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Dichloro{2,2′-thiobis[(4*S*)-4-isopropyl-1,3-oxazolinylphenyl]}zinc(II)

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Key indicators

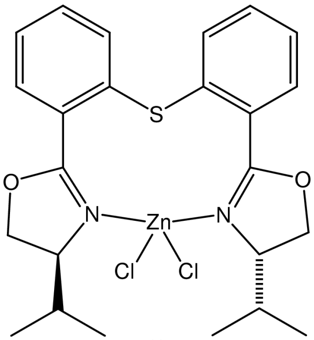
Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.004 Å
R factor = 0.028
wR factor = 0.063
Data-to-parameter ratio = 19.3

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

The title compound, $[ZnCl_2(C_{24}H_{28}N_2O_2S)]$, consists of a tetrahedral Zn atom coordinated by a C_2-symmetric bis-oxazoline ligand. In order to participate in complexation, the ligand becomes bowl-shaped, which results in a distance between the Zn and S atoms of 5.2237 (8) Å.

Comment

Bidentate bis-oxazolines constitute an important class of chiral ligands. Due to their efficient transition-metal binding properties, they have been used with much success in a broad range of asymmetric catalytic transformations, such as the Diels–Alder, cyclopropanation and allylic nucleophilic substitution reactions (Corey & Wang, 1993; Evans *et al.*, 1993; Fritschi *et al.*, 1986; Togni & Venanzi, 1994). The bite angle and the steric bulk of the oxazoline substituents determine the extent to which the ligand envelopes the metal and are therefore crucial parameters for the performance of the complex in a catalytic reaction in terms of transfer of stereochemical information. The present structural analysis was carried out to determine if a five-coordinate metal complex with a metal–sulfur interaction is feasible, with the relatively rigid diphenyl sulfide moiety as a spacer. The title compound, (I), however, displays a very long Zn⋯S distance of 5.2237 (8) Å, similar to other zinc complexes with an *N*,*N*,*S*-donor set (Darensbourg *et al.*, 1995; Gregorzik & Vahrenkamp, 1994).



(I)

The packing displays a short contact between C14—H14 and the ring C1–C6($-\frac{1}{2}+x$, $\frac{3}{2}-y$, $1-z$), with H⋯*Cg* = 2.92 Å and C—H⋯*Cg* = 149° (*Cg* is the geometrical centre of the ring).

Experimental

For the preparation of 2,2′-thiobis[(4*S*)-2-phenyl-4-isopropyl-1,3-oxazoline], dry $ZnCl_2$ (200 mg) and $S(2\text{-}PhCN)_2$ (3.03 g, 12.8 mmol) were dried under vacuum. (*S*)-Valinol (3.41 g, 33 mmol) and 100 ml chlorobenzene were added. After refluxing overnight, the solvent was

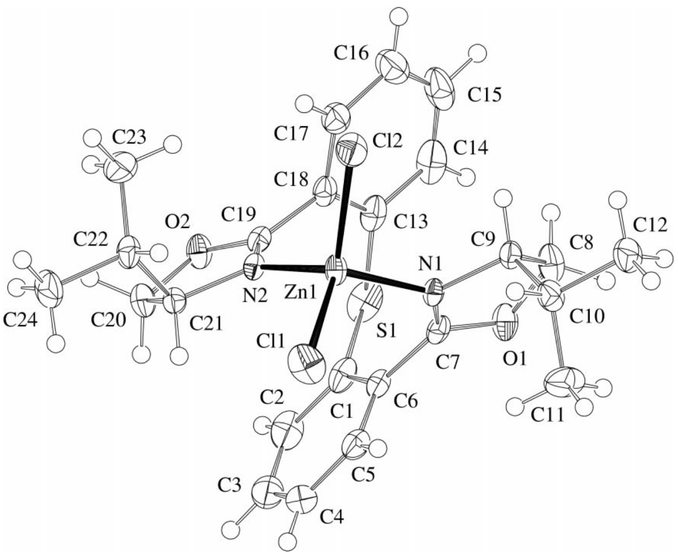


Figure 1
Displacement-ellipsoid plot of the title compound, drawn at the 50% probability level (Spek, 2001). H atoms have an arbitrary radius.

distilled off. The residue was taken up in CH_2Cl_2 and washed with 3 × 50 ml water. The combined water layers were washed with 50 ml CH_2Cl_2. The organic layers were dried on sodium sulfate. Evaporation yielded 5.00 g (96%) of a yellow oil which was sufficiently pure for complexation reactions. Recrystallization from toluene yielded analytically pure white cubes. ^{1}H NMR ($CDCl_3$, 200 MHz, p.p.m.): 0.86 (*d*, 6H, *J* = 7 Hz, CH_3), 0.89 (*d*, 6H, *J* = 7 Hz, CH_3), 2.20 [*m*, 2H, C*H*(CH_3)$_2$], 3.69 (*m*, 4H, OCH_2), 4.21 (*m*, 2H, NCH), 7.50–7.61 (*m*, 6H), 7.97 (*d*, 2H, *J* = 7 Hz). ^{13}C NMR ($CDCl_3$, p.p.m.): 15.4 (CH_3), 18.2 (CH_3), 30.7 [*C*H(CH_3)$_2$], 67.8 (CH_2O), 70.2 (CHN), 126.4 [Ar*C*C=N], 128.1, 131.9, 132.3, 133.9 (ArCH). C—S and C—*C*=N were not resolved. 1643 (CN), 1242 (CO). MS (EI): 408 (M$^+$). HRMS calculated 408.187, found 408.187.

For the of preparation dichloro{2,2′-thiobis[(4*S*)-4-isopropyl-1,3-oxazolinylphenyl]}zinc(II), dry $ZnCl_2$ (93 mg, 0.68 mmol) was dissolved in 7.0 ml THF. At room temperature, a solution of the bis-oxazoline ligand (278 mg, 0.68 mmol) in 11 ml THF was added. The volatiles were evaporated and the resulting solid slowly recrystallized from 15 ml methanol. Two crops of white crystals yielded 368 mg (99%). Crystals suitable for single-crystal X-ray diffraction were obtained from the first fraction. ^{1}H NMR (CD_3CN, 200 MHz, p.p.m.): 0.80 (*d*, 6H, *J* = 7 Hz, CH_3), 0.84 (*d*, 6H, *J* = 7 Hz, CH_3), 2.05 [*m*, 2H, C*H*(CH_3)$_2$], 3.59 (*m*, 2H, CHO), 3.75 (*t*, 2H, *J* = 9 Hz, CHO), 4.28 (*dd*, 2H, *J* = 9 Hz, *J* = 6 Hz CHN), 7.49–7.86 (*m*, 8H). ^{13}C NMR (CD_3CN, p.p.m.): 15.48 (CH_3), 17.95 (CH_3), 31.45 [*C*H(CH_3)$_2$], 68.43 (CHN), 71.17 (CH_2O), 126.99 (ArC—S), 128.77, 133.11, 133.77, 134.01 (ArCH), 133.0 (*C*—C=N), 170.1 (C—*C*=N). Analysis found (calculated) for $C_{24}H_{28}Cl_2N_2O_2SZn$: C 52.52 (52.91); H 5.12 (5.18); S 5.80 (5.89); Zn 11.79% (12.00%).

Crystal data

[$ZnCl_2(C_{24}H_{28}N_2O_2S)$]
M_r = 544.84
Orthorhombic, $P2_12_12_1$
a = 9.5848 (6) Å
b = 15.6021 (9) Å
c = 16.4734 (9) Å
V = 2463.5 (2) Å^3
Z = 4
D_x = 1.469 Mg m^{-3}

Mo*Kα* radiation
Cell parameters from 25 reflections
θ = 11.5–14.1°
μ = 1.32 mm^{-1}
T = 150 K
Irregular, colourless
0.50 × 0.45 × 0.38 mm

Data collection

Enraf–Nonius CAD-4 Turbo diffractometer
$\omega/2\theta$ scans
6371 measured reflections
5650 independent reflections
5246 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.019

$\theta_{\rm max}$ = 27.5°
$h = 0 \rightarrow 12$
$k = -20 \rightarrow 20$
$l = 0 \rightarrow 21$
3 standard reflections
frequency: 60 min
intensity decay: 8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.063
S = 1.05
5650 reflections
293 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0352P)^2 + 0.52P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.003
$\Delta\rho_{\rm max}$ = 0.27 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.21 e Å^{-3}
Absolute structure: Flack (1983), 2463 Friedel pairs
Flack parameter = −0.007 (8)

Table 1
Selected geometric parameters (Å, °).

Zn1—S1	5.2237 (8)	S1—C1	1.778 (3)
Zn1—Cl1	2.2289 (7)	S1—C13	1.764 (3)
Zn1—Cl2	2.2107 (7)	N1—C7	1.271 (3)
Zn1—N1	2.0357 (17)	N2—C19	1.279 (3)
Zn1—N2	2.0363 (18)		
Cl1—Zn1—Cl2	116.70 (3)	N1—Zn1—N2	99.70 (7)
Cl1—Zn1—N1	109.53 (6)	C1—S1—C13	105.86 (10)
Cl1—Zn1—N2	106.50 (6)	Zn1—N1—C7	129.45 (14)
Cl2—Zn1—N1	109.46 (5)	Zn1—N2—C19	128.39 (15)
Cl2—Zn1—N2	113.56 (6)		
C13—S1—C1—C6	−40.3 (2)	C1—C6—C7—N1	118.9 (2)
C1—S1—C13—C18	−42.9 (2)	C13—C18—C19—N2	123.4 (3)

2463 Friedel pairs were measured, *i.e.* 77.3% of the symmetry-unique reflections. The reported Flack x parameter (Flack, 1983) was derived during the final structure-factor calculation. The value obtained for a structure with reversed chirality was 1.009 (16). H atoms were placed at calculated postions, riding on their carrier atoms. The methyl H atoms were refined as rigid groups, allowing for rotation around the C—C bond. Isotropic displacement parameters were coupled to the equivalent isotropic displacement parameter of the carrier atom.

Data collection: locally modified *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *SET*4 (de Boer & Duisenberg, 1984); data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *DIRDIF* (Beurskens *et al.*, 1992); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *PLATON* (Spek, 2001); software used to prepare material for publication: *PLATON*.

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