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Bis{μ-2′-[1-(4-chloro-2-oxidophenyl)ethylidene]thiophene-2-carbohydrazidato}bis[pyridinezinc(II)]

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.048
wR factor = 0.138
Data-to-parameter ratio = 17.9

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

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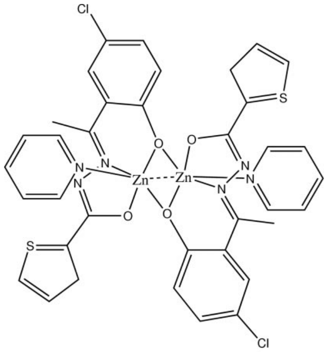
The title compound, $[Zn_2(C_{13}H_9ClN_2O_2S)_2(C_5H_5N)_2]$, is dimeric *via* Zn—O bridges with an average Zn—O distance of 2.027 Å. The Zn···Zn separation is 3.1003 (5) Å and the geometry of both Zn atoms is square pyramidal.

Comment

The coordination of dimethyl sulfoxide (DMSO) molecules in zinc–Schiff base complexes, such as in $[Zn(C_{26}H_{34}O_6)(DMSO)_2]$ (Morgant *et al.*, 1998), $[Zn(C_{15}H_{12}N_2O_2)_2(DMSO)_2]$ and $[Zn(C_{12}H_{10}N_2O_2S)_2(DMSO)]$ (Ali, Kadir *et al.*, 2003; Ali, Omar *et al.*, 2003), has displayed a variety of geometries at the zinc metal centre. The complexes can also be either monomeric or dimeric. The title compound, (I), shows the coordination of pyridine when $[Zn(C_{13}H_{10}N_2O_2SCl]$ was recrystallized from pyridine. The molecule is dimeric *via* Zn—O bridges, with an average Zn—O distance of 2.027 Å. The Zn1···Zn2 distance of 3.1004 (5) Å is shorter than in $[Zn(C_{15}H_{12}N_2O_2)(DMSO)_2]$ [3.1370 (13) Å; Ali, Kadir *et al.*, 2003].



(I)

Both Zn atoms have geometry between square pyramidal and trigonal bipyrimidal, but are closer to the former. Atoms O1, O2, O3 and N1 occupy the equatorial positions, with atom N5 located at the apex of the pyramid (Table 2). The structural dimensions of the *O,N,O*-tridentate ligands are normal (Orpen *et al.*, 1989; Allen *et al.*, 1987). The Schiff base ligands are essentially planar, with the Cl1/O1/O2/N2/C1–C7/C9 plane [maximum deviation of 0.052 (1) Å for Cl1] making an angle of 8.33 (11)° with S1/C9/C10–C13 [maximum deviation of 0.020 (4) Å for C13]. The pyridine ring (N5/C27–C31) is inclined to the Cl1/O1/O2/N2/C1–C7/C9 fragment by 80.02 (2)°.

There are C2—H2*B*···O4 and C15—H15*A*···O2 intramolecular interactions, involving the O atoms of the chelated NNC(O) fragments and the H atoms on the chloro-substituted benzene rings. In the crystal structure, the mol-

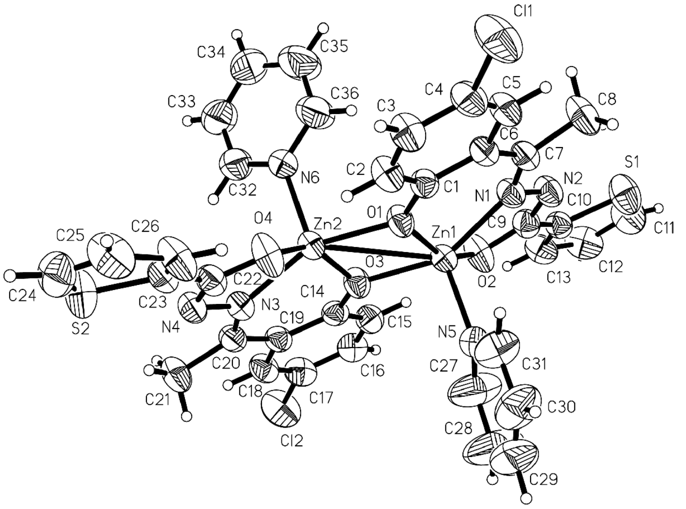


Figure 1
The molecular structure of the title compound, (I), shown with 50% probability displacement ellipsoids.

ecule is stabilized by intermolecular C26—H26*A*···Cl2^i interactions (symmetry code as in Table 2), forming L-shaped dimers which are arranged parallel to the *b* axis (Fig. 2).

Experimental

The title complex was synthesized by the template condensation of 5-chloro-2-hydroxyacetophenone (2.40 g, 14 mmol) and 2-thiophenecarbohydrazide (2.00 g, 14 mmol) with zinc acetate dihydrate (1.54 g, 7 mmol), by refluxing and stirring in a methanol–ethanol mixture for 6 h. The yellow solid was filtered off and recrystallized from pyridine–ethanol.

Crystal data

$[Zn_2(C_{13}H_9ClN_2O_2S)_2(C_5H_5N)_2]$
$M_r = 874.40$
Monoclinic, $P2_1/n$
$a = 18.367$ (2) Å
$b = 10.201$ (2) Å
$c = 20.242$ (2) Å
$\beta = 107.318$ (3)°
$V = 3620.4$ (8) Å^3
$Z = 4$

$D_x = 1.604$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9860 reflections
$\theta = 1.3$–27.6°
$\mu = 1.64$ mm^{-1}
$T = 293$ (2) K
Block, yellow
0.44 × 0.39 × 0.37 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.499$, $T_{max} = 0.546$
23971 measured reflections

8380 independent reflections
6706 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 27.6°$
$h = -23 \rightarrow 23$
$k = -12 \rightarrow 13$
$l = -16 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.138$
$S = 1.06$
8380 reflections
469 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0743P)^2 + 2.3755P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.88$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ e Å^{-3}

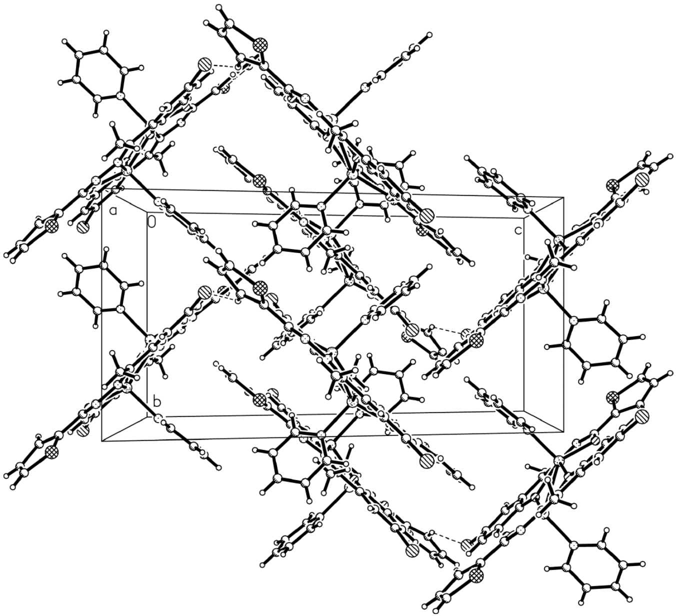


Figure 2
Packing diagram of the title complex, viewed down the *a* axis. The dashed lines denote C—H···Cl hydrogen bonds.

Table 1
Selected geometric parameters (Å, °).

Zn1—O1	2.015 (2)	Zn2—N6	2.065 (3)
Zn1—O2	1.991 (2)	Cl1—C4	1.744 (3)
Zn1—O3	2.047 (2)	Cl2—C17	1.742 (3)
Zn1—N1	2.065 (2)	O1—C1	1.335 (3)
Zn1—N5	2.050 (3)	O2—C9	1.282 (4)
Zn1—Zn2	3.1003 (5)	O3—C14	1.333 (3)
Zn2—O1	2.0366 (19)	O4—C22	1.282 (3)
Zn2—O3	2.009 (2)	N1—C7	1.294 (4)
Zn2—O4	1.991 (2)	N2—C9	1.303 (4)
Zn2—N3	2.070 (2)	N3—C20	1.291 (4)
O2—Zn1—O1	152.81 (11)	O4—Zn2—O3	149.11 (11)
O2—Zn1—O3	102.69 (9)	O4—Zn2—O1	102.24 (8)
O1—Zn1—O3	80.02 (8)	O3—Zn2—O1	80.41 (8)
O2—Zn1—N5	104.05 (12)	O4—Zn2—N6	108.25 (12)
O1—Zn1—N5	102.33 (11)	O3—Zn2—N6	101.48 (10)
O3—Zn1—N5	97.79 (10)	O4—Zn2—N3	78.08 (9)
O2—Zn1—N1	78.71 (10)	O3—Zn2—N3	87.10 (9)
O1—Zn1—N1	86.45 (9)	O1—Zn2—N3	155.34 (10)
O3—Zn1—N1	151.68 (10)	N6—Zn2—N3	103.65 (10)
N5—Zn1—N1	109.41 (11)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2*B*···O4	0.93	2.21	3.065 (3)	153
C15—H15*A*···O2	0.93	2.19	3.049 (4)	154
C26—H26*A*···Cl2^i	0.93	2.71	3.501 (4)	143

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

After location in a difference map, all H atoms were positioned geometrically at ideal positions and allowed to ride on their parent C atom, with C—H = 0.93–0.96 Å and $U_{iso}(H) = 1.2$ or $1.5U_{eq}(C)$.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine

m124 Hapipah Ali *et al.* • $[Zn_2(C_{13}H_9ClN_2O_2S)_2(C_5H_5N)_2]$ *Acta Cryst.* (2004). E**60**, m123–m125

structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL, PARST* (Nardelli, 1995) and *PLATON* (Spek, 2003).

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Acta Cryst. (2004). E**60**, m123–m125 Hapipah Ali *et al.* • $[Zn_2(C_{13}H_9ClN_2O_2S)_2(C_5H_5N)_2]$ **m125**