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Bis(μ-4-formyl-2-methoxyphenolato)-bis[aquachloridozinc(II)] dihydrate

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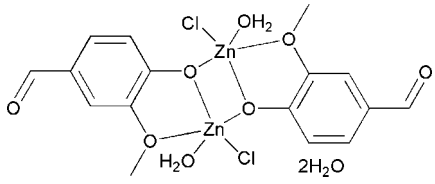
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.003 Å; R factor = 0.030; wR factor = 0.087; data-to-parameter ratio = 16.9.

In the centrosymmetric dinuclear molecule of the title compound, $[Zn_2(C_8H_7O_3)_2Cl_2(H_2O)_2]$, the Zn ions are bridged by two phenolate O atoms, with a Zn···Zn distance of 3.1216 (6) Å, forming a Zn_2O_2 four-membered ring. Each Zn coordination is completed by a further bidentate 4-hydroxy-3-methoxybenzaldehyde ion, one chloride ion and one water molecule. The water molecules are involved in hydrogen bonds, which stabilize the crystal structure.

Related literature

For related crystal structures, see: Ding *et al.* (2005); Kunert *et al.* (2000); Olmstead *et al.* (1991). For common applications of these complexes, see: Rice-Evans *et al.* (1996); Tumer *et al.* (1999).



Experimental

Crystal data

$[Zn_2(C_8H_7O_3)_2Cl_2(H_2O)_2]$
M_r = 576.02
Monoclinic, $P2_1/n$
a = 7.0896 (6) Å
b = 15.9772 (10) Å
c = 10.1193 (7) Å
β = 107.559 (4)°
V = 1092.83 (14) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 2.49 mm^{-1}
T = 296 (2) K
0.26 × 0.17 × 0.07 mm

Data collection

Bruker SMART diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.517, T_{max} = 0.840
9933 measured reflections
2500 independent reflections
2046 reflections with $I > 2\sigma(I)$
R_{int} = 0.028

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.088
S = 1.06
2500 reflections
148 parameters
6 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.57 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1WA···O3^{i}	0.827 (17)	1.847 (18)	2.666 (3)	171 (4)
O1W—H1WB···O2W^{ii}	0.819 (17)	1.854 (18)	2.671 (3)	175 (3)
O2W—H2WA···Cl1	0.833 (19)	2.40 (3)	3.190 (3)	158 (6)
O2W—H2WB···Cl1^{iii}	0.83 (4)	2.43 (4)	3.258 (3)	178 (6)

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

Data collection: *SMART* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2002); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RK2052).

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supplementary materials

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Bis(μ-4-formyl-2-methoxyphenolato)bis[aquachloridozinc(II)] dihydrate

H.-M. Guo, H.-D. Xian and G.-L. Zhao

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). We report here the zinc dinuclear vanillin complex bis[aqua-chloro-(4-hydroxy-3-methoxybenzaldehyde)-zinc(II)] dihydrate (**I**).

The structural features of the **I** dimer shown in Fig. 1. The complex is centrosymmetric with an inversion center in the middle of the Zn_2O_2 core. Similar binuclear zinc(II) phenol *O*-bridged complexes with a planar Zn_2O_2 core have been reported by Olmstead *et al.*, (1991) and Kunert *et al.*, (2000). Each Zn atom employs one oxygen donor - O1, from the vanillin ligands to form the Zn_2O_2 unit, while the second oxygen atom, O2, from this bridging vanillin ligand is terminally coordinated to the Zn atom. This complex contains a central four-membered Zn—O—Zn—O ring can be described as parallelogram. The atom O1 as a bridge atom coordinate with two Zn atoms. The Zn—O bond lengths of the terminal bonds (Zn1—O2 = 2.2907 (17) Å) are significantly larger than the bridging Zn—O—Zn moiety (Zn1—O1 = 1.9851 (17) Å, Zn1—O1A = 2.0349 (16) Å) but still less than the Zn—O bond length (2.444 Å) reported by Ding *et al.*, (2005). The coordinated water molecules and chloride ion are located *trans* with respect to the Zn_2O_2 plane. The bridging vanillin ligands are coplanar. There are two water molecules in the lattice. The O1w H atoms make intermolecular hydrogen bonds to the O2w atoms [(symmetry code: −1 + *x*, *y*, *z*) with d(O···O) = 2.671 (3)Å and angle O–H···O = 175.(3)°] and uncoordinated O3 atoms [(symmetry code: *x* − 1, *y*, *z* − 1) with d(O···O) = 2.666 (3)Å and angle O–H···O = 170.(4)°]. The O2w H atoms also make intermolecular hydrogen bonds to the Cl atoms [(symmetry code: 1/2 + *x*, 0.5 − *y*, 1/2 + *z*) with d(O···O) = 3.259 (3)Å and angle O–H···O = 178.(4)°]. The vanillin O atoms, the water O atoms and chloride ion contribute to the formation of a hydrogen-bonded three-dimensional network.

Experimental

$ZnCl_2$(1 mmol, 136 mg), 2-methoxy-4-[(4-nitrophenylimino)methyl]phenol (2 mmol, 545 mg) were dissolved in ethanol (25 ml) solution and the mixture was stirred for 2 h at room temperature. The yellow solution was kept aside, and the orange crystal was abtained after several weeks.

Refinement

The H atoms bonded to C atoms were positioned geometrically and refined using a riding model: aromatic C–H = 0.93Å and aliphatic C–H = 0.96 Å, U_{iso}(H) = 1.2U_{eq}(C) for aromatic and U_{iso}(H) = 1.5U_{eq}(C) for aliphatic. The H atoms bonded to O atoms were located in a difference Fourier maps and refined with O–H distance restraints of 0.85 (2) and U_{iso}(H) = 1.5U_{eq}(O).

Figures

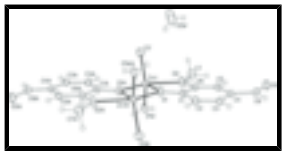

Fig. 1. The molecular structure of **I**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are presented as a spheres of arbitrary radius.

Bis(μ-4-formyl-2-methoxyphenolato)bis[aquachloridozinc(II)] dihydrate

Crystal data

$[Zn_2(C_8H_7O_3)_2Cl_2(H_2O)_2]$	F_{000} = 584
M_r = 576.02	D_x = 1.750 Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2yn	Cell parameters from 3431 reflections
a = 7.0896 (6) Å	θ = 2.5–27.5º
b = 15.9772 (10) Å	μ = 2.49 mm^{-1}
c = 10.1193 (7) Å	T = 296 (2) K
β = 107.559 (4)º	Plate, orange
V = 1092.83 (14) Å^3	0.26 × 0.17 × 0.07 mm
Z = 2	

Data collection

Bruker P4 diffractometer	2500 independent reflections
Radiation source: Fine-focus sealed tube	2046 reflections with $I > 2\sigma(I)$
Monochromator: Graphite	R_{int} = 0.028
T = 296(2) K	θ_{max} = 27.5º
ω–scans	θ_{min} = 2.5º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	h = −9→8
T_{min} = 0.517, T_{max} = 0.840	k = −20→20
9933 measured reflections	l = −13→12

Refinement

Refinement on F^2	Secondary atom site location: Difmap
Least-squares matrix: Full	Hydrogen site location: Geom
$R[F^2 > 2\sigma(F^2)]$ = 0.030	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.088	$w = 1/[\sigma^2(F_o^2) + (0.0464P)^2 + 0.539P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.06	$(\Delta/\sigma)_{max}$ = 0.001
2500 reflections	$\Delta\rho_{max}$ = 0.57 e Å^{-3}

148 parameters
6 restraints
Primary atom site location: Direct

$\Delta\rho_{min} = -0.48$ e Å^{-3}
Extinction correction: None

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 $F^2 > 2\sigma(F^2)$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Zn1	−0.05704 (4)	0.407241 (18)	0.51776 (3)	0.03079 (12)
Cl1	0.06529 (12)	0.29032 (5)	0.45511 (8)	0.0496 (2)
C1	0.1385 (3)	0.50285 (15)	0.7681 (2)	0.0275 (5)
C2	0.2207 (4)	0.57134 (16)	0.8483 (3)	0.0330 (5)
H2A	0.2306	0.6222	0.8063	0.040*
C3	0.2887 (4)	0.56405 (17)	0.9918 (3)	0.0338 (6)
H3A	0.3432	0.6103	1.0455	0.041*
C4	0.2758 (4)	0.48843 (16)	1.0555 (2)	0.0316 (5)
C5	0.1889 (4)	0.41882 (16)	0.9764 (2)	0.0309 (5)
H5A	0.1790	0.3681	1.0188	0.037*
C6	0.1187 (4)	0.42698 (15)	0.8348 (2)	0.0289 (5)
C7	0.0128 (5)	0.28292 (17)	0.7989 (3)	0.0460 (7)
H7A	0.0587	0.2848	0.8983	0.055*
H7B	0.0934	0.2448	0.7661	0.055*
H7C	−0.1221	0.2643	0.7687	0.055*
C8	0.3641 (4)	0.48144 (19)	1.2047 (3)	0.0390 (6)
H8A	0.4148	0.5299	1.2534	0.047*
O1	0.0780 (3)	0.50395 (10)	0.63014 (17)	0.0345 (4)
O1W	−0.3382 (3)	0.39772 (14)	0.5103 (2)	0.0426 (5)
H1WA	−0.434 (4)	0.406 (2)	0.441 (3)	0.064*
H1WB	−0.377 (5)	0.3628 (19)	0.555 (3)	0.064*
O2	0.0256 (3)	0.36493 (11)	0.74433 (18)	0.0406 (5)
O2W	0.5141 (4)	0.2849 (3)	0.6469 (3)	0.1013 (13)
H2WA	0.393 (3)	0.294 (4)	0.616 (5)	0.152*
H2WB	0.525 (8)	0.265 (4)	0.725 (3)	0.152*
O3	0.3765 (3)	0.41693 (14)	1.2706 (2)	0.0489 (5)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.03931 (19)	0.02613 (18)	0.02405 (17)	−0.00240 (12)	0.00521 (12)	0.00208 (11)
Cl1	0.0609 (5)	0.0417 (4)	0.0420 (4)	0.0132 (3)	0.0091 (3)	−0.0052 (3)
C1	0.0291 (11)	0.0315 (12)	0.0207 (11)	0.0014 (10)	0.0059 (9)	0.0043 (9)
C2	0.0396 (14)	0.0289 (12)	0.0303 (13)	−0.0015 (11)	0.0101 (11)	0.0014 (10)
C3	0.0373 (14)	0.0339 (13)	0.0276 (12)	0.0030 (11)	0.0060 (11)	−0.0051 (10)
C4	0.0304 (12)	0.0401 (14)	0.0229 (11)	0.0059 (11)	0.0062 (10)	0.0001 (10)
C5	0.0330 (13)	0.0341 (13)	0.0243 (12)	0.0017 (10)	0.0067 (10)	0.0070 (10)
C6	0.0309 (12)	0.0311 (12)	0.0219 (11)	0.0000 (10)	0.0037 (9)	0.0019 (9)
C7	0.0607 (19)	0.0308 (14)	0.0410 (15)	−0.0087 (13)	0.0069 (14)	0.0087 (12)
C8	0.0405 (15)	0.0511 (16)	0.0232 (12)	0.0051 (13)	0.0062 (11)	−0.0026 (12)
O1	0.0518 (11)	0.0286 (9)	0.0195 (8)	−0.0056 (8)	0.0053 (7)	0.0034 (7)
O1W	0.0363 (11)	0.0565 (13)	0.0303 (10)	−0.0027 (9)	0.0031 (8)	0.0117 (9)
O2	0.0574 (12)	0.0298 (9)	0.0249 (9)	−0.0113 (9)	−0.0020 (8)	0.0053 (7)
O2W	0.0647 (17)	0.154 (3)	0.0694 (18)	−0.045 (2)	−0.0035 (14)	0.058 (2)
O3	0.0529 (13)	0.0624 (14)	0.0254 (10)	0.0024 (10)	0.0027 (9)	0.0092 (9)

Geometric parameters (Å, °)

Zn1—O1W	1.978 (2)	C5—C6	1.374 (3)
Zn1—O1	1.9851 (17)	C5—H5A	0.9300
Zn1—O1^{i}	2.0350 (16)	C6—O2	1.375 (3)
Zn1—Cl1	2.2307 (8)	C7—O2	1.435 (3)
Zn1—O2	2.2905 (17)	C7—H7A	0.9600
Zn1—Zn1^{i}	3.1216 (6)	C7—H7B	0.9600
C1—O1	1.331 (3)	C7—H7C	0.9600
C1—C2	1.382 (3)	C8—O3	1.217 (3)
C1—C6	1.415 (3)	C8—H8A	0.9300
C2—C3	1.390 (4)	O1—Zn1^{i}	2.0350 (16)
C2—H2A	0.9300	O1W—H1WA	0.827 (17)
C3—C4	1.385 (4)	O1W—H1WB	0.819 (17)
C3—H3A	0.9300	O2W—H2WA	0.833 (19)
C4—C5	1.400 (4)	O2W—H2WB	0.83 (4)
C4—C8	1.454 (3)		
O1W—Zn1—O1	112.85 (9)	C5—C4—C8	120.7 (2)
O1W—Zn1—O1^{i}	100.15 (8)	C6—C5—C4	118.7 (2)
O1—Zn1—O1^{i}	78.12 (7)	C6—C5—H5A	120.7
O1W—Zn1—Cl1	113.49 (7)	C4—C5—H5A	120.7
O1—Zn1—Cl1	130.77 (6)	C5—C6—O2	125.2 (2)
O1^{i}—Zn1—Cl1	108.86 (5)	C5—C6—C1	121.4 (2)
O1W—Zn1—O2	88.06 (8)	O2—C6—C1	113.4 (2)
O1—Zn1—O2	73.91 (6)	O2—C7—H7A	109.5
O1^{i}—Zn1—O2	151.87 (7)	O2—C7—H7B	109.5
Cl1—Zn1—O2	91.91 (6)	H7A—C7—H7B	109.5

O1W—Zn1—Zn1^{i}	111.21 (6)	O2—C7—H7C	109.5
O1—Zn1—Zn1^{i}	39.64 (5)	H7A—C7—H7C	109.5
O1^{i}—Zn1—Zn1^{i}	38.48 (5)	H7B—C7—H7C	109.5
Cl1—Zn1—Zn1^{i}	128.75 (3)	O3—C8—C4	124.9 (3)
O2—Zn1—Zn1^{i}	113.49 (5)	O3—C8—H8A	117.6
O1—C1—C2	123.4 (2)	C4—C8—H8A	117.6
O1—C1—C6	117.7 (2)	C1—O1—Zn1	122.51 (15)
C2—C1—C6	118.9 (2)	C1—O1—Zn1^{i}	135.20 (15)
C1—C2—C3	119.9 (2)	Zn1—O1—Zn1^{i}	101.88 (7)
C1—C2—H2A	120.1	Zn1—O1W—H1WA	126 (2)
C3—C2—H2A	120.1	Zn1—O1W—H1WB	122 (2)
C4—C3—C2	120.6 (2)	H1WA—O1W—H1WB	105 (2)
C4—C3—H3A	119.7	C6—O2—C7	118.4 (2)
C2—C3—H3A	119.7	C6—O2—Zn1	112.32 (14)
C3—C4—C5	120.4 (2)	C7—O2—Zn1	128.87 (16)
C3—C4—C8	118.8 (2)	H2WA—O2W—H2WB	103 (3)
O1—C1—C2—C3	−177.0 (2)	Cl1—Zn1—O1—C1	−81.56 (19)
C6—C1—C2—C3	2.2 (4)	O2—Zn1—O1—C1	−3.26 (18)
C1—C2—C3—C4	0.4 (4)	Zn1^{i}—Zn1—O1—C1	173.7 (2)
C2—C3—C4—C5	−1.9 (4)	O1W—Zn1—O1—Zn1^{i}	−96.13 (9)
C2—C3—C4—C8	174.7 (2)	O1^{i}—Zn1—O1—Zn1^{i}	0.0
C3—C4—C5—C6	0.6 (4)	Cl1—Zn1—O1—Zn1^{i}	104.76 (8)
C8—C4—C5—C6	−175.9 (2)	O2—Zn1—O1—Zn1^{i}	−176.94 (10)
C4—C5—C6—O2	−178.3 (2)	C5—C6—O2—C7	−5.1 (4)
C4—C5—C6—C1	2.1 (4)	C1—C6—O2—C7	174.5 (2)
O1—C1—C6—C5	175.7 (2)	C5—C6—O2—Zn1	−178.4 (2)
C2—C1—C6—C5	−3.6 (4)	C1—C6—O2—Zn1	1.2 (3)
O1—C1—C6—O2	−3.9 (3)	O1W—Zn1—O2—C6	−113.56 (18)
C2—C1—C6—O2	176.8 (2)	O1—Zn1—O2—C6	0.91 (16)
C3—C4—C8—O3	−173.8 (3)	O1^{i}—Zn1—O2—C6	−5.5 (3)
C5—C4—C8—O3	2.8 (4)	Cl1—Zn1—O2—C6	133.00 (17)
C2—C1—O1—Zn1	−175.52 (19)	Zn1^{i}—Zn1—O2—C6	−1.22 (18)
C6—C1—O1—Zn1	5.2 (3)	O1W—Zn1—O2—C7	74.0 (2)
C2—C1—O1—Zn1^{i}	−4.3 (4)	O1—Zn1—O2—C7	−171.5 (3)
C6—C1—O1—Zn1^{i}	176.41 (17)	O1^{i}—Zn1—O2—C7	−177.9 (2)
O1W—Zn1—O1—C1	77.54 (19)	Cl1—Zn1—O2—C7	−39.4 (2)
O1^{i}—Zn1—O1—C1	173.7 (2)	Zn1^{i}—Zn1—O2—C7	−173.6 (2)

Symmetry codes: (i) −*x*, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1W—H1WA···O3^{ii}	0.827 (17)	1.847 (18)	2.666 (3)	171 (4)
O1W—H1WB···O2W^{iii}	0.819 (17)	1.854 (18)	2.671 (3)	175 (3)
O2W—H2WA···Cl1	0.833 (19)	2.40 (3)	3.190 (3)	158 (6)

O2W—H2WB···Cl1^{iv}	0.83 (4)	2.43 (4)	3.258 (3)	178 (6)

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

Fig. 1