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Intramolecular Interactions in Crystals of Tris(2,6-diisopropylphenoxy)silanethiol and Its Sodium Salts

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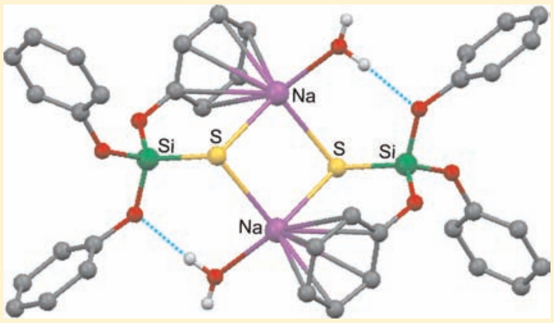
Supporting Information

ABSTRACT: Hydrolytically stable silanethiol tris(2,6-diisopropylphenoxy)-silanethiol (TDST) has been synthesized and reacted with sodium metal. In solid state TDST exhibits π-interactions between the S−H unit and the π-system of the arene, replaced by cation-π interactions in its sodium salts. The interactions are documented by crystal structures and FT-IR spectroscopy.



1. INTRODUCTION

Most silicon—sulfur compounds are very susceptible to hydrolysis.[1−3] Yet the enclosure of the silicon−sulfur bond by a hydrophobic environment slows down or almost entirely prevents the reaction with water, hampering the access of molecules of water to the positively charged atom of silicon. Tri-*tert*-butoxysilanethiol (TBST) was the first silicon−sulfur compound protected against hydrolysis in this way.[2] TBST was used to synthesize a large number of thiolate complexes and salts with main group elements and transition metals, and the reactions were often carried out in biphasic systems consisting of water and organic solvent.[4] Some of the described products were air- and moisture-sensitive depending on the relative stability of their metal−sulfur bonds.[5] Nearly 100 metal tri-*tert*-butoxysilanethiolates were structurally characterized;[6] the bioinorganic aspect of the structural studies was reviewed.[7] Similar bulk tri-*tert*-butylsilyl (supersilyl) thiolates have been used to construct transition-metal centers.[8] Other voluminous protection groups, such as 2,4,6-tris[bis(trimethylsilyl)methyl]-phenyl and 2,4,6-trimethylphenyl have been described to stabilize compounds with silanedithiolate[9] and silanethione functional groups.[10]

Silanethiolate complexes with less sterical hindrance about the silicon atom were usually reported as the potential precursors to metal−sulfur clusters and particles. These included trimethylsilanethiolates,[11] triisopropylsilanethiolate,[12] and triphenylsilanethiolates.[3,13] Mixed-ligand silanethiolate cadmium complexes were probed as precursors of CdS thin films.[14]

Alkali metal thiolates and silanethiolates were often obtained and described as byproducts[15] or substrates for the further synthesis of coordination compounds.[16] Systematic studies undertaken to analyze the influence of metal, ligand, and solvent on the structure of thiolates of group 1 elements were reviewed.[17] Because of the well recognized ability of thiolato ligands to form bridges between metal ions,[18] alkali metal thiolates exhibit the varying extent of aggregation; they crystallize as rare, mononuclear species,[19] common, four-membered M_2S_2 rings,[16,19b,20] ladders,[15,20c,21] cubanes,[8a,16b,21b] or other coordination oligomers and polymers.[19b,20c,d,21b,22] The aggregation can be prevented by the increase of the steric hindrance of thiolato ligand[7,18,19a,20] and/or addition of coligands such as tetrahydrofuran[16b,19,20c,d] or *N*,*N*,*N*′,*N*′-tetramethylethylenediamine.[16a,19b,20c,21a,22a] It is possible to obtain crystalline compounds with separate or contact thiolato anions and alkali metal cations surrounded either by water[13a] or crown ethers.[19b,20c,22b,23] Quite unusual ion pairs of different character, $2Li(TBST)_2^-$ $Li_2(D_2O)_6^{2+}$[24] and $Na(TBST)_2^-$ $Na(DME)_2^+$,[25] were structurally characterized by the researchers from our department. Introduction of other functional groups into the molecule of thiol greatly influences the structure of the resulting alkali metal thiolate (e.g., ref 26), but this research is not reviewed in detail here.

In this paper we present the continuation of our studies on silicon−sulfur compounds stabilized by the presence of bulky organoxy substituents on silicon atom. With the method developed by Wojnowski and Piękoś[27] we have obtained new aryloxysilanethiols. The crystal structure of tri(mesityloxy)-silanethiol (TMST) was communicated in 2010.[28] Herein we describe the new member of the family, highly resistant toward hydrolysis tris(2,6-diisopropylphenoxy)silanethiol, TDST. The synthesis of sodium salt of TDST is reported with the prospect

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of further utilization in a synthetic route to transition metal-chalcogenolates. The intra- and intermolecular interactions in the title compounds are characterized by X-ray diffraction and FT-IR spectroscopy.

2. EXPERIMENTAL SECTION

2.1. Synthesis - General Remarks. *n*-Hexane was dried over Na/K and distilled under nitrogen prior to use. Silicon disulfide (raw material that contained 45% of pure SiS_2 as confirmed by the analysis of sulfides content) was obtained by the direct reaction of sulfur and silicon. 2,6-Diisopropylphenol (Alfa-Aesar, 97%) and toluene were used as purchased. Naphtho-15-crown-5 was synthesized as described in ref 29 and purified as in ref 30.

Elemental analyses were performed on an Elemental Analyzer EA 1108 (Carlo Erba Instruments).

*2.1.1. Synthesis of Tris(2,6-diisopropylphenoxy)silanethiol TDST (**1**).* TDST was obtained by phenolysis of SiS_2 as described for tris(2,6-dimethylphenoxy)silanethiol[27c] and tri(mesityloxy)silanethiol (TMST)[28] SiS_2 (54.4 g) and 2,6-diisopropylphenol (257 g) were stirred and heated for 80 h in 150−180 °C under the stream of nitrogen. After that 250 mL of toluene was added to the reaction mixture, and the unreacted SiS_2 was removed by centrifugation. Toluene and the excess phenol were removed by vacuum distillation. The crude red-brownish solid (32 g, ∼20% yield with regard to SiS_2) was dissolved in *n*-hexane. Large colorless crystals of TDST (see Supporting Information) were obtained at 0 °C. Melting point: 105.3 °C, Anal. Calcd.: C-72.9; H-8.84; S-5.41; Anal. Found: C-72.8; H-8.75; S-5.42, ^{1}H NMR (500 MHz) in $CDCl_3$: δ 0.50 (s, 1H), 1.12 (d, 36H), 3.53 (sept, 6H), 6.95 (m, 3H), 7.01 (d, 6H) ppm. ^{13}C NMR (125 MHz) in $CDCl_3$: δ 23.81 ($CH(CH_3)_2$), 27.58 ($CH(CH_3)_2$), 124.16 (aromatic ring 4-C), 124,20 (aromatic ring 3,5-C), 139.31 (aromatic ring 2,6-C), 148.00 (aromatic ring *C*−O-Si). FT-IR (solid, cm^{-1}) 3073 m, 3026 m, 2970vs, 2931vs, 2872s, 2552 m, 1930w,br, 1868w, 1853w, 1752w,br, 1718w, 1703w, 1659w, 1591w, 1465s, 1443vs, 1383 m, 1362 m, 1329s, 1257s, 1189vs, 1157w, 1115s, 1107 m,sh, 1046s, 973vs, 934s,sh, 884w, 795 m, 790w,sh, 755vs FT-IR (solution in carbon tetrachloride, cm^{-1}) 3141w, 3067w, 3026vw, 2967vs, 2930 m, 2906 m,sh, 2870 m, 2758w, 2691w, 2657w,sh, 2558w, 2531vw,sh, 1615w, 1588vw, 1465s, 1441vs, 1384 m, 1363 m, 1340 m,sh, 1330s, 1270 m, 1257s, 1187vs, 1163w,sh, 1148w, 1113 m, 1099 m, 1058w, 1047 m, 975vs, 935 m, 882vw, 790vs, 653 m, 644 m,sh, 624vw, 587w,sh, 576w,sh, 564 m, 534 m, 504w, 444vw, 422w.

*2.1.2. Synthesis of Sodium Tris(2,6-diisopropylphenoxy)-silanethiolate (**2**).* TDST (0.500 g, 0.843 mmol) was dissolved in *n*-hexane (20 mL). To the solution of TDST an excess of sodium (0.046 g, 2 mmol) was added. The reaction mixture was stirred and heated for 2 days under nitrogen. White powder of sodium tri(2,6-diisopropylphenoxy)silanethiolate was separated with the reversing frit (under nitrogen) and vacuum-dried. Yield of **2** approximately 60% (the pieces of sodium were removed mechanically under the stream of nitrogen and the remaining white powder was weighed in a nitrogen-filled flask). Anal. Calcd. $C_{72}H_{102}O_6S_2Si_2Na_2$ (MW 1229.9) C-70.31; H-8.36; S-5.21. Anal. Found: C-70.08; H-8.74; S-4.93. ^{1}H NMR (500 MHz) in C_6D_6: δ 1.21 (d, 72H), 3.81 (sept, 12H), 6.88 (t, 6H), 7.03 (d, 12H) ppm, the admixture of *n*-hexane visible at 0.89 ppm (triplet, 1 molecule per 6 molecules of thiolato residue). ^{13}C NMR (125 MHz) in C_6D_6: δ 23.98 ($CH(CH_3)_2$), 27.61 ($CH(CH_3)_2$), 122.80 (aromatic ring 4-*C*), 123,80 (aromatic ring 3,5-C), 140.62 (aromatic ring 2,6-*C*), 150.05 (aromatic ring *C*−O-Si), the admixture of *n*-hexane visible as three signals of small intensity at 14.31, 23.01, 31.92 ppm. Hydration of sodium thiolate was observed in the FT-IR spectra obtained in the air (very weak bands at 3413 and 3178 cm^{-1}, the spectrum is presented in the Supporting Information, Figure 5S. FT-IR (solid, white precipitate, cm^{-1}) 3413w,br, 3178w,br, 3073 m,sh, 3063w, 3025w, 2965vs, 2928vs, 2901s,sh, 2868s, 2751w, 2718w, 2707w, 1912w, 1851w, 1588w, 1466vs, 1451s, 1441s, 1381 m, 1360s, 1348w, 1334s, 1297w, 1258vs, 1199vs, 1158w, 1138 m,sh, 1111vs, 1060 m, 1047 m, 1018 m, 933vs, 902 m, 881 m, 864w,sh, 841w, 799 m, 758s, 734 m.

*2.1.2.1. {μ-Tris(2,6-diisopropylphenoxy)silanethiolato-κ^2-O:S:O′:S′}-sodium-{μ-tris(2,6-diisopropylphenoxy)silanethiolato-κ^7-η^6C25,C26,C27,C28,C29,C30:S:η^6C25′,C26′,C27′,C28′,C29′,C30′:S′}-sodium n-Hexane Solvate (**3**).* Slow crystallization of **2** from diluted *n*-hexane solution at room temperature yielded few crystals of **3**. which were characterized by X-ray diffraction.

*2.1.2.2. Di-aqua-Bis{μ-tris(2,6-diisopropylphenoxy)silanethiolato-κ^8-S:S′:η^6C25,C26,C27,C28, C29,C30}-disodium (**4**).* Recrystallization of **2** from commercial *n*-hexane at room temperature produced crystals of **4** suitable for X-ray analysis. FT-IR (solid, cm^{-1}) 3666s, 3407s, 3200w, 3067w, 3020w, 2968vs, 2935s,sh, 2870s, 2810w, 1619 m, 1587w, 1462s, 1440vs, 1382 m, 1361 m, 1331s, 1253s, 1203 m,sh, 1192s, 1181s, 1164w,sh, 1109 m, 1098 m, 1059w, 1044 m, 940s, 909s, 880 m, 800 m, 762vs, 734 m.

*2.1.3. Synthesis of Tris(2,6-diisopropylphenoxy)silanethiolate of Naphtho-15-crown-5 Complexed Sodium (**5**).* **2** (0.01043 g, 1.696 × 10^{-5} mol) and naphtho-15-crown-5 (0.01079 g, 3.393 × 10^{-5} mol) were dissolved in a mixture of 1 mL of *n*-hexane and 1 mL of toluene. The reaction mixture which was kept in the temperature of 255 K yielded few colorless crystals of **5**. FT-IR (solid, cm^{-1}) 3565 m,vbr, 3235 m,br, 3058 m, 3024 m, 2959vs, 2938s,sh, 2921vs, 2864s, 1631 m, 1603 m, 1588w, 1512s, 1491s, 1461vs, 1452vs, 1418s, 1377 m, 1361 m, 1348 m, 1335s, 1292w, 1268vs, 1252s,sh, 1201s, 1183s, 1149 m,sh 1132vs, 1106s, 1080s, 1056vs, 1048vs, 945 m, 940 m, 914vs, 881w, 864 m, 852 m, 838w, 796 m, 756s, 740vs.

2.2. Physical Measurements. *2.2.1. X-ray Crystallographic Analysis.* Experimental diffraction data were collected on KM4CCD kappa-geometry diffractometer, equipped with a Sapphire2 CCD detector. Enhanced X-ray MoK_α radiation source with a graphite monochromator was used. Determination of the unit cells and data collection were carried out at 120 K. Data reduction, absorption correction, and space group determination were made using the CrysAlis software package (Oxford Diffraction, 2008).[31] Solutions and refinements were carried out using the SHELX-97 program package.[32]

Structures of **1**, **3**, **4**, **5** were solved by direct methods, and all non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares procedure based on F^2. Hydrogen atoms were usually refined using the isotropic model with *Uiso*(H) values fixed to be 1.5 times *Ueq* of C atoms for CH_3 or 1.2 times *Ueq* for CH_2 and CH groups. Hydrogen of SH bond in **1** and hydrogens of OH bonds in **4** were positioned from differential electron-density maps and refined freely. In crystals of **3** there is a disordered *n*-hexane molecule, which lays in a special position on a 2-fold axis. It was refined with the occupancy ratio 50:50. A summary of the crystallographic data for **1**, **3**, **4**, **5** is listed in Table 1.

2.2.2. FT-IR Spectra. FT-IR spectra of solids were measured with a Momentum microscope (IR detector) attached to a Mattson Genesis II Gold spectrometer (IR source). Spectra acquisition was controlled by WINFIRST software package

FT-IR spectra of TBST solutions were recorded in ATR mode on a Nicolet 8700 FT-IR spectrometer, using the Turbo mode of the EverGlo infrared source. A total of 128 scans were made with a selected resolution of 4 cm^{-1}. Spectra acquisition was controlled by the OMNIC 7.2a software package (Thermo Electron Corporation, Madison, WI). Thereafter the spectra were transformed to GRAMS file format and analyzed using GRAMS/32 software (Galactic Industries Corporation, Salem, MA) and RAZOR program (Spectrum Square Associates, Ithaca, NY) run under GRAMS/32. This analysis was also carried out for FT-IR spectra of solid **4**.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Molecular Structure. Similar to its predecessor compounds tri(*o*-xylenoxy)silanethiol and tri-(mesityloxy)silanethiol (TMST),[27c,28] tris(2,6-diisopropylphenoxy)-silanethiol (TDST) was isolated as the only product of the reaction between SiS_2 and 2,6-diisopropylphenol. The reaction was carried out in a high temperature of 180 °C under nitrogen. The high temperature favors the formation of silanethiol,[27c] and the atmosphere of nitrogen prevents combustion of the phenol

Table 1. Crystal Data and Structure Refinement Parameters for Compounds 1, 3, 4, 5

	1	**3**	**4**	**5**
empirical formula	$C_{36}H_{52}O_3SSi$	$C_{78}H_{116}Na_2O_6S_2Si_2$	$C_{72}H_{106}Na_2O_8S_2Si_2$	$C_{86}H_{111}NaO_{13}SSi$
formula weight	592.93	1315.99	1265.85	1435.89
temperature/K	120(2)	120(2)	120(2)	120(2)
wavelength (Mo K_α)/Å	0.71073	0.71073	0.71073	0.71073
crystal system	monoclinic	orthorhombic	triclinic	triclinic
space group	*Cc*	$P2_12_12$	$P\bar{1}$	$P\bar{1}$
a /Å	11.4061(8)	12.6124(7)	10.7839(5)	15.0557(6)
b /Å	35.0837(9)	24.0235(9)	12.1344(6)	16.9264(8)
c /Å	10.2841(4)	12.7530(4)	16.0385(8)	16.9715(7)
α /deg	90	90	86.689(4)	82.752(4)
β /deg	122.677(4)	90	72.849 (4)	87.179(4)
γ /deg	90	90	66.292(5)	68.636(4)
V /Å ^{3}	3464.0(3)	3864.1(3)	1831.72(15)	3995.6(3)
Z	4	2	1	2
D_c /Mg m^{-3}	1.137	1.134	1.148	1.193
μ /mm^{-1}	0.160	0.161	0.168	0.122
$F(000)$	1288	1428	684	1544
Θ range/deg	2.32 to 25.5	2.33 to 25.5	2.16 to 25.5	2.42 to 25.5
Index ranges	$-13 \le h \le 13$	$-15 \le h \le 15$	$-9 \le h \le 13$	$-14 \le h \le 18$
	$-38 \le k \le 42$	$-11 \le k \le 29$	$-9 \le k \le 14$	$-19 \le k \le 20$
	$-12 \le l \le 12$	$-8 \le l \le 14$	$-19 \le l \le 19$	$-20 \le l \le 20$
reflections collected/unique	10968/5572 [R(int) = 0.0151]	7890/5871 [R(int) = 0.0235]	11349/6812 [R(int) = 0.0243]	25869/14837 [R(int) = 0.0433]
data/restraints/parameters	5572/2/382	5871/2/418	6812/0/408	14837/0/933
goodness of fit on F^2	1.057	1.013	0.949	1.080
final R indices [$I > 2\sigma(I)$]	R_1 = 0.0316	R_1 = 0.0409	R_1 = 0.0404	R_1 = 0.0686
	$w R_2$ = 0.0778	$w R_2$ = 0.104	$w R_2$ = 0.0961	$w R_2$ = 0.1977
R indices (all data)	R_1 = 0.0323	R_1 = 0.0471	R_1 = 0.0573	R_1 = 0.0973
	$w R_2$ = 0.0783	$w R_2$ = 0.1067	$w R_2$ = 0.1008	$w R_2$ = 0.2063
largest diff. peaks [e Å $^{-3}$]	0.256, −0.214	0.765, −0.375	0.509, −0.225	1.143 −0.363
CCDC no.	**830182**	**830184**	**830183**	**830185**

and reaction products. The raw, brownish product was recrystallized from *n*-hexane. The solutions of TDST in hexane showed no signs of decomposition (such as turbidity) even in direct contact with water. TDST easily forms large and well-shaped crystals having a very faint odor of burning rubber (Supporting Information, Figure 1S). The molecular structure of TDST is presented in Figure 1. Important bond lengths and angles are gathered in Table 2. The molecular structure of TDST is similar to the structure of its congener TMST[28] with one exception, which is the position of the SH bond. In TDST the SH hydrogen weakly interacts with one of the phenyl rings, which is seen both in the crystal structure (Figure 2a) and FT-IR spectrum, which will be discussed later. The interaction influences the geometry of the molecule and forces the rotation of one of the phenyl rings so that the weak hydrogen bond can be created. In the structure of TMST the SH bond was initially refined in the "opposite direction" (see Figure 2b).[28] Now we have decided the hydrogen position should rather be refined as disordered between several states. Satisfactory results have been obtained for two-position disorder with hydrogen occupancies 72/28. Position occupied in 28% is analogous to location of H1a in TDST (Figure 2c) whereas in the position occupied in 72% the hydrogen interacts with the phenyl ring of the neighboring molecule of TMST. In this model the isotropic temperature factors of split hydrogen atom substantially decrease, and the overall R factor is lowered by 0.02%. Distances between H1a and carbon atoms of the interacting ring are shorter in TDST than in TMST (see Figure.2 caption). Both the absence of disorder and the shortened distances are logically connected with the growing, electron-releasing effect of alkyl substituents. The corrected cif file and the pictures illustrating different intermolecular interactions in solid TMST and TDST are included in Supporting Information, Figures 2S and 3S.

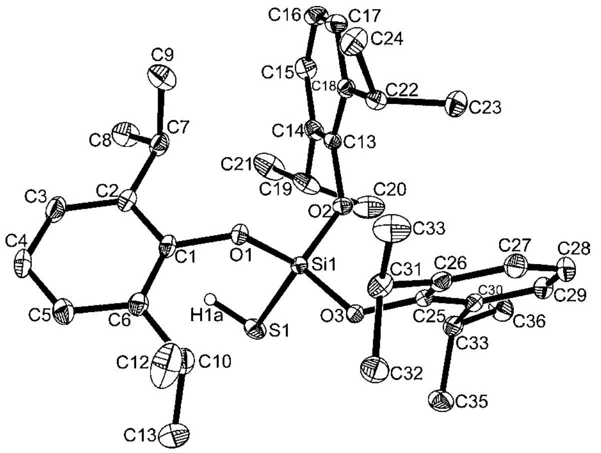


Figure 1. Molecular structure of TDST (**1**). Hydrogen atoms (except for H1a) have been removed for clarity of the picture.

Silicon atom in TDST is surrounded by hydrophobic alkyl substituents and practically inaccessible to solvent molecules which explains its increased resistance toward hydrolysis.

Sodium silanethiolates **2**, **3**, and **4** were obtained in the reaction of sodium metal with TDST in *n*-hexane solution

Table 2. Crystallographic Data for 1–4[a]

	1	3	4	5
		Bond Lengths [Å]		
S1–H1	1.1074			
Na1–Na1^{i}/Na2		3.791(2)	3.7625(14)	
Na1–S1		2.7474(13)	2.7582(9)	
Na1^{i}-S1			2.7631(8)	
Na1–S1^{ii}		2.7474(13)		
Na2–S1		2.7830(14)		
Na1^{i}/Na2–C25		2.833(3)	2.9896(19)	
Na1^{i}/Na2–C26		2.954(3)	2.9567(19)	
Na1^{i}/Na2–C27		3.010(3)	2.8951(19)	
Na1^{i}/Na2–C28		3.033(3)	2.897(2)	
Na1^{i}/Na2–C29		2.965(3)	2.959(2)	
Na1^{i}/Na2–C30		2.881(3)	3.031(2)	
Na1^{i}/Na2–centroid		2.596	2.606	
Na1–O2		2.4327(17)		
Na1–O4				
Si1–S1	2.1145(6)	2.0289(9)	2.0248(7)	2.0053(12)
		Bond Angles [deg]		
Si1–S1–H1	94.1			
Na1–S1–Na1^{i}/Na2		86.54(4)	85.91(2)	
S1–Na1–S1^{i}			94.09(2)	
Si1–S1–Na1		80.82(3)	113.71(3)	
Si1–S1–Na1^{i}/Na2		103.81(3)	112.85(3)	
S1 Na1 S1^{ii}		94.25(6)		
S1 Na2 S1^{ii}		92.68(6)		
O4/O2 Na1 S1		70.98(5)	95.29(5)	
O4/O2 Na1 S1$^{i/ii}$		112.41(6)	126.47(5)	
O2 Na1 O2^{ii}		175.35(13)		
centroid–Na2–centroid^{ii}		132.24		
centroid–Na1/Na2–S1		101.43	97.70	
centroid–Na1/Na2–S1^{i}		111.15	116.73	
O4–Na1–centroid^{i}			123.63	

[a] **3**, ii (1−*x*, 1−*y*, *z*); **4**, i (1−*x*, 1−*y*, −*z*).

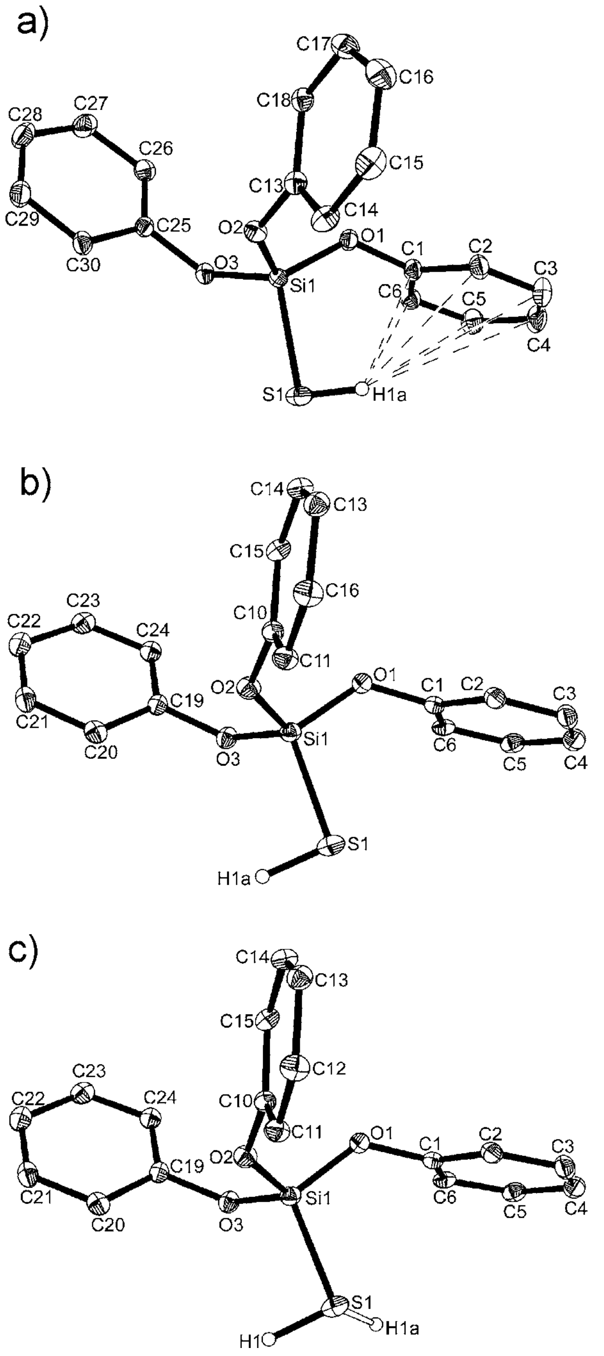


Figure 2. Molecular structures of (a) TDST (**1**), marked distances between and H1a and C1–C6 carbons are between 2.823 −4.444 Å; (b) TMST;[28] (c) TMST-split model, distances between and H1a and C1–C6 carbons are between 3.127 −4.514 Å. Hydrogen atoms (except for H1/H1a) and isopropyl (TDST) or methyl (TMST) substituents have been removed for clarity of the picture.

similar to the sodium thiolates[17] and silanethiolates[25,33] described previously. The reaction in *n*-hexane was rather slow, requiring continuous stirring and heating. The white, powdery precipitate of sodium silanethiolate **2** was separated from the rest of the solution by filtration and characterized by NMR and elemental analysis (see Experimental Section). Two types of crystals (compounds **3** and **4**) that were characterized by X-ray diffraction were obtained from the filtrate. Both of them contained dimeric sodium thiolate.

Compound **3** is a dimeric sodium thiolate with the planar Na_2S_2 core (Figure 3), but each atom of sodium in **3** exhibits different coordination. Na1 is coordinated by two O atoms and two S atoms in a distorted seesaw geometry. Na2 is also tetracoordinated by two S atoms and two aryl groups with the geometry that is closer to the trigonal pyramidal than to tetrahedral (τ_4 = 0.827[34]). The two independent Na–S distances in **3** are 2.7474(13) and 2.7830(14) and Na–O distance is 2.4327(17) Å (Table 2) which is relatively long as the bond constitutes a part of the strained deltoid ring. The Na2-centroid distance of 2.596 Å is significantly shorter than in sodium salts of HSC_6H_3-2,6-Trip$_2$ (2.701 Å) described in 1996 by Niemeyer and Power.[20b] TDST and HSC_6H_3-2,6-Trip$_2$ are compared in Scheme 1. It is probably the result of greater flexibility of phenyl rings in TDST compared to HSC_6H_3-2,6-Trip$_2$ which allows the aryl-cation interaction to strengthen. The coordination manner of arene ligands is similar to that in the sodium-arene complex described in 1990.[35]

The structure of **4** presented in Figure 4 resembles the structures of dimeric lithium and sodium salts of sterically hindered (HSC_6H_3-2,6-Trip$_2$).[20b] Compound **4** has a crystallographically

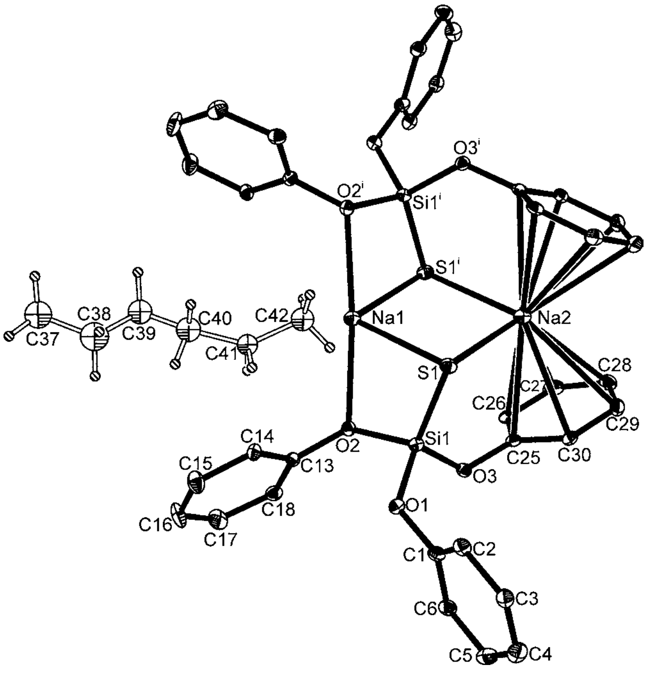
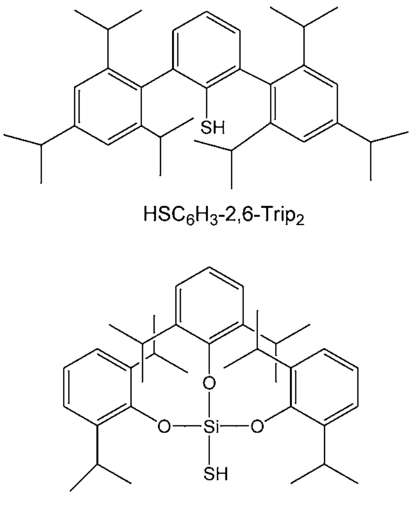


Figure 3. Molecular structure of **3**. Hydrogen atoms (except for solvating *n*-hexane moiety) and isopropyl substituents have been removed for clarity of the picture.

Scheme 1



HSC_6H_3-2,6-$Trip_2$

TDST

required center of symmetry and exhibits a planar Na_2S_2 core with two independent Na−S distances of 2.7582(9) and 2.7631(8) Å (see Table 2 for important bond lengths and angles). The internal Na_2S_2 ring angles are 85.91(2) and 94.09(2)°. Similar to **3** the sodium interacts with one of the phenyl rings of TDST with the Na−C distances ranging from 2.8951(19) to 3.031(2) Å. Interestingly in both complexes **3** and **4** the sodium-to-centroid distances are definitely shorter than the sodium-to-sulfur bond lengths (the difference is ca. 0.15 Å or more). In **4** sodium is additionally coordinated by the oxygen atom of a single molecule of water. In the hydrophobic environment formed by the silanethiolate ligands water forms only one "classical" hydrogen bond with the adjacent O-atom of phenoxy moiety (parameters of the hydrogen bond are given in the Figure 4 caption). There is a weak interaction in the crystal between the other OH bond of water and the phenyl ring of the adjacent molecule of **4** (Supporting Information, Figure 4S). The situation is confirmed by the FT-IR spectrum of solid **4** and will be discussed in the next section.

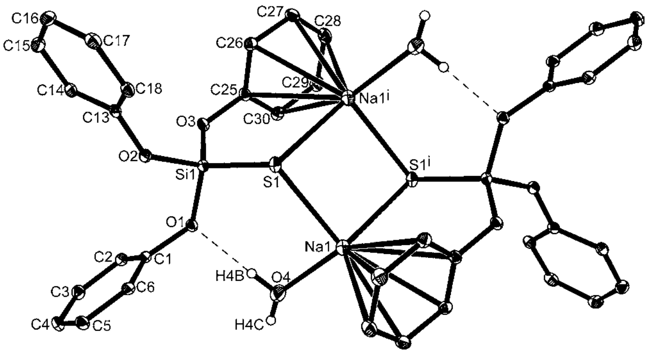


Figure 4. Molecular structure of **4**. Hydrogen atoms (except for water molecule) and isopropyl substituents have been removed for clarity of the picture. Parameters of the hydrogen bond O4−H4B···O1: D−H 0.85(3) Å; H···A 1.96(3) Å; D···A 2.800(2) Å; ∠ DHA 172(3) deg.

Herman and Chojnacki investigated the effect of deprotonation of the silanethiol on the Si−S bond length and found that it results in a shortening of the Si−S bond length.[36] Chojnacki analyzed the relationship between Si−S bond length and the character of the S−M bond in silanethiolate metal complexes and concluded that the increase in the ionic character of S−M is accompanied by the decrease of Si−S distance.[37] We decided to test these predictions experimentally and produce separate sodium-thiolate ion pairs applying the approach described by Chadwick and co-workers.[23] Crown ethers can coordinate and separate metal cations from anions and so that isolated anions are obtained in crystals. Using several crown ethers and mixtures of solvents we produced one such crystalline ion pair **5** in small amounts. The crystal structure of **5** consists of silanethiolate anions and [Na(naphtho-15-crown-5)$_2$]$^+$ cations (Figure 5). The sulfur and sodium atoms are separated by a distance of 7.124 Å, the nearest distances between sulfur and adjacent atoms are those to TDST oxygens (ca. 3.15 Å) and additionally: S1 C72 3.480 Å (nearest distance to one of crown ether atoms), S1 C13 3.505 Å, S1 C31 3.677 Å, S1 C7 3.757 Å, S1 C25 3.771 Å,

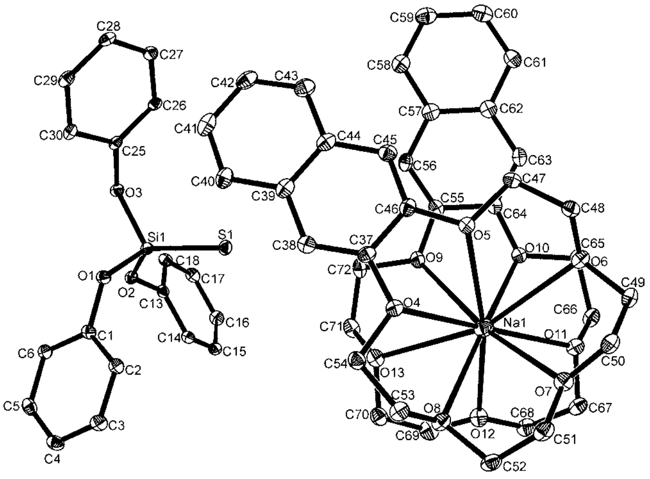


Figure 5. Structure of **5**. H atoms and isopropyl substituents of TDST removed for clarity of the picture.

S1 C71 3.786 Å, S1 C33 3.804 Å, S1 C14 3.825 Å, S1 C19 3.843 Å, S1 C8 3.943 Å. The remaining distances of sulfur-to-atom exceed 4 Å. Sodium Na1 is ten-coordinated by oxygen atoms from two crown ether molecules complexed in a sandwich manner and the geometry of pentagonal antiprism.

We expected that sodium would rather fit the ligand cavity as it usually does with crown ethers of this type and size,[38] but we underestimated the influence of the counterion. Earlier infrared spectroscopic studies revealed that benzo-15-crown-5 ether forms a similar 2:1 sandwich with Na$^+$, if the anion is tetraphenyl borate.[39] It was explained that such anion could not provide donor atoms for the Na$^+$ which then coordinates a second crown to complete the coordination sphere.[40] Though this explanation is not entirely satisfactory, since sodium can be in fact solvated by the phenyl rings, the coordination of Na$^+$ which is a hard Lewis acid with oxygen must be preferred, and complex **5** is a structural evidence of this. The geometry of sandwich-type cation [Na(naphtho-15-crown-5)2]$^+$ strongly resembles the geometry of analogous complex [K(naphtho-15-crown-5)$_2$]$^+$ including the rotation of crown ether molecules in the complex so that the angle between the aromatic rings is approximately 30 deg.[30,41] The distances Na−O vary in the wide range 2.597−3.012 Å with an average Na−O distance equal to 2.784 Å, whereas analogous potassium complexes exhibit distances K−O between 2.784 and 3.096 Å with an average of approximately 2.903 Å.[30,41]

As predicted and explained by theoretical methods, the Si1−S1 bond length in this definitely ionic compound is considerably shorter than in **1** and also still significantly shorter than in **3** and **4** (see Table 2).[36,37]

3.2. FT-IR Spectroscopy. The FT-IR spectrum of the solid sample of TDST exhibits a relatively narrow band of SH stretching vibration at 2552 cm^{-1}, comparable to that of TMST, which is located at 2662 cm^{-1}.[28] Such frequency is not quite typical neither of (Si)−S-H nor of (C)−S-H stretching mode, and the red-shift amounts to approximately 35−40 cm^{-1}; for example, tri-*tert*-butoxysilanethiol exhibits ν_{SH} at 2592 cm^{-1}.[42] On the basis of X-ray molecular structure we attributed this difference, at least partly, to the formation of the intramolecular SH-π interaction. To strengthen this hypothesis we analyzed FT-IR ATR spectra of tri-*tert*-butoxysilanethiol in CCl_4 and CCl_4-xylene solutions. Stretching mode ν_{SH} of tri-*tert*-butoxysilanethiol dissolved in xylene-CCl_4 mixture shows the band at 2572 cm^{-1}, which is 20 cm^{-1} red-shifted in comparison to the solution in CCl_4 (Figure 6). Experimentally, very similar shifts were observed upon the formation of the SH---π interaction between molecules of organic thiols[43] and for the intermolecular interactions between hydrogen sulfide and indole.[44] Interestingly the preference for the formation of SH---π over the formation of NH---S was observed in the latter case. Computational studies indicate that the energy of the SH---π interaction is either comparable with that of XH---π (where X = O)[45] or even the SH---π interaction is the strongest among the studied XH---π (where X = C, N, and O).[44] The SH---π interaction is preferred over SH---S,[45] which is confirmed by the crystal packing of both TMST and TDST (see Figure.2 and Supporting Information, Figure 3S).

In sodium salts of TDST SH---π interactions are replaced by cation-π noncovalent forces. Cation-π bonds are relatively strong interactions that are recognized as important for molecular recognition and stability of protein structure.[46] The studies on synthetic receptors established that a hydrophobic binding site composed of aromatic rings can compete with aqueous solvation.[46c] The main features of the cation-π interactions are well explained by classical electrostatic trends: smaller ions with greater charge have larger affinities for aromatic rings.[46e]

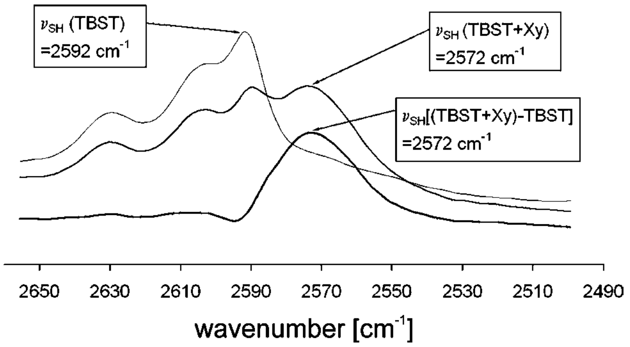


Figure 6. ATR FT-IR absorbance spectra of tri-*tert*-butoxysilanethiol (TBST) and tri-*tert*-butoxysilanethiol-xylene mixtures in CCl_4.

Noncovalent interactions in ion-benzene-water clusters have been studied by the infrared predissociation spectroscopy and ab initio calculations for lithium and sodium clusters consisting of metal cation, water, and benzene molecules: $Li^+(C_6H_6)_x(H_2O)_y$ and $Na^+(C_6H_6)_x(H_2O)_y$.[47] The position of water W1 in the argonated cluster $Na^+(C_6H_6)_2(H_2O)_2Ar_1$ (Figure 7) corresponds to the environment of water in the compound **2**. There were four experimentally observed OH stretching frequencies for the two molecules of water in this cluster. No detectable interaction between the benzene and water W2 was reflected by the OH symmetric and asymmetric stretches at 3649 and 3733 cm^{-1} (W2 in Figure 7). Stretching bands of water W1 were located at 3712 (free) and 3435 cm^{-1} (water−water H-bond)[47]. In the FT-IR spectrum of our compound **4** there are two strong bands of the water molecule at 3666 and 3406 cm^{-1}. The latter must be certainly ascribed to the OH---O hydrogen-bonded to the oxygen atom (Figures 4 and 8). However, there is a considerable discrepancy of 50 cm^{-1} between the values of free OH in the cluster $Na^+(C_6H_6)_2(H_2O)_2Ar_1$ (3712 cm^{-1}[47]) and in compound **4** (3666 cm^{-1}). We analyzed the crystal packing of **4** and found out that there is an OH-π interaction between the "free" OH of water and the phenyl ring of the adjacent molecule of the sodium thiolate. The intermolecular distances between the H atom of water and C atoms of the Ph ring are between 2.860 and 4.880 Å (see Supporting Information,

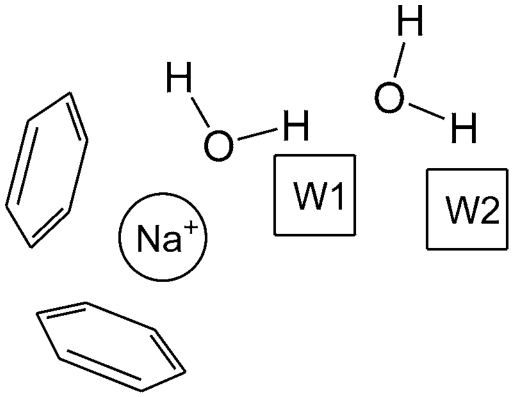


Figure 7. Cluster $Na^+(C_6H_6)_2(H_2O)_2Ar_1$.[47]

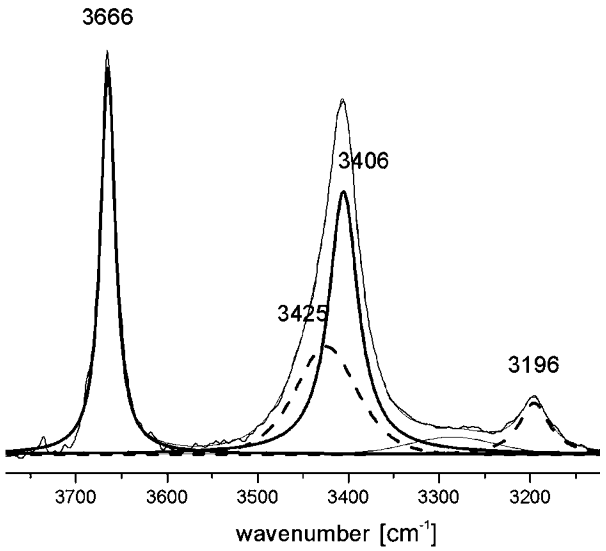


Figure 8. Analysis of FT-IR absorbance spectra of **4** in the OH stretching range.

Figure 4S for illustration). For comparison the experimental value of the OH stretch for the OH---π interacting bond in the cluster $Na^+(C_6H_6)_2(H_2O)_2Ar_1$ was 3690 cm^{-1}.[47]

More discriminating analysis of the FT-IR spectrum of **4** in the range of OH stretching vibration reveals also less numerous water molecules in a different state, compared to the molecules in the crystal structure of **4** (Figure 8). The band position of these new water molecules may correspond to the asymmetric (3425 cm^{-1}) and symmetric (3196 cm^{-1}) OH stretching vibration, in a state of approximately symmetric and strong H-bond formation. They result from the slow hydration of sodium thiolate in a thin layer in contact with air. Most probably, these few water molecules are H-bonded to the adjacent oxygen atoms of silanethiolate residue.

4. CONCLUSIONS

A new silanethiol with 2,6-diisopropylphenoxy substituents at the silicon atom is resistant toward hydrolysis, which can be explained by the hindered access of water molecules to the Si−S bond. The thiol forms sodium salts in a slow reaction with sodium metal in *n*-hexane. If no other donor atoms are provided, sodium ions in these salts are coordinated by neutral phenyl rings. SH---π and OH---π interactions in crystals of sodium silanethiolates are evidenced by X-ray diffraction and cause approximately 20 and 50 cm^{-1} shifts of the stretching ν_{SH} and ν_{OH} modes, respectively.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic information files (the crystal structures of compounds **1**, **3**, **4**, and **5** have been also deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC-830182, CCDC-830184, CCDC-830183, and CCDC-830185). Figures 1S (crystal of TDST), 2S (crystal packing of TDST), 3S (crystal packing of TMST), 4S (crystal packing of **4**), 5S (FT-IR spectrum of **2**), and 6S (FT-IR spectrum of **4**). This material is available free of charge via the Internet at http://pubs.acs.org.

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