

Tetrakis(μ -triisopropylsilanethiolato)-1:2 κ^4 S:S;2:3 κ^4 S:S-bis(triisopropylsilanethiolato)-1 κ S,3 κ S-trizinc(II)

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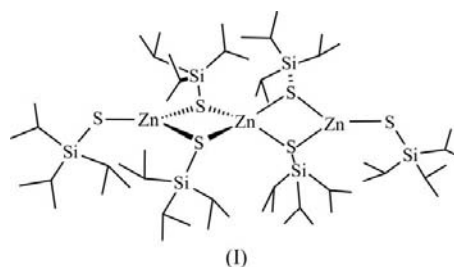
The title compound, $[\text{Zn}_3(\text{C}_9\text{H}_{21}\text{SiS})_6]$ or $[(^i\text{Pr}_3\text{SiS})\text{Zn}(\mu\text{-SSi}^i\text{Pr}_3)_2\text{Zn}(\mu\text{-SSi}^i\text{Pr}_3)_2\text{Zn}(\text{SSi}^i\text{Pr}_3)]$, is the first structurally characterized homoleptic silanethiolate complex of zinc. A near-linear arrangement of three Zn^{II} ions is observed, the metals at the ends being three-coordinate with one terminally bound silanethiolate ligand. The central Zn^{II} ion is four-coordinate and tetrahedral, with two bridging silanethiolate ligands joining it to each of the two peripheral Zn^{II} ions. The nonbonding intermetallic distances are 3.1344 (11) and 3.2288 (12) Å, while the $\text{Zn}\cdots\text{Zn}\cdots\text{Zn}$ angle is 172.34 (2)°. A trimetallic silanethiolate species of this type has not been previously identified by X-ray crystallography for any element.

Comment

The study of metal chalcogenolate complexes is of interest due to their current application as precursors for metal sulfide/selenide materials (nanoparticles, thin films and bulk materials). It is well known that the chemistry of group 12 metal chalcogenolates is complicated due to the formation of oligomeric networks supported by bridging chalcogenolate ligands with tetrahedral metal ion coordination (Bonasia & Arnold, 1992). A wide variety of synthetic methods have been developed to synthesize these compounds; the use of bulky aryl substituents is a common practice in order to reduce molecularity and enhance solubility. It is also common to modify the degree of aggregation in these compounds by blocking some coordination sites either with donor atoms from the thiolate ligand or with coligands (e.g. 1,10-phenanthroline).

The chemistry of metal thiocarboxylates has been widely studied (Nyman *et al.*, 1997; Vittal & Ng, 2006). Neutral complexes of general formula $\text{Zn}(\text{SOCR})_2\text{Lut}_2$ (Lut = 3,5-dimethylpyridine) were found to be monomeric, with dis-

torted tetrahedral metal centers and monodentate S-bound thiocarboxylate ligands. The anionic complexes $[\text{M}(\text{SC}(\text{O})\text{-Ph})_3]^-$ ($M = \text{Zn}, \text{Cd}, \text{Hg}$) present a trigonal planar MS_3 geometry, supported by one or more intramolecular $M\cdots\text{O}$ interactions (Vittal & Dean, 1996). Pentacoordinated zinc complexes with a trigonal-bipyramidal geometry have been reported (Zhang *et al.*, 1991; Pérez-Lourido *et al.*, 1999). These neutral thiolate complexes are composed of a metal center bonded to unsaturated S ligands $[\text{Ph}(\text{SCH}_3)\text{C}=\text{C}(\text{SH})\text{Ph}]$ (Zhang *et al.*, 1991), as well as to arenephosphinothiol ligands $[\text{RP}(\text{SH})_x, x = 1 \text{ or } 2]$ (Pérez-Lourido *et al.*, 1999). The former are examples of labile compounds that quickly undergo ligand exchange forming adducts with N-containing ligands [4-(dimethylamino)pyridine (dmapy), pyridine (py) and 2,2'-bipyridine (bipy)] that adopt tetra-, penta- and hexacoordinated structures.



There are not many examples of silylated metal (Zn) chalcogenolate complexes. The compounds (N,N,N',N' -tmeda) $\text{Zn}(\text{SSiMe}_3)_2$ (N,N,N',N' -tmeda = tetramethylethylenediamine) and $(3,5\text{-Me}_2\text{C}_5\text{H}_3\text{N})_2\text{Zn}(\text{SSiMe}_3)_2$ exist in the solid state as monomeric species with terminally bonded silylated groups and a distorted tetrahedral geometry at the Zn center (DeGroot & Corrigan, 2005). We have previously reported the synthesis and characterization of coordination metal complexes (groups 11 and 13) containing $-\text{ESiR}_3$ ($E = \text{O}, \text{S}, \text{Se}; R = \text{Ph}, ^i\text{Pr}$) ligands (Medina, 2005). The group 13 complexes are mainly dimeric with an M_2E_2 central core, whereas group 11 complexes were found to be monomeric. In this paper, we report the crystal structure of trinuclear $[(^i\text{Pr}_3\text{SiS})\text{Zn}(\mu\text{-SSi}^i\text{Pr}_3)_2\text{Zn}(\mu\text{-SSi}^i\text{Pr}_3)_2\text{Zn}(\text{SSi}^i\text{Pr}_3)]$, (I).

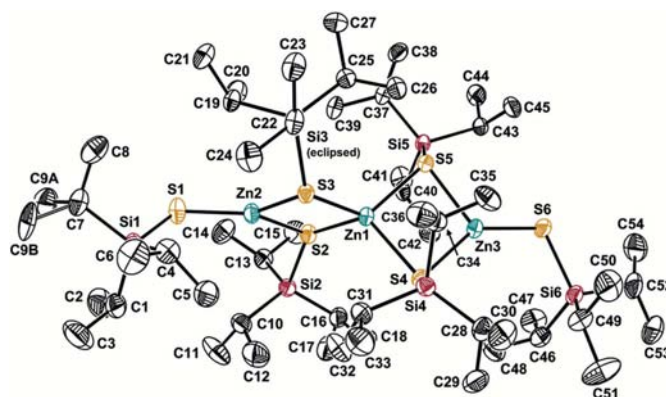


Figure 1
The molecular structure of the title compound, shown with 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

The structural characteristics of the compound reported here are consistent with structural data for other examples of tri- and tetracoordinated zinc sulfide complexes; nevertheless, this spiro compound has a unique structure containing both trigonal planar and tetrahedral metal centers bonded to S atoms. The two terminal Zn ions are both three-coordinate and have a single nonbridging silanethiolate ligand (Fig. 1). The central Zn ion is four-coordinate and tetrahedral, with two bridging silanethiolate ligands to each of the two Zn atoms at the ends of the molecule (Table 1). The idealized point-group symmetry within the $S-Zn(\mu-S)_2Zn(\mu-S)_2Zn-S$ inorganic core of the molecule is C_{2v} . The nonbonding intermetallic distances are 3.2288 (12) and 3.1344 (11) Å for $Zn1 \cdots Zn2$ and $Zn1 \cdots Zn3$, respectively. The $Zn2 \cdots Zn1 \cdots Zn3$ angle is 172.34 (2)°, consistent with the linear description of the compound. The overall packing of the molecules within the crystal appears to be governed by intermolecular aliphatic interactions. The periphery of the molecule is an essentially uniform hydrocarbon surface that offers numerous points for favorable hydrophobic intermolecular contacts. Thus, the individual molecules pack in an end-to-end fashion with the molecular axis essentially collinear with the *b* axis and numerous intermolecular contacts made between molecules along the length of the molecule.

Structurally identified homoleptic silanethiolate complexes are comparatively few in number. The title compound represents not only the first such example for zinc but also the first crystallographically characterized trimetallic species with this ligand type for any element. Dimetallic (Sydora *et al.*, 2006) and cyclic tetrametallic silanethiolate molecules (Komuro *et al.*, 2002, 2004; Kückmann *et al.*, 2005), possibly with metal-metal bonding interactions (Kückmann *et al.*, 2005), have been described. The structure type observed for (I) also does not appear to have a precedent within the larger body of structurally authenticated homoleptic alkanethiolate complexes of Zn. This larger set of complexes includes two- (Nguyen *et al.*, 2005; Ellison & Power, 1994), three- (Gruff & Koch, 1989; Matsunaga *et al.*, 2005) and four-coordinate mononuclear zinc thiolates (Ueyama *et al.*, 1988; Silver *et al.*, 1993), three- (Grützmaier *et al.*, 1992; Bochmann *et al.*, 1993) and four-coordinate dinuclear Zn thiolates (Watson *et al.*, 1985; Abrahams *et al.*, 1987; Gelinsky & Vahrenkamp, 2002) and adamantanoid-type tetranuclear anions with tetrahedral coordination at zinc (Hencher *et al.*, 1985; Gelinsky & Vahrenkamp, 2002), but no species with mixed coordination numbers at the metal. The closest analogs to compound (I), showing coordination numbers of both three and four, are the arenethiolate complexes $[(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3\text{S})E(\mu\text{-}2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3\text{S})_2E(\mu\text{-}2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3\text{S})_2E(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3\text{S})]$ ($E = \text{Sn}$ or Pb) (Hitchcock *et al.*, 1983). These molecules, however, reveal a pronounced nonlinear arrangement of the metal atoms.

Experimental

A 1.0 M solution of diethylzinc in hexanes (5 ml, 0.005 mol) was added dropwise to a solution (2.15 ml, 0.01 mol) of HSSi^iPr_3 in the

same solvent (25 ml), which resulted in immediate gas evolution. This reaction mixture was stirred for 12 h and the solvent was removed under reduced pressure. The solid residue was dissolved with hexanes (~5 ml) and cooled to 273 K for 24 h. Clear colorless crystals were obtained. The solvent was removed with a syringe in order to eliminate impurities. The crystals were redissolved in hexanes (~5 ml), and the solution was again cooled to 273 K for 24 h. Clear colorless crystals were obtained. The solvent was removed, and the crystals were dried under reduced pressure.

Crystal data

$[\text{Zn}_3(\text{C}_9\text{H}_{21}\text{SSi})_6]$	$V = 7396$ (6) Å ³
$M_r = 1332.56$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 15.179$ (7) Å	$\mu = 1.26$ mm ⁻¹
$b = 13.746$ (6) Å	$T = 100$ K
$c = 36.180$ (16) Å	$0.35 \times 0.29 \times 0.25$ mm
$\beta = 101.564$ (7)°	

Data collection

Bruker SMART APEX CCD diffractometer	63046 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2008a)	17610 independent reflections
$T_{\min} = 0.665$, $T_{\max} = 0.744$	15542 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.030$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$	669 parameters
$wR(F^2) = 0.111$	H-atom parameters constrained
$S = 1.28$	$\Delta\rho_{\max} = 0.58$ e Å ⁻³
17610 reflections	$\Delta\rho_{\min} = -0.45$ e Å ⁻³

Table 1

Selected geometric parameters (Å, °).

Zn1—S2	2.3907 (14)	Zn2—S2	2.3025 (14)
Zn1—S3	2.3764 (13)	Zn2—S3	2.3179 (13)
Zn1—S4	2.3818 (11)	Zn3—S4	2.3144 (11)
Zn1—S5	2.3549 (11)	Zn3—S5	2.3333 (11)
Zn2—S1	2.1902 (13)	Zn3—S6	2.1888 (12)
S2—Zn1—S3	91.20 (3)	S1—Zn2—S2	122.86 (4)
S2—Zn1—S4	118.15 (4)	S1—Zn2—S3	141.90 (4)
S3—Zn1—S4	116.93 (3)	S2—Zn2—S3	94.98 (3)
S2—Zn1—S5	119.06 (3)	S4—Zn3—S5	96.47 (4)
S3—Zn1—S5	119.74 (4)	S4—Zn3—S6	142.21 (4)
S4—Zn1—S5	94.09 (4)	S5—Zn3—S6	120.77 (4)

Tertiary H atoms were placed in calculated positions (C—H = 0.98–0.99 Å) and included as riding contributions with isotropic displacement parameters 1.2–1.5 times those of the attached C atoms. All methyl H atoms were similarly refined as riding atoms with fixed C—H distances of 0.98 Å but with the rotational disposition of the methyl group determined as an optimal fit using the refinement software. One methyl C atom of one isopropyl group was disordered over two positions and was refined with a split-atom model as a 69:31 distribution.

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2008); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008b); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008b); molecular graphics: SHELXTL (Sheldrick, 2008b); software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3038). Services for accessing these data are described at the back of the journal.

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