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Key indicators

Single-crystal X-ray study
T = 150 K
Mean $\sigma(C-C)$ = 0.004 Å
Disorder in main residue
R factor = 0.038
wR factor = 0.097
Data-to-parameter ratio = 16.3

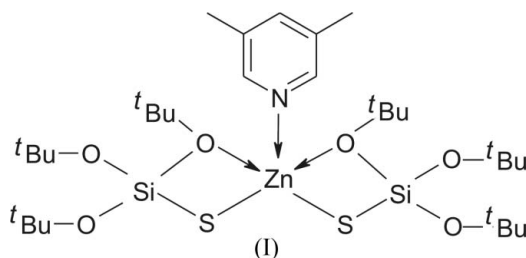
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

(3,5-Dimethylpyridine)bis(tri-*tert*-butoxysilane-thiolato)zinc(II)

The title compound, $[Zn(C_{12}H_{27}O_3SSi)_2(C_7H_9N)]$, is a molecular zinc thiolate containing, as an additional ligand, 3,5-dimethylpyridine. The Zn^{II} ion coordination is distorted trigonal-bipyramidal, formed by two S, two O and one N atom, with the Zn atom lying on a twofold rotation axis. Molecules pack as discrete units, with no intermolecular contacts shorter than those arising from van der Waals forces.

Comment

Owing to their vast biological representation, zinc complexes with nitrogen, oxygen and sulfur ligands have been extensively studied. Interest derives from both human curiosity and the hope of applying the revealed mechanisms in practice. Zinc coordination sites in living organisms, divided into catalytic, cocatalytic, structural and protein interfaces, were reviewed by Auld (2001). Several review articles have been devoted to synthetic zinc complexes with N and S ligands, and their potential use as catalysts (Fleischer, 2005; Parkin, 2004; Rauchfuss, 2004). Another reason behind the interest in zinc complexes with S ligands is the possible use of molecular zinc thiolates as substrates for the chemical vapour deposition technique (e.g. Cheon *et al.*, 1997).



In the above context, we present the structure of the title complex, (I). Tri-*tert*-butoxysilanethiol, used as a source of the thiolate ligand, is very resistant to hydrolysis (Wojnowski, 1974), a feature that allows reactions with a variety of amines without decomposition of thiol. The steric hindrance of the tri-*tert*-butoxy groups, together with the negative induction effect of oxygen substituents on silicon, allow one to obtain monomeric molecular tri-*tert*-butoxysilanethiolates of group 12 metals by relatively simple procedures (Wojnowski *et al.*, 1985, 1992; Becker *et al.*, 1996; Dołęga *et al.*, 2004)

The crystal structure of the title compound consists of discrete molecules with twofold rotational symmetry (Fig. 1). The central Zn atom is coordinated by five atoms: two S (S1 and S1ⁱ; symmetry code as in Table 1 and Fig. 1), one N (N1) and two O atoms (O1 and O1ⁱ). The Zn1–S1 and Zn1–N1 bond lengths (Table 1) are within the typical range for such

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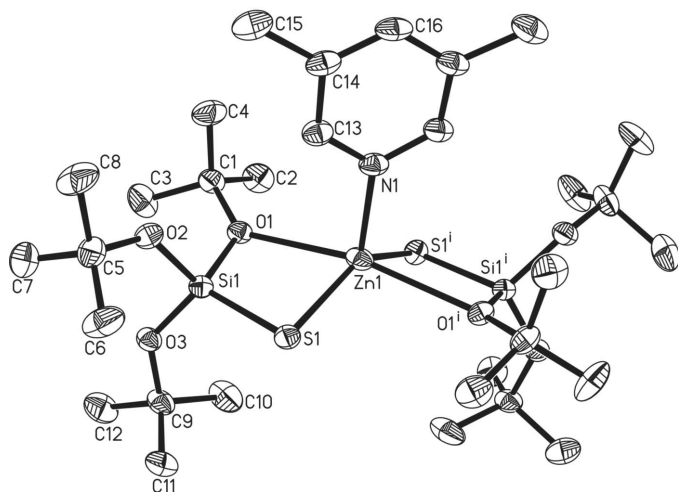


Figure 1
ORTEP (Johnson, 1976) view of the molecule of (I), showing the atom-labelling scheme [symmetry code: (i) $-x, y, \frac{1}{2} - z$]. Displacement ellipsoids are drawn at the 30% probability level; H atoms and the minor component of the disordered CH_3 group have been omitted.

bonds in four- or five-coordinate zinc complexes (Fleischer, 2005). The $\text{Zn1}-\text{O1}$ distance [2.539 (2) Å] distinctly exceeds the sum of covalent radii for Zn and O atoms, which is equal to 1.91 Å. It is comparable, however, with Zn–O distances in zinc–aldehyde complexes, where the zinc–oxygen interactions are very weak (Müller & Vahrenkamp, 1999). We have already described a similar coordination pattern, *i.e.* a metal–oxygen interaction, for homoleptic mercury and cadmium silanethiolates (Wojnowski *et al.*, 1985, 1992). It was also found in heteroleptic zinc and cobalt silanethiolates (Becker *et al.*, 1996, 2001; Dołęga *et al.*, 2004). The $M-\text{O}$ distances in the above-mentioned compounds were longer than the typical lengths of the respective covalent bonds, but the geometries of the complexes obviously indicated the interaction between the metal and one of the O atoms from the *tert*-butoxy group. In the case of zinc tri-*tert*-butoxysilanethiolates, the measured Zn–O distance ranged from 2.38 to 2.57 Å (Becker *et al.*, 1996; Dołęga *et al.*, 2004).

The geometry of the coordinating atoms around zinc may be described as distorted trigonal–bipyramidal. The equatorial trigonal plane is formed by atoms S1, S1ⁱ and N1, with atom Zn1 lying exactly in the plane. Atoms O1 and O1ⁱ occupy the two axial positions of the bipyramid. The $\text{S1}-\text{Zn1}-\text{S1}^i$, $\text{S1}-\text{Zn1}-\text{N1}$ and $\text{S1}^i-\text{Zn1}-\text{N1}$ angles deviate significantly from the ideal value of 120°, the $\text{S1}-\text{Zn1}-\text{S1}^i$ angle being the widest [139.40 (4)°]. The distortion is caused by at least two factors. First, there is the influence of the repulsion of lone pairs of electrons present at the S atom. In a homoleptic mercury thiolate (Wojnowski *et al.*, 1985), the $\text{S}-\text{Hg}-\text{S}$ angle is 180°. The steric hindrance of the tri-*tert*-butoxysilane groups, the second structure-forming factor, is of minor influence in our opinion. The perpendicular distance between O1 and the $\text{S1}/\text{S1}^i/\text{N1}$ plane is 2.539 (2) Å. The $\text{O1}-\text{Zn1}-\text{O1}^i$ angle is 166.47 (7)°, which means that the $\text{Zn1}-\text{O1}$ vector intersects the equatorial plane in an oblique manner at an approximate angle of 83°.

Experimental

Compound (I) was synthesized by a method already described (Dołęga *et al.*, 2004). It crystallizes from the reaction mixture in acetonitrile as colourless plates suitable for X-ray analysis.

Crystal data

$[\text{Zn}(\text{C}_{12}\text{H}_{27}\text{O}_3\text{SSi})_2(\text{C}_7\text{H}_9\text{N})]$
 $M_r = 731.53$
 Monoclinic, $C2/c$
 $a = 14.542$ (3) Å
 $b = 12.806$ (3) Å
 $c = 22.265$ (4) Å
 $\beta = 101.39$ (3)°
 $V = 4064.6$ (15) Å³
 $Z = 4$

$D_x = 1.195$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 13393 reflections
 $\theta = 1.94\text{--}25.97^\circ$
 $\mu = 0.80$ mm⁻¹
 $T = 150$ (2) K
 Thick plate, colourless
 $0.4 \times 0.4 \times 0.2$ mm

Data collection

Stoe IPDS-2 diffractometer
 φ scans
 Absorption correction: integration
 (*X-RED*; Stoe & Cie, 1997)
 $T_{\min} = 0.484$, $T_{\max} = 0.657$
 8313 measured reflections
 3845 independent reflections

3585 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.035$
 $\theta_{\max} = 26.0^\circ$
 $h = -13 \rightarrow 17$
 $k = -13 \rightarrow 15$
 $l = -27 \rightarrow 27$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.097$
 $S = 1.08$
 3845 reflections
 236 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0421P)^2 + 5.0297P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.47$ e Å⁻³
 $\Delta\rho_{\min} = -0.43$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

$\text{Zn1}-\text{S1}$	2.2484 (8)	$\text{Si1}-\text{O2}$	1.6259 (18)
$\text{Zn1}-\text{N1}$	2.071 (3)	$\text{Si1}-\text{O3}$	1.6206 (18)
$\text{Si1}-\text{O1}$	1.6458 (18)		
$\text{S1}-\text{Zn1}-\text{N1}$	110.30 (4)	$\text{O1}-\text{Si1}-\text{O3}$	113.06 (10)
$\text{S1}^i-\text{Zn1}-\text{N1}$	110.30 (4)	$\text{O2}-\text{Si1}-\text{O3}$	105.94 (10)
$\text{Zn1}-\text{S1}-\text{Si1}$	89.57 (4)	$\text{O3}-\text{C9}-\text{C10}$	110.3 (2)
$\text{S1}-\text{Si1}-\text{O1}$	103.34 (7)	$\text{O3}-\text{C9}-\text{C11}$	108.5 (2)
$\text{S1}-\text{Si1}-\text{O2}$	115.19 (7)	$\text{O3}-\text{C9}-\text{C12}$	104.9 (2)
$\text{S1}-\text{Si1}-\text{O3}$	114.59 (8)	$\text{N1}-\text{C13}-\text{C14}$	122.89
$\text{O1}-\text{Si1}-\text{O2}$	104.45 (9)		

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

Two $\text{C}_{\text{ar}}-\text{H}$ atoms were initially located in a difference Fourier map. All H atoms of CH_3 groups, including those of the lutidine ligand, were positioned geometrically. The methyl groups were allowed to rotate to fit the electron density. A riding model with $\text{C}_{\text{ar}}-\text{H}$ distances of 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, or 0.98 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for the methyl groups, was used. A disordered *tert*-butyl group was refined with geometrical restraints on bond lengths and angles, with occupancy factors of 0.604 (7):0.396 (7).

Data collection: *X-AREA* (Stoe & Cie, 1997); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP II* (Johnson, 1976); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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