

Diaquabis(2-hydroxy-5-methoxybenzoato- κO^1)zinc

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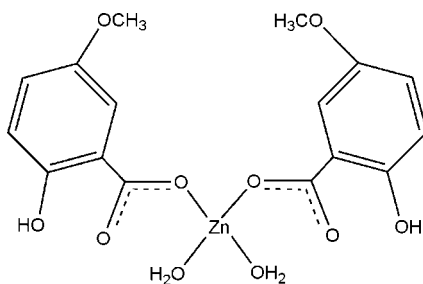
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Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(C-C) = 0.002$ Å; R factor = 0.030; wR factor = 0.082; data-to-parameter ratio = 14.6.

The title compound, $[Zn(C_8H_7O_4)_2(H_2O)_2]$, has been synthesized by hydrothermal methods. The Zn^{II} atom, whose symmetry element is a twofold axis, is four coordinated by two O atoms from 5-methoxysalicylate anions and two aqua O atoms in a distorted tetrahedral geometry. In the crystal, molecules are linked into a layer by $O-H \cdots O$ hydrogen bonds, which stabilize the packing.

Related literature

For coordination polymers constructed by hydrogen bonds, see: Li *et al.* (2006); Jiang *et al.* (2011). For the structure of the complex with 5-methoxysalicylate ligands and its analogues, see: Půčeková-Repická *et al.* (2007); Valigura *et al.* (2006).



Experimental

Crystal data

 $[Zn(C_8H_7O_4)_2(H_2O)_2]$
 $M_r = 435.67$

Monoclinic, $C2/c$
 $a = 25.113$ (4) Å
 $b = 5.5065$ (6) Å
 $c = 12.648$ (3) Å
 $\beta = 97.845$ (12)°
 $V = 1732.7$ (5) Å³

$Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 1.47$ mm⁻¹
 $T = 173$ K
 $0.20 \times 0.20 \times 0.20$ mm

Data collection

Rigaku Mercury CCD/AFC diffractometer
 Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2007)
 $T_{min} = 0.745$, $T_{max} = 0.752$

6403 measured reflections
 1986 independent reflections
 1837 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.027$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.082$
 $S = 1.08$
 1986 reflections
 136 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{max} = 0.27$ e Å⁻³
 $\Delta\rho_{min} = -0.69$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O3-H1 \cdots O1$	0.87 (3)	1.76 (3)	2.5771 (19)	155 (2)
$O4-H4A \cdots O2^i$	0.73 (3)	1.93 (3)	2.643 (2)	169 (3)
$O4-H4B \cdots O5^{ii}$	0.84 (3)	1.97 (3)	2.790 (2)	167 (3)

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

Data collection: *CrystalClear* (Rigaku, 2007); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZK2017).

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supplementary materials

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Diaquabis(2-hydroxy-5-methoxybenzoato- κO^1)zinc

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Comment

Generally, the self-assembly of inorganic metal species and organic ligands can be achieved by the use of noncovalent contacts. Among the noncovalent contacts, hydrogen bonds have the great influence in determining the geometry of the obtained metal complexes (Li *et al.* 2006; Jiang *et al.* 2011). In the other hand, the reactions of transition metal ions with 5-MeOsal ligands and its analogues are relatively rare (Valigura *et al.*, 2006; Púčeková-Repická *et al.*, 2007). In this paper we present results of hydrothermal reactions of ZnCl₂ and 5-MeOsal ligand. Title Compound was isolated as molecular complex and the intermolecular O—H—O hydrogen bonds in (I) together with intramolecular O—H—O hydrogen bonds promote the molecules into two-dimensional structure.

A single-crystal X-ray diffraction study of (I) reveals a discrete coordination complex that crystallizes in the space group *C2/c*. Coordination of the Zn atoms in (I) is a slightly distorted tetrahedral geometry with each Zn atom bonding to four oxygen atoms, in which two from the monodentate 5-MeOsal ligands and two from the waters (Fig.1). Further inspection into the structure reveals that there are O—H—O intramolecular and intermolecular hydrogen bonds. (Table 1). As described in Figure 2, the intramolecular hydrogen bonds from hydroxyl hydrogen atom of the 5-MeOsal anions to the coordinated carboxylate oxygen atoms O3—H—O1 with the distance of 2.577 (1) Å, then create six-membered rings (O₂C₃H), and stabilize the structure. The mean deviation from the planes C(2)—C(3)—C(4)—C(5)—C(6)—(7), and O(1)—H(13)—O(3)—C(3)—C(2)—C(1) are 0.0032 and 0.0229 Å, respectively. Furthermore the dihedral angles between planes is 0.9°, indicating a planar structure for this ligand. Furthermore the uncoordinated oxygen atoms of the carboxyl group and methoxy group of the 5-MeOsal anions (O2, O5) are hydrogen bonded with the hydrogen atoms of coordinated water with the distances of 2.643 (2) and 2.790 (2) Å, respectively. As a result every coordinated water molecule is connected by two oxygen atoms through hydrogen bonds and the isolated units are to be form a 2-D layer. A prospective view of the structure packing from *a* direction is presented in Fig. 3.

Experimental

The title compound was hydrothermally synthesized under autogenous pressure. A mixture of ZnCl₂ (68 mg, 0.5 mmol), 5-MeOsal (84 mg, 0.5 mmol), and H₂O (6 ml) was sealed in a stainless reactor with Teflon liner, which was heated to 358 K for two days. After slow cooling to room temperature, prism pale yellow crystals were obtained as a major phase by filtration, which were washed with distilled water, and finally dried in air (65% yield). Anal. calc. for C₁₆H₁₈O₁₀Zn: C, 44.11; H, 4.16; O, 36.72%; Found: C, 44.32; H, 4.15; O, 36.23%. IR (KBr pellet): 3448(*w*), 3290(*w*), 2839(*w*), 2615(*w*), 1661(*s*), 1616(*s*), 1486(*s*), 1428(*s*), 1223(*s*), 1188(*s*), 1033(*m*), 824(*m*), 788(*m*), 761(*m*), 678(*m*), 555(*m*), 464(*w*).

Refinement

All the hydrogen atoms were discernible in the difference electron density maps. However, the H atoms were situated into idealized positions and constrained by the riding model approximation: O—H_{hydroxyl} = 0.869, C_{aryl}—H_{aryl} = 0.95,

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$C_{\text{methyl}}\text{---}H_{\text{methyl}} = 0.98$ and $U_{\text{iso}H_{\text{aryl}}} = 1.2U_{\text{eq}}(\text{C})$, $U_{\text{iso}H_{\text{methyl}}} = 1.5U_{\text{eq}}(\text{C})$. The highest electron-density peak is situated 1.2 Å from Zn1 and the deepest hole 0.78 Å from Zn1.

Figures

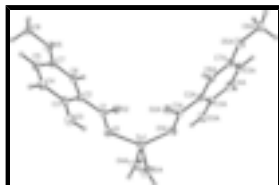


Fig. 1. Displacement ellipsoids are drawn at the 30% probability level. $(-x, y, -z + 1/2)$

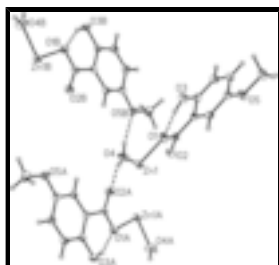


Fig. 2. The intramolecular and intermolecular hydrogen bonds (the dashed lines) in title compound. Symmetry codes: (A) $x, -y + 2, z + 1/2$; (B) $x, -y + 1, z + 1/2$.

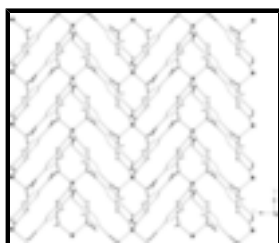


Fig. 3. The 2-D layer of title compound by O—H—O interactions (black dash lines) viewed from a direction.

Diaquabis(2-hydroxy-5-methoxybenzoato- κO^1)zinc(II)

Crystal data

$[\text{Zn}(\text{C}_8\text{H}_7\text{O}_4)_2(\text{H}_2\text{O})_2]$

$M_r = 435.67$

Monoclinic, $C2/c$

Hall symbol: $-C 2yc$

$a = 25.113$ (4) Å

$b = 5.5065$ (6) Å

$c = 12.648$ (3) Å

$\beta = 97.845$ (12)°

$V = 1732.7$ (5) Å³

$Z = 4$

$F(000) = 896$

$D_x = 1.670$ Mg m⁻³

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

Cell parameters from 2689 reflections

$\theta = 2.1\text{--}27.5^\circ$

$\mu = 1.47$ mm⁻¹

$T = 173$ K

Prism, pale yellow

$0.20 \times 0.20 \times 0.20$ mm

Data collection

Rigaku Mercury CCD/AFC
diffractometer

Radiation source: fine-focus sealed tube

1986 independent reflections

1837 reflections with $I > 2\sigma(I)$

graphite $R_{\text{int}} = 0.027$
 φ and ω scans $\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 3.3^\circ$
 Absorption correction: multi-scan
 (*CrystalClear*; Rigaku, 2007) $h = -31 \rightarrow 32$
 $T_{\text{min}} = 0.745$, $T_{\text{max}} = 0.752$ $k = -7 \rightarrow 7$
 6403 measured reflections $l = -16 \rightarrow 15$

Refinement

Refinement on F^2 Primary atom site location: structure-invariant direct methods
 Least-squares matrix: full Secondary atom site location: difference Fourier map
 $R[F^2 > 2\sigma(F^2)] = 0.030$ Hydrogen site location: inferred from neighbouring sites
 $wR(F^2) = 0.082$ H atoms treated by a mixture of independent and constrained refinement
 $S = 1.08$ $w = 1/[\sigma^2(F_o^2) + (0.0494P)^2]$
 1986 reflections where $P = (F_o^2 + 2F_c^2)/3$
 136 parameters $(\Delta/\sigma)_{\text{max}} = 0.001$
 0 restraints $\Delta\rho_{\text{max}} = 0.27 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.69 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.0000	0.94430 (5)	0.2500	0.03390 (13)
O1	0.07205 (5)	0.8141 (2)	0.23289 (10)	0.0398 (3)
O2	0.01520 (5)	0.6023 (2)	0.12225 (11)	0.0379 (3)
O3	0.17146 (5)	0.6892 (3)	0.27805 (10)	0.0433 (3)
O4	0.02830 (7)	1.1674 (3)	0.36768 (14)	0.0556 (4)
O5	0.12868 (6)	-0.0192 (3)	-0.03081 (11)	0.0432 (3)
C1	0.06216 (6)	0.6401 (3)	0.16527 (12)	0.0294 (3)
C2	0.10816 (6)	0.4881 (3)	0.14311 (13)	0.0269 (3)
C3	0.15997 (7)	0.5201 (3)	0.19989 (13)	0.0301 (3)
C4	0.20140 (7)	0.3720 (4)	0.17747 (14)	0.0358 (4)
H4	0.2364	0.3946	0.2153	0.043*

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C5	0.19295 (7)	0.1916 (3)	0.10108 (14)	0.0355 (4)
H5	0.2219	0.0912	0.0866	0.043*
C6	0.09982 (6)	0.3065 (3)	0.06567 (12)	0.0297 (3)
H6	0.0651	0.2848	0.0266	0.036*
C7	0.14159 (7)	0.1582 (3)	0.04532 (12)	0.0307 (3)
C8	0.17070 (8)	-0.1737 (4)	-0.05639 (16)	0.0470 (5)
H8A	0.1989	-0.0751	-0.0818	0.070*
H8B	0.1562	-0.2881	-0.1123	0.070*
H8C	0.1859	-0.2639	0.0074	0.070*
H1	0.1412 (11)	0.767 (5)	0.275 (2)	0.065 (8)*
H4A	0.0164 (10)	1.283 (5)	0.378 (2)	0.052 (7)*
H4B	0.0570 (12)	1.135 (6)	0.407 (2)	0.081 (9)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.02475 (17)	0.03398 (19)	0.0432 (2)	0.000	0.00526 (12)	0.000
O1	0.0334 (6)	0.0375 (7)	0.0492 (7)	-0.0006 (5)	0.0087 (5)	-0.0142 (5)
O2	0.0256 (6)	0.0363 (6)	0.0511 (7)	0.0028 (5)	0.0025 (5)	-0.0042 (5)
O3	0.0319 (7)	0.0497 (8)	0.0462 (7)	-0.0039 (6)	-0.0015 (6)	-0.0164 (6)
O4	0.0486 (9)	0.0465 (9)	0.0660 (10)	0.0189 (8)	-0.0124 (8)	-0.0210 (8)
O5	0.0393 (7)	0.0429 (7)	0.0464 (8)	0.0083 (6)	0.0020 (6)	-0.0165 (6)
C1	0.0283 (8)	0.0280 (8)	0.0330 (8)	-0.0011 (7)	0.0081 (6)	0.0022 (6)
C2	0.0244 (8)	0.0279 (7)	0.0288 (8)	-0.0005 (7)	0.0051 (6)	0.0021 (6)
C3	0.0277 (8)	0.0338 (8)	0.0287 (8)	-0.0039 (7)	0.0027 (6)	-0.0002 (6)
C4	0.0237 (8)	0.0458 (9)	0.0366 (8)	0.0012 (8)	-0.0002 (7)	0.0002 (7)
C5	0.0279 (8)	0.0418 (9)	0.0372 (8)	0.0090 (7)	0.0053 (7)	0.0016 (7)
C6	0.0251 (7)	0.0330 (8)	0.0302 (7)	-0.0006 (6)	0.0015 (6)	-0.0004 (6)
C7	0.0321 (8)	0.0309 (8)	0.0291 (7)	0.0017 (7)	0.0045 (6)	-0.0003 (6)
C8	0.0519 (12)	0.0448 (11)	0.0466 (10)	0.0112 (9)	0.0155 (9)	-0.0063 (8)

Geometric parameters (\AA , $^\circ$)

Zn1—O4	1.9852 (15)	C2—C6	1.395 (2)
Zn1—O4 ⁱ	1.9852 (15)	C2—C3	1.409 (2)
Zn1—O1	1.9854 (13)	C3—C4	1.382 (2)
Zn1—O1 ⁱ	1.9854 (13)	C4—C5	1.382 (3)
O1—C1	1.286 (2)	C4—H4	0.9500
O2—C1	1.247 (2)	C5—C7	1.395 (2)
O3—C3	1.360 (2)	C5—H5	0.9500
O3—H1	0.87 (3)	C6—C7	1.381 (2)
O4—H4A	0.73 (3)	C6—H6	0.9500
O4—H4B	0.84 (3)	C8—H8A	0.9800
O5—C7	1.379 (2)	C8—H8B	0.9800
O5—C8	1.427 (2)	C8—H8C	0.9800
C1—C2	1.484 (2)		
O4—Zn1—O4 ⁱ	103.54 (11)	C4—C3—C2	119.37 (16)
O4—Zn1—O1	93.83 (6)	C3—C4—C5	121.33 (15)

O4 ⁱ —Zn1—O1	112.34 (7)	C3—C4—H4	119.3
O4—Zn1—O1 ⁱ	112.34 (7)	C5—C4—H4	119.3
O4 ⁱ —Zn1—O1 ⁱ	93.83 (6)	C4—C5—C7	119.43 (16)
O1—Zn1—O1 ⁱ	137.66 (7)	C4—C5—H5	120.3
C1—O1—Zn1	104.20 (10)	C7—C5—H5	120.3
C3—O3—H1	102.2 (17)	C7—C6—C2	120.63 (14)
Zn1—O4—H4A	125 (2)	C7—C6—H6	119.7
Zn1—O4—H4B	120 (2)	C2—C6—H6	119.7
H4A—O4—H4B	115 (3)	O5—C7—C6	115.91 (14)
C7—O5—C8	118.04 (15)	O5—C7—C5	124.02 (15)
O2—C1—O1	120.00 (15)	C6—C7—C5	120.07 (15)
O2—C1—C2	122.53 (15)	O5—C8—H8A	109.5
O1—C1—C2	117.46 (14)	O5—C8—H8B	109.5
C6—C2—C3	119.16 (15)	H8A—C8—H8B	109.5
C6—C2—C1	119.38 (14)	O5—C8—H8C	109.5
C3—C2—C1	121.45 (15)	H8A—C8—H8C	109.5
O3—C3—C4	117.55 (15)	H8B—C8—H8C	109.5
O3—C3—C2	123.07 (16)		

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

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>
O3—H1 \cdots O1	0.87 (3)	1.76 (3)	2.5771 (19)	155 (2)
O4—H4A \cdots O2 ⁱⁱ	0.73 (3)	1.93 (3)	2.643 (2)	169 (3)
O4—H4B \cdots O5 ⁱⁱⁱ	0.84 (3)	1.97 (3)	2.790 (2)	167 (3)

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

Fig. 1

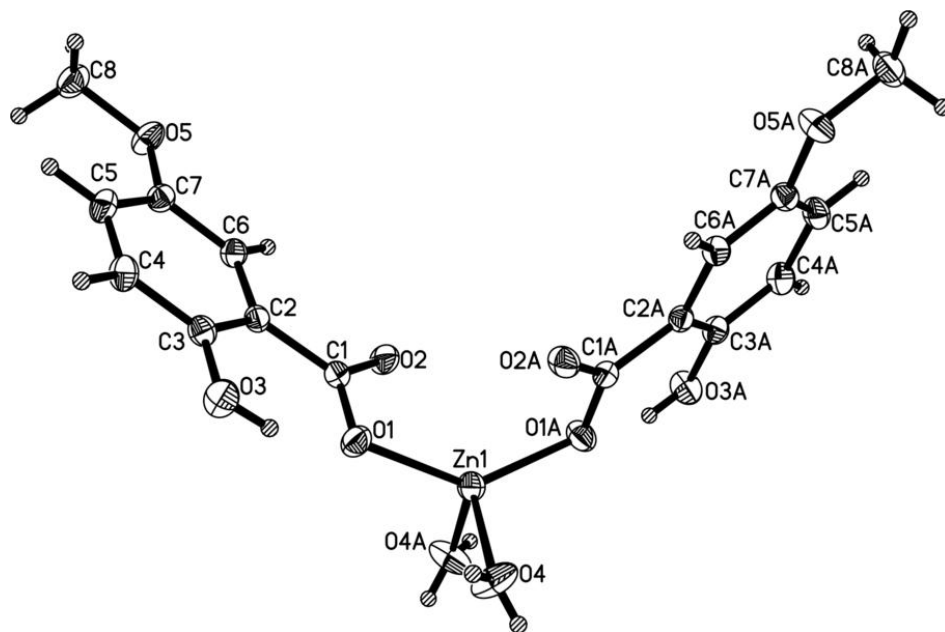


Fig. 2

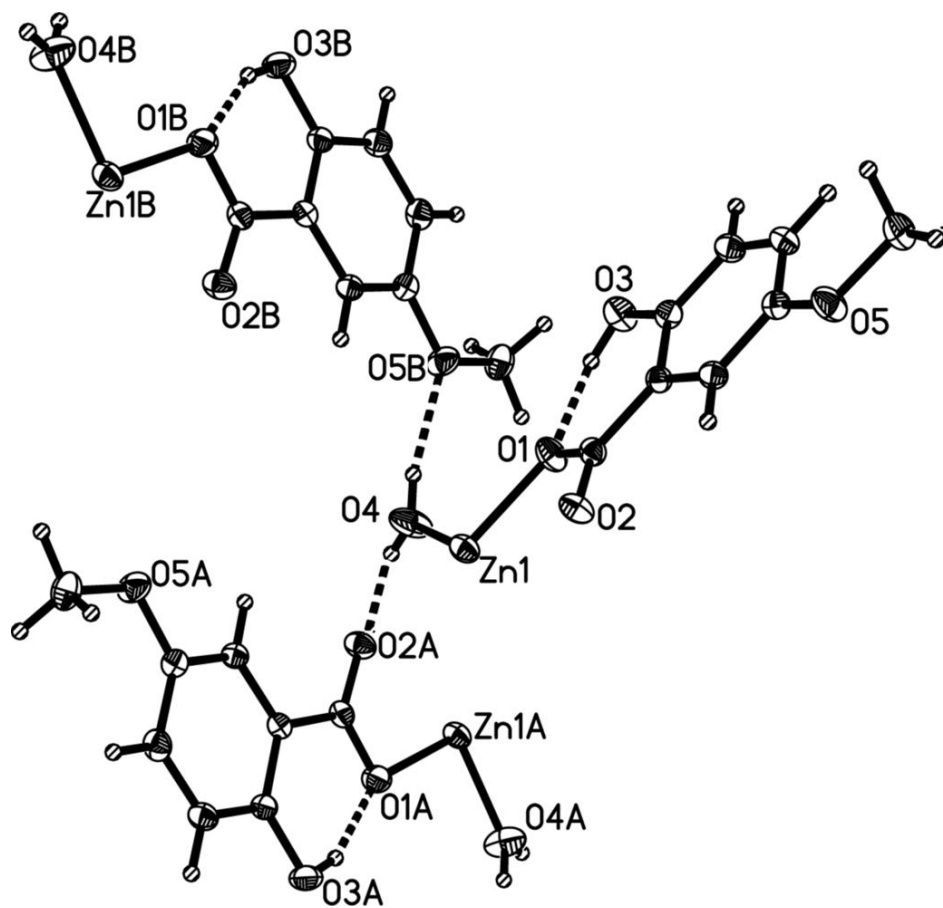


Fig. 3

