.0239 (10)	0.0312 (10)	0.0009 (8)	0.0054 (7)	0.0060 (8)
O2	0.0121 (9)	0.0233 (10)	0.0443 (12)	-0.0014 (8)	0.0025 (8)	-0.0025 (9)
F1	0.0282 (9)	0.0390 (10)	0.0500 (11)	0.0008 (8)	-0.0028 (8)	0.0232 (9)
O3	0.0132 (9)	0.0315 (11)	0.0350 (11)	-0.0020 (8)	-0.0020 (8)	0.0111 (9)
O4	0.0139 (10)	0.0277 (11)	0.0497 (13)	0.0020 (8)	-0.0017 (9)	-0.0155 (10)

Geometric parameters (Å, °)

Zn1—O4	1.966 (2)	C4—C5	1.380 (4)
Zn1—O4 ⁱ	1.966 (2)	C4—H4	0.9500
Zn1—O1	1.9716 (17)	C5—C6	1.381 (4)
Zn1—O1 ⁱ	1.9717 (17)	C5—H5	0.9500
C1—O2	1.246 (3)	C6—F1	1.359 (3)
C1—O1	1.289 (3)	C6—C7	1.369 (4)
C1—C2	1.487 (4)	C7—H7	0.9500
C2—C7	1.394 (4)	O3—H3	0.803 (18)
C2—C3	1.406 (4)	O4—H4A	0.834 (18)
C3—O3	1.367 (3)	O4—H4B	0.834 (19)
C3—C4	1.388 (4)		
O4—Zn1—O4 ⁱ	100.61 (13)	C5—C4—H4	120.1
O4—Zn1—O1	121.01 (8)	C3—C4—H4	120.1
O4 ⁱ —Zn1—O1	94.50 (8)	C4—C5—C6	119.0 (2)
O4—Zn1—O1 ⁱ	94.50 (8)	C4—C5—H5	120.5
O4 ⁱ —Zn1—O1 ⁱ	121.01 (8)	C6—C5—H5	120.5
O1—Zn1—O1 ⁱ	124.62 (11)	F1—C6—C7	119.0 (2)
O2—C1—O1	121.2 (2)	F1—C6—C5	118.7 (2)
O2—C1—C2	121.3 (2)	C7—C6—C5	122.3 (2)
O1—C1—C2	117.4 (2)	C6—C7—C2	119.5 (2)
C7—C2—C3	118.6 (2)	C6—C7—H7	120.3
C7—C2—C1	119.8 (2)	C2—C7—H7	120.3
C3—C2—C1	121.6 (2)	C1—O1—Zn1	108.44 (15)
O3—C3—C4	117.2 (2)	C3—O3—H3	108 (2)
O3—C3—C2	122.1 (2)	Zn1—O4—H4A	128 (2)
C4—C3—C2	120.7 (2)	Zn1—O4—H4B	123 (3)
C5—C4—C3	119.9 (2)	H4A—O4—H4B	109 (4)
O2—C1—C2—C7	-7.8 (4)	C4—C5—C6—F1	-179.0 (2)
O1—C1—C2—C7	174.9 (2)	C4—C5—C6—C7	0.4 (4)
O2—C1—C2—C3	169.2 (2)	F1—C6—C7—C2	-179.9 (2)
O1—C1—C2—C3	-8.1 (4)	C5—C6—C7—C2	0.7 (4)

C7—C2—C3—O3	-179.6 (2)	C3—C2—C7—C6	-1.5 (4)
C1—C2—C3—O3	3.3 (4)	C1—C2—C7—C6	175.6 (2)
C7—C2—C3—C4	1.2 (4)	O2—C1—O1—Zn1	-8.5 (3)
C1—C2—C3—C4	-175.8 (2)	C2—C1—O1—Zn1	168.89 (17)
O3—C3—C4—C5	-179.3 (2)	O4—Zn1—O1—C1	73.68 (18)
C2—C3—C4—C5	-0.1 (4)	O4 ⁱ —Zn1—O1—C1	178.91 (17)
C3—C4—C5—C6	-0.7 (4)	O1 ⁱ —Zn1—O1—C1	-48.07 (15)

Symmetry code: (i) $-x+1, y, -z+3/2$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

<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>
O3—H3 \cdots O1	0.80 (2)	1.84 (2)	2.564 (3)	149 (3)
O4—H4 <i>A</i> \cdots O2 ⁱⁱ	0.83 (2)	1.83 (2)	2.641 (3)	162 (3)
O4—H4 <i>B</i> \cdots O3 ⁱⁱⁱ	0.83 (2)	1.89 (2)	2.711 (3)	170 (4)

Symmetry codes: (ii) $x, y-1, z$; (iii) $x-1/2, y-1/2, z$.