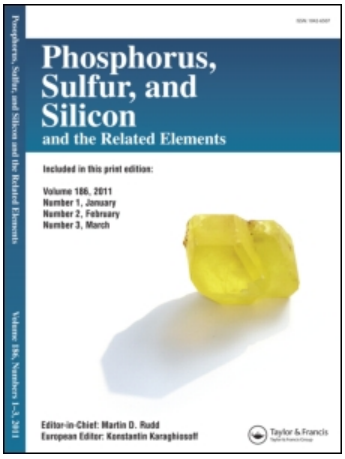

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Potassium Tri-*tert*-butoxysilanethiolates: Synthesis, Properties, and Crystal and Molecular Structures of $[(^{t}BuO)_3SiSK]_6[THF]_2\cdot 2THF$, $\{[(^{t}BuO)_3SiS]_2K_2\}_n$, and $[(^{t}BuO)_3SiSK]_4[H_2O]_4\cdot C_6H_6$

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Potassium Tri-*tert*-butoxysilanethiolates: Synthesis, Properties, and Crystal and Molecular Structures of $[(^tBuO)_3SiSK]_6[THF]_2 \cdot 2THF$, $\{[(^tBuO)_3SiS]_2K_2\}_n$, and $[(^tBuO)_3SiSK]_4[H_2O]_4 \cdot C_6H_6$

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*The synthesis and characterization of a family of potassium silanethiolates is described. $[(^tBuO)_3SiSK]_6[THF]_2 \cdot 2THF$ (**1**), $\{[(^tBuO)_3SiS]_2K_2\}_n$(**2**), and $[(^tBuO)_3SiSK]_4[H_2O]_4 \cdot C_6H_6$ (**3**) were synthesized by treatment of $(^tBuO)_3SiSH$ with potassium metal in various solvents. The target molecules were characterized by single crystal X-ray crystallography. Compounds **1**, **2**, and **3** form hexameric, polymeric, and tetrameric units correspondingly, in the solid state. $[(^tBuO)_3SiSK]_6[THF]_2 \cdot 2THF$ contains three, differently coordinated potassium ions and crystallizes in the space group $P2_1/c$, $a = 15.227(4)$, $b = 14.650(5)$, $c = 32.067(9)$ Å, $\beta = 117.001(18)^\circ$, $V = 6374(3)$ Å^3. $\{[(^tBuO)_3SiS]_2K_2\}_n$ crystallizes in the space group P-1, $a = 11.6305(14)$, $b = 13.348(3)$, $c = 13.531(4)$ Å, $\alpha = 67.27(2)^\circ$, $\beta = 76.064(16)^\circ$, $\gamma = 88.706(14)^\circ$, $V = 1874.6(8)$ Å^3. $[(^tBuO)_3SiSK]_4[H_2O]_4 \cdot C_6H_6$ crystallizes in the space group P-4b2, $a = 20.854(3)$, $b = 20.854(3)$, $c = 9.283(2)$ Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 4037{,}1(12)$ Å^3.*

Keywords Coordination chemistry; crystal structure; hydrogen bonds; potassium; silanethiolate ligands

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Dedicated to Professor Marian Mikołajczyk, CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

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INTRODUCTION

The structure and chemistry of silanethiolates have been the subject of our research for over 20 years[1] and also have generated some interest among other scientific groups.[2] The silanethiolate ligand contains a sulfur atom bonded to a silicon instead of carbon atom.

Structural studies on thiolates, selenolates, and tellurolates of s-block elements are important because the compounds often serve as very convenient starting materials in both inorganic and organic syntheses.[3] The potential of alkali metal thiolates, selenolates, and tellurolates in synthetic chemistry as well as various technical applications has sparked a very recent interest in the chemistry of alkali metal thiolates, selenolates, and tellurolates. As a result, an increasing body of work concerned with exploration of synthetic routes to these compounds, analysis of the influence of metal and ligand on the structural chemistry, and correlation between structure and function has appeared in the literature, mostly in the last few years.[4] Since structural factors critically affect physical properties and consequently the suitability of the target compounds in various applications, detailed investigations into factors modulating structural parameters are important. Of specific interest are variables determining aggregation chemistry, but possibly even more critical is information on how association in both solution and the solid state. As a consequence, multiple studies have been undertaken to investigate the role of metal, ligand, solvent, and donors on the structural chemistry of alkali metal chalcogenolates.[4] In contrast to this, the silanethiolate derivatives have received much less attention. Silanethiolate compounds are a subject of our research for a long time. In the majority of our works, we used tri-*tert*-butoxysilanethiolate $(^{t}BuO)_3SiS^-$ as a model ligand, due to its specific features. Among others, it is worth mentioning that the large steric hindrance at the Si atom created by three bulky *tert*-butoxy groups, its chelating capability as an O-and S-donor ligand, its nonpolar exterior and polar interior, and solubility in common organic solvents. Most of our articles have been devoted to the discussion of structural features of tri-*tert*-butoxysilanothiolates of transition and *p*-block metals.[5,6] So far only, scant structural data for silanethiolates of the *s*-block elements are known. A whole series of silanethiolates of s-block metals was obtained and characterized in 1974,[7] but the first structure of alkali metal silanethiolate was described in 1986—it was very interesting, ionic sodium triphenylsilanotihiolate trihydrate $NaSSiPh_3 \cdot 3H_2O$.[8] Structurally characterized lithium silanethiolate species include the dimeric $[LiSSi(O^tBu)_3 \cdot THF]_2$,[9] hydrated octameric $[Li_8\{(^tBuO)_3SiS\}_6(OH)_2(H_2O)_2] \cdot 2C_7H_8$,[10] the polymeric

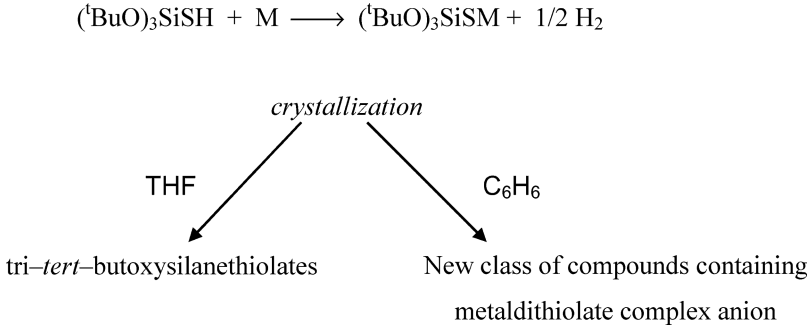
$[LiSSi(O^tBu)_3]_2DME$,[9] and $[(TMEDA)LiSSiMe_2^tBu]_2$.[11] The examples of heavier alkali metal silanethiolates are limited to only two sodium compounds, $NaSSiPh_3 \cdot H_2O$,[8] and hexameric $[(NaSSiPh_3)_6(toluene)_2]$,[12] and one monomeric potassium silanethiolate K^+, 18-crown-6, $[C_6H_4\text{-}2\text{-}C(CF_3)_2OSiPhCH(CH_2^tBu)S]^-$.[13] This small group of structurally characterized alkali metal silanethiolates indicates rich structural chemistry.

In this article, we want to present three new potassium silanethiolates synthesized with the use of sterically demanding tri-*tert*-butoxysilanethiolate ligand.

RESULTS AND DISCUSSION

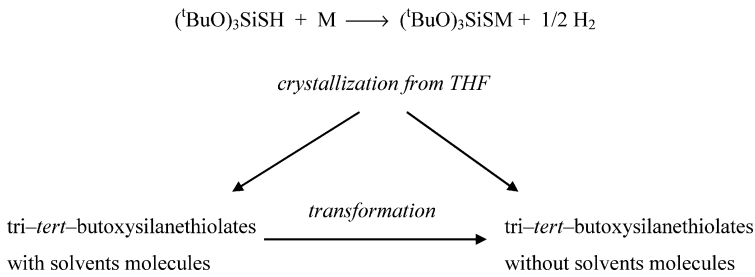
The compounds 1–3 were synthesized in a straightforward manner by the reaction between $(^tBuO)_3$ SiSH and potassium metal with hydrogen elimination, with or without solvents in quantitative yields.

The solvent nature has a great influence on the solid state structure of the obtained compounds. Depending on the kind of solvent, we previously obtained lithium and sodium silanethiolates, which belong to two different classes. With the use of a solvent devoid of donor atoms, we obtained an unknown class of compounds with a metal atom in the center of the metaldithiolates complex anion.[14] The reaction scheme is presented in Scheme 1



SCHEME 1 Synthesis of silanethiolates of s-block metals, part 1.

Crystallization in THF resulted in the formation of two different silanethiolate compounds, one of them heteroleptic, with solvent molecules complexed to metal ion and the other homoleptic silanethiolate. The first of these two compounds is unstable and loses solvent molecules decomposing to homoleptic compound as is shown in Scheme 2.



SCHEME 2 Synthesis of silanethiolates of the s-block metals, part 2.

In this article we describe compounds obtained in reactions between potassium metal and tri-*tert*-butoxysilanethiol. The reactions were carried out according to Schemes 1 and 2.

Structural Description

[(tBuO)3SiSK]6[THF]2·2THF (1)

The structure of **1** is shown in Figure 1, crystallographic date are summarized in Table I, while selected structural parameters are listed in Table II.

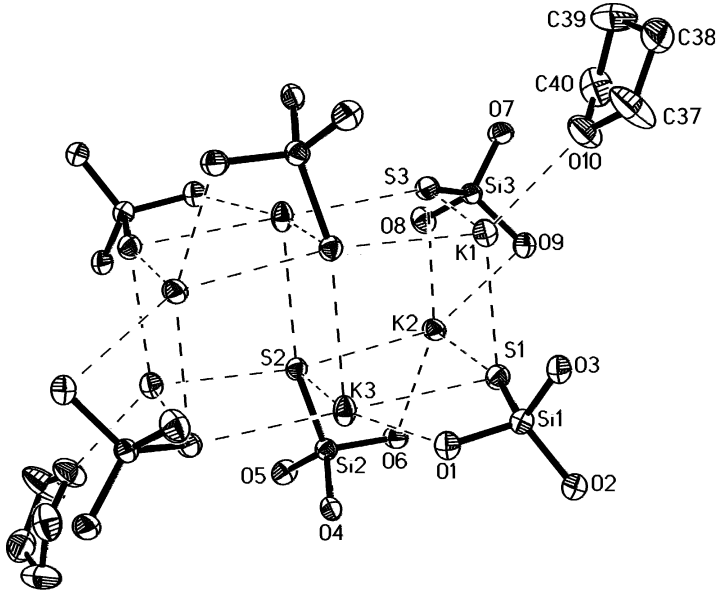


FIGURE 1 The molecular structure of **1**, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. All *tert*-butyl groups and hydrogen atoms have been omitted for clarity.

TABLE I Crystallographic Data, Measurement Conditions, and Refinement Parameters for Compounds 1–3

Compound	1	2	3
Diffractometer	KUMA KM4	KUMA KM4	KUMA KM4
Radiation	Mo Kα,/graphite	Mo Kα,/graphite	Mo Kα,/graphite
Empirical formula	$C_{88}H_{194}K_6O_{22}S_6Si_6$	$C_{24}H_{54}K_2O_6S_2Si_2$	$C_{54}H_{122}K_4O_{16}S_4Si_4$
Formula weight	2199.93	637.19	1424.52
Crystal size, mm	0.4 × 0.4 × 0.2	0.4 × 0.1 × 0.1	0.4 × 0.3 × 0.3
Temperature, K	150	150	200(2)
Crystal system	Monoclinic	Triclinic	Tetragonal
Space group	$P2_1/c$	$P\bar{1}$	P-4b2
a, Å	15.227(4)	11.6305(14)	20.854(3)
b, Å	14.650(5)	13.348(3)	20.854(3)
c, Å	32.067(9)	13.531(4)	9.283(2)
α,°	90	67.27(2)	90
β,°	117.001(18)	76.064(16)	90
γ,°	90	88.706(14)	90
Volume, Å^3	6374(3)	1874.6(8)	4037.1(12)
Z	2	2	2
d_x, gcm^{-3}	1.146	1.129	1.172
μ,mm^{-1}	0.414	0.458	0.435
2θmax,°	50.1	56	51
No. reflections collected	36760	16166	7359
No. of independent reflections	11837	8991	3566
R(int)	0.1344	0.09	0.0887
Data/restraints /parameters	11837/21/630	8991/0/344	3566/0/187
Goodness of fit	1. 790	1.163	1.109
Final R indices [I>2σ(I)]	R = 0.1545	R = 0.1169	R = 0.0639
	R_w = 0.4261	R_w = 0.2684	R_w = 0.1536
Final R indices [all data]	R = 0.1752	R = 0.1667	R = 0.1035
	R_w = 0.4590	R_w = 0.3067	R_w = 0.1824

Standard deviations are in parentheses.

Compound **1** crystallizes as a hexameric molecule. The overall geometry may be described as an array of trimers of dimers—three dimeric units form a box-shaped molecular or face-fused cuboidal geometry. An asymmetric unit contains half of the hexamer, while the second half of the hexamer is generated by a center of symmetry located in the central K_2S_2 ring. In addition, one THF solvent molecule is identified in each asymmetric unit. Each S atom is attached to one R group and is connected to three or four potassium atoms in the outer and central units, respectively. The geometry of the potassium atoms located in the

TABLE II Selected Bond Lengths and Angles for 1, 2, and 3

$[(^t\text{BuO})_3\text{SiSK}]_6[\text{THF}]_2\cdot 2\text{THF}$ (**1**)			
S(1)-Si(1)	2.058(2)	K(1)-S(2)	3.186(2)
S(2)-Si(2)#1	2.069(2)	K(1)-S(3)	3.255(2)
S(3)-Si(3)	2.054(2)	K(2)-O(6)	2.691(5)
O(1)-Si(1)	1.651(5)	K(2)-O(9)	2.887(5)
O(2)-Si(1)	1.632(5)	K(2)-S(1)	3.120(2)
O(3)-Si(1)	1.648(5)	K(2)-O(8)	3.162(6)
O(4)-Si(2)	1.646(5)	K(2)-S(2)#1	3.163(2)
O(5)-Si(2)	1.639(5)	K(2)-S(3)	3.213(2)
O(6)-Si(2)	1.658(5)	K(3)-O(1)	2.719(4)
O(7)-Si(3)	1.624(5)	K(3)-S(2)#1	3.165(2)
O(8)-Si(3)	1.654(5)	K(3)-S(3)#1	3.241(2)
O(9)-Si(3)	1.655(5)	K(3)-S(1)	3.277(2)
K(1)-O(10)	2.834(6)	K(3)-O(4)	3.412(5)
K(1)-S(1)	3.166(2)	K(3)-S(2)	3.503(3)
O(1)-K(3)-S(1)	58.64(10)	S(1)-K(1)-S(3)	90.48(6)
S(2)#1-K(3)-S(1)	94.51(5)	S(2)-K(1)-S(3)	86.98(5)
S(3)#1-K(3)-S(1)	177.80(6)	O(10)-K(1)-S(1)	132.55(17)
O(1)-K(3)-S(2)	90.90(11)	O(10)-K(1)-S(2)	129.03(18)
S(2)#1-K(3)-S(2)	94.97(6)	S(1)-K(1)-S(2)	95.62(6)
S(3)#1-K(3)-S(2)	91.27(5)	O(10)-K(1)-S(3)	105.21(15)
S(1)-K(3)-S(2)	87.86(6)	O(6)-K(2)-S(1)	96.41(12)
K(2)-S(1)-K(1)	90.19(6)	O(9)-K(2)-S(1)	99.87(12)
K(2)-S(1)-K(3)	83.12(5)	O(6)-K(2)-O(9)	135.84(15)
K(1)-S(1)-K(3)	90.40(6)	S(1)-K(2)-S(2)#1	97.72(6)
K(2)#1-S(2)-K(3)#1	84.28(5)	O(6)-K(2)-S(2)#1	61.22(11)
K(2)#1-S(2)-K(1)	169.41(7)	O(9)-K(2)-S(2)#1	153.05(12)
K(3)#1-S(2)-K(1)	93.83(6)	O(6)-K(2)-S(3)	158.69(12)
K(2)#1-S(2)-K(3)	83.34(5)	O(9)-K(2)-S(3)	60.88(11)
K(3)#1-S(2)-K(3)	85.03(6)	S(1)-K(2)-S(3)	92.08(6)
K(1)-S(2)-K(3)	86.12(5)	S(2)#1K(2)-S(3)	98.33(6)
K(2)-S(3)-K(3)#1	86.91(6)	O(1)-K(3)-S(2)#1	152.32(11)
K(2)-S(3)-K(1)	87.01(6)	O(1)-K(3)-S(3)#1	119.38(11)
# 1 –x, -y, -z+1			
$\{[(^t\text{BuO})_3\text{SiS}]_2\text{K}_2\}_n$(**2**)			
S(1)-Si(1)	2.047(2)	K(1)-O(1)	2.757(5)
S(2)-Si(2)	2.047(2)	K(1)-O(4)	2.941(5)
Si(1)-O(1)	1.651(4)	K(1)-S(2)#1	3.119(2)
Si(1)-O(2)	1.640(5)	K(1)-S(1)	3.1435(19)
Si(1)-O(3)	1.641(5)	K(1)-S(2)	3.310(2)
Si(2)-O(4)	1.638(4)	K(2)-S(1)	3.117(2)
Si(2)-O(5)	1.618(5)	K(2)-S(1)#2	3.1046(19)
Si(2)-O(6)	1.655(4)	K(2)-S(2)	3.094(2)
S(1)-K(2)#2	3.1046(19)	K(2)-O(6)	2.670(4)
S(2)-K(1)#1	3.119(2)		
O(1)-Si(1)-O(3)	105.0(3)	S(2)#1-K(1)-S(1)	134.00(7)

(Continued on next page)

TABLE II Selected Bond Lengths and Angles for 1, 2, and 3 *(Continued)*

O(1)-Si(1)-O(2)	110.8(2)	O(1)-K(1)-S(2)	148.60(10)
O(3)-Si(1)-O(2)	103.6(3)	O(4)-K(1)-S(2)	58.94(9)
O(1)-Si(1)-S(1)	106.15(18)	S(2)#1-K(1)-S(2)	92.49(6)
O(3)-Si(1)-S(1)	115.3(2)	S(1)-K(1)-S(2)	94.38(5)
O(2)-Si(1)-S(1)	115.5(2)	O(6)-K(2)-S(2)	61.11(10)
O(5)-Si(2)-O(4)	105.0(2)	O(6)-K(2)-S(1)#2	143.11(10)
O(5)-Si(2)-O(6)	110.2(2)	S(2)-K(2)-S(1)#2	151.50(7)
O(4)-Si(2)-O(6)	104.0(2)	O(6)-K(2)-S(1)	93.48(11)
O(5)-Si(2)-S(2)	117.9(2)	S(2)-K(2)-S(1)	99.36(6)
O(4)-Si(2)-S(2)	113.62(18)	S(1)#2-K(2)-S(1)	94.18(6)
O(6)-Si(2)-S(2)	105.32(17)	K(2)#2-S(1)-K(2)	85.82(6)
O(1)-K(1)-O(4)	116.62(15)	K(2)#2-S(1)-K(1)	165.11(7)
O(1)-K(1)-S(2)#1	118.10(11)	K(2)-S(1)-K(1)	82.14(5)
O(4)-K(1)-S(2)#1	101.20(9)	K(2)-S(2)-K(1)	79.86(5)
O(1)-K(1)-S(1)	59.92(9)	K(2)-S(2)-K(1)#1	147.40(7)
O(4)-K(1)-S(1)	121.08(9)	K(1)#1-S(2)-K(1)	87.51(6)
# 1 -x, -y + 1, –z # 2 -x + 1, -y + 1, -z			
	$[(t\text{-}BuO)_3SiSK]_4[H_2O]_4 \cdot C_6H_6$ (**3**)		
S(1)-Si(1)	2.0592(18)	K(1)-S(1)#1	3.1345(19)
Si(1)-O(1)	1.640(4)	K(1)-S(1)#2	3.3849(19)
Si(1)-O(2)	1.634(4)	S(1)-K(1)#2	3.1345(19)
Si(1)-O(3)	1.652(3)	S(1)-K(1)#1	3.3849(19)
K(1)-O(3)	2.753(4)	0(1)-C(10)	1.450(6)
K(1)-O(7)	2.851(4)	O(2)-C(20)	1.438(7)
K(1)-S(1)	3.2177(17)	O(3)-C(30)	1.458(6)
O(3)-K(1)-O(7)	116.01(11)	S(1)#1-K(1)-S(1)#2	94.22(5)
O(3)-K(1)-S(1)#1	154.01(8)	S(1)-K(1)-S(1)#2	90.61(5)
O(7)-K(1)-S(1)#1	89.76(9)	O(1)#1-K(1)-S(1)#2	151.55(8)
O(3)-K(1)-S(1)	59.61(7)	K(1)#2-S(1)-K(1)	88.99(5)
O(7)-K(1)-S(1)	171.28(10)	K(1)#2-S(1)-K(1)#1	85.76(5)
S(1)#1-K(1)-S(1)	95.31(5)	K(1)-S(1)-K(1)#1	84.77(4)
O(3)-K(1)-O(1)#1	112.94(11)	O(2)-Si(1)-O(1)	105.0(2)
O(7)-K(1)-O(1)#1	96.40(11)	O(2)-Si(1)-O(3)	110.55(18)
S(1)#1-K(1)-O(1)#1	57.34(7)	O(1)-Si(1)-O(3)	104.98(19)
S(1)-K(1)-O(1)#1	92.31(8)	O(2)-Si(1)-S(1)	115.13(15)
O(3)-K(1)-S(1)#2	92.84(9)	O(1)-Si(1)-S(1)	113.69(16)
O(7)-K(1)-S(1)#2	81.92(9)	O(3)-Si(1)-S(1)	107.08(14)
# 1 -y + 1, x, -z +1 # 2 y, -x + 1, -z + 1			

outer K_2S_2 rings is defined by their position as "corner" atoms in the hexamer. There are two different potassium atoms in the outer K_2S_2 dimeric unit. Each of the outer potassium atoms is bound to three sulfur atoms of thiolate ligands with angles close to 90 degrees. One of them, K(1), is additionally connected to an oxygen atom from THF molecule, giving distorted tetrahedral geometry. Each K(2) potassium atom is five-coordinated and is additionally bound to two oxygen atoms that

come from the two tert-butoxy group of the two different silanethiolate ligands.

The potassium atoms located in the central K_2S_2 ring are pentacoordinated and are connected to four S atoms of silanethiolate ligands displaying angles of 90 degrees and 180 degrees,respectively. In addition, each K(3) potassium atom is connected to one oxygen atom from the tert-butoxy group of the silanethiolate ligand. Different K-S distances for the three potassium centers are observed. The longest K—S bond is found for five-coordinate K(3) in the central K_2S_2 dimeric unit (3.296 Å average), and the shortest metal contacts for the five-coordinate K(2) centers in the outer K_2S_2 ring (3.165 Å average). The K(1)–O(10) (from THF) distance is found to be 2.834 Å; the other potassium–oxygen distances observed for the five-coordinate potassium centers range form 2.691 Å to 2.887 Å. The sulfur–silicon distance is 2.060(2) Å (average).

$\{[(^tBuO)_3SiS]_2K_2\}_n$ (2)

Shown in Figure 2, it exhibits a two-dimensional, polymeric, puckered, ladder-type structure with alternating potassium and silicon atoms arranged in nearly square planar K_2S_2 arrangements.

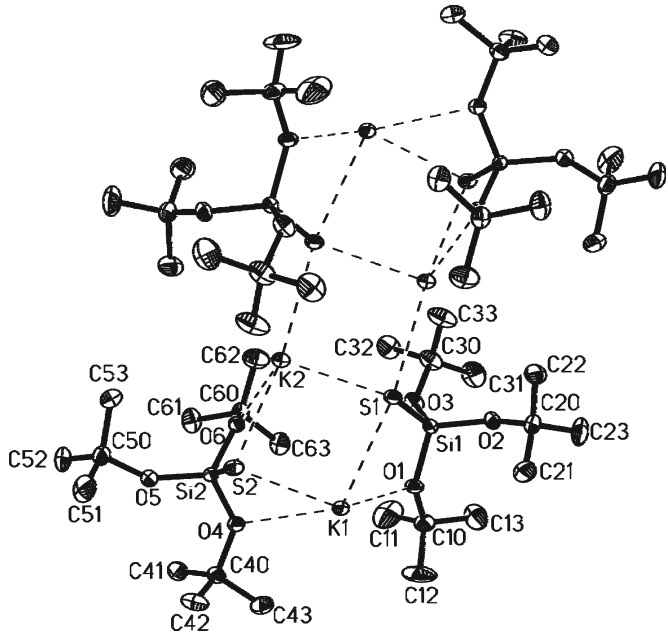


FIGURE 2 The molecular structure of **2**, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. All hydrogen atoms have been omitted for clarity.

This compound shows example of two different coordination spheres. At potassium K(1), atoms are pentacoordinated, exhibiting three bonds and two oxygen bonds. The coordination at potassium K(1) can be described as distorted trigonal bipiramidal with angles at the potassium between 58.94(9)degrees and 148.60(10) degrees. The potassium K(2) atoms are four-coordinate, with three atoms and one oxygen atom in a distorted tetrahedral coordination geometry and angles at the potassium ranging from 61.11(10) degrees to 151.50(7) degrees. The potassium bonds are on average slighly longer for the five-coordinate [3.19(2) Å average] then for the four-coordinate [3.10(2) Å average] potassium centers. Accordingly, longer potassium–oxygen bonds [2.85(5) Å average] are observed for the five-coordinate then for the four-coordinate [2.670(4) Å] potassium atoms.

The sulfur–silicon distance is found at 2.047(2) Å. Important crystallographic data are summarized in Table I, while selected structural parameters are listed in Table II. The polymeric nature of **2** is shown in Figure 3.

[(^{t}BuO)$_3$SiSK]$_4$[H$_2$O]$_4$·C$_6$H$_6$ (3)

Shown in Figure 4; crystallographic data for **3** are summarized in Table I, and selected structural parameters are listed in Table II. This compound crystallizes as a tetrameric molecule with a cuboidal geometry. Each metal atom is five-coordinate by three silicons and two

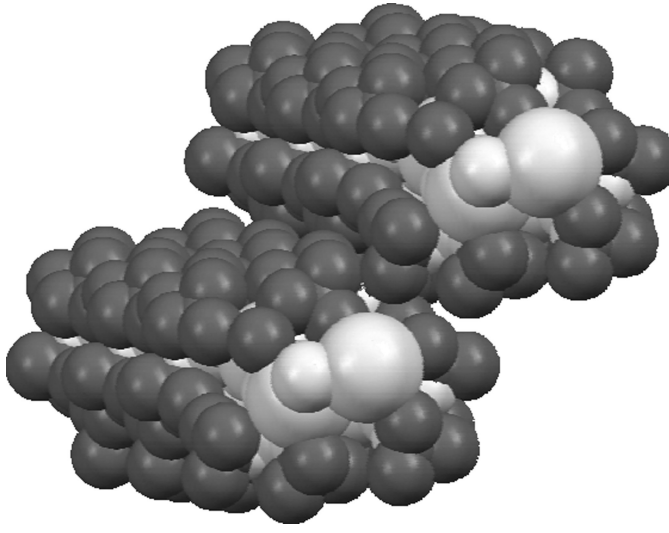


FIGURE 3 Visualization of the polymeric nature of **2** showing internal hydrophilic core and external hydrophobic coat.

TABLE III Hydrogen Bonds in Compound 3

D–H···A	d(D–H) /Å	D(H···A) /Å	d(D···A) /Å	<(DHA) /°
O(7)–H(7A)···O(7)#1	0.88	2.01	2.850(6)	158.2
O(7)–H(7B)···S(1)#2	0.88	2.51	3.273(4)	142.1

Symmetry codes: #1: x, –y+1, –z +2; #2: x, y, z+1

oxygens, with a distorted trigonal bipiramidal geometry at each potassium. The geometry of the potassium atoms is partially defined by their position as "corner" atoms in the tetramer; therefore S–K–S angles close to 90 degrees are observed. One of the oxygen atoms O(3) is donated by the tert-butoxy group of silanethiolate ligand and the second, O(7), by a water molecule. Angles at potassium atom range between 57.34(7) degrees and 171.28(10) degrees, potassium distances are located between 3.134(19) Å and 3.385(19) Å, while the potassium–oxygen bonds are 2.753(4) Å for O(3) oxygen atoms and 2.851(4) Å for O(7) atoms from water molecules. The sulfur–silicon distance is found to be 2.059(18) Å.

The intermolecular hydrogen bond system (Table III) in **3** is shown in Figure 5. The intermolecular hydrogen bonds are shown with a dashed line.

Hydrogen bonds are grouped in the hydrophilic core, while the organic, hydrocarbon groups form hydrophobic coat in the crystal. This is a common feature for many polymeric structures having a polar inside core and a non-polar outside coat (see Figure 6).

EXPERIMENTAL

All manipulations were carried out using a standard vacuum and N_2 line and Schlenk techniques. The starting $(^tBuO)_3SiSH$ was prepared according to the literature.[15] The solvents were dried by standard methods and were distilled under argon prior to use. Elemental analyses were performed on an Elemental Analyzer Ea 1108 (Carlo Erba Instruments).

Tetrakis[μ_3-(tri-*tert*-butoxysilanethiolate)]bis[μ_4-(tri-*tert*-butoxysilanothiolate)]bis(tetra-hydrofuran)hexapotassium(I) Tetrahydrofuran (1)

To 5 mL (16.5 mmol) of tri-*tert*-butoxysilanethiol, 0.66 g (17 mmol) of metallic potassium was added. The mixture was stirred and heated until the potassium was covered with a white precipitate and the reaction stopped. The precipitate was dissolved in 10 mL THF. The solution

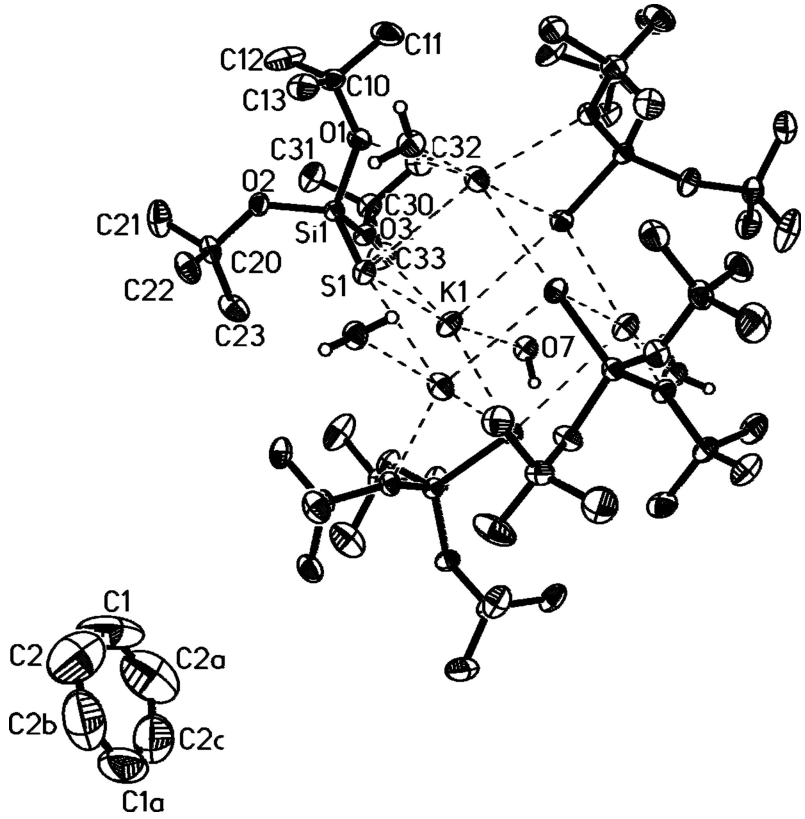


FIGURE 4 The molecular structure of **3**, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms from *tert*-butyl groups have been omitted for clarity.

was separated from metal by filtration. Limpid solution was left at 0–5°C. After one week, colorless crystals were obtained. The crystals were labile and decomposed quickly.

Catena-poly-bis[μ_3-(tri-tert-butoxysilanethiolate)] dipotassium(I) (2)

To 5 mL (16.5 mmol) tri-*tert*-butoxysilanethiol, 0.70 g (18 mmol) of metallic potassium was added. The mixture was stirred and heated, yielding a white precipitate. The precipitate was dissolved in 25 mL THF. The solution was separated from potassium metal by filtration. Limpid solution was left for slow crystallization at 0–5°C. After two

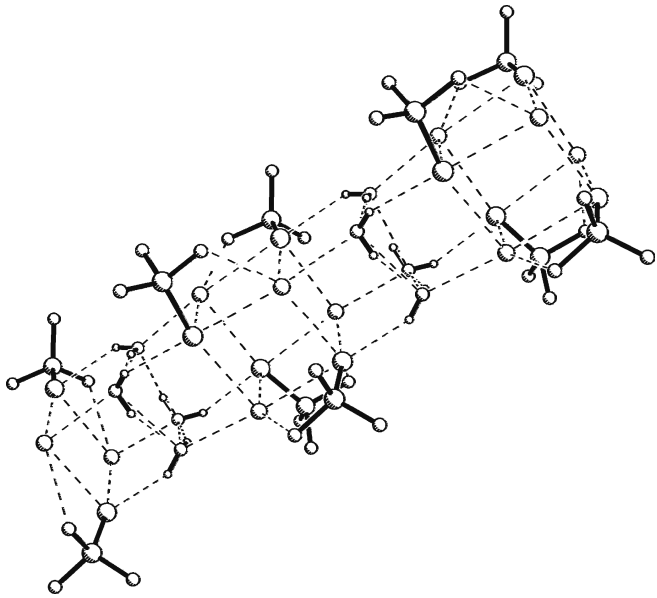


FIGURE 5 Packing diagram for **3**. For better presentation of the H-bond network, all *tert*-butyl groups are omitted.

weeks, colorless crystals were obtained. $C_{24}H_{54}O_6S_2Si_2K_2$ (637.19): Calculated (%): C, 45.2; H, 8.5; S, 10.0; Found: C, 46.3; H, 8.9; S, 9.6.

Tetraaqua-tetrakis[μ_3-(tri-tert-butoxysilanethiolate)] tetrapotassium(I) Benzene Solvate (3)

To 5 mL (16.5 mmol) tri-*tert*-butoxysilanethiol, 0.72 g (20 mmol) of metallic potassium was added. The mixture was stirred and heated,

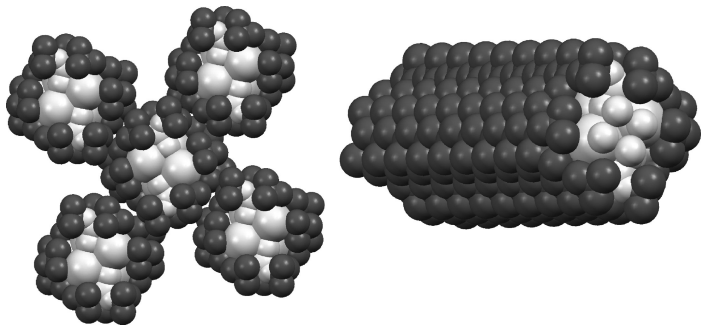


FIGURE 6 Visualization of polymeric nature of (**3**) showing internal hydrophilic core and external hydrophobic coat.

yielding a white precipitate. The precipitate was dissolved in 10 mL benzene. The solution was separated from metal by filtration. Limpid solution was allowed to stand at room temperature; slow crystallization afforded colorless crystals. $C_{54}H_{122}O_{16}S_4Si_4K_4$ (1424.52): Calculated (%): C, 45.5; H, 8.6; S, 9.0; Found: C, 46.8; H, 9.1; S, 9.6; Mp 202–203°C (decomposition).

X-Ray Diffraction Measurements

The crystals were removed from the Schlenk tube and immediately covered with a layer of viscous hydrocarbon oil. A suitable crystal was selected under a microscope, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream of the diffractometer. Diffraction date was recorded on a KUMA KM4 diffractometer with graphite-monochromated M_0K_α radiation, equipped with Sapphire 2 CCD camera (Oxford Diffraction). Numerical absorption corrections were applied. The structures have been solved by direct methods and refined with the SHELX-97[16] software package. All non-hydrogen atoms have been refined in anisotropic approximation. Hydrogen atoms were refined in a geometrically idealized position with isotropic temperature factors 1.2 times the equivalent isotropic temperature factors U_{eq} of their attached atoms (1.5 for CH_3 groups). One *tert*-butyl group in (**1**) was found disordered in two positions: C30–C32 with probabilities of 0.54(2) and 0.46(2). Disorder in (**1**) in the THF molecules: C41–C44 (s.o.f 0.554(17)/0.446(17)).

Crystallographic data for the structures **1**, **2**, and **3** have been deposited with the Cambridge Crystallographic Data Centre, 670202–670204,(respectively. Copies of the data can be obtained free of charge upon application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code +(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk; e-mail for deposition: deposit@ccdc.cam.ac.uk).

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