Contributions to the chemistry of silicon–sulphur compounds 70.

Zinc silanethiolates: synthesis and properties. Crystal structures of bis(tri-*tert*-butoxysilanethiolato)(acetonitrile)zinc(II) and bis(tri-*tert*-butoxysilanethiolato)(bipyridine)zinc(II) [1]

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Abstract

Reactions of tri-*tert*-butoxysilanethiol with inorganic zinc compounds such as $[Zn(H_2O)_4]^{2+}$, $[Zn(NH_3)_4]^{2+}$, basic zinc carbonate, $ZnCl_2$ or with metallic zinc in water, benzene, or in the absence of solvent are described. Heteroleptic zinc silanethiolates such as $\{[('BuO)_3SiS]_2Zn(H_2O)_n]_m$, and $\{[('BuO)_3SiS]_2Zn(NH_3)\}_2$ have been obtained. In acetonitrile as solvent $[('BuO)_3SiS]_2Zn(NCMe)$ is formed. All three of these new complexes reacted with the strong nitrogen donor species pyridine, 1-methylimidazole, 2,2'-bipyridine and 1,10-phenanthroline to give complexes of formula $[('BuO)_3SiS]_2ZnL_2$ (L = py, 1-meimid or L_2 = bipy, phen). Some reactions leading to cadmium complexes were also performed. The crystal structures of two compounds were determined. Orthorhombic crystals of $[('BuO)_3SiS]_2Zn(NCMe)$ consist of molecules in which the zinc atom is bonded to two sulphur atoms, two oxygen atoms and one nitrogen atom in a distorted trigonal bipyramidal arrangement. In the triclinic crystals $[('BuO)_3SiS]_2Zn(bipy)$ there is a ZnN_2S_2 core with distorted tetrahedral geometry.

Keywords: Silicon; Zinc; Silanethiolates; Crystal structure

1. Introduction

Complexes involving thiolate ligands are of considerable interest for a number of reasons, including the question of the nature of the metal–sulphur bond in metal sulphides and hydrosulphides and the importance of metal ligation in biological systems by cysteine thiolate function. Compared with those of simple ions such as S^{2-} and SH^-, the properties of thiolate ligands RS^- can be much more readily varied since their electronic and steric properties can be changed by appropriate choice of the substituent R on sulphur. Thus metal thiolates show great structural diversity, and structures of newly prepared complexes, frequently polymeric, are sometimes very hard to predict [2].

Our main research interest concerns the chemistry of compounds containing silicon–sulphur bonds. Thus, when some years ago we became interested in the structural chemistry of metal thiolates, we initiated the use of thiolate ligands derived from silanethiols instead of organic thiols. The idea of combining organosilicon chemistry, thiolate chemistry, and coordination chemistry in studies of metal silanethiolates, so gaining a novel insight into a borderline area, was rather attractive. The silanethiol chosen was tri-*tert*-butoxysilanethiol, $('BuO)_3SiSH$, and the first compound we prepared with an Si–S metal linkage was the silver complex $[('BuO)_3SiSAg]_4$ [3]. We thought it likely that factors such as the steric congestion imposed by the bulky $('BuO)_3Si$ substituent on sulphur and the presence of Si–S and Si–O bonds in the same ligand would lead to new interesting compounds. Their synthesis and properties, with special emphasis on structural aspects, have become one of the research projects of our group.

We previously reported on homoleptic tri-*tert*-butoxysilanothiolates of some main group metals, namely Tl(I) [4], Pb(II) [5], the copper group metals [3,6,7], Hg(II) [8], and Cd(II) [9]. Some heteroleptic

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[1] Dedicated to Professor Robert Corriu in recognition of his outstanding contributions to organosilicon chemistry. BB will always appreciate her time in Professor Corriu's laboratory, the chemistry she learned there, and the friendship she found.
For Part 69 see Ref. [1].

silanethiolates of transition elements were also obtained, bis(tri-*tert*-butoxysilanethiolato)(acetonitrile)cobalt(II) being the most recent example [10]. In the present paper we describe the preparation and properties of several zinc complexes containing the $(^tBuO)_3SiS$ ligand, and X-ray structures of two of them, namely bis(tri-*tert*-butoxysilanethiolato)(acetonitrile)zinc(II), $[(^tC_4H_9O)_3-SiS]_2Zn(NCCH_3)$, and bis(tri-*tert*-butoxysilanethiolato)-(bipyridine)zinc(II), $[(^tC_4H_9O)_3SiS]_2Zn(bipy)$.

2. Experimental

Tri-*tert*-butoxysilanethiol, $(^tBuO)_3SiSH$, was prepared as described previously [11]. All other chemicals were commercial products. Solvents were dried by standard procedures.

2.1. Preparation of $\{[(^tBuO)_3SiS]_2Zn(H_2O)_n\}_m$ 1A–C

2.1.1. Method A′

Tri-*tert*-butoxysilanethiol (8.4 g, 30 mmol) and triethylamine (3.03 g, 30 mmol) were mixed with 150 ml of water to give a clear solution. Addition of an aqueous solution of $ZnCl_2$ (2.043 g, 15 mmol) resulted within a few moments in formation of a glue-like hydrophobic substance. When the mixture was vigorously shaken for ca. 2 h the substance formed a precipitate. This was filtered off on a Büchner funnel, thoroughly washed with water, and dried in an air stream to give a white solid, to which was added 120 ml of n-hexane. The insoluble material was removed by filtration, the filtrate washed with water, and the organic layer separated and dried over anhydrous magnesium sulfate. Concentration of the solution, followed by cooling, gave some poorly formed crystals (1A′₁, 4.2 g), which were filtered off. The remaining solution yielded a second crop (*1A′₂*, 1.9 g) of crystals. Crystals of both crops melted over a wide temperature range, 130–135°C.

When the same procedure as above was repeated but starting from $CdCl_2$, it gave exclusively the known $\{[(^tBuO)_3SiS]_2Cd\}_2$ [9] in high yield.

2.1.2. Method A″ (small scale)

Tri-*tert*-butoxysilanethiol (1.4 g, 5 mmol) and triethylamine (0.5 g, 5 mmol) were mixed with 25 ml of water to give a clear solution. After addition of a solution of $ZnCl_2$ (0.341 g, 2.5 mmol), the mixture was shaken for ca. 2 h. Work-up of the mixture was essentially as described in Method A′, but only one crop of product was collected (1A″, 0.9 g), m.p. 138–141°C.

2.1.3. Method B

A solution of $(^tBuO)_3SiSH$ (17.33 g, 62 mmol) in anhydrous benzene was added to 15 g of basic zinc carbonate (approximate formula $2ZnCO_3 \cdot 3Zn(OH)_2$)

and stirred for 6 h at room temperature. Evolution of CO_2 was observed. The mixture was stirred under reflux for 2 h and insoluble material then removed by filtration. The benzene was evaporated from the solution in vacuo to leave a viscous oily residue which partially crystallized after exposure for several hours to air. (Crushing of the solidified but still wet particles can significantly reduce the crystallisation time.) The quasi-solid residue was dried between two sheets of filter-paper and recrystallised from a small volume of anhydrous n-hexane to yield 11.022 g (ca. 59%) of crystalline **1B**, m.p. 138–139°C. Anal. Found: C, 46.13; H, 8.85; S, 10.30. $[(^tBuO)_3SiS]_2Zn$, $ZnS_2Si_2O_6C_{24}H_{54}$ Calc.: C, 46.17; H, 8.72; S, 10.27%. Molecular weight determined by cryoscopy in benzene: $M = 900$.

The mass spectrum showed no ions with m/z values higher than those originating from monomeric $[(^tBuO)_3SiS]_2Zn$ molecules (m/z 623, relative abundance 5.7%). The main decomposition pathway is characterised by stepwise elimination of C_4H_8.

NMR (ppm): ^1H 1.39; ^{13}C 31.53 (CH_3), 75.60 (CMe_3); ^{29}Si 62.35. All signals were sharp singlets.

2.1.4. Method C

In a small glass bottle a two-fold excess of zinc powder was mixed with pure tri-*tert*-butoxysilanethiol (mobile liquid at room temperature) under argon. The bottle was then closed with a rubber septum and left to stand at room temperature. It was opened when the liquid became so viscous that it did not move when the bottle was shaken (c.a. 1–2 months required). When the mixture was exposed to air crystallisation started almost immediately and when it was complete the mixture was extracted with n-hexane. The extract was concentrated and kept at −10°C to give colourless crystals of **1C**, and these were filtered off. Yield ca. 65%, m.p. 134–137°C.

No attempts were made to optimise the procedure. The examples of preparation of **1** given above refer to cases in which some analytical data were collected. The procedures were repeated several times with very similar results, although there were small differences in melting points and IR spectra even for products obtained by the same method and on the same scale. These variations cause no complications in the use of **1** in further syntheses, and even the initial viscous liquid products can be used satisfactorily.

2.2. Preparation of $\{[(^tBuO)_3SiS]_2Zn(NH_3)\}_2$ 2

To a solution of $ZnCl_2$ (1.7 g, 12.5 mmol) in 100 ml of water, a concentrated ammonia solution was added dropwise until the initially formed precipitate completely disappeared. Neat tri-*tert*-butoxysilanethiol (7.0 g, 25 mmol) was slowly added to the stirred mixture, a white hydrophobic glue-like substance being immedi-

ately formed. The mixture was vigorously shaken for ca. 1 h until the glue-like substance had turned to a white precipitate. This was filtered, washed with dilute ammonia solution then with water, and finally dried in an air stream. The solid obtained was finely crushed and added to 200 ml of n-hexane. A little insoluble material was filtered off and the filtrate dried over anhydrous magnesium sulfate. Concentration and cooling of the solution led to 3.05 g of very long, hair-like crystals of **2** which were filtered off. Concentration of the mother liquor gave a second crop (1.90 g) of **2**. Yield 62%, m.p. 118–119°C. The residues from similar syntheses can be combined and recrystallised to give further product.

Anal. Found: C, 44.60; H, 9.12; N, 2.29. $Zn_2S_4Si_4O_{12}N_2C_{48}H_{114}$ Calc.: C, 44.94; H, 8.96; N, 2.18%. Molecular weight (cryoscopy in benzene): Found $M = 1140$, Calc. $M = 1284$. When the procedure described above was repeated with $CdCl_2$ as substrate the known $\{[('BuO)_3SiS]_2Cd\}_2$ [9] was obtained exclusively in high yield.

2.3. Some comments

Because of the very high solubility of **1** and **2** in common organic solvents crystallisation is very difficult, and the yields reflect this. All filtrations should be carried out by exerting a small gas pressure rather than under normal or reduced pressure.

2.4. Preparation of $[('BuO)_3SiS]_2Zn(NCCH_3)$ 3

A. Triethylamine (0.484 g, 4.8 mmol) was added to a stirred solution of 1.120 g (4 mmol) of tri-*tert*-butoxy-silanethiol in 50 cm³ of acetonitrile. The resulting yellowish solution was then mixed with a solution of $ZnCl_2$ (0.272 g, 2 mmol) in 150 cm³ of acetonitrile. The mixture was stirred for ca. 30 min at room temperature and then evaporated to dryness in vacuo. The solid residue was then treated with 30 cm³ of dry THF, insoluble material removed by filtration, and the solution again evaporated to dryness to give crude **3**. This was dissolved in a minimum volume of THF and the solution was diluted with a three-fold excess of acetonitrile and left to stand for 24 h at 0°C. Well-formed crystals of pure **3** suitable for X-ray analysis were filtered off, washed with acetonitrile, and dried in vacuo (0.943 g, yield 71%).

B. An alternative procedure involves simply dissolving 1A–C in a minimum volume of THF then adding a three-fold excess of acetonitrile. Crystals of **3** separate on cooling.

Complexes **4–7** were prepared starting from **1, 2** or **3**. Experimental procedures are similar and so only those in which **1B** was used are described in detail. In reactions with **2** as substrate elimination of ammonia was observed.

2.5. Preparation of $[('BuO)_3SiS]_2Zn(py)_2$ 4 and $[('BuO)_3SiS]_2Cd(py)_2$ 8

Pyridine (0.158 g, 2 mmol) was added to a solution of 0.623 g (ca. 1 mmol) of **1B** in 7.5 ml of anhydrous n-hexane. A white voluminous precipitate formed almost instantaneously. The mixture was refluxed under nitrogen as more hexane was added until dissolution was complete (20 ml). The clear solution was left to stand overnight at room temperature, and the colourless crystals (0.606 g) were then filtered off, washed with hexane, and dried in vacuo. A second crop of crystals (0.101 g) was obtained from the filtrate by very slow evaporation of the solvent. A total of 0.707 g of **4** (90%) was collected. The fractions were combined and recrystallised from n-hexane to give rhombohedral crystals melting at 178–179°C.

Anal. Found: C, 52.00; H, 8.32; N, 3.53. $ZnS_2Si_2O_6N_2C_{34}H_{64}$ Calc.: C, 52.18; H, 8.24; N, 3.58%.

When the homoleptic cadmium silanethiolate $\{[('BuO)_3SiS]_2Cd\}_2$ [9] was used instead of **1B**, rhombohedral crystals of **8** were obtained in 93% yield, m.p. 143–144°C.

Anal. Found: C, 48.69; H, 7.84; N, 3.24. $CdS_2Si_2O_6N_2C_{34}H_{64}$ Calc.: C, 49.23; H, 7.77; N, 3.38%.

2.6. Preparation of $[('BuO)_3SiS]_2Zn(1-meimid)_2$ 5 and $[('BuO)_3SiS]_2Cd(1-meimid)_2$ 9

1-Methylimidazole (0.164 g, 2 mmol) was added to a solution of 0.623 g (ca. 1 mmol) of **1B** in 10 ml of anhydrous n-hexane. A white voluminous precipitate was formed immediately. The mixture was refluxed under nitrogen atmosphere as more hexane was added until dissolution was complete (110 ml). The clear solution was left to stand at room temperature, and the colourless needles of **5** (0.713 g, 90%) were then filtered off, washed with hexane, and dried in vacuo m.p. 176°C (decomp.).

Anal. Found: C, 48.41; H, 8.47; N, 6.99. $ZnS_2Si_2O_6N_4C_{32}H_{66}$ Calc.: C, 48.74; H, 8.44; N, 7.10%.

When the homoleptic cadmium silanethiolate $\{[('BuO)_3SiS]_2Cd\}_2$ [9] was used instead of **1B**, colourless needles of **9** were obtained in 92% yield, m.p. 163°C (decomp.).

Anal. Found: C, 45.44; H, 7.98; N, 6.54. $CdS_2Si_2O_6N_4C_{32}H_{66}$ Calc.: C, 45.99; H, 7.96; N, 6.70%.

2.7. Preparation of $[('BuO)_3SiS]_2Zn(L_2)$ complexes $(L_2 = bipy, 6; L_2 = phen, 7)$

A solution of **1B** $\{[('BuO)_3SiS]_2Zn(H_2O)_n\}_m$ (approximately 1 mmol) in benzene was mixed with a

Table 1

Summary of crystal data, intensity collection and structure refinement for **3** (KUMA KM4, four-circle diffractometer) and **6** (Siemens, four-circle diffractometer)

Compound	3	6
Empirical formula	$C_{26}H_{57}NO_6S_2Si_2Zn$	$C_{34}H_{62}N_2O_6S_2Si_2Zn$
Formula weight	665.40	780.53
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Triclinic
Space group	$Fdd2$	$P\bar{1}$
Unit cell dimensions	$a = 17.845(4)$ Å	$a = 9.588(2)$ Å
	$b = 45.811(9)$ Å	$b = 14.569(3)$ Å
	$c = 9.059(2)$ Å	$c = 16.498(3)$ Å
	$\alpha = 90°$	$\alpha = 107.57(3)°$
	$\beta = 90°$	$\beta = 95.21(3)°$
	$\gamma = 90°$	$\gamma = 98.84(3)°$
Volume (Å³)	7406(3)	2139.7(7)
Z	8	2
Density (calculated) (Mg m⁻³)	1.194	1.211
Absorption coefficient (mm⁻¹)	0.874	0.767
F(000)	2864	836
Crystal size (mm³)	$0.3 \times 0.3 \times 0.4$	$0.4 \times 0.4 \times 0.3$
Theta range for data collection	1.78 to 27.52°	3.64 to 22.51°
Index ranges	$-23 \le h \le 23$	$-10 \le h \le 10$
	$-59 \le k \le 59$	$-15 \le k \le 14$
	$0 \le l \le 10$	$-7 \le l \le 17$
Reflections collected	8667	5469
Independent reflections	2223 [R(int) = 0.0682]	5401 [R(int) = 0.0424]
Reflections with $I > 2\sigma(I)$	1929	4738
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2223/33/179	5390/62/457
Goodness-of-fit on F^2	1.042	1.060
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0304$, $wR_2 = 0.0649$	$R_1 = 0.0352$, $wR_2 = 0.0829$
R indices (all data)	$R_1 = 0.0376$, $wR_2 = 0.0675$	$R_1 = 0.0430$, $wR_2 = 0.0929$
Absolute structure parameter	0.011(12)	
Extinction coefficient	0.00022(4)	0.0025(6)
Largest diff. peak and hole (e Å⁻³)	0.378 and -0.188	0.374 and -0.374

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **3**

Atom	x	y	z	U_{eq}
Zn	2500	2500	2317	47(1)
S	1379(1)	2485(1)	3448(1)	48(1)
Si	1409(1)	2038(1)	3138(1)	37(1)
O1	2180(1)	1997(1)	2157(2)	42(1)
C10	2609(2)	1736(1)	1806(4)	51(1)
C11	3110(2)	1820(1)	534(6)	87(2)
C12	3060(3)	1654(1)	3120(6)	88(1)
C13	2086(2)	1497(1)	1334(5)	65(1)
O2	1525(1)	1844(1)	4602(2)	56(1)
C20	1025(2)	1714(1)	5629(4)	64(1)
C21	700(4)	1442(1)	4987(6)	115(2)
C22	416(2)	1925(1)	6025(5)	89(1)
C23	1495(3)	1643(1)	6966(5)	103(2)
O3	685(1)	1904(1)	2344(3)	47(1)
C30	154(2)	2004(1)	1274(4)	54(1)
C31	−447(2)	2173(1)	2053(5)	82(1)
C32	528(2)	2191(1)	138(4)	79(1)
C33	−148(3)	1728(1)	583(6)	103(2)
N	2500	2500	13(4)	50(1)
C1	2500	2500	−1203(6)	56(1)
C2	2500	2500	−2800(7)	93(2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

solution of the bidentate ligand (2,2'-bipyridine or 1,10-phenanthroline monohydrate, 2 mmol), also in benzene. A white voluminous precipitate separated immediately. More benzene was added and the mixture was refluxed under argon until a clear solution was obtained (the total volume of benzene required was 12 ml for bipy and 50 ml for phen). Slow cooling to room temperature produced colourless thin needle-shaped

crystals, which were washed with benzene and dried in vacuo. The following compounds were obtained. $[(^tBuO)_3SiS]_2Zn(bipy)$ 6: yield 92%, m.p. 233°C. Anal. Found: C, 52.12; H, 8.02; S, 8.19; N, 3.56. $ZnS_2Si_2O_6N_2C_{34}H_{62}$ Calc.: C, 52.32; H, 8.01; S, 8.22; N, 3.59%. $[(^tBuO)_3SiS]_2Zn(phen)$ 7: yield 86%, m.p. 225–226°C. Anal. Found: C, 53.68; H, 7.80; S, 7.86; N, 3.48. $ZnS_2Si_2O_6N_2C_{36}H_{62}$ Calc.: C, 53.74; H, 7.77; S,

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for 6

Atom	x	y	z	U_{eq}
Zn	2836(1)	234(1)	1768(1)	21(1)
S1	1345(1)	−278(1)	2592(1)	27(1)
Si1	1005(1)	−1814(1)	2168(1)	22(1)
O110	−248(2)	−2218(1)	1327(1)	26(1)
C110	−823(3)	−3212(2)	731(2)	29(1)
C111	−1240(4)	−3917(2)	1222(2)	39(1)
C112	270(4)	−3546(3)	154(2)	39(1)
C113	−2147(4)	−3131(3)	195(2)	43(1)
O120	2377(2)	−2278(2)	1850(1)	27(1)
C120	3472(3)	−2625(2)	2269(2)	31(1)
C121	4539(4)	−2827(3)	1644(3)	43(1)
C122	2802(4)	−3579(3)	2414(3)	49(1)
C123	4183(4)	−1841(3)	3102(2)	47(1)
O130	569(2)	−2242(2)	2940(1)	29(1)
C130	−179(3)	−1959(2)	3668(2)	32(1)
C131	817(4)	−1159(3)	4402(2)	47(1)
C132	−573(5)	−2881(3)	3909(3)	52(1)
C133	−1501(4)	−1598(4)	3419(3)	59(1)
S2	2948(1)	1759(1)	1615(1)	22(1)
Si2	3986(1)	2652(1)	2841(1)	21(1)
O210	3073(2)	3421(2)	3359(1)	27(1)
C210	1582(3)	3498(2)	3323(2)	32(1)
C211	1170(4)	3794(3)	2544(2)	41(1)
C212	1528(4)	4317(3)	4156(3)	52(1)
C213	64(4)	2540(3)	3298(2)	41(1)
O220	5523(2)	3318(2)	2813(1)	28(1)
C220	5896(3)	4238(2)	2637(2)	32(1)
C221	5706(4)	5076(2)	3399(3)	42(1)
C222	4991(4)	4197(3)	1817(2)	42(1)
C223	7474(4)	4340(3)	2523(3)	46(1)
O230	4371(2)	1918(2)	3366(1)	26(1)
C230	4919(4)	2100(3)	4267(2)	43(1)
C231	6675(10)	2471(7)	4289(6)	56(3)
C232	4505(12)	2932(8)	4867(5)	69(4)
C233	4733(19)	1176(12)	4458(12)	50(4)
C234	3476(10)	2235(9)	4734(5)	44(3)
C235	5988(12)	2939(9)	4662(6)	62(4)
C236	5147(24)	1122(17)	4314(13)	66(7)
N1	4836(3)	−126(2)	1614(2)	22(1)
N2	2450(3)	−715(2)	493(2)	21(1)
C1	6001(3)	189(2)	2218(2)	26(1)
C2	7296(3)	−77(2)	2071(2)	30(1)
C3	7394(3)	−686(2)	1267(2)	30(1)
C4	6221(3)	−994(2)	631(2)	25(1)
C5	4939(3)	−708(2)	823(2)	21(1)
C6	3609(3)	−1012(2)	183(2)	21(1)
C7	3536(3)	−1554(2)	−680(2)	25(1)
C8	2251(4)	−1770(2)	−1223(2)	30(1)
C9	1058(3)	−1475(2)	−899(2)	31(1)
C10	1202(3)	−951(2)	−39(2)	26(1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

7.97; N, 3.48%. The same compounds were obtained when the amount of ligand used was doubled.

2.8. Spectral measurements

Instruments and procedure were as follows.

IR: Specord 75, C. Zeiss Jena, 4000–400 cm^{-1}, KBr, solutions in CCl_4 (for 1 and 2 also in n-hexane).

^{1}H NMR: Varian 360A (60 MHz), solution in CCl_4 (TMS int.).

^{13}C NMR: Bruker AM250 (v_0 = 62.896 MHz), solution in $CDCl_3$ (TMS int.).

^{29}Si NMR: Bruker AM250 (v_0 = 49.689 MHz), solution in $CDCl_3$ (TMS int.); $Cr(acac)_3$ as a relaxation reagent at room temperature with inverse gated broad band proton noise decoupling.

Mass spectra: Varian Mat 8230 (EI, 80 eV), direct inlet.

2.9. Crystallographic analysis

The crystal structures of 3 and 6 were determined by single-crystal X-ray diffraction studies. Details of the determinations are given in Table 1. Atomic coordinates and equivalent isotropic displacement parameters for 3 and 6 ...e listed in Tables 2 and 3. The structures were solved by direct methods followed by full-matrix least-squares refinement based on F^2 [12]. Further information on the crystal structure determinations (full lists of atomic positional coordinates, displacement factor coefficients, bond lengths and angles and lists of F_o/F_c values, 10 pages for 3 and 18 pages for 6) can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany on quoting the depository number CSD-59193.

3. Results and discussion

The heavier members of the zinc group, cadmium and mercury, readily form homoleptic, neutral silanethiolates. We have shown previously that tri-*tert*-butoxysilanethiolates of Hg(II) and Cu(I) can be prepared directly from appropriate oxides and tri-*tert*-butoxysilanethiol [6,8]. Zinc oxide, however, did not dissolve in (^{t}BuO)$_3$SiSH to any appreciable extent, even during ca. 10 h at 80°C. This can be plausibly attributed to the fact that a soft base (thiolate) should react much more readily with a soft acid (mercury) than a hard acid (zinc).

We thus tried zinc acetate as a metal source, an approach that was successful in cadmium silanethiolate syntheses [9]. Zinc acetate did react slowly at room temperature with tri-*tert*-butoxysilanethiol in benzene–water and acetic acid was eliminated, but the resulting

Zn-containing highly viscous oily product (partially soluble in benzene and hexane) solidified only on prolonged standing (ca. 3–4 months), to give a white solid with a very broad melting point (90–110°C).

Metal thiolates are commonly prepared according to Eq. (1) from a metal salt, the thiol, and in the presence of a tertiary amine (for example triethylamine) in a polar solvent:

$$MX_n + nRSH + nNEt_3 \rightarrow M(SR)_n + n[NEt_3H]X \quad (1)$$

Tri-*tert*-butoxysilanethiol readily forms a salt-like adduct with triethylamine that shows quite good solubility in water, and so we chose water as the reaction medium. The products obtained were extremely soluble in common organic solvents, including non-polar ones, but contained water that was not removed by use of anhydrous magnesium sulphate during the standard work-up or to prolonged vacuum pumping of the solid at 50–60°C. The presence of water was shown by the infrared spectra of isolated species 1A'$_1$ and 1A'$_2$ as well as 1A'' (see Experimental section), in which the wide band at 3000–3500 cm^{-1} characteristic of hydrogen-bonded OH groups was clearly visible. The very high solubility of the products in non-polar solvents (e.g. hexane) suggested that they were neutral rather than ionic species. In the absence of any other OH-containing species the band could be attributed only to water used as the solvent. Since preparative results were not completely reproducible, as exemplified by differing and wide melting points for products obtained by the same method it was concluded that the water content in the products can vary. It is noteworthy that under the same reaction conditions but starting from with $CdCl_2$ the known homoleptic cadmium tri-*tert*-butoxysilanethiolate [9] is exclusively formed.

Dance [13] used basic zinc carbonate in his syntheses of zinc benzenethiolate derivatives. We used the same compound, but instead of the recommended acetone or MeOH we used benzene as a solvent to exclude any possibility of solvent coordination. The viscous oily product solidified only upon exposure to air. The solid thus obtained was recrystallised from hexane to give colourless crystals of 1B with a sharp melting point and elemental composition consistent with the formula [(^{t}BuO)$_3$SiS]$_2$Zn. However, the IR spectrum of 1B again contained a wide band in the region 3000–3500 cm^{-1}, although less intense than that from products 1A, and there was no doubt that 1B also contained water.

The higher acidity of silanethiols than organic thiols [14] prompted us to try another preparative route, involving direct reaction between the metal and silanethiol in the absence of added solvent. The reaction was very slow and the product was a highly viscous liquid. On contact with air it solidified to a substance 1C, in which water was again detected by IR spectroscopy. A similar result was obtained when zinc powder was

treated with a 1/2 mixture (by volume) of tri-*tert*-butoxysilanethiol and anhydrous benzene.

In the light of the above results we concluded that zinc tri-*tert*-butoxysilanethiolate is stabilised in some way by capturing water molecule(s). To the best of our knowledge, structural data for water-stabilised zinc thiolate complexes are rare, but at least one example is known, namely the very stable 2-mercaptobenzothiazole complex of zinc [n-Bu$_4$N][Zn(C$_7$H$_4$NS$_2$)$_3$(OH$_2$)], which is readily formed in the presence of traces of moisture [15].

Our findings correspond very well with those reported by Dance [13], who observed that reactions of benzenethiol with basic zinc carbonate in alcohols gave alcohol-containing products. He described the X-ray structure of one such complex, polymeric *catena*-(μ-SPh)[(μ-SPh)$_6$Zn$_4$(CH$_3$OH)(SPh)].

Some other zinc thiolate complexes are known in which additional oxygen-containing ligands enter the zinc coordination sphere. Thus Bochmann et al. [16] prepared chalcogenolato complexes of zinc bearing additional aldehyde and ketone ligands and structurally characterised the dimeric complex {(2,4,6-^{t}Bu$_3$C$_6$H$_2$-Se)$_2$Zn(OCHC$_6$H$_4$OCH$_3$))}$_2$. Furthermore, Power and Shoner [17] prepared and characterised an unusual compound monomeric zinc thiolate (2,4,6-^{t}Bu$_3$C$_6$H$_2$S)$_2$Zn(OEt$_2$) in which an ether molecule is bonded to the metal.

The observations made in the syntheses leading to 1A–C and the examples mentioned above suggest that a different small molecule capable of coordination to zinc might fulfil a role analogous to those of water and ammonia suggested itself as the most appropriate choice. When tri-*tert*-butoxysilanethiol was treated with [Zn(NH$_3$)$_4$](OH)$_2$ (prepared in situ from ZnCl$_2$ and concentrated aqueous NH$_3$) in water, complex 2 was obtained as very long and thin hair-like crystals. Elemental analysis pointed to the stoichiometric formula [(^{t}BuO)$_3$SiS]$_2$Zn(NH$_3$). The preparations were fully reproducible regardless of the small variations in the reaction conditions and ratio of the reagents, only 2 being isolated in all cases. Like 1A–C, compound 2 is very soluble in common organic solvents, including non-polar ones, but insoluble in water and is indefinitely stable under normal conditions. The ammonia, clearly identified by the appearance of the characteristic broad N–H band at 3500–3000 cm^{-1} arising from hydrogen bonding, could not be removed by pumping under vacuum but was released (and easily detected) in reactions of 2 with strong nitrogen donor ligands. The same synthetic procedure used in the case of cadmium gave only known homoleptic cadmium tri-*tert*-butoxysilanethiolate [9].

To the best of our knowledge 2 is the first example of zinc complexes in which metal is coordinated by two ligands such as thiolate and ammonia.
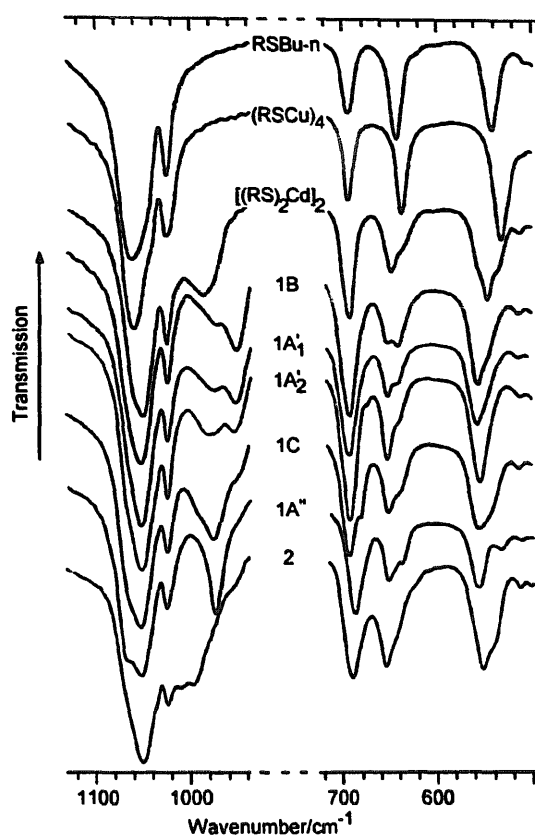

Fig. 1. Selected sections of the infrared spectra of products 1A–C, 2, and related compounds with R = (^{t}BuO)$_3$Si.

The vibrational spectra of solutions of 1A–C and 2 in carbon tetrachloride exhibit very similar features. Besides O–H and N–H stretching frequencies, above 3000 cm^{-1} the spectra are dominated by a set of essentially invariant bands arising from the (^{t}BuO)$_3$SiS group and therefore present in the spectra of all the tri-*tert*-butoxysilanethiolates so far obtained. A detailed examination, however, revealed some peculiarities in the regions usually attributed to the Si–O–C (near 1000 cm^{-1}) and Si–S (near 600 cm^{-1}) vibrations. Relevant portions of the spectra are shown in Fig. 1 which for comparison also includes spectra of the alkyl derivative (^{t}BuO)$_3$SiS^{n}Bu and those of cadmium(II) and copper(I) tri-*tert*-butoxysilanethiolates.

The fact that there are only minor differences in the spectra of the products containing water (1A$_1$, 1A$_2$, 1A$''$, 1B and 1C) is consistent with the assumption that these species are all mixtures of very similar compounds. At 940–1000 cm^{-1} the spectra of these products contain at least two superimposed bands with varying intensities. Close similarities are also observed in the 520–670 cm^{-1} region, all the compounds containing the (^{t}BuO)$_3$SiS group show two bands of medium intensity in this range. These bands are either sharp and symmetric (so far we have observed such bands only for those compounds in which exclusively terminal or ex-

clusively bridging sulphur is present, in the present work (^{t}BuO)$_3$SiSBu and [(^{t}BuO)$_3$SiSCu]$_4$ respectively) or are composed of at least two superimposed bands and unsymmetrical (those where both terminal and bridging sulphur is present, as in {[(^{t}BuO)$_3$SiS]$_2$Cd}$_2$). The spectra of 1A–C belong to the latter group, suggesting that both types of sulphur are present. Of the species 1A–C only 1B, with a sharp melting point seemed to be homogeneous; attempts to characterise it by X-ray diffraction studies failed owing to the low quality of the crystals.

The spectrum recorded for 2 exhibits essentially the features described above, but with more intense absorption near 1000 cm^{-1}. We assumed that 2 was the dimeric species {[(^{t}BuO)$_3$SiS]$_2$Zn(NH$_3$)}$_2$, and this was confirmed by a cryoscopic molecular weight determination that differed by only ca. 10% from the calculated value. The structures of several known zinc thiolates are of the generic type (RS)Zn(μ-SR)$_2$Zn(SR) (see Refs. [18,19]), and the dimeric formulation proposed for 2 is by no means unique. Cadmium bis(tri-$tert$-butoxysilanethiolate) is also dimeric [9]. Unfortunately, the very thin and long hair-like crystals of 2 were not suitable for an X-ray study, and the spatial arrangement of the ligands and possible intramolecular interactions (for example)N–H $\cdots$ O(and)N–H $\cdots$ S(hydrogen bonding) is a matter for speculation.

Acetonitrile is one of the most frequently employed solvents in the synthesis of thiolates. In the reaction of tri-$tert$-butoxysilanethiol with ZnCl$_2$ in the presence of Et$_3$N in acetonitrile one molecule of solvent was taken up, complex 3, with the formula [(^{t}BuO)$_3$SiS]$_2$Zn-(NCMe) was obtained. The same complex was obtained by addition of an excess of acetonitrile to concentrated solutions of 1A–C in THF. Formation of zinc thiolates

containing acetonitrile was observed by Dance [13], but none of the complexes were isolated in a pure state.

The crystals of 3 are insoluble in water, very poorly soluble in acetonitrile, hexane, or benzene, slightly more soluble in carbon tetrachloride, and very soluble in THF. They begin to melt at ca. 85°C with some loss of weight, leaving a liquid which completely decomposes at 180–190°C with gas evolution.

The structure of 3 revealed by X-ray diffraction shows the zinc-like pentacoordinate (with a ZnS$_2$O$_2$N core), clearly demonstrating that coordination of zinc by both sulphur and oxygen from the same tri-$tert$-butoxy-silanethiolate ligand is possible.

Compounds 1, 2 and 3 are readily accessible and therefore can serve as convenient substrates for syntheses of other heteroleptic zinc tri-$tert$-butoxysilanethio-lates. We found that they react easily with strong nitrogen donor ligands such as pyridine, 1-methylimidazole, 1,10-phenanthroline and 2,2'-bipyridine. In all cases colourless crystalline compounds with the formula [(^{t}BuO)$_3$SiS]$_2$Zn(L$_2$), where L = py 4, L = 1-meimid 5, L$_2$ = bipy 6, and L$_2$ = phen 7, were obtained. We described previously the cadmium complexes with a similar composition to that of 6 and 7 [9], and we have now prepared two more such complexes, [(^{t}BuO)$_3$SiS]$_2$-Cd(py)$_2$ 8 and [(^{t}BuO)$_3$SiS]$_2$Cd(1-meimid)$_2$ 9. Complexes of zinc with S$_{4-n}$N$_n$ ($n = 0$ to 2) cores are of interest from at least two points of view: (i) they frequently serve as structural models for the immediate ligand environment of zinc in DNA-binding proteins and certain zinc-containing enzymes (see, for example, Refs. [20–23]), and (ii) some derivatives of arenethiols and N-heterocyclic bidentate ligands show luminescence (see, for example, Ref. [24]). Complexes with the ZnS$_2$N$_2$ core are thus well known, but according to our

Table 4
Selected bond lengths and angles for 3 (standard deviations in parentheses)

Bonds (Å)			
Zn–N	2.087(4)	Si–O1	1.648(2)
Zn–S	2.2491(8)	Si–O2	1.612(2)
Zn–O1	2.378(2)	Si–O3	1.602(2)
S–Si	2.0680(11)	O1–C10	1.457(4)
N–C1	1.102(6)	O2–C20	1.420(4)
C1–C2	1.446(9)	O3–C30	1.433(3)
Angles (°)			
N–Zn–S	117.09(2)	O3–Si–O2	105.07(12)
S'–Zn–S	125.81(5)	O3–Si–O1	112.77(11)
S–Zn–O1	77.59(5)	O2–Si–O1	105.83(11)
S–Zn–O1'	105.69(5)	O3–Si–S	114.91(9)
N–Zn–O1	86.51(5)	O2–Si–S	116.08(10)
O1'–Zn–O1	173.02(10)	O1–Si–S	102.03(8)
Si–S–Zn	86.81(3)	C10–O1–Si	130.6(2)
Si–O1–Zn	93.26(9)	C10–O1–Zn	133.1(2)

Symmetry transformations used to generate equivalent atoms: $-x + 0.5$, $-y + 0.5$, z.

knowledge 4–7 and the cadmium analogues are the first examples containing a silanethiolate ligand. The crystal structure of bis(tri-tert-butoxysilanethiolato)(bypyri-dine)zinc(II) 6 was determined, as is described below.

3.1. Structure of [(^{t}C$_4$H$_9$O)$_3$SiS]$_2$Zn(NCCH$_3$)] 3

The complex [(^{t}C$_4$H$_9$O)$_3$SiS]$_2$Zn(NCCH$_3$)] 3 gives colourless plates of orthorhombic crystals. They consist of discrete, monomeric bis(tri-tert-butoxysilanethiol-ato)(acetonitrile)zinc(II) units. Fig. 2 gives a view of the molecule, and selected interatomic distances and angles are listed in Tables 2 and 4 respectively.

In 3 there is a distorted trigonal bipyramidal arrangement around the central zinc(II) atom (ZnS$_2$NO$_2$ core). It has crystallographically imposed C$_2$ symmetry with the ZnNCMe portion lying on a two-fold rotational axis. Both silanethiolate ligands are bonded to zinc in a bidentate fashion, through sulphur and oxygen atoms from one of the alkoxy groups located on silicon. The sulphur atoms occupy two equatorial positions and the oxygen atoms two axial ones. The acetonitrile molecule is in the remaining equatorial position. The Zn–N bond length of 2.087 Å is comparable with the Zn–N bond lengths found in several zinc thiolate complexes bearing nitrogen ligands [23], including Zn–N1 and Zn–N2 bonds of 2.090 and 2.097 Å found in 6. The N–C bond length in 3, 1.102 Å, is shorter than that in free MeCN (1.6 Å). The N≡C bond length in nitriles is usually shortened upon coordination, and distances between 1.11 and 1.15 Å are usually reported [25]. The Zn–S bond length of 2.2491 Å in 3 lies between those usually observed for thiolates with four- or pentacoordinated zinc (usually ca. 2.3 Å or larger [21–23]), and those found for three-coordinated zinc as in the trigonal pla-nar anion [Zn(S–Me$_4$C$_6$H-2,3,5,6)]$_3^-$ (2.243–2.217 Å) [26] or the dimeric [Zn(S–^{t}Bu$_3$C$_6$H$_2$-2,4,6)$_2$]$_2$ (Zn–S$_t$ 2.184 and 2.203 Å) [19].

The Zn–O bond seems to be rather weak since its length (2.378 Å) significantly exceeds the sum of the Zn and O covalent radii (1.91 Å) (cf. also the Zn–O bond length of 2.133 Å in [(Et$_2$O)Zn(S–^{t}Bu$_3$C$_6$H$_2$-2,4,6)$_2$] [17]). However, its presence is clearly demon-strated by the distortions in the geometry at the Si atom. Thus the Si–O1 bond, which forms part of a four-mem-bered chelate ring, is ca. 0.04 Å longer than the other two Si–O bonds, and the S–Si–O1 angle is 13–14° smaller than the other two S–Si–O angles. Furthermore, the O1–C10 bond is ca. 0.03 Å shorter than the O–C bonds to the O2 and O3 atoms. The ZnSSiO chelate rings are essentially planar; the mean deviation from the best least-squares plane is 0.0363 Å (with Zn and Si above, and S and O1 below, the plane) and the sum of relevant angles is 359.7°.

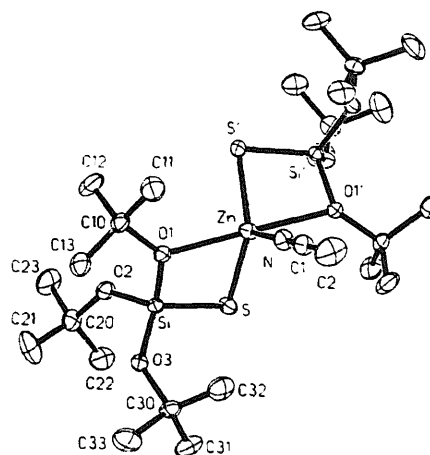Distortions from ideal trigonal bipyramidal geometry in 3 are revealed by the spatial arrangement of atoms

Fig. 2. Molecular structure of [(^{t}BuO)$_3$SiS]$_2$Zn(NCMe) 3 with atom labelling (hydrogen atoms are omitted for clarity). ORTEP plot with 30% probability ellipsoids.

forming the basal trigonal plane, where S–Zn–S and S–Zn–N angles of 125.81° and 117.09° deviate from the ideal value of 120°, and the Zn–O bonds are not strictly colinear, the angle O–Zn–O being 173.0°. Fur-thermore, they are not perpendicular to the basal ZnS$_2$N plane, forming an angle of 77.6° with this plane. An-other important feature of 3 is a very short Si–S bond of 2.068 Å.

The features of 3 are closely related to those of the cobalt(II) complex [(^{t}C$_4$H$_9$O)$_3$SiS]$_2$Co(NCCH$_3$)] [10], the complexes being isomorphous and isostructural. In contrast, [Zn(S–Me$_4$C$_6$H-2,3,5,6)$_3$]$^-$ does not react with acetonitrile [26] even though the corresponding cobalt(II) complex [Co(S–Me$_4$C$_6$H-2,3,5,6)$_3$(CH$_3$CN)]$^-$ can be readily obtained [27]. Furthermore, the neutral [Zn(S–^{t}Pr$_2$C$_6$H$_3$-2,6)$_2$(bipy)] is four-coordinate, whereas [Co(S–^{t}Pr$_2$C$_6$H$_3$-2,6)$_2$(bipy)] adds CH$_3$CN to give the five-coordinate complex [Co(S–^{t}Pr$_2$C$_6$H$_3$-2,6)$_2$(bipy)-(CH$_3$CN)] [21,28]. Our results thus confirm the conclu-sion of Schrautzer and coworkers [22] that, when it bears the appropriate ligands, Zn(II) can also form penta-coordinated species.

Recently, the crystal structure of monometallic pyri-dine-bis(4,6-dimethylpyrimidine-2-thiolato)zinc(II), [Zn(4,6-Me$_2$pymt)$_2$(py)], was reported [29]. In it the zinc atom has a distorted trigonal bipyramidal geometry with the pyridine nitrogen and two sulphur atoms occu-pying equatorial positions and one nitrogen atom of each bidentate 4,6-Me$_2$pymt$^-$ moiety occupying an ax-ial position. The Zn–N$_{pyrim}$ bonds are judged to be relatively weak. It is remarkable that this complex and 3 have very similar structures, although containing signif-icantly different types of ligand.

3.2. Structure of [(^{t}BuO)$_3$SiS]$_2$Zn(bipy) 6

Bis(tri-tert-butoxysilanethiolate)(bipyridine)zinc(II) 6 forms monoclinic colourless crystals melting at 206–

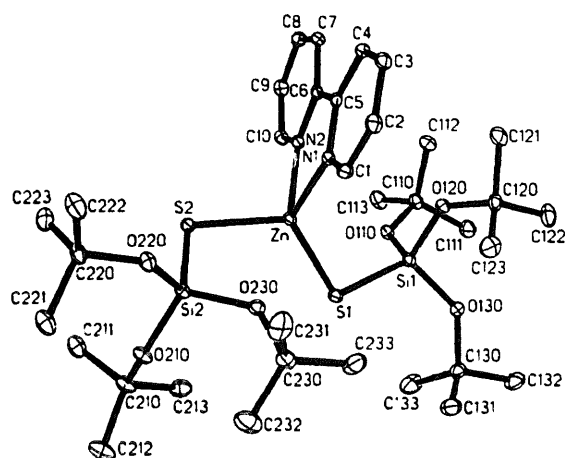Fig. 3. Molecular structure of [('BuO)₃SiS]₂Zn(bipy) 6 with atom labelling (hydrogen atoms are omitted for clarity). ORTEP plot with 20% probability ellipsoids.

207°C. Fig. 3 gives a view of the molecule. Atom coordinates are shown in Table 3 and selected bond distances and angles in Table 5. The methyls in one of the *tert*-butyl groups (at C230) are disordered (site occupancy factor 0.5), and only one of the forms is shown.

The molecular structure of [('BuO)₃SiS]₂Zn(bipy) 6 is based on a tetrahedral ZnS₂N₂ core, necessarily

distorted as the result of the small bite of the 2,2'-bipyridine. The bipyridine ligand is essentially planar with mean deviation from the best least-squares plane of 0.038 Å. The bond lengths and angles within the ligand are unexceptional. It is bound symmetrically to zinc and the N–Zn–N angle is 78.3°. Correspondingly the S1–Zn–S2 angle is larger (120.4°) than expected for ideal tetrahedral geometry. The Zn–N bond lengths are comparable with those commonly reported [21,22,29]. The two Zn–S bond lengths differ by 0.05 Å, and the shorter bond, Zn–S1 (2.2475 Å), has essentially the same length as the Zn–S bond in 3.

The two Si–S bonds have the same length (within experimental error) and are only slightly longer than the Si–S bond in 3 (mean 2.0917 Å vs. 2.0680 Å). One ('BuO)₃SiS group is bent back over the bipyridine moiety in such a manner that the mean bipyridine plane and the plane defined by Si1, O110, and O120 atoms are almost parallel (interplanar angle 4.5°). This brings two ('BuO)₃Si groups near to the bipyridine plane, but without apparent crowding. The second ('BuO)₃SiS group is directed away from the bipyridine. The spatial arrangement of ligands is reflected in the wide Si1–S1–Zn angle of 106.12°, compared with 99.95° for Si2–S2–Zn, and in the angles S1–Zn–N being larger than the angles S2–Zn–N. There are no interactions between oxygen and zinc like those in 3. The closest O–Zn

Table 5
Selected bond lengths and angles for 6 (standard deviations in parentheses)

Bonds (Å)			
Zn–N1	2.090(2)	Zn–N2	2.097(3)
Zn–S1	2.2475(10)	Zn–S2	2.2970(9)
S1–Si1	2.0908(13)	S2–Si2	2.0927(14)
Si1–O110	1.636(2)	Si2–O210	1.626(2)
Si1–O120	1.637(2)	Si2–O220	1.632(2)
Si1–O130	1.634(2)	Si2–O230	1.633(2)
O110–C110	1.461(4)	O210–C210	1.451(4)
O120–C120	1.448(4)	O220–C220	1.449(4)
O130–C130	1.444(4)	O230–C230	1.458(4)
N1–C1	1.341(4)	N2–C6	1.349(4)
N1–C5	1.347(4)	N2–C10	1.344(4)

Angles (°)			
N1–Zn–N2	78.31(10)	S1–Zn–S2	120.40(4)
N1–Zn–S1	124.97(7)	N2–Zn–S1	112.72(7)
N1–Zn–S2	107.40(7)	N2–Zn–S2	103.17(7)
Si1–S1–Zn	106.12(5)	Si2–S2–Zn	99.95(5)
O110–Si1–O120	105.79(11)	O210–Si2–O220	106.02(11)
O110–Si1–O130	112.33(12)	O210–Si2–O230	111.85(12)
O120–Si1–O130	105.58(11)	O220–Si2–O230	105.43(11)
O110–Si1–S1	107.14(9)	O210–Si2–S2	113.96(9)
O120–Si1–S1	115.74(9)	O220–Si2–S2	112.39(10)
O130–Si1–S1	110.29(9)	O230–Si2–S2	106.94(9)
C110–O110–Si1	131.0(2)	C210–O210–Si2	136.6(2)
C120–O120–Si1	133.2(2)	C220–O220–Si2	132.2(2)
C130–O130–Si1	136.9(2)	C230–O230–Si2	132.1(2)
C1–N1–C5	118.6(2)	C10–N2–C6	119.3(3)
C1–N1–Zn	125.9(2)	C10–N2–Zn	125.1(2)
C5–N1–Zn	115.5(2)	C6–N2–Zn	115.2(2)

distance is 3.049 Å for O230–Zn, well beyond the sum of the respective van der Waals radii (2.9 Å).

The observed arrangement of ligands in **6** resembles that reported for $(p\text{-}CH_3C_6H_4S)_2Zn(phen)$ [30], in which one thiolate group is bent back over the phenanthroline and the second directed away, and is different from that reported for $(2,4,6\text{-}^iPr_3C_6H_2S)_2Zn(bipy)$ [21], in which both thiolate ligands are directed towards bipyridine. It is noteworthy that despite the difference in the types of thiolate the principal structural features of **3** and these two complexes are similar.

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