2-28-2009

**Diaquabis(5-fluoro-2-hydroxybenzoato-κO\textsubscript{1})zinc(II)**

Diana Rishmawi  
*Francis Marion University*

Jennifer Kelley  
*Francis Marion University*

Mark D. Smith  
*University of South Carolina - Columbia*

LeRoy Peterson  
*Francis Marion University, lpeterson@fmarion.edu*

Hans-Conrad zur Loye  
*University of South Carolina - Columbia, zurloye@sc.edu*

Follow this and additional works at: [https://scholarcommons.sc.edu/chem_facpub](https://scholarcommons.sc.edu/chem_facpub)

Part of the Chemistry Commons

**Publication Info**  
Published in *Acta Crystallographica Section E*, Volume E65, Issue 3, 2009, pages m331-.
DOI: 10.1107/S1600536809005716
Publisher’s Version: [http://dx.doi.org/10.1107/S1600536809005716](http://dx.doi.org/10.1107/S1600536809005716)

This Article is brought to you by the Chemistry and Biochemistry, Department of at Scholar Commons. It has been accepted for inclusion in Faculty Publications by an authorized administrator of Scholar Commons. For more information, please contact dillarda@mailbox.sc.edu.
Diaquabis(5-fluoro-2-hydroxybenzoato-κO1)zinc(II)

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

Acta Cryst. (2009). E65, m331

This open-access article is distributed under the terms of the Creative Commons Attribution Licence http://creativecommons.org/licenses/by/2.0/uk/legalcode, which permits unrestricted use, distribution, and reproduction in any medium, provided the original authors and source are cited.

Acta Crystallographica Section E: Structure Reports Online is the IUCr’s highly popular open-access structural journal. It provides a simple and easily accessible publication mechanism for the growing number of inorganic, metal-organic and organic crystal structure determinations. The electronic submission, validation, refereeing and publication facilities of the journal ensure very rapid and high-quality publication, whilst key indicators and validation reports provide measures of structural reliability. In 2007, the journal published over 5000 structures. The average publication time is less than one month.

Crystallography Journals Online is available from journals.iucr.org
Diaquabis(5-fluoro-2-hydroxybenzoato-κO³)zinc(II)

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

Abstract

The title compound, [Zn(C₇H₄FO₃)₂(H₂O)₂], is a monomeric Zn²⁺ complex. The Zn²⁺ 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. O—H…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).

Table 1

| Selected geometric parameters (Å, °) |
|-------------------------------------|
| Zn1—O4 1.966 (2) Zn1—O1 1.9716 (17) |
| O4—Zn1—O4' 100.61 (13) O4—Zn1—O1' 94.50 (8) |
| O4—Zn1—O1' 121.01 (8) O1—Zn1—O1' 124.62 (11) |

Symmetry codes: (i) −x + 1, y, −z + 1/2; (ii) x, y − 1, z; (iii) x + 1/2, y − 1, z.

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)

Refinement

\( R(F^2 > 2\sigma(F^2)) = 0.035 \)
\( wR(F^2) = 0.081 \)
1520 independent reflections
287 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

Financial support from the National Science Foundation, awards CHE-0714555 and CHE-0714439, is gratefully acknowledged.

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

References

Brandenburg, K. (1999). DIAMOND. Crystal Impact GbR, Bonn, Germany.
Brownless, J. B., Edwards, D. A. & Mahon, M. F. (1999). Inorg. Chim. Acta, 287, 89–94.
Bruker (2001). SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2007). SMART and SAINT-Plus. Bruker AXS Inc., Madison, Wisconsin, USA.
Ellsworth, J. M. & zur Loye, H.-C. (2008). Dalton Trans. pp. 5823–5835.
Janiak, C. (2003). Dalton Trans. pp. 2781–2804.
Mehrotra, R. C. & Bohra, R. (1983). In Metal Carboxylates. London: Academic Press.
Sheldrick, G. M. (2008). Acta Cryst. A64, 112–122.
Wang, Z., Zhang, H., Chen, Y., Huang, C., Sun, R., Cao, Y. & Yu, X. (2006). J. Solid State Chem. 179, 1536–1544.
Wasuke, M., Tomohiko, S., Tesushi, O., Chika, N. K. & Tohru, T. (2005). J. Solid State Chem. 178, 2555–2573.
supplementary materials
supplementary materials

*Acta Cryst.* (2009). E65, m331  [doi:10.1107/S1600536809005716]

Diaquabis(5-fluoro-2-hydroxybenzoato-\(\text{H}\)\(\text{O}\)\(^2\))zinc(II)

D. Rishmawi, J. Kelley, M. D. Smith, L. R. Peterson Jr and H.-C. zur Loye

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 Zn(5-fsalcyl)_2(H_2O)_2 (Fig. 1) (5-fsalcyl = 5-fluorosalicylate). The asymmetric unit consists of one Zn\(^{II}\) atom that lies on a twofold rotation axis, one 5-fsalcyl 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—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-fsalcyl 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-fsalcyl 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-fsalcyl 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).

Experimental

All chemicals and solvents were purchased from commercial sources and used without further purification. 5-Fluorosalicylic 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 Zn(NO_3)_2\(_2\).\_6\_H_2\_O. Single crystals of the title compound were formed in four weeks after complete evaporation of the solution under ambient conditions.

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.
supplementary materials

Figures

**Fig. 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) \(-x+1, y, -z+3/2\).]

**Fig. 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)zinc(II)**

Crystal data

\[\text{[Zn(C}_2\text{H}_4\text{FO}_3)_2(\text{H}_2\text{O})_2]}\]
\[M_r = 411.61\]
Monoclinic, \(C2/c\)
Hall symbol: \(-C\ 2\ yc\)
\(a = 15.3096\ (10)\ \text{Å}\)
\(b = 5.4706\ (4)\ \text{Å}\)
\(c = 17.7741\ (12)\ \text{Å}\)
\(\beta = 91.674\ (1)^\circ\)
\(V = 1487.99\ (18)\ \text{Å}^3\)
\(Z = 4\)

\(F_{000} = 832\)
\(D_x = 1.837\ \text{Mg m}^{-3}\)
Mo \(K\alpha\) radiation
\(\lambda = 0.71073\ \text{Å}\)
Cell parameters from 2066 reflections
\(\theta = 2.7–24.1^\circ\)
\(\mu = 1.72\ \text{mm}^{-1}\)
\(T = 150\ \text{K}\)
Plate, colorless
0.16 × 0.12 × 0.05 mm

Data collection

Bruker SMART APEX CCD
diffractometer
Radiation source: fine-focus sealed tube
Monochromator: graphite
\(T = 150\ \text{K}\)
\(\varphi\) and \(\omega\) scans
Absorption correction: multi-scan
(SADABS, Bruker, 2001)
\(T_{\text{min}} = 0.893, T_{\text{max}} = 1.000\)
8435 measured reflections
1520 independent reflections
1341 reflections with \(I > 2\sigma(I)\)

Refinement

Refinement on \(F^2\)
Least-squares matrix: full
Secondary atom site location: difference Fourier map
\(R[F^2 > 2\sigma(F^2)] = 0.035\)
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

sup-2
supplementary materials

\[ wR(F^2) = 0.081 \]
\[ w = 1/[\sigma^2(F_o^2) + (0.0397P)^2 + 0.7409P] \]
\[ S = 1.09 \]
\[ (\Delta\sigma)_{\text{max}} < 0.001 \]
1520 reflections
\[ \Delta\rho_{\text{max}} = 0.43 \text{ e Å}^{-3} \]
126 parameters
\[ \Delta\rho_{\text{min}} = -0.27 \text{ e Å}^{-3} \]
3 restraints
Primary atom site location: structure-invariant direct methods

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

|   |   |   |   |   |
|---|---|---|---|---|
| ZnI | 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 (Å²)

|   | U¹¹ | U¹² | U¹³ | U²² | U²³ | U³³ |
|---|-----|-----|-----|-----|-----|-----|
| ZnI | 0.0113 (2) | 0.0178 (2) | 0.0149 (3) | 0.0000 | 0.0000 | 0.0000 |
| C1 | 0.0169 (13) | 0.0199 (13) | 0.0245 (14) | 0.0015 (10) | 0.0036 (10) | -0.0006 (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) |
supplementary materials

**Geometric parameters (Å, °)**

| Bond                  | Distance   | Angle         |
|-----------------------|------------|---------------|
| Zn1—O4                | 1.966 (2)  | C4—C5 1.380 (4) |
| Zn1—O4<sup>i</sup>   | 1.966 (2)  | C4—H4 0.9500 |
| Zn1—O1                | 1.9716 (17)| C5—C6 1.381 (4) |
| Zn1—O1<sup>i</sup>   | 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<sup>i</sup>| 100.61 (13)| C5—C4—H4 120.1 |
| O4—Zn1—O1             | 121.01 (8) | C3—C4—H4 120.1 |
| O4<sup>i</sup>—Zn1—O1 | 94.50 (8)  | C4—C5—C6 119.0 (2) |
| O4—Zn1—O1<sup>i</sup>| 94.50 (8)  | C4—C5—H5 120.5 |
| O4<sup>i</sup>—Zn1—O1<sup>i</sup>| 121.01 (8) | C6—C5—H5 120.5 |
| O1—Zn1—O1<sup>i</sup>| 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<sup>i</sup>—Zn1—O1—C1 178.91 (17) |
| C3—C4—C5—C6           | −0.7 (4)   | O1<sup>i</sup>—Zn1—O1—C1 −48.07 (15) |

Symmetry codes: (i) −x+1, y, −z+3/2.

**Hydrogen-bond geometry (Å, °)**

|        | D—H—A       | D—H   | H—A   | D···A  | D—H···A |
|--------|--------------|-------|-------|--------|---------|
| O3—H3—O1 | 0.803 (18)  | 1.84 (2) | 2.564 (3) | 149 (3) |
supplementary materials

|                |        |        |        |        |
|----------------|--------|--------|--------|--------|
| O4—H4A···O2
   Symmetry code: (ii) x, y=1, z; (iii) x=1/2, y=1/2, z. | 0.834 (18) | 1.83 (2) | 2.641 (3) | 162 (3) |
| O4—H4B···O3
   Symmetry code: (ii) x, y=1, z; (iii) x=1/2, y=1/2, z. | 0.834 (19) | 1.89 (2) | 2.711 (3) | 170 (4) |
supplementary materials

Fig. 2