(2,2′-Bipyridine)bis(tri-tert-butoxy-silanethiolato-κS)lead(II) and (4,7-diphenyl-1,10-phenanthroline-κ²N,N′)bis(tri-tert-butoxysilanethiol-ato-κS)lead(II) benzene hemisolvate

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In the title mononuclear lead silanethiolates, [Pb($C_{12}H_{27}O_3$-$SSi)_2(C_{10}H_8N_2)$], (I), and [Pb($C_{12}H_{27}O_3SSi)_2(C_{24}H_{16}N_2)$]·$0.5C_6H_6$, (II), the Pb atom shows a distorted square-pyramidal coordination with a $PbON_2S_2$ core in which one S atom lies in an axial position. Intermolecular π–π and C—H···π interactions stabilize the structures. The benzene solvent molecule in (II) lies on an inversion centre.

Comment

The present study is a continuation of our investigation of silanethiolate complexes of various metals (see, for example, Kloskowska *et al.*, 2006). The compounds often show interesting structural features and are potential precursors for the generation of structurized metal sulfides (Tran *et al.*, 2000). Only three structures containing an Si–S–Pb sequence were
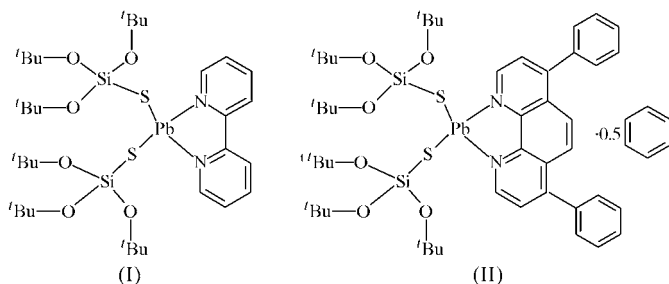
found in the Cambrigde Structural Database (CSD; Version 5.28, May 2007 update; Allen, 2002). The dimeric lead tri-*tert*-butoxysilanethiolate, in the form of the diglyme solvate, was obtained by reaction of silanethiol with PbO (Wojnowski *et al.*, 1986). Another complex, Pb{SSi(OC$_4$H$_9$)$_3$}$_2$N$_2$C$_{12}$H$_8$, or (*ortho*-phenanthroline)bis(tri-*tert*-butoxysilanethiolato)lead(II), a mononuclear and heteroleptic compound, was obtained

about ten years later by the incorporation of a chelating nitrogen ligand (Peters *et al.*, 1997). Finally, a metal–organic compound, namely a plumbolane (2,2,3,3-tetramethyl-5,5-diphenyl-1,4,2,3,5-dithiadisilaplumbolane), has been reported (Herzog & Rheinwald, 2002). Several attempts to obtain and characterize heteroleptic silanethiolates with PPh$_3$ or simple heteroaromatic nitrogen bases as additional ligands have so far failed. We present here the syntheses and structures of two mononuclear complexes, namely (2,2′-bipyridine)bis(tri-*tert*-butoxysilanethiolato)lead(II), (I), and (4,7-diphenyl-1,10-phenanthroline)bis(tri-*tert*-butoxysilanethiolato)lead(II) benzene hemisolvate, (II). To our knowledge, no lead complexes with this latter heterocyclic ligand have been structurally characterized by X-ray diffraction to date.

Both compounds show a distorted square-pyramidal coordination of the Pb atoms. The impact of the 'inert pair effect' on the structure is clearly manifested. The base plane contains N, N, S and O atoms, whereas the second S atom, found in the apical position, belongs to the *O,S*-chelating tri-*tert*-butoxysilanethiolate ligand. A widening of the valence angles at the S atoms by *ca* 4° in the silanethiolate ligands not involved in chelation is observed in both structures (Tables 1 and 2). It is worth noting the influence of the steric effect of the S-atom lone pairs on the coordination of sulfur. In (I), the Pb—N bond lengths differ, although the difference is small. This is not the case in (II), where Pb—N2 is about 0.2 Å longer than Pb—N1. The Si—S bond lengths are shorter and Pb—S distinctly longer compared with the respective bonds in the plumbolane (Si—S *ca* 2.14 Å and Pb—S *ca* 2.50 Å). This probably indicates a partially ionic character of the metal–ligand bonds in (I) and (II) (Baranowska *et al.*, 2006). The Si2—O4 bond length is slightly longer than the other Si—O bonds in (I), due to chelation; this effect was noted previously by Jesionka *et al.* (2005). In (II), the situation is complicated by disorder.

In structure (I), the aromatic 2,2′-bipyridine rings of two neighbouring molecules are linked by a π–π interaction. Even
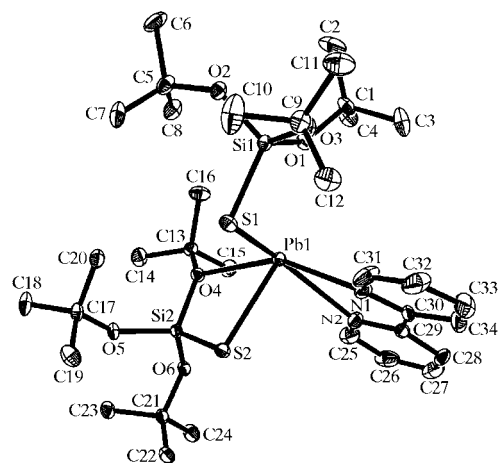

Figure 1
The molecular structure of (I), showing the atom-numbering scheme and displacement ellipsoids drawn at the 25% probability level. H atoms have been omitted.

if such an arrangement of heterocyclic rings is not possible in complex (II), due to the nonplanar character of 4,7-diphenyl-1,10-phenanthroline, it is possible between the phenyl substituents of the heteroaromatic base. In addition to this, some C—H$\cdots\pi$ interactions complete the packing interaction scheme (Table 3).

The large dihedral angles between the phenanthroline residue and its phenyl substituents C37–C42 and C43–C48 [49.5 (2) and 51.1 (2)°, respectively] indicate that π electrons in the phenanthroline group are not coupled with the phenyl substituents. The same behaviour (shown in Fig. 3, with data extracted from the CSD) has been observed in all 43 complexes of the 4,7-diphenyl-1,10-phenanthroline ligand known to date (for example, Brandi-Blanco *et al.*, 2005).

The benzene solvent molecule in (II) sits on the inversion centre at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, filling voids within the structure. Its linkage to the main frame is by way of a C—H$\cdots\pi$ interaction (final entry in Table 3).

Experimental

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk techniques. The solvents were purified and dried by standard methods (Perrin & Armarego, 1988).

Compound (I) was prepared by the addition of [{(^{t}BuO)$_3$SiS}$_2$Pb]$_2$ (0.3 g, 0.20 mmol) (Wojnowski *et al.*, 1986) dissolved in hexane–pentane (40:60 *v/v*, 25 ml) to a solution of 2,2'-bipyridine (130 mg, 0.83 mmol) in hexane–pentane (40:60 *v/v*, 5 ml). The mixture was shaken for a few minutes and subsequently left at *ca* 273 K for 15 h. The solid material was filtered off and the solution concentrated to half its initial volume and then left for crystallization at *ca* 273 K. After a week, good quality crystals of (I) (m.p. 433 K) were obtained in moderate yield (*ca* 50%, not optimized) with consistent elemental analyses for C, H, S and N.

Solid [{(^{t}BuO)$_3$SiS}$_2$Pb]$_2$ (0.3 g, 0.20 mmol) (Wojnowski *et al.*, 1986) and 4,7-diphenyl-1,10-phenanthroline (bathophenanthroline) (250 mg, 0.40 mmol) were added to hexane (20 ml). The mixture was shaken for 10 min and subsequently left at *ca* 273 K for 5 h. The solid material was filtered off and the solution concentrated to form a raw product. Recrystallization from hexane–benzene (1:1 *v/v*) solution was carried out at *ca* 273 K. After a month, crystals of (II) (m.p. 440 K) separated (yield *ca* 40%, not optimized). Elemental analyses for C, H, S and N were consistent with the assumed formula.
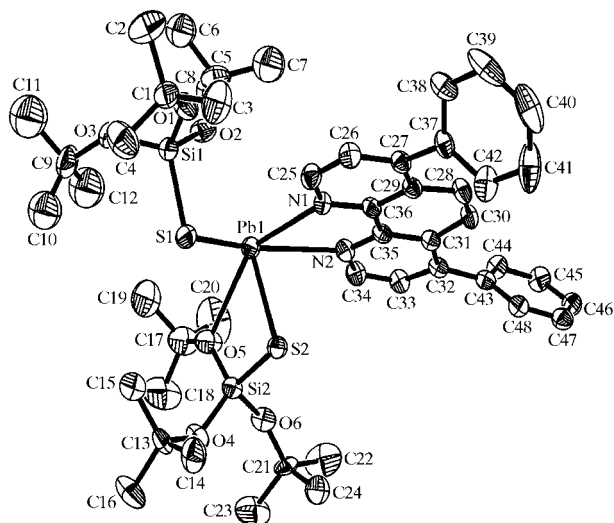

Figure 2
The molecular structure of (II), showing the atom-numbering scheme and displacement ellipsoids drawn at the 25% probability level. H atoms and the solvent benzene molecule have been omitted. Only the major part of the disordered group is shown.
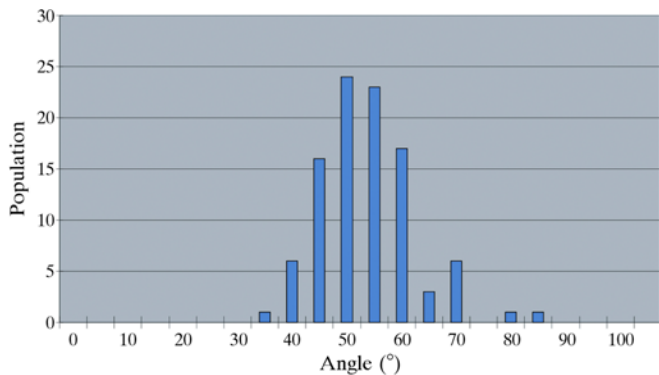

Figure 3
Histogram of phenyl–heterocycle dihedral angles in 4,7-diphenyl-1,10-phenanthroline complexes currently (May 2007) deposited in the CSD.

Compound (I)

Crystal data

[Pb(C$_{12}$H$_{27}$O$_3$SSi)$_2$(C$_{10}$H$_8$N$_2$)]	$\gamma = 101.086\ (4)°$
$M_r = 922.35$	$V = 2144.1\ (2)$ Å^3
Triclinic, $P\bar{1}$	$Z = 2$
$a = 9.4053\ (4)$ Å	Mo $K\alpha$ radiation
$b = 13.8617\ (7)$ Å	$\mu = 4.13$ mm^{-1}
$c = 18.0405\ (9)$ Å	$T = 120\ (2)$ K
$\alpha = 107.361\ (5)°$	$0.49 \times 0.13 \times 0.09$ mm
$\beta = 99.069\ (4)°$	

Data collection

Oxford Diffraction KM-4 CCD diffractometer	17997 measured reflections
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2006)	10174 independent reflections
	9037 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.030$
$T_{min} = 0.503$, $T_{max} = 0.695$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$	442 parameters
$wR(F^2) = 0.099$	H-atom parameters constrained
$S = 1.16$	$\Delta\rho_{max} = 2.11$ e Å^{-3}
10174 reflections	$\Delta\rho_{min} = -1.55$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

Pb1—N1	2.610 (4)	Si1—O3	1.625 (3)
Pb1—S2	2.6705 (11)	Si1—O2	1.627 (3)
Pb1—S1	2.7034 (13)	Si1—O1	1.633 (3)
Pb1—N2	2.725 (4)	Si2—O5	1.628 (3)
S1—Si1	2.0730 (17)	Si2—O6	1.632 (3)
S2—Si2	2.0861 (16)	Si2—O4	1.641 (3)
N1—Pb1—S2	95.78 (10)	S2—Pb1—N2	85.70 (9)
N1—Pb1—S1	86.96 (11)	S1—Pb1—N2	145.90 (9)
S2—Pb1—S1	87.14 (4)	Si1—S1—Pb1	97.90 (5)
N1—Pb1—N2	60.74 (14)	Si2—S2—Pb1	94.17 (5)

Compound (II)

Crystal data

$[Pb(C_{12}H_{27}O_3SSi)_2(C_{24}H_{16}N_2)]\cdot$
  $0.5C_6H_6$
$M_r = 1137.6$
Triclinic, $P\bar{1}$
$a = 10.204$ (2) Å
$b = 13.359$ (3) Å
$c = 21.109$ (4) Å
$\alpha = 84.57$ (3)°

$\beta = 83.05$ (3)°
$\gamma = 85.29$ (3)°
$V = 2836.2$ (10) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 3.13$ mm^{-1}
$T = 293$ (2) K
$0.6 \times 0.41 \times 0.32$ mm

Data collection

Oxford Diffraction KM-4 single-
  point diffractometer
Absorption correction: ψ scan
  (North *et al.*, 1968)
  $T_{min} = 0.198$, $T_{max} = 0.359$
10564 measured reflections

10091 independent reflections
7445 reflections with $I > 2\sigma(I)$
$R_{int} = 0.053$
3 standard reflections
  every 200 reflections
  intensity decay: 5.7%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.118$
$S = 1.00$
10091 reflections
648 parameters

115 restraints
H-atom parameters constrained
$\Delta\rho_{max} = 0.84$ e Å^{-3}
$\Delta\rho_{min} = -0.80$ e Å^{-3}

Table 2
Selected geometric parameters (Å, °) for (II).

Pb1—N1	2.594 (5)	Pb1—N2	2.801 (5)
Pb1—S2	2.6331 (18)	S1—Si1	2.075 (2)
Pb1—S1	2.6976 (18)	S2—Si2	2.071 (2)
N1—Pb1—S2	87.77 (11)	S2—Pb1—N2	81.17 (11)
N1—Pb1—S1	89.44 (11)	S1—Pb1—N2	148.25 (10)
S2—Pb1—S1	88.41 (6)	Si1—S1—Pb1	99.04 (9)
N1—Pb1—N2	60.42 (14)	Si2—S2—Pb1	94.28 (8)

Table 3
π–π and C—H$\cdots\pi$ contacts for (I) and (II).

DA is the dihedral angle between planes, DCC is the length of the CC (centroid-to-centroid) vector in π–π interactions, DCH is the length of the CH (centroid to H) vector in C—H$\cdots\pi$ interactions and τ is the angle(s) subtended by the plane normal(s) to CC or CH. $Cg1$ is the centroid of ring N1/C30–C34, $Cg2$ of ring N2/C25–C9, $Cg3$ of ring C37–C42, $Cg4$ of ring C28–C31/C35–C36 and $Cg5$ of ring C49–C51/(C49–C51)^{iii}.

Compound	Group 1/Group 2	DA (°)	DCC/DCH (Å)	τ (°)
(I)	$Cg1/Cg2^i$	5.6	3.797 (4)	24, 31
(II)	$Cg3/Cg3^{ii}$	0.0	3.717 (5)	17.1
(II)	C51—H51/$Cg4$		2.98	13.6
(II)	C48—H48/$Cg5$		2.81	6.6

Symmetry codes: (i) $1 - x, 2 - y, -z$; (ii) $-x, 2 - y, 1 - z$; (iii) $1 - x, 1 - y, 1 - z$.

All H atoms were refined as riding on their parent C atoms, with methyl C—H = 0.98 Å, methylene C—H = 0.99 Å and aromatic C—H = 0.95 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic, $1.3U_{eq}(C)$ for CH$_2$ and $1.5U_{eq}(C)$ for methyl groups. In the case of (II), eluci-

dation of the structure from diffraction data required special treatment. The two butoxy groups at O4 and O6 were each refined as being disordered over two positions, with occupancies of 0.714 (12) and 0.286 (12). Atoms C5–C8 and C10–C12 were refined with ISOR/SIMU instructions (*SHELXL97*; Sheldrick, 1997) simulating isotropic behaviour because of the unacceptable parameters of their ellipsoids. The highest electron-density peaks were located 0.78 Å from atom Pb1 in (I) and 0.86 Å from Pb1 in (II).

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006) for (I); *KM4 System* (Gałdecki, Kowalski, Kucharczyk & Uszyński, 1996) for (II). Cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006) for (I); *KM4 System* for (II). Data reduction: *CrysAlis RED* for (I); *DATAPROC* (Gałdecki, Kowalski & Uszyński, 1996) for (II). For both compounds, program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Mercury* (Version 1.5; Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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