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Key indicators

Single-crystal X-ray study
 $T = 295$ K
 Mean $\sigma(\text{C}-\text{C}) = 0.005$ Å
 R factor = 0.043
 wR factor = 0.126
 Data-to-parameter ratio = 12.8

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

cis-Diaquabis(4-formyl-2-methoxyphenolato)-zinc(II)

The title compound, $[\text{Zn}(\text{C}_8\text{H}_7\text{O}_3)_2(\text{H}_2\text{O})_2]$, is a mononuclear complex. The Zn^{II} atom lies on a twofold axis and is coordinated by four O atoms from two 4-formyl-2-methoxyphenolate anionic ligands and two O atoms from two water molecules, to form a very distorted tetragonal–bipyramidal geometry. The formyl O atoms of the ligand, the water O atoms and the phenolate O atoms contribute to the formation of a hydrogen-bonded three-dimensional network.

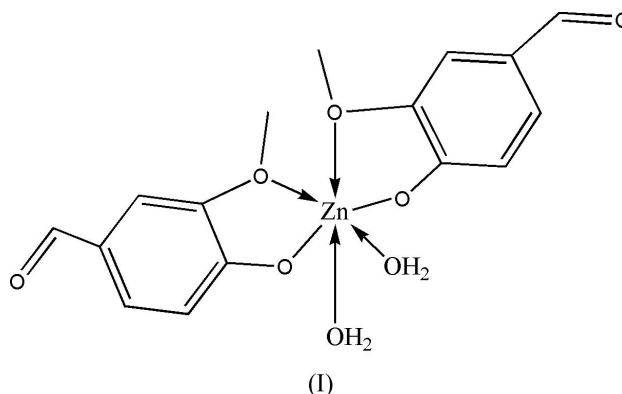
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Comment

In recent years, phenolic compounds have attracted the interest of researchers because they show promise of being powerful antioxidants that can protect the human body from free radicals (Rice-Evans *et al.*, 1996). Their complexes are becoming increasingly important as biochemical, analytical and antimicrobial reagents (Tumer *et al.*, 1999).



4-Hydroxy-3-methoxybenzaldehyde, which is well known as the flavoring material vanillin (Walton *et al.*, 2003), is a

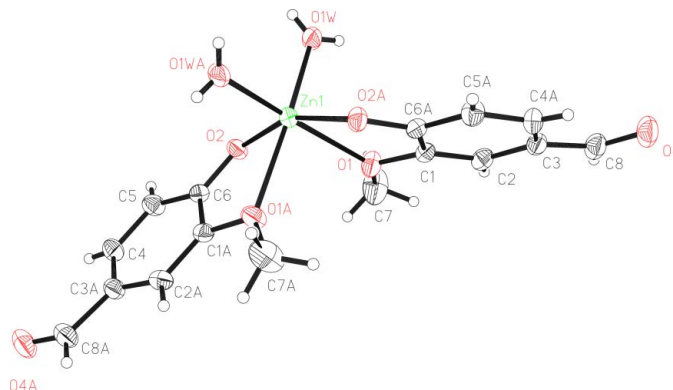


Figure 1

The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

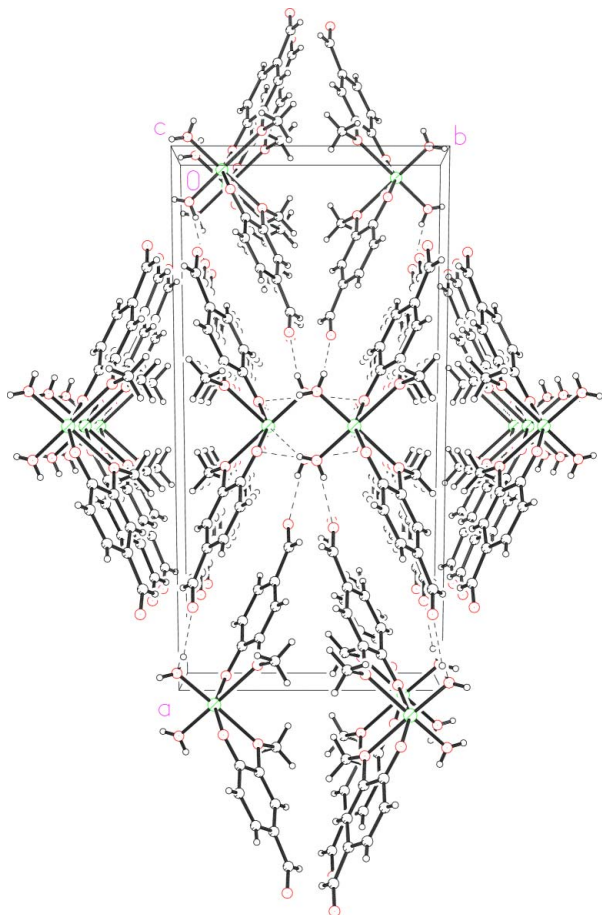


Figure 2
The crystal packing of (I), viewed along the *c* axis. The O—H...O hydrogen-bonding interactions are shown as dashed lines.

potential bidentate ligand with versatile binding modes. However, the reported crystal structures of metal complexes with vanillin are rare and mainly focus on mononuclear copper(II) complexes. We report here the zinc vanillin complex *cis*-diaquabis(4-formyl-2-methoxyphenolato)zinc(II), (I).

In the crystal structure of (I), the asymmetric unit is composed of a Zn^{II} ion, one 4-formyl-2-methoxyphenolate anion and one coordinated water molecule. The molecular structure of (I) is shown in Fig. 1. The 4-formyl-2-methoxyphenolate ligand bears a formal charge of -1 , being deprotonated at phenol atom O2. The Zn^{II} ion lies on a twofold axis. The Zn^{II} ion is six-coordinated and the coordination geometry can be described as very distorted tetragonal–bipyramidal. One axial position is occupied by water atom O1W. The other axial position is occupied by methoxy atom O1A, with a Zn—O distance of 2.331 (3) Å, which is longer than the other four Zn—O bonds, but still less than the Zn—O bond length (2.444 Å) reported by Ding *et al.* (2005). In some sense, the Zn coordination geometry can also be described as a distorted tetrahedron, for the bonds to the methoxy group are long and

have less than half the bond valence (bond order) that the other four bonds have. The Zn atom is displaced from the center of its octahedron toward the centre of a tetrahedron formed by the four strong bonds. The four strong bonds have bond valences (Brown & Altermatt, 1985; Brese & O’Keeffe, 1991) of 0.47 and 0.42 (they would be 0.50 in a tetrahedron) and two weak bonds of bond valence 0.18. In a regular octahedron, all bonds would have valences of 0.33.

The 4-hydroxy-2-methoxyphenolate anion coordinates to the central zinc ion as a bidentate ligand. In the crystal structure, the coordinated water molecules form intermolecular hydrogen bonds (Table 2) with formyl atom O4 and coordinated phenolate O2 acceptors. These hydrogen bonds link the molecules into a three-dimensional network (Fig. 2).

Experimental

Zn(NO₃)₂·4H₂O (1 mmol, 261 mg), 4-hydroxy-3-methoxybenzaldehyde (2 mmol, 304 mg) and pyrimidine (2 mmol, 148 mg) were dissolved in an ethanol solution and the mixture was stirred for 2 h at room temperature. The resulting clear yellow solution was kept in air and, after slow evaporation of the solvent over a period of a week, yellow crystals of (I) were formed at the bottom of the vessel. The crystals were isolated and washed three times with ethanol and dried in a vacuum desiccator using anhydrous CaCl₂ (yield 38%). Analysis calculated for C₁₆H₁₈O₈Zn: C 47.60, H 4.49%; found: C 47.36, H 4.72%.

Crystal data

[Zn(C ₈ H ₇ O ₃) ₂ (H ₂ O) ₂]	$D_x = 1.538 \text{ Mg m}^{-3}$
$M_r = 403.67$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 1601 reflections
$a = 22.172 (4) \text{ \AA}$	$\theta = 2.5\text{--}26.9^\circ$
$b = 10.5547 (16) \text{ \AA}$	$\mu = 1.45 \text{ mm}^{-1}$
$c = 7.7884 (12) \text{ \AA}$	$T = 295 (2) \text{ K}$
$\beta = 106.909 (5)^\circ$	Block, yellow
$V = 1743.8 (5) \text{ \AA}^3$	$0.34 \times 0.31 \times 0.25 \text{ mm}$
$Z = 4$	

Data collection

Bruker SMART CCD area-detector diffractometer	1538 independent reflections
φ and ω scans	1378 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.032$
$T_{\text{min}} = 0.621$, $T_{\text{max}} = 0.710$	$\theta_{\text{max}} = 25.0^\circ$
4251 measured reflections	$h = -26 \rightarrow 24$
	$k = -12 \rightarrow 8$
	$l = -9 \rightarrow 9$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0765P)^2 + 2.1873P]$
$R[F^2 > 2\sigma(F^2)] = 0.043$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.126$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.08$	$\Delta\rho_{\text{max}} = 0.91 \text{ e \AA}^{-3}$
1538 reflections	$\Delta\rho_{\text{min}} = -0.34 \text{ e \AA}^{-3}$
120 parameters	
H atoms treated by mixture of independent and constrained refinement	

Table 1

Selected geometric parameters (Å, °).

Zn1—O2	1.981 (2)	Zn1—O1	2.331 (3)
Zn1—O1W	2.027 (3)		
O2—Zn1—O2 ⁱ	156.77 (15)	O1W—Zn1—O1 ⁱ	171.25 (11)
O2—Zn1—O1W ⁱ	98.85 (11)	O2—Zn1—O1	89.00 (9)
O2—Zn1—O1W	96.97 (11)	O1W—Zn1—O1	89.07 (12)
O1W ⁱ —Zn1—O1W	93.76 (17)	O1 ⁱ —Zn1—O1	89.35 (15)
O2—Zn1—O1 ⁱ	74.40 (9)		

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

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H1WB \cdots O2 ⁱⁱ	0.830 (19)	1.87 (2)	2.695 (4)	175 (4)
O1W—H1WA \cdots O4 ⁱⁱⁱ	0.826 (19)	1.91 (2)	2.725 (4)	169 (5)

Symmetry codes: (ii) $1 - x, 1 - y, -z$; (iii) $\frac{3}{2} - x, \frac{1}{2} - y, 1 - z$.

H atoms bonded to C atoms were placed in calculated positions and were allowed to ride on their parent C atoms, with a distance of 0.93 Å for aromatic H atoms and 0.97 Å for methyl H atoms, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$. The aqua H atoms were placed in calculated positions and refined with an O—H distance restraint of 0.85 (1) Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{iso}}(\text{O1W})$.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINTE* (Siemens, 1996); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b); software used to prepare material for publication: *SHELXTL*.

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