

{[μ -*N,N'*-Bis(salicylidene)-1,3-propanediaminato-*N,N'*-dimethylformamide]zinc(II)]dichlorozinc(II)}

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Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.007\text{ \AA}$

R factor = 0.029

wR factor = 0.090

Data-to-parameter ratio = 10.8

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

The title compound, $[\text{Zn}_2\text{Cl}_2(\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2)(\text{C}_3\text{H}_7\text{NO})]$, is a doubly oxygen-bridged dinuclear complex with non-crystallographic mirror symmetry. One of the Zn^{2+} ions has a distorted square-pyramidal environment involving two O and two N atoms of the bis(salicylidene)-1,3-propanediaminate ligand, and an O atom of dimethylformamide in the axial position. The other Zn^{2+} ion has a distorted tetrahedral coordination, with average $\text{Zn}-\text{O}$ and $\text{Zn}-\text{Cl}$ distances of 1.994 (3) and 2.2108 (14) \AA . The $\text{Zn}\cdots\text{Zn}$ distance is 3.161 (1) \AA .

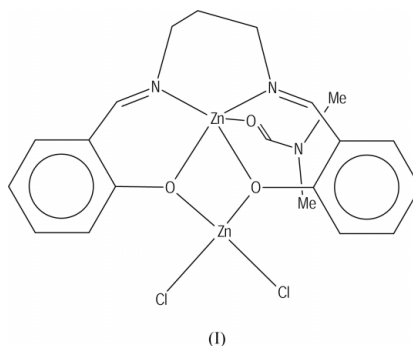
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Comment

Dinuclear complexes with double oxygen bridges are of interest because of the magnetic superexchange interactions between the bridged metal ions. The magnetic properties of homo- and heteropolynuclear compounds are currently under investigation (Tuna *et al.*, 1999). The synthesis and structures of oxygen-bridged polynuclear complexes based on Schiff base ligands, such as $[\text{Zn}\{\text{Zn}(\text{CH}_3\text{COO})(\text{SALPD})\}_2]$ (Ülkü *et al.*, 2001, and references therein), $[\text{ZnBr}_2\text{Ni}(\text{SALPD})(\text{C}_3\text{H}_7\text{NO})_2]$ (Arıcı *et al.*, 2001), $[\text{ZnCl}_2\text{Cu}(\text{SALPD})]$ (Tatar *et al.*, 1999), $[\text{ZnCl}_2\text{Zn}(\text{SALPD})(\text{C}_2\text{H}_7\text{O}_2)]$ (Atakol, Tatar *et al.*, 1999), $[\text{ZnCl}_2\text{Ni}(\text{SALPD})(\text{C}_6\text{H}_7\text{N})_2]$ (Atakol, Ercan *et al.*, 1999), $[\text{ZnI}_2\text{Cu}(\text{SALPD})]$ (Ercan, Arıcı, Ülkü *et al.*, 1999) and $[\text{ZnI}_2\text{Cu}(\text{SALPD})(\text{C}_6\text{H}_7\text{N})]$ (Ercan, Arıcı, Akay *et al.*, 1999) [SALPD is *N,N'*-bis(salicylidene)-1,3-propanediaminate ($\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2$)], have been the subject of considerable interest in our laboratory.



In the present work, a zinc–Schiff base complex, $[\text{ZnCl}_2\text{Zn}(\text{SALPD})(\text{C}_3\text{H}_7\text{NO})]$, (I), consisting of a doubly oxygen-bridged homodinuclear structure was prepared, and the crystal structure of this new complex determined. The coordination around the Zn1 ion is a distorted square pyramid. The basal plane, defined by the atoms O1, O2, N1

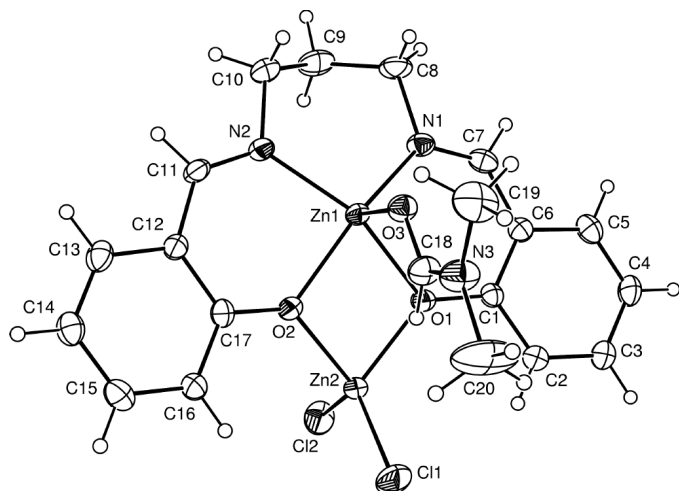


Figure 1
ORTEP-3 (Farrugia, 1997) drawing of $[\text{Zn}_2\text{Cl}_2(\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2)(\text{C}_3\text{H}_7\text{NO})]$ with the atom-numbering schemes. The displacement ellipsoids are drawn at the 40% probability level.

and N2, consists of two N atoms and two bridging O atoms from a bis(salicylidene)-1,3-propanediaminate (SALPD^{2-}) ligand. The axial position of the square pyramid is occupied by an O atom [$\text{Zn1}-\text{O3}$ 2.041 (3) Å] of the dimethylformamide ligand. Within the coordination sphere, the average $\text{Zn1}-\text{N}$ and $\text{Zn1}-\text{O}$ (SALPD^{2-}) bond lengths are 2.043 (3) and 2.053 (3) Å, respectively. The bond angles in the five-coordinate polyhedron have values between 75.90 (10) ($\text{O1}-\text{Zn1}-\text{O2}$) and 105.60 (14) ($\text{O3}-\text{Zn1}-\text{N1}$). The dihedral angle between the $\text{O1}-\text{Zn1}-\text{O2}$ and $\text{N1}-\text{Zn1}-\text{N2}$ planes is 32.78 (1)°. The Zn1 ion is located 0.412 (3) Å from the basal plane, towards the O3 atom.

The Zn2 ion has a distorted tetrahedral coordination involving two bridging O atoms from the SALPD^{2-} ligand and two chloro ligands. The $\text{Zn2}-\text{O1}$, $\text{Zn2}-\text{O2}$, $\text{Zn2}-\text{Cl1}$ and $\text{Zn2}-\text{Cl2}$ bond lengths are 1.991 (3), 1.997 (3), 2.2163 (14) and 2.2054 (14) Å, respectively. The $\text{Cl1}-\text{Zn2}-\text{Cl2}$ and $\text{O1}-\text{Zn2}-\text{O2}$ angles are 119.75 (7) and 78.56 (10)°, respectively, and these two planes are almost perpendicular to each other, the dihedral angle being 89.82 (1)°.

The bridged core ($\text{Zn1}-\text{O1}-\text{Zn2}-\text{O2}$) in the title compound is not exactly planar, as also observed in the corresponding $\text{Cu}-\text{Zn}$ complex [(II), Tatar *et al.*, 1999]. The dihedral angle between the planes through atoms $\text{O1}-\text{Zn1}-\text{O2}$ and $\text{O1}-\text{Zn2}-\text{O2}$ is 3.07 (1)°; this is smaller than the value of 14.04 (4)° observed in (II). The bridged core and the coordination plane composed of atoms O1, N1, O2 and N2 around the Zn1 ion form a dihedral angle of 16.03 (1)°, which is greater than the values for related compounds: 0.44 (9)° (Atakol, Ercan *et al.*, 1999), 1.9 (3)° (Ercan, Arıcı, Ülkü *et al.*, 1999), 8.6 (5)° (Tatar *et al.*, 1999), and 11.4 (4)° (Ercan, Arıcı, Akay *et al.*, 1999). The $\text{Zn1}\cdots\text{Zn2}$ separation is 3.161 (1) Å.

In compound (I), the SALPD^{2-} ligand is not planar; the six-membered chelate ring composed of atoms Zn1, N1, C8, C9, C10 and N2 has a chair conformation and the atoms Zn1 and C9 are displaced from the plane defined by the other four

atoms of the ring by 0.278 (3) and -0.717 (3) Å, respectively. The phenyl rings are essentially planar and their average bond lengths and bond angles are 1.390 Å and 120.0°.

Experimental

The ligand *N,N'*-bis(salicylidene)-1,3-propanediamine (0.282 g, 1 mmol) was dissolved by heating in a dimethylformamide (dmf)–acetonitrile (MeCN) mixture (30 ml, 1:2). A solution of ZnCl_2 (0.272 g, 2 mmol) in hot dmf (20 ml) was added. The resulting mixture was set aside for 10 d and the crystals which formed were filtered off and dried in air.

Crystal data

$[\text{Zn}_2\text{Cl}_2(\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2)(\text{C}_3\text{H}_7\text{NO})]$
 $M_r = 555.09$
 Orthorhombic, $P2_12_12_1$
 $a = 10.1959$ (9) Å
 $b = 14.443$ (3) Å
 $c = 15.8359$ (15) Å
 $V = 2332.0$ (5) Å³
 $Z = 4$
 $D_x = 1.581$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 10.4\text{--}18.3^\circ$
 $\mu = 2.31$ mm⁻¹
 $T = 293$ K
 Prism, colorless
 0.40 × 0.40 × 0.40 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.383$, $T_{\max} = 0.397$
 2929 measured reflections
 2927 independent reflections
 2718 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.015$
 $\theta_{\text{max}} = 27.2^\circ$
 $h = 0 \rightarrow 13$
 $k = 0 \rightarrow 18$
 $l = -20 \rightarrow 0$
 3 standard reflections
 frequency: 120 min
 intensity decay: 2%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.090$
 $S = 1.11$
 2927 reflections
 272 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0568P)^2 + 0.9618P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.68$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.41$ e Å⁻³
 Extinction correction: *SHELXL*
 Extinction coefficient: 0.0136 (8)
 Absolute structure: (Flack, 1983), no Friedel pairs
 Flack parameter = -0.01 (2)

Table 1

Selected geometric parameters (Å, °).

Zn1–Zn2	3.161 (1)	O1–Zn2	1.991 (3)
Cl1–Zn2	2.2163 (14)	O1–Zn1	2.058 (3)
Cl2–Zn2	2.2054 (14)	O2–Zn2	1.997 (3)
N1–Zn1	2.040 (3)	O2–Zn1	2.048 (3)
N2–Zn1	2.046 (3)	O3–Zn1	2.041 (3)
C7–N1–Zn1	125.1 (3)	O3–Zn1–O2	98.58 (12)
C8–N1–Zn1	118.5 (3)	N1–Zn1–O2	152.58 (14)
C11–N2–Zn1	124.0 (3)	N2–Zn1–O2	88.28 (12)
C10–N2–Zn1	119.8 (3)	O3–Zn1–O1	97.17 (12)
C1–O1–Zn2	130.5 (2)	N1–Zn1–O1	88.27 (13)
C1–O1–Zn1	126.9 (2)	N2–Zn1–O1	155.53 (13)
Zn2–O1–Zn1	102.65 (12)	O2–Zn1–O1	75.90 (10)
C17–O2–Zn2	130.5 (3)	O1–Zn2–O2	78.56 (10)
C17–O2–Zn1	126.0 (3)	O1–Zn2–Cl2	111.93 (10)
Zn2–O2–Zn1	102.79 (13)	O2–Zn2–Cl2	112.63 (9)
C18–O3–Zn1	119.6 (3)	O1–Zn2–Cl1	113.28 (10)
O3–Zn1–N1	105.60 (14)	O2–Zn2–Cl1	113.59 (9)
O3–Zn1–N2	103.66 (13)	Cl2–Zn2–Cl1	119.75 (7)
N1–Zn1–N2	98.22 (13)		

The achiral molecule of the title compound, with non-crystallographic mirror symmetry, crystallizes in a chiral space group. The H atoms were positioned geometrically with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, and a riding model was used during the refinement process.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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