

Lewis Base Coordination versus Cation– π Interaction in Monomeric and Hexameric Potassium Thiolates

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The synthesis and structural identification of a family of crown-ether-coordinated and crown-ether-free potassium thiolates are described. [Li(15-crown-5)(SCPh₃)] (**1**), [K(18-crown-6)(SCPh₃)(C₆H₆)_{0.5}] (**2**), [K(18-crown-6)(SCPh₃)(thf)_{0.5}] (**3**), [K(dibenzo-18-crown-6)(SCPh₃)-(hmpa)_{0.5}] (hmpa = hexamethylphosphoramide; **4**), and [K(dibenzo-18-crown-6)(SCPh₃)(tol)] (tol = toluene; **5**) are available *via* metathesis of nBuLi or KH with triphenylmethanethiol in toluene, added crown ether, and respective Lewis donors. In the absence of crown ether, however, metathesis with NaH or KH and triphenylsilanethiol or triphenylmethanethiol in toluene leads to the hexameric aggregates [(NaSSiPh₃)₆(tol)₂] (**6**), [(KSCPh₃)₆(hmpa)₂]·2 tol (**7**), and [(KSCPh₃)₆(tol)₂] (**8**). It is shown that the strongly coordinating hmpa can ligate the hexameric framework in **7**; employment of stoichiometric amounts of pyridine, 1,4-dioxane, or chelating pmdta (*N,N,N,N,N'*-pentamethyldiethylenetriamine) results in the isolation of toluene-coordinated **8**. Compounds **1–8** were unequivocally identified by X-ray crystallography, ¹H NMR, ¹³C NMR (depending on solubility), IR spectroscopy, and melting point. The monomeric formulations of **1–5** are clearly related to the ability of the appropriate crown ether to sequester the alkali-metal cation, thereby satiating much of its coordination environment. In contrast, aggregation is observed in the absence of crown ether (compounds **6–8**), where the M₆S₆ hexameric core is stabilized through numerous cation– π interactions with several of the 18 phenyl groups comprising the organic periphery and two donor molecules.

Introduction

Alkali-metal chalcogenolates occupy a central role in organic and inorganic synthetic methodology. Chemistry based on the alkali-metal cation–oxygen bond has been the most thoroughly developed with regard to application and solution and solid-state investigation, and it is still an active area of research.¹ Further, interesting solution and solid-state chemistry has been recently reported for heavier alkali-metal cation–alkoxide, –aryloxide, and –silyloxide complexes.² In marked contrast, considerably less attention has been paid to developing the synthetic potential of alkali-metal thiolates, selenolates, and tellurolates and to elucidating the solution and solid-state structures.^{1g,3} One goal of our research program, then, is to identify the param-

eters affecting solution and solid-state structural chemistry in families of alkali-metal thiolates and apply this information in the design of synthetic reagents.

The structural chemistry observed in lithium thiolates is influenced by subtle changes in the organic ligand and the presence or absence of Lewis bases. Monomers and dimers are the most common formulations, which often result from the propensity of lithium to adopt a four-coordinate environment. Higher aggregation numbers such as trimers, tetramers, hexamers, and polymers have also been structurally characterized, although they are generally less prevalent.^{4–7} For sodium and potassium thiolates, however, very few compounds have been thoroughly characterized. The heavier alkali-metal thiolates elucidated to date point to a varied and interesting solid-state structural chemistry. For example, recent work from this laboratory has delineated a family of sodium and potassium arenethiolates, which exhibit monomeric, dimeric, hexameric, and polymeric structural motifs. The observed structural modifications of the [MStrip(D)]_n (M = Na, K; Trip = C₆H₂-2,4,6-

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PrI_3 ; D = various Lewis donors; $n = 1-\infty$) complexes were shown to be dependent on cation radii, donor stoichiometry, and especially donor hapticity.^{8,9} In other recent work, a combination of ligand steric bulk with concomitant intramolecular arene coordination was used to isolate dimeric $[\text{MSC}_6\text{H}_3\text{-2,6-Trip}_2]_2$ ($M = \text{Na}, \text{K}$).^{4a} The first structurally characterized oligomeric sodium thiolate was shown to be a hexameric aggregate resulting from a reduced ligand steric presence in conjunction with Lewis base stabilization. $[\text{Na}(\text{SNC}_5\text{H}_2\text{-3,6-(SiMe}_2\text{Bu}^t)_2)_6]$ exhibits a distorted-hexagonal-prismatic framework, with intramolecular stabilization *via* the silyl-substituted 2-pyridinethiolate inhibiting polymerization.¹⁰ Significant within this structure, no external Lewis bases are required to stabilize the core framework. In contrast, the perfluorinated thiol HSR_f ($R_f = \text{HSC}_6\text{H}_2\text{-2,4,6-(CF}_3)_3$) leads to the ladder-type polymers $[\text{Na}(\text{thf})_2\text{SR}_f]_\infty$ and $[\text{K}(\text{thf})\text{SR}_f]_\infty$, exhibiting significant secondary interactions between the metal centers and neighboring $o\text{-CF}_3$ groups to facilitate one-dimensional polymerization.¹¹⁻¹⁵

Herein are detailed the synthesis and structural identification of monomeric and hexameric alkali-metal thiolates, where the use of sterically cumbersome triphenylmethanethiol with crown ethers in a metathesis protocol leads to the formation of monomeric $[\text{Li}(15\text{-}$

crown-5)(SCPh_3)] (**1**), $[\text{K}(18\text{-crown-6})(\text{SCPh}_3)(\text{C}_6\text{H}_6)_{0.5}]$ (**2**), $[\text{K}(18\text{-crown-6})(\text{SCPh}_3)(\text{thf})_{0.5}]$ (**3**), $[\text{K}(\text{dibenzo-18-crown-6})(\text{SCPh}_3)(\text{hmpa})_{0.5}]$ ($\text{hmpa} = \text{hexamethylphosphoramide}$; **4**), and $[\text{K}(\text{dibenzo-18-crown-6})(\text{SCPh}_3)(\text{tol})]$ ($\text{tol} = \text{toluene}$; **5**). Remarkably, and quite unexpectedly, reaction of sodium or potassium hydride with triphenylsilylanethiol or triphenylmethanethiol in toluene, in the absence of crown ether, leads to the arene-stabilized hexamers $[(\text{NaSSiPh}_3)_6(\text{tol})_2]$ (**6**), $[(\text{KSCPh}_3)_6(\text{hmpa})_2] \cdot 2 \text{ tol}$ (**7**), and $[(\text{KSCPh}_3)_6(\text{tol})_2]$ (**8**), where hmpa or toluene completes the coordination environment at the metal center. Each hexameric aggregate is composed of an M_6S_6 core stabilized primarily through an organic periphery consisting of 18 phenyl groups.

Experimental Section

General Procedures. All reactions were performed under a purified nitrogen atmosphere by using modified Schlenk techniques and a Braun Labmaster 100 drybox. Toluene was distilled just prior to use from a Na/K alloy followed by two freeze-pump-thaw cycles. Hexamethylphosphoramide (hmpa) was stirred over CaH_2 for 1 h and distilled under vacuum. Commercially available 15-crown-5 (15C5) was dried over 3 Å molecular sieves, while 18-crown-6 (18C6) was dissolved in freshly distilled diethyl ether and stirred with finely cut sodium metal for 1 day. After filtration from the metal, the crown was recrystallized at -20°C and used as isolated. Dibenzo-18-crown-6 (DB18C6) was used as received. Readily available $n\text{BuLi}$ was used as a 1.6 M solution in hexanes. Mineral oil suspensions of NaH and KH were each washed repeatedly with freshly distilled hexane and dried under vacuum. Triphenylmethanethiol (HSCPh_3) and triphenylsilyl thiol (HSSiPh_3) were both dried by warming under vacuum for several hours. ^1H NMR (300 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker DPX-300 spectrometer. Infrared spectra were recorded as Nujol mulls between KBr plates (unless otherwise noted) on a Perkin-Elmer PE 1600 FT-IR spectrometer. Elemental analysis was precluded by the extreme thermal and moisture sensitivity of all compounds reported. For example, typical working time for mounting crystals was less than 15 min before decomposition occurred, even while the crystals were stored under a heavy hydrocarbon oil.

The synthesis of compounds **1-8** was affected *via* a straightforward metathesis reaction of the appropriate alkali-metal reagent ($n\text{BuLi}$, NaH, or KH) with HSCPh_3 or HSSiPh_3 in an aromatic or ethereal solvent and under the addition of crown ether if required. All reaction stoichiometries involve an equimolar ratio of reactants. A representative experimental procedure is given for compound **1**.

[Li(15C5)(SCPh₃)] (1). To a 100 mL Schlenk flask was added 0.44 g (2.0 mmol) of 15C5 and 0.55 g (2.0 mmol) of HSCPh_3 . A 25 mL portion of toluene was added, followed by the dropwise addition of 1.3 mL (2.0 mmol) of $n\text{BuLi}$ in hexanes. Initially, a bright, clear red solution formed, which faded to light yellow over 1 h at room temperature. Filtration through a Celite padded frit and storage at -20°C for several

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days led to the isolation of colorless plates in 83% yield (0.83 g). Mp: decomposes to a brown oil at >100 °C. ^1H NMR (thf- d_6): δ 7.58–7.55 (m, 6H), 7.02–6.90 (m, 9H), 3.56 (s, 20H). $^{13}\text{C}\{^1\text{H}\}$ NMR (thf- d_6): δ 156.57, 131.39, 126.53, 124.33, 71.24. IR (cm^{-1} ; Nujol): 3045 m, 2930 s, 1586 m, 1465 s, 1377 s, 1350 m, 1300 m, 1250 m, 1236 m, 1105 s, 1030 m, 957 m, 833 m, 765 m, 742 s, 709 s, 694 s, 616 m, 505 m.

[K(18C6)(SCPh₃)(C₆H₆)_{0.5}] (2). X-ray-quality crystals formed, on cooling the filtrate to room temperature, in 30% yield (0.19 g). Mp: decomposes at >150 °C. ^1H NMR (thf- d_6): δ 7.64 (d, 6H), 7.30 (C₆H₆), 6.94 and 6.84 (t, 9H), 3.55 (s, 24H). $^{13}\text{C}\{^1\text{H}\}$ NMR (thf- d_6): δ 131.71, 131.53, 127.06, 126.18, 123.59, 71.09. IR (cm^{-1} ; Nujol, NaCl): 2934 s, 1587 w, 1463 s, 1377 m, 1348 w, 1280 w, 1247 w, 1102 m, 1027 w, 961 m, 835 w, 747 w, 698 w.

[K(18C6)(SCPh₃)(thf)_{0.5}] (3). After the filtrate was cooled to 0 °C, pale yellow plates gradually formed over several days in 60% yield (0.74 g). Mp: decomposes at >180 °C. ^1H NMR (thf- d_6): δ 7.65 (d 6H), 6.93 (t, 6H), 6.82 (t, 3H), 3.55 (s, 24H). $^{13}\text{C}\{^1\text{H}\}$ NMR (thf- d_6): δ 158.15, 131.50, 126.09, 123.48, 71.02. IR (cm^{-1} ; Nujol): 2870 bs, 1588 m, 1467 s, 1377 s, 1348 m, 1280 m, 1246 m, 1102 s, 1028 m, 961 s, 835 m, 748 s, 697 s, 673 w, 615 w.

[K(DB18C6)(SCPh₃)(hmpa)_{0.5}] (4). X-ray-quality crystals quickly grew from the filtrate at room temperature in 59% yield (0.45 g). Mp: decomposes at >110 °C. ^1H NMR (thf- d_6): δ 7.78–6.87 (broad overlapping m), 3.99 (broad diffuse d), 2.57 (d, hmpa). Integration was unreliable due to low solubility and prohibited ^{13}C NMR. IR (cm^{-1} ; Nujol): 3044 w, 2924 s, 1594 s, 1504 s, 1454 s, 1377 m, 1252 s, 1218 s, 1063 m, 958 m, 944 s, 747 s, 700 s, 617 m.

[K(DB18C6)(SCPh₃)(tol)] (5). Clear colorless rods gradually formed from the filtrate at 0 °C over 24 h in 50% yield (0.34 g). Mp: decomposes to a brown solid at >185 °C. ^1H NMR (thf- d_6): δ 7.67 (d, 6H), 6.90–6.76 (m, 17H), 4.03 (m, 8H), 3.94 (m, 8H). $^{13}\text{C}\{^1\text{H}\}$ NMR (thf- d_6): δ 157.57, 148.62, 131.59, 126.28, 123.70, 121.57, 111.64, 69.44, 68.38. IR (cm^{-1} ; Nujol): 3042 w, 2923 s, 1593 m, 1503 s, 1455 s, 1377 m, 1252 s, 1218 s, 1123 s, 1063 s, 958 m, 943 m, 747 s, 704 m, 617 w.

[NaSSiPh₃]₆(tol)₂ (6). Clear plates formed from the filtrate after 24 h at -20 °C in 62% yield (0.22 g). Mp: decomposes at >220 °C. ^1H NMR (thf- d_6): δ 7.71–7.66 (m, 6H), 7.15–7.12 (m, 9H and residual tol), 2.31 (s, tol). $^{13}\text{C}\{^1\text{H}\}$ NMR (thf- d_6): δ 146.13, 136.54, 127.85, 127.35. IR (cm^{-1} ; Nujol): 3044 w, 2918 s, 1597 w, 1492 w, 1463 s, 1426 s, 1377 m, 1304 w, 1260 w, 1103 s, 1028 w, 997 w, 742 s, 700 s, 684 s, 576 s, 501 s, 470 w, 431 w.

[K(SCPh₃)₆(hmpa)₂] \cdot 2tol (7). Storage of the filtrate at room temperature led to the formation of colorless plates in 54% yield (0.40 g, based on the toluene-free formula C₁₂₆H₁₂₆K₆N₆O₂P₂S₆). Mp: decomposes at >175 °C. ^1H NMR (tol- d_6): δ 7.76 (d, 6H), 7.11–6.94 (m, 9H and solvent), 2.37 (d, 9.33 Hz, hmpa). $^{13}\text{C}\{^1\text{H}\}$ NMR (tol- d_6): δ 154.89, 131.60, 130.21, 127.29, 36.75. IR (cm^{-1} ; Nujol): 3055 m, 2926 m, 1589 m, 1464 s, 1377 m, 1296 m, 1205 s, 1068 w, 1029 m, 984 s, 739 s, 698 s, 617 m, 483 m.

[K(SCPh₃)₆(tol)₂] (8). At room temperature, the filtrate produced small colorless plates in 46% yield (0.16 g). Mp: decomposes at >230 °C. ^1H NMR (thf- d_6): δ 7.55 (d, 6H), 7.19–6.93 (m, 9H and residual tol), 2.31 (s, tol). $^{13}\text{C}\{^1\text{H}\}$ NMR (thf- d_6): δ 153.85, 128.36, 124.52, 122.13. IR (cm^{-1} ; Nujol): 3042 w, 2918 s, 1589 m, 1464 s, 1377 s, 1178 w, 1076 w, 766 m, 742 s, 698 s, 674 m, 617 w.

X-ray Crystallographic Studies. X-ray-quality crystals for all compounds were grown as described in the Experimental Section. The crystals were removed from the Schlenk tube under a stream of N₂ and immediately covered with a layer of viscous hydrocarbon oil (Paratone N, Exxon). A suitable crystal was selected with the aid of a microscope, attached to a glass fiber, and immediately placed in the low-temperature

N₂ stream of the diffractometer.¹⁶ Data sets for compounds **2** and **3** were collected at -60 °C using a Rigaku AFC5S diffractometer equipped with a Molecular Structure Corp. low-temperature device and graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Three standard reflections were measured every 150 reflections and showed in both cases only statistical variation of the intensity ($<1.5\%$). The intensities were corrected for Lorentz and polarization effects; extinction was disregarded. An absorption correction was applied using semiempirical ψ scans. The intensity data sets for compounds **1** and **4–8** were collected utilizing a Siemens SMART system, complete with three-circle goniometer and CCD detector operating at -54 °C. Each data set was collected at -123 °C using a Cryojet low-temperature device from Oxford Instruments and by employing graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The data collections nominally covered a hemisphere of reciprocal space utilizing a combination of three groups of exposures, each with a different ϕ angle and each exposure covering 0.3° in ω . Crystal decay was monitored by repeating a set of initial frames at the end of the data collection and comparing the duplicate reflections, whereby no decay was observed for all compounds reported. An absorption correction was applied utilizing the program SADABS.¹⁷ The crystal structures of all compounds were solved by direct methods, as included in the SHELXTL program package.^{18,19} Missing atoms were located in subsequent difference Fourier maps and included in the refinement. The structures of compounds **1** and **4–8** were refined by full-matrix least-squares refinement on F^2 (SHELXL-93),¹⁸ while compounds **2** and **3** were refined by full-matrix least-squares calculations on $|F_o|$ (SHELX-76).¹⁹ Hydrogen atoms were placed geometrically and refined using a riding model, including free rotation of methyl groups. Compounds **1** and **4–8** were refined with U_{iso} constrained at 1.2 (for non-methyl groups), and 1.5 (for methyl groups) times U_{eq} of the carrier C atom. Thermal parameters for hydrogen atoms in compounds **2** and **3** were included using fixed $U_{iso} = 0.08$. The crystallographic programs used for structural refinement were installed on a PC clone (SHELX-76) or a Silicon Graphics Indigo² R10000 solid Impact (SHELXL-93). Scattering factors were those provided by the SHELX program. All non-hydrogen atoms, with the exception of some disordered or restrained positions, were refined anisotropically. Disorder was typically handled by including split positions for the affected groups and included the refinement of the respective occupancies. Generally, a set of restraints was applied to aid in modeling.¹⁸ The ligating thf molecule in compound **3** was taken as half-occupied. In compound **4**, the hmpa molecule is shared equally by two symmetry-related [K(DB18C6)(SCPh₃)] units, such that the donor is taken as half-occupied with five unique methyl groups, while the sixth methyl group is common to both symmetry-related positions. In compound **6**, disorder about phenyl C(37)–C(42) was handled through introduction of a second aryl ring orientation, the occupancies of which were refined. Both ring orientations were refined anisotropically. The remaining electron density associated with highly disordered solvent molecules in compounds **4–6** was treated using SQUEEZE (Platon).²⁰ In each treatment, the geometrical parameters and accompanying estimated standard deviations for the main molecules showed no changes when compared to the refinement incorporating modeled solvent molecules of crystallization. The SQUEEZE refinement, however, did

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result in an improved *R* factor and difference map. In **4–6**, the void volume and associated electron density was found to describe four toluene molecules each. In **4**, the calculated solvent area volume is 751.8 Å³/unit cell with an electron count/unit cell of 200.7, and the void center is located at $-0.046, -0.041, 0.455$. Closest contacts to the main molecule are above 3.58 Å. In **5**, the calculated solvent area volume is 770.3 Å³/unit cell with an electron count/unit cell of 205.7, and the void center is located at 0.500, 1.000, 1.079. Closest contacts to the ligated toluene molecule are 1.82 Å to C(46) and 3.03 Å to C(41) with remaining distances above 3.1 Å. In **6**, the calculated solvent area volume is 774.5 Å³/unit cell with an electron count/unit cell of 201.2, and the void center is located at $-0.021, 0.0, 0.0$. Closest contacts to the main molecule are above 3.90 Å. The molecular formulas in Table 1 for compounds **4–6** are only for the main molecules. The synthesis of compound **8** was repeated several times in an attempt to obtain a data set which could be refined to a more acceptable *R* value and lower esds. In each case, however, an essentially identical refinement was obtained. The slightly increased esds in the geometrical data for **8** should be noted in comparison to those for compounds **6** and **7**. Further details about the refinements and how disorder was handled are outlined in the Supporting Information. Crystallographic parameters for compounds **1–8** are summarized in Table 1, while selected bond distances and angles can be found in Table 2.

Results and Discussion

Compounds **1–8** are readily available through methathesis of *n*BuLi or appropriate alkali-metal hydride with triphenylmethanethiol or triphenylsilylthiol in various donor solvents, including toluene. The presence of adjunct donor ligands was expected to affect the structural outcome of the nascent lithium, sodium, and potassium chalcogenolates, as had been observed with a small group of related alkali-metal thiolates.^{4,5,8–11} Addition of crown ethers, 15-crown-5 (15C5) for lithium or 18-crown-6 (18C6) and dibenzo-18-crown-6 (DB18C6) for potassium, has led to the isolation of the monomeric alkali-metal triphenylmethanethiolates [Li(15C5)(SCPh₃)] (**1**), [K(18C6)(SCPh₃)(C₆H₆)_{0.5}] (**2**), [K(18C6)(SCPh₃)(thf)_{0.5}] (**3**), [K(DB18C6)(SCPh₃)(hmpa)_{0.5}] (**4**), and [K(DB18C6)(SCPh₃)(tol)] (**5**). Surprising, however, was the isolation of high-quality crystals from crown-ether-free reaction mixtures and the subsequent structural identification of the hexameric aggregates [(NaSSiPh₃)₆(tol)₂] (**6**), [(KSCPh₃)₆(hmpa)₂]·2 tol (**7**), and [(KSCPh₃)₆(tol)₂] (**8**). The M₆S₆ box-shaped core of these hexamers is stabilized via a number of intramolecular π interactions with the metal cations (out of 18 phenyl groups surrounding the framework) and donor solvation from toluene or hmpa at two open coordination sites.

The monomeric formulation of compound **1** (Figure 1) can be attributed to pairing of pentacoordinate 15C5 and the sterically demanding triphenylmethanethiolate ligand, with Li(1)–O contacts ranging between 2.197(4) and 2.454(4) Å and a Li(1)–S(1) bond distance of 2.501(4) Å. This is the first example of a six-coordinate cation in lithium thiolate structural chemistry, and the Li–S bond distance correlates well (that is, slightly longer) with those in related monomeric structures.^{4,5} For example, [Li(12C4)(SCPh₃)] exhibits a broader range of Li–oxygen contacts between 1.895(6) and 2.450(5) Å but a significantly shorter Li–S bond at 2.399(4) Å, attributable to a lower coordination number about the cation.^{4c} Other monomeric lithium thiolates display

Table 1. Crystallographic Data for Compounds 1–8

	1	2	3	4	5	6	7	8
formula	C ₂₉ H ₃₅ LiO ₅ S	C ₃₄ H ₄₂ KO ₆ S	C ₃₃ H ₄₃ KO _{6.5} S	C ₄₂ H _{46.5} KNi _{1.5} O _{6.5} P _{0.5} S	C ₆ H ₇ KO ₆ S	C ₁₂₂ H ₁₀₈ Na ₆ S ₆ Si ₆	C ₁₄₀ H ₁₄₂ K ₆ N ₆ O ₂ P ₂ S ₆	C ₁₂₈ H ₁₀₄ K ₆ S ₆
fw	502.57	617.18	614.9	764.46	767.00	2070.90	2429.50	2069.08
cryst shape	colorless plate	yellow plate	pale yellow plate	colorless needle	colorless rod	colorless plate	colorless plate	colorless plate
cryst size (mm)	0.40 × 0.40 × 0.08	0.35 × 0.30 × 0.08	0.20 × 0.20 × 0.08	0.45 × 0.15 × 0.08	0.40 × 0.15 × 0.10	0.50 × 0.50 × 0.10	0.40 × 0.40 × 0.18	0.40 × 0.30 × 0.04
a (Å)	14.5192(2)	9.358(2)	9.382(2)	14.1554(7)	13.9684(2)	16.1995(2)	14.3242(7)	16.0780(2)
b (Å)	12.7911(2)	10.480(2)	10.434(2)	14.1987(7)	13.9701(1)	16.3657(2)	14.4693(7)	21.0961(4)
c (Å)	15.8199(2)	17.232(3)	17.087(3)	14.8107(7)	14.0663(3)	16.3680(1)	16.9522(8)	32.0614(7)
α (deg)	90	95.75(3)	95.790(1)	103.990(1)	109.196(1)	73.765(1)	75.506(1)	90
β (deg)	113.977(1)	94.97(3)	93.88(3)	97.124(1)	90.606(1)	63.484(1)	71.992(1)	90
γ (deg)	90	92.30(3)	94.59(3)	112.860(1)	98.633(1)	62.160(1)	80.723(1)	90
V (Å ³)	2684.49(7)	1673.1(8)	1654.3(8)	2581.2(2)	2557.62(7)	3419.76(6)	3221.6(3)	10874.7(3)
Z	4	2	2	2	2	1	1	4
space group	P2 ₁ /c	P1	P1	P1	P1	P1	P1	Pbca
d _{calc} (g/cm ³)	1.243	1.226	1.235	0.982	0.996	1.006	1.252	1.264
lin abs coeff (mm ⁻¹)	0.157	0.262	0.266	0.197	0.183	0.211	0.378	0.406
radiation	Mo K α	Mo K α	Mo K α	Mo K α	Mo K α	Mo K α	Mo K α	Mo K α
T (K)	150	213	213	150	150	150	150	150
2 θ range, deg	3–57	0–55	0–45	3–50	3–57	3–57	3–57	3–50
no. of indep rflns	6212	7704	4670	8483	10 584	14 748	14 013	9546
no. of obsd rflns (>2 σ)	4551	4032 (>5 σ)	2340 (>3 σ)	4487	4591	10 190	11 228	6560
no. of params	320	379	370	515	487	643	730	631
R1, wR2 (all data) ^a	0.0910, 0.1037	N/A ^b	N/A ^c	0.1264, 0.1685	0.1509, 0.2095	0.0803, 0.1616	0.0655, 0.1153	0.1615, 0.1437
R1, wR2 (>2 σ)	0.0586, 0.0935	0.0534, 0.0552 (>5 σ)	0.0633, 0.0551 (>3 σ)	0.0685, 0.1479	0.0818, 0.1794	0.0561, 0.1475	0.0475, 0.1050	0.1037, 0.1285

^a R1 = $\sum ||F_o| - |F_c|| / \sum |F_o|$, wR2 = $\sum w(F_o - F_c)^2 / \sum w(F_o)^2$, R = $\sum ||F_o| - |F_c|| / \sum |F_o|$, and R_w = $\sum w||F_o| - |F_c|| / \sum w|F_o|^{1/2}$. ^b Refined on |F_o| with F > 5.0 σ (F) (SHELX 76); listed are R and R_w. ^c Refined on |F_o| with F > 3.0 σ (F) (SHELX 76); listed are R and R_w.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds 1–8

Compound 1							
Li(1)–S(1)	2.501(4)	Li(1)–O(3)	2.197(4)	S(1)–C(1)	1.855(2)	C(1)–C(14)	1.560(3)
Li(1)–O(1)	2.326(4)	Li(1)–O(4)	2.454(4)	C(1)–C(2)	1.544(3)		
Li(1)–O(2)	2.368(4)	Li(1)–O(5)	2.219(4)	C(1)–C(8)	1.561(3)		
Li(1)–S(1)–C(1)	117.60(10)	O(3)–Li(1)–S(1)	140.0(2)	C(2)–C(1)–S(1)	104.62(12)		
O(1)–Li(1)–S(1)	99.67(14)	O(4)–Li(1)–S(1)	96.83(13)	C(8)–C(1)–S(1)	112.38(13)		
O(2)–Li(1)–S(1)	106.40(14)	O(5)–Li(1)–S(1)	89.93(13)	C(14)–C(1)–S(1)	111.54(13)		
Compound 2							
K(1)–S(1)	3.135(1)	K(1)–O(3)	2.965(2)	K(1)–O(6)	2.800(2)	C(1)–C(8)	1.552(5)
K(1)–O(1)	2.959(3)	K(1)–O(4)	2.846(2)	S(1)–C(1)	1.867(3)	C(1)–C(14)	1.544(4)
K(1)–O(2)	2.763(3)	K(1)–O(5)	2.860(3)	C(1)–C(2)	1.543(5)		
K(1)–S(1)–C(1)	112.1(1)	O(4)–K(1)–S(1)	102.1(1)	S(1)–C(1)–C(8)	111.9(2)		
O(1)–K(1)–S(1)	102.2(1)	O(5)–K(1)–S(1)	89.2(1)	S(1)–C(1)–C(14)	107.2(2)		
O(2)–K(1)–S(1)	113.5(1)	O(6)–K(1)–S(1)	81.7(1)				
O(3)–K(1)–S(1)	126.6(1)	S(1)–C(1)–C(2)	109.6(2)				
Compound 3							
K(1)–S(1)	3.158(2)	K(1)–O(3)	2.950(4)	K(1)–O(6)	2.767(4)	C(1)–C(2)	1.548(9)
K(1)–O(1)	2.920(5)	K(1)–O(4)	2.831(4)	K(1)–O(1S)	3.249(6)	C(1)–C(8)	1.559(8)
K(1)–O(2)	2.729(5)	K(1)–O(5)	2.868(5)	S(1)–C(1)	1.847(6)	C(1)–C(14)	1.547(8)
K(1)–S(1)–C(1)	112.8(2)	O(4)–K(1)–S(1)	100.2(1)	S(1)–C(1)–C(2)	109.9(4)		
O(1)–K(1)–S(1)	99.8(1)	O(5)–K(1)–S(1)	87.3(1)	S(1)–C(1)–C(8)	113.0(4)		
O(2)–K(1)–S(1)	112.0(1)	O(6)–K(1)–S(1)	77.7(1)	S(1)–C(1)–C(14)	107.3(4)		
O(3)–K(1)–S(1)	124.2(1)	O(1S)–K(1)–S(1)	153.1(2)				
Compound 4							
K(1)–S(1)	3.216(1)	K(1)–O(4)	2.817(3)	S(1)–C(1)	1.864(4)	O(7)–P(1)	1.433(7)
K(1)–O(1)	2.760(3)	K(1)–O(5)	2.769(2)	C(1)–C(2)	1.540(5)	P(1)–N(1)	1.677(10)
K(1)–O(2)	2.786(3)	K(1)–O(6)	2.782(3)	C(1)–C(8)	1.527(5)	P(1)–N(2)	1.639(12)
K(1)–O(3)	2.765(3)	K(1)–O(7)	2.770(7)	C(1)–C(14)	1.556(5)	P(1)–N(3)	1.680(13)
K(1)–S(1)–C(1)	126.69(12)	O(5)–K(1)–S(1)	98.09(6)	S(1)–C(1)–C(14)	110.2(2)		
O(1)–K(1)–S(1)	91.97(7)	O(6)–K(1)–S(1)	94.42(6)	O(7)–P(1)–N(1)	110.0(5)		
O(2)–K(1)–S(1)	92.79(6)	S(1)–K(1)–O(7)	164.7(2)	O(7)–P(1)–N(2)	120.2(6)		
O(3)–K(1)–S(1)	102.14(6)	S(1)–C(1)–C(2)	107.6(2)	O(7)–P(1)–N(3)	109.7(7)		
O(4)–K(1)–S(1)	104.15(6)	S(1)–C(1)–C(8)	110.4(3)				
Compound 5							
K(1)–S(1)	3.127(1)	K(1)–O(4)	2.686(3)	K(1)···C(41)	3.905(6)	C(1)–C(2)	1.521(6)
K(1)–O(1)	2.714(3)	K(1)–O(5)	2.796(3)	K(1)···C(44)	3.956(8)	C(1)–C(8)	1.523(6)
K(1)–O(2)	2.743(3)	K(1)–O(6)	2.763(3)	K(1)···C(45)	3.561(7)	C(1)–C(14)	1.551(5)
K(1)–O(3)	2.738(3)	K(1)···C(40)	3.524(6)	S(1)–C(1)	1.861(4)		
K(1)–S(1)–C(1)	132.15(14)	O(4)–K(1)–S(1)	88.13(7)	S(1)–C(1)–C(8)	109.7(3)		
O(1)–K(1)–S(1)	101.97(6)	O(5)–K(1)–S(1)	91.77(7)	S(1)–C(1)–C(14)	109.1(3)		
O(2)–K(1)–S(1)	90.16(6)	O(6)–K(1)–S(1)	100.78(6)				
O(3)–K(1)–S(1)	86.55(7)	S(1)–C(1)–C(2)	110.6(3)				
Compound 6							
Na(1)–S(1)	2.892(1)	Na(1)···X	2.972	Na(2)···C(61)	3.027(3)	Si(1)–C(13)	1.893(2)
Na(1)–S(2A)	2.777(1)	Na(2)–S(1)	2.817(1)	Na(2)···X1	2.665	S(2)–Si(2)	2.081(1)
Na(1)–S(3A)	2.728(1)	Na(2)–S(2)	2.751(1)	Na(3)–S(1)	2.981(1)	Si(2)–C(19)	1.893(2)
Na(1)–S(av)	2.799	Na(2)–S(3)	2.803(1)	Na(3)–S(1A)	3.182(2)	Si(2)–C(25)	1.885(2)
Na(1)···C(13)	2.852(2)	Na(2)–S(av)	2.791	Na(3)–S(2A)	2.782(1)	Si(2)–C(31)	1.899(2)
Na(1)···C(14)	2.853(3)	Na(2)···C(56)	3.115(3)	Na(3)–S(3)	2.826(1)	S(3)–Si(3)	2.081(1)
Na(1)···C(15)	3.278(3)	Na(2)···C(57)	3.048(3)	Na(3)–S(av)	2.944	Si(3)–C(37)	1.923(2)
Na(1)···C(16)	3.661(3)	Na(2)···C(58)	2.935(3)	S(1)–Si(1)	2.088(1)	Si(3)–C(37')	1.893(5)
Na(1)···C(17)	3.664(3)	Na(2)···C(59)	2.896(4)	Si(1)–C(1)	1.887(2)	Si(3)–C(43)	1.867(3)
Na(1)···C(18)	3.285(3)	Na(2)···C(60)	2.930(4)	Si(1)–C(7)	1.885(2)	Si(3)–C(49)	1.897(3)
S(1)–Na(1)–S(2A)	92.23(3)	S(3)–Na(3)–S(1A)	93.47(4)	S(2)–Si(2)–C(19)	111.40(8)		
S(1)–Na(1)–S(3A)	102.44(4)	Si(1)–S(1)–Na(1)	87.51(3)	S(2)–Si(2)–C(25)	112.45(8)		
S(2A)–Na(1)–S(3A)	93.72(3)	Si(1)–S(1)–Na(2)	105.66(3)	S(2)–Si(2)–C(31)	111.81(8)		
S(1)–Na(2)–S(2)	88.03(3)	Si(1)–S(1)–Na(3)	131.02(4)	Si(3)–S(3)–Na(1A)	120.67(4)		
S(1)–Na(2)–S(3)	92.18(3)	Si(1)–S(1)–Na(3A)	137.44(4)	Si(3)–S(3)–Na(2)	150.41(4)		
S(2)–Na(2)–S(3)	92.64(3)	S(1)–Si(1)–C(1)	111.94(8)	Si(3)–S(3)–Na(3)	100.51(4)		
S(2A)–Na(3)–S(3)	173.85(5)	S(1)–Si(1)–C(7)	113.20(8)	S(3)–Si(3)–C(37)	104.87(7)		
S(1)–Na(3)–S(1A)	92.30(3)	S(1)–Si(1)–C(13)	109.46(7)	S(3)–Si(3)–C(37')	115.6(2)		
S(1)–Na(3)–S(2A)	90.27(3)	Si(2)–S(2)–Na(1A)	104.32(3)	S(3)–Si(3)–C(43)	113.59(10)		
S(1)–Na(3)–S(3)	88.36(3)	Si(2)–S(2)–Na(2)	124.39(4)	S(3)–Si(3)–C(49)	111.57(8)		
S(2A)–Na(3)–S(1A)	80.60(3)	Si(2)–S(2)–Na(3A)	132.14(4)				

Table 2 (Continued)

Compound 7							
K(1)–S(1)	3.109(1)	K(1)⋯C(42)	3.546(3)	K(2)⋯C(13A)	3.556(3)	C(1)–C(14)	1.544(3)
K(1)–S(2)	3.196(1)	K(2)–S(1A)	3.117(1)	K(2)⋯C(32)	3.398(2)	S(2)–C(20)	1.853(2)
K(1)–S(3)	3.230(1)	K(2)–S(2)	3.117(1)	K(3)–S(1A)	3.180(1)	C(20)–C(21)	1.543(3)
K(1)–S(3A)	3.310(1)	K(2)–S(3)	3.314(1)	K(3)–S(2)	3.028(1)	C(20)–C(27)	1.544(3)
K(1)–S(av)	3.212	K(2)–S(av)	3.183	K(3)–S(3A)	3.252(1)	C(20)–C(33)	1.553(3)
K(1)⋯C(21)	3.244(2)	K(2)⋯C(52)	3.246(2)	av K(3)–S	3.154	S(3)–C(39)	1.875(2)
K(1)⋯C(22)	3.430(2)	K(2)⋯C(53)	3.127(2)	K(3)–O(1)	2.538(2)	C(39)–C(40)	1.543(3)
K(1)⋯C(23)	3.491(2)	K(2)⋯C(54)	3.253(3)	K(3)⋯C(40)	3.532(2)	C(39)–C(46)	1.537(3)
K(1)⋯C(24)	3.375(2)	K(2)⋯C(55)	3.495(3)	K(3)⋯C(45)	3.367(3)	C(39)–C(52)	1.548(3)
K(1)⋯C(25)	3.180(2)	K(2)⋯C(56)	3.626(3)	K(3)⋯C(47)	3.307(3)	O(1)–P(1)	1.478(2)
K(1)⋯C(26)	3.104(2)	K(2)⋯C(57)	3.513(2)	S(1)–C(1)	1.860(2)	P(1)–N(1)	1.652(2)
K(1)⋯X	2.999	K(2)⋯X1	3.079	C(1)–C(2)	1.538(3)	P(1)–N(2)	1.647(2)
K(1)⋯C(41)	3.225(2)	K(2)⋯C(8A)	3.571(2)	C(1)–C(8)	1.553(3)	P(1)–N(3)	1.657(2)
S(1)–K(1)–S(2)	175.17(2)	O(1)–K(3)–S(2)	111.38(5)	S(2)–C(20)–C(33)	112.50(14)		
S(1)–K(1)–S(3)	86.50(2)	O(1)–K(3)–S(3A)	140.73(5)	C(39)–S(3)–K(1)	112.68(7)		
S(1)–K(1)–S(3A)	88.18(2)	C(1)–S(1)–K(1)	135.26(7)	C(39)–S(3)–K(1A)	159.92(7)		
S(2)–K(1)–S(3)	89.32(2)	C(1)–S(1)–K(2A)	103.53(7)	C(39)–S(3)–K(3)	87.55(6)		
S(2)–K(1)–S(3A)	94.46(2)	C(1)–S(1)–K(3A)	125.09(8)	C(39)–S(3)–K(2A)	96.06(7)		
S(3)–K(1)–S(3A)	93.04(2)	S(1)–C(1)–C(2)	106.95(14)	S(3)–C(39)–C(40)	106.06(14)		
S(1A)–K(2)–S(2)	91.23(2)	S(1)–C(1)–C(8)	107.43(14)	S(3)–C(39)–C(46)	113.64(14)		
S(1A)–K(2)–S(3)	87.99(2)	S(1)–C(1)–C(14)	112.2(2)	S(3)–C(39)–C(52)	106.14(14)		
S(2)–K(2)–S(3)	89.18(2)	C(20)–S(2)–K(1)	100.16(6)	O(1)–P(1)–N(1)	109.24(11)		
S(1A)–K(3)–S(2)	91.70(2)	C(20)–S(2)–K(2)	107.83(7)	O(1)–P(1)–N(2)	119.32(11)		
S(1A)–K(3)–S(3A)	84.97(2)	C(20)–S(2)–K(3)	161.00(7)	O(1)–P(1)–N(3)	109.09(11)		
S(2)–K(3)–S(3A)	98.95(2)	S(2)–C(20)–C(21)	104.10(13)				
O(1)–K(3)–S(1A)	117.25(5)	S(2)–C(20)–C(27)	110.43(14)				
Compound 8							
K(1)–S(1)	3.214(2)	K(1)⋯C(24)	3.539(6)	K(2)⋯C(56)	3.171(5)	K(3)⋯C(62)	3.735(10)
K(1)–S(2)	3.304(2)	K(1)⋯C(25)	3.271(6)	K(2)⋯C(57)	3.116(5)	S(1)–C(1)	1.871(5)
K(1)–S(3A)	3.102(2)	K(1)⋯C(26)	3.125(5)	K(2)⋯X1	2.988	C(1)–C(2)	1.540(7)
av K(1)–S	3.207	K(1)⋯X	3.121	K(3)–S(1A)	3.117(2)	C(1)–C(8)	1.535(7)
K(1)⋯C(14)	3.289(5)	K(2)–S(1)	3.203(2)	K(3)–S(2)	3.213(2)	C(1)–C(14)	1.546(7)
K(1)⋯C(15)	3.275(5)	K(2)–S(2)	3.320(2)	K(3)–S(3)	3.001(2)	S(2)–C(20)	1.878(5)
K(1)⋯C(16)	3.627(5)	K(2)–S(3)	3.257(2)	K(3)–S(av)	3.110	C(20)–C(21)	1.538(7)
K(1)⋯C(17)	3.956(6)	K(2)–S(2A)	3.184(2)	K(3)⋯C(32)	3.338(5)	C(20)–C(27)	1.545(7)
K(1)⋯C(18)	3.972(6)	K(2)–S(av)	3.241	K(3)⋯C(33)	3.286(5)	C(20)–C(33)	1.546(6)
K(1)⋯C(19)	3.654(5)	K(2)⋯C(38)	3.349(5)	K(3)⋯C(34)	3.173(5)	S(3)–C(39)	1.856(5)
K(1)⋯X	3.365	K(2)⋯C(52)	3.265(5)	K(3)⋯C(35)	3.727(5)	C(39)–C(40)	1.545(7)
K(1)⋯C(21)	3.272(5)	K(2)⋯C(53)	3.408(5)	K(3)⋯C(59)	3.845(10)	C(39)–C(46)	1.546(7)
K(1)⋯C(22)	3.571(6)	K(2)⋯C(54)	3.449(6)	K(3)⋯C(60)	3.270(8)	C(39)–C(52)	1.542(7)
K(1)⋯C(23)	3.675(7)	K(2)⋯C(55)	3.351(6)	K(3)⋯C(61)	3.205(7)		
S(1)–K(1)–S(2)	92.42(5)	S(2)–K(3)–S(3)	98.30(5)	S(2)–C(20)–C(21)	106.2(3)		
S(1)–K(1)–S(3A)	89.21(5)	C(1)–S(1)–K(1)	96.8(2)	S(2)–C(20)–C(27)	113.3(3)		
S(2)–K(1)–S(3A)	89.10(4)	C(1)–S(1)–K(2)	130.3(2)	S(2)–C(20)–C(33)	105.4(3)		
S(1)–K(2)–S(3)	169.41(5)	C(1)–S(1)–K(3A)	131.7(2)	C(39)–S(3)–K(1A)	112.5(2)		
S(1)–K(2)–S(2)	92.33(4)	S(1)–C(1)–C(2)	107.0(3)	C(39)–S(3)–K(2)	100.1(2)		
S(1)–K(2)–S(2A)	81.57(4)	S(1)–C(1)–C(8)	112.9(4)	C(39)–S(3)–K(3)	155.0(2)		
S(2)–K(2)–S(3)	91.29(4)	S(1)–C(1)–C(14)	107.2(3)	S(3)–C(39)–C(40)	112.6(4)		
S(2)–K(2)–S(2A)	89.12(4)	C(20)–S(2)–K(1)	96.8(2)	S(3)–C(39)–C(46)	110.5(3)		
S(3)–K(2)–S(2A)	88.55(4)	C(20)–S(2)–K(2)	117.3(2)	S(3)–C(39)–C(52)	103.4(3)		
S(1A)–K(3)–S(2)	82.45(4)	C(20)–S(2)–K(3)	83.8(2)				
S(1A)–K(3)–S(3)	92.93(5)	C(20)–S(2)–K(2A)	151.4(2)				

typically a four-coordinate cation with Li–S distances of less than 2.45 Å: Li–S bonding in [Li(thf)₃(S–C₆H₂–2,4,6-Bu₃)] is 2.45(1) Å,^{4h} in [Li(NC₅H₅)₃(S–C₆H₄–2-Me)] is 2.412(6) Å,^{4g} in [Li(thf)₃(S–C₆H₂–2,4,6-Ph₃)] is 2.43(1) Å,^{4f} and in [Li(pmdta)(SCPh₃)] (pmdta = *N,N,N,N,N'*-pentamethyldiethylenetriamine) and [Li(pmdta)(STrip)] is 2.412(7) and 2.366(7) Å, respectively.^{4c} In the absence of crown ether or other Lewis basic donors, however, aggregation behavior is observed with a concomitant increase in Li–S bond distances.^{4,5} Specifically, [Li(SCPh₃)] dimerizes in the presence of thf, yielding [Li(SCPh₃)(thf)₂]₂ where the Li–S bonds range from 2.466(5) to 2.494(5) Å (CN = 4).^{4c} A similar dimeric compound was observed in [Li(OSiPh₃)(dme)]₂, where ethereal chelation results in a four-coordinate cation.²¹ Crown ether solvation of lithium triphenylmethane-

thiolates, then, provides enough in the way of coordinative saturation and steric presence to preclude aggregation past a monomeric species.

The crown-complexed monomeric potassium thiolates **2–5** are the first family of such compounds reported, facilitating a comparison of donor effects on molecular structure. In the asymmetric unit of **2**, K(1) (CN = 7) is coordinated to six crown oxygens and the thiolato sulfur atom (Figure 2). The broad range of K(1)–O interactions, 2.763(3)–2.965(2) Å, reflects the displacement of K(1) above the crown oxygen plane by 0.63 Å, while the K(1)–S(1) bond distance is 3.135(1) Å. A benzene molecule is included in the lattice at an inversion center, such that the asymmetric unit contains

(21) McGeary, M. J.; Folting, K.; Streib, W. E.; Huffman, J. C.; Caulton, K. G. *Polyhedron* **1991**, *10*, 2699.

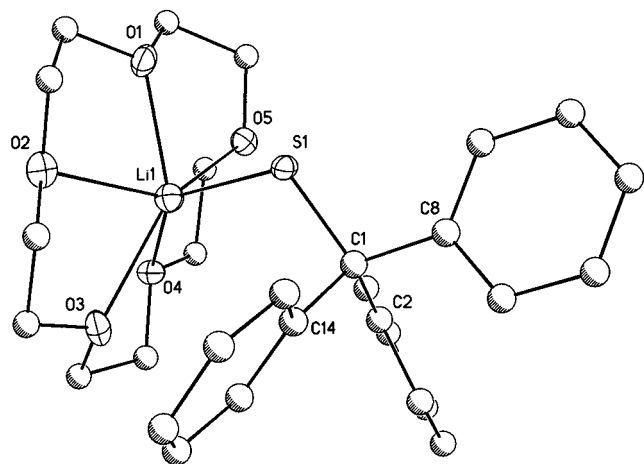


Figure 1. Computer-generated plot of **1** with anisotropic displacement parameters depicting 30% probability. The hydrogen atoms have been omitted for clarity.

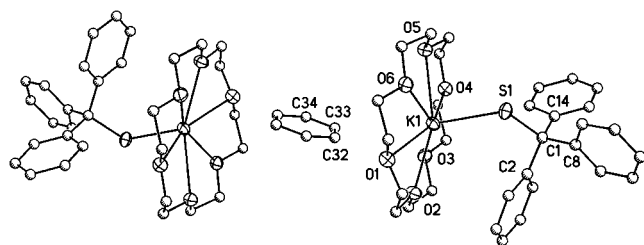


Figure 2. Computer-generated plot of **2** with anisotropic displacement parameters depicting 30% probability. The symmetry-generated second molecule is shown. Hydrogen atoms have been omitted for clarity.

half of C_6H_6 . When the reaction is run in thf, compound **3** is obtained, where a molecule of thf also resides over a crystallographic inversion center but interacts weakly with potassium at 3.249(6) Å. Interestingly, in a 50:50 thf–benzene solvent system, **2** is the sole isolated product in good yield, corroborating the weak K(1)–thf interaction. Geometrical data for **3** are very similar to those for the thf-free analogue: K(1)–O interactions range broadly over 2.729(5)–2.950(4) Å, in accord with a cation displacement from the crown oxygen plane by 0.520 Å. The K(1)–S(1) bond distance of 3.158(2) Å is comparable to the 3.135(1) Å K(1)–S(1) bond in **2**, suggesting K(1) in compound **3** can be viewed as formally seven-coordinate. Further, both compounds exhibit almost identical angles about S(1), 112.1(1)° in **2** and 112.8(2)° in **3**.

K(1)–S(1)–C(1) bond angles in **2** and **3** are related to the balance between potassium–crown oxygen coordination, cation displacement above the crown plane, and the steric interaction of trityl phenyl rings and crown ether. Specifically, the orientation of trityl to crown is such that S(1)–K(1)–O(5), O(6) angles are acute, while the remaining S(1)–K(1)–oxygen angles are all obtuse. As a result of the skewed crown plane with respect to the K–S vector, the K–S–C bond angle can relax toward the more distant crown edge (O(2)–O(3)). The K–S–C angles in **2** and **3** can be compared to the 77.68(7)° K–Te–C angle in [K(18C6)(TeTrip)], where longer K–Te and Te–C bond lengths (3.499(1) and 2.150(3) Å, respectively) allow for a more closed geometry about tellurium.¹⁵ The monomeric formulation of compounds **2** and **3** can be contrasted to [K(18C6)-OSiPh₃]₂, where dimerization occurs through K–O

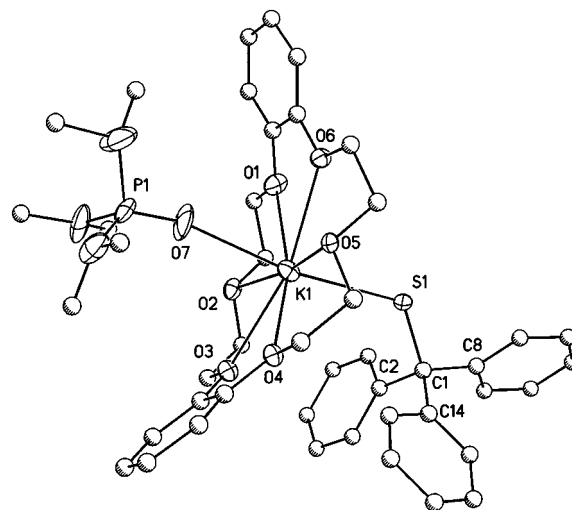


Figure 3. Computer-generated plot of **4** with anisotropic displacement parameters depicting 30% probability. The hydrogen atoms have been omitted for clarity.

(crown) contacts and not the anionic ligands.²¹ The intercrown K–O bonds in the dimer are 2.918 and 3.112 Å, whereas coordinating thf in compound **3** is located 3.249 Å from K(1). The stronger K–O contacts in the former serve to stabilize the aggregate.²²

In contrast to the cation displacement from the mean crown oxygen plane in **2** and **3**, DB18C6-coordinated **4** and **5** exhibit little cation deviation from the crown oxygen plane, a narrow distribution of K–O contacts, considerably wider K–S–C angles, and an accompanying tight range of S–K–O(crown) bond angles. K(1) in **4** is formally eight-coordinate, with six crown oxygen contacts in the range of 2.760(3)–2.817(3) Å, one hmpa ligand trans to the thiolate at 2.770(7) Å, and a thiolate interaction of 3.216(1) Å (Figure 3). The longer K–S bond length (compared to **2** and **3**) can be attributed to the higher cation coordination number. In comparison, [K(DB18C6)STrip(thf)] exhibits similar geometrical parameters with respect to the metal coordination environment: K–oxygen distances range between 2.700(5) and 2.868(7) Å, and the average K–S bond length of 3.197 Å reflects an eight-coordinate metal center.^{8,23} Potassium displacement out of the crown oxygen plane in **4** is nominal at 0.15 Å, while the K(1)–S(1)–C(1) angle has opened to 126.7(1)°. The cup-shaped DB18C6 solid-state conformation facilitates a strong K–S interaction with maximized K–O bonding, which is at the expense of a wider K–S–C bond angle, however. The K(1)–hmpa interaction in **4** is in accord with other potassium–hmpa interactions. For example, [K(SCN)₃(hmpa)₅] exhibits K–O contacts in the range of 2.712(5)–2.748(8) Å.²⁴ When the metalation reaction is carried out in the absence of donors other than crown ether, a toluene-coordinated monomer can be isolated. In **5**, K(1) exhibits a narrow range of ethereal interactions over 2.686(3)–2.796(3) Å, nominal displacement from the crown oxygen plane of 0.153 Å, and a wider

(22) The monomeric [K(18C6)(SSiPh₃)] also features a significant cation displacement above the crown oxygen plane, which likely precludes any interaction from a donor trans to the thiolate (unpublished results).

(23) In the monomeric potassium thiolate [K(18C6)(S-2-NC₃H₄)] with an eight-coordinate cation, the K–S bond distance is 3.256 Å (manuscript in preparation).

(24) Barr, D.; Doyle, M. J.; Drake, S. R.; Raithby, P. R.; Snaith, R.; Wright, D. S. *Inorg. Chem.* **1989**, *28*, 1767.

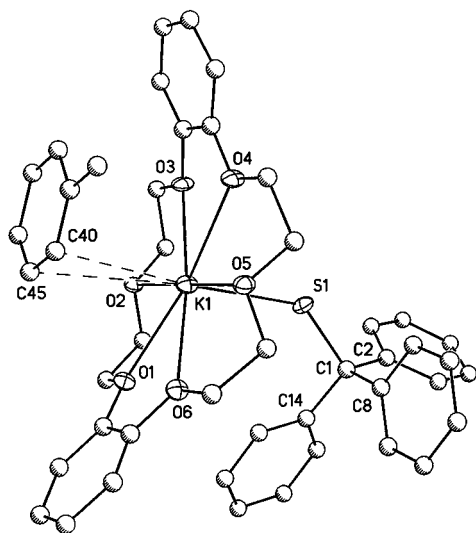


Figure 4. Computer-generated plot of **5** with anisotropic displacement parameters depicting 30% probability. The hydrogen atoms have been omitted for clarity.

K(1)–S(1)–C(1) angle at 132.2(1)° (Figure 4). Toluene is partially coordinated to K(1), with the closest, albeit very weak, contacts to C(40) and C(45) of 3.524(6) and 3.561(7) Å, respectively (*vide infra*).²⁵ Accordingly, the K(1)–S(1) bond distance of 3.127(1) Å suggests that the cation can be viewed as seven-coordinate, where the shorter bond in **5** can be correlated with the wider K(1)–S(1)–C(1) angle. Comparative geometrical data for compounds **2–5** and related potassium chalcogenolates can be found in Table 3.²⁶

Sodium hydride metalation of triphenylsilylanethiol in toluene leads to hexameric [(NaSSiPh₃)₆(tol)₂] (**6**), shown in Figures 5 and 6. The box-shaped core can be viewed as two face-fused cubes, or alternatively as dimerized three-rung Na₃S₃ ladders or as a trimer of Na₂S₂ dimers. Compound **6** is one of the few examples of a box motif for a sodium chalcogenolate. Related examples of hexameric Na₆(ER)₆ species are known. For example, in the sodium thiolate box [(NaSTrip)₂(Na(Et₂O)STrip)₄],⁸ a combination of steric saturation and ethereal donor coordination stabilizes the framework. Further, the hexagonal-prismatic structure of [Na(S-2-NC₅H₂-3,6-(SiMe₂Bu^t)₂)₆]¹⁰ and the box-shaped [NaOC₆H₄(CH₂-NMe₂)-2]₆^{2b} feature intramolecular nitrogen coordination of the Na₆E₆ core, while in [NaOC(CH₃)₃]₆²⁷ the framework is stabilized via bulky *tert*-butyl groups.²⁸ In compound **6**, the Na₆S₆ grid is stabilized by an organic periphery consisting of 18 phenyl groups from triphenylsilyl ligands and two coordinating toluene solvent molecules. Three unique four-coordinate metal environments exist: Na(1) resides at a corner position, with three thiolate contacts and η⁶-arene solvation from C(13)–C(18); Na(2) occupies the other corner position

(25) The structure of [K(18C6)(SCPh₃)]·tol does not show any cation–π interaction, which may be linked to the steric presence of 18C6 and the cation displacement toward the thiolate (unpublished results).

(26) No intermolecular contacts were observed for compounds **1–8** in packed structures.

(27) Greiser, T.; Weiss, E. *Chem. Ber.* **1977**, *110*, 3388.

(28) A number of hexameric lithium silyloxides (alkoxides) are known. For example: (a) Jones, R. A.; Koschmieder, S. U.; Atwood, J. L.; Bott, S. G. *J. Chem. Soc., Chem. Commun.* **1992**, 726. (b) Chisholm, M. H.; Drake, S. R.; Naiini, A. A.; Streib, W. E. *Polyhedron* **1991**, *10*, 805. (c) Bazhenova, T. A.; Lobkovskaya, R. M.; Shibaeva, R. P.; Shilov, A. E.; Shilova, A. K. *J. Organomet. Chem.* **1987**, *330*, 9.

in the asymmetric unit, also with three thiolate bonds and a strong η⁶-arene interaction to toluene C(55)–C(61); Na(3) is located at the internal site, exhibiting four thiolate interactions and no significant π contacts with the triphenylsilyl periphery.

Within the framework, no clear trend is discernible regarding the range of Na–S contacts, which deviate over 0.457 Å. The average Na–S bond distance of 2.845 Å in **6** is comparable to that in other hexameric sodium thiolates. For example, the Na–S bond distances in [(NaSTrip)₂(Na(Et₂O)STrip)₄]⁸ and [Na(S-2-NC₅H₂-3,6-(SiMe₂Bu^t)₂)₆]¹⁰ range between 2.822(2) and 2.918(1) Å and between 2.785(4) and 2.857(5) Å, respectively. Several other sodium thiolates exhibit Na–S distances in a comparable range: 2.808(1)–2.848(1) Å and 2.770(1)–2.773(1) Å in [Na(pmdta)STrip]₂ and [Na(tmeda)STrip]_∞ (tmeda = *N,N,N,N*-tetramethylethylenediamine), respectively,⁸ and 2.825(2)–2.838(2) Å in [Na(thf)₂SR_f]_∞.¹¹ Shorter Na–S distances are observed in [NaSC₆H₃-2,6-Trip₂]₂ (2.684(2)–2.762(2) Å) due to a lower coordination number for the cation.^{4a} Angles involving the corner metal sites and the central position in **6** exhibit nominal deviations from 90° and 180°: 92.23(3)–102.44(4)° about Na(1) and 88.03(3)–92.64(3)° about Na(2), while the four thiolate contacts to Na(3) describe a slightly distorted seesaw geometry with angles at 80.60(3)–93.47(4) and 173.85(5)°.

Both Na(1) and Na(2) exhibit significant η⁶-arene interactions with proximal phenyl groups. Numerous examples exist of arene solvation in alkali-metal complexes.²⁹ Perhaps most pertinent, however, is the recently characterized [NaSC₆H₃-2,6-Trip₂]₂, where the sodium cations are ligated in an η⁶ fashion by *ortho* phenyl groups in the range of 2.839(5)–3.244(5) Å with Na–centroid distances of 2.720 and 3.076 Å.^{4a} In compound **6**, one strong and one weaker sodium–η⁶-arene interaction are observed. The weaker contact is about Na(1), with Na(1) to C(13)–C(18) distances ranging from 2.852(2) to 3.664(3) Å and a Na(1)–centroid distance of 2.972 Å, while toluene C(56)–C(61) is very close to Na(2), with contacts ranging from 2.896(4) to 3.115(3) Å and a Na(2)–centroid distance of 2.665 Å. For comparison, Na–π contacts in [{Na⁺(thf)₂}]₄-(rubrene⁴⁻) range from 2.60 to 2.93 Å.^{29d} Importantly,

(29) For lead references to the cation–π model and both neutral and anionic aryl ligation of alkali-metal cations see: (a) Ma, J. C.; Dougherty, D. A. *Chem. Rev.* **1997**, *97*, 1303. (b) Clegg, W.; Drummond, A. M.; Mulvey, R. E.; O'Shaughnessy, P. *J. Chem. Soc., Chem. Commun.* **1997**, 1301. (c) Dougherty, D. A. *Science* **1996**, *271*, 163. (d) Bock, H.; Gharagozloo-Hubmann, K.; Näther, C.; Nagel, N.; Havlas, Z. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 631. (e) Mecozzi, S.; West, A. P.; Dougherty, D. A. *J. Am. Chem. Soc.* **1996**, *118*, 2307. (f) Clark, D. L.; Gordon, J. C.; Huffman, J. C.; Vincent-Hollis, R. L.; Watkin, J. G.; Zwick, B. D. *Inorg. Chem.* **1994**, *33*, 5903. (g) Kumpf, R. A.; Dougherty, D. A. *Science* **1993**, *261*, 1708. (h) Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1501. (i) Hitchcock, P. B.; Lappert, M. F.; Lawless, G. A.; Royo, B. *J. Chem. Soc., Chem. Commun.* **1993**, 554. (j) Bock, H.; Ruppert, K.; Näther, C.; Havlas, Z.; Herrmann, H.-F.; Arad, C.; Göbel, I.; John, A.; Meuret, J.; Nick, S.; Rauschenbach, A.; Seitz, W.; Vaupel, T.; Solouki, B. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 550. (k) Bock, H.; Näther, C.; Ruppert, K. *J. Chem. Soc., Chem. Commun.* **1992**, 765. (l) Clark, D. L.; Watkin, J. G.; Huffman, J. C. *Inorg. Chem.* **1992**, *31*, 1554. (m) Fuentes, G. R.; Coan, P. S.; Streib, W. E.; Caulton, K. G. *Polyhedron* **1991**, *10*, 2371. (n) Rabe, G.; Roesky, H. W.; Stalke, D.; Pauer, F.; Sheldrick, G. M. *J. Organomet. Chem.* **1991**, *403*, 11. (o) Bock, H.; Ruppert, K.; Havlas, Z.; Fenske, D. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1042. (p) Lorberth, J.; Shin, S.-H.; Wocadlo, S.; Massa, W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 735. (q) Bock, H.; Ruppert, K.; Fenske, D. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1685. (r) Jutzki, P.; Leffers, W.; Hampel, B.; Pohl, S.; Saak, W. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 583. (s) Prior to 1987 see Schade, C.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1987**, *27*, 169; and references cited therein.

Table 3. Bond Distances in 2–5, 7, and 8 and Related Potassium Thiolates

compd	CN	K–S (Å)	K–donor (Å)	K \cdots arene (Å)	K \cdots centroid (Å)	ref
2	7	3.135(1)	2.763(3)–2.965(2)	NA	NA	<i>b</i>
3	7 (+1)	3.158(2)	2.729(5)–2.950(4)	NA	NA	<i>b</i>
4	8	3.216(1)	2.760(3)–2.817(3)	NA	NA	<i>b</i>
5	7 (+1)	3.127(1)	2.686(3)–2.796(3)	3.524(6)–4.274(8)	3.678	<i>b</i>
7	3 (+6)	3.183 (av)		3.127(2)–3.626(3)	3.079	<i>b</i>
	4 (+6)			3.104(2)–3.491(2)	2.999	
	4		2.538(2)	NA		
8	3 (+6) (+ 6)	3.186 (av)		3.125(5)–3.972(6)	3.121, 3.365	<i>b</i>
	3 (+2)			3.205(7)–3.270(8)	NA	
	4 (+6)			3.116(5)–3.449(6)	2.988	
[KSR] ₂	2 (+6) (+6)	3.055 (av)		3.279(5)–3.564(5)	3.067, 3.093	4a
					3.140, 3.152	
[(KSR')(thf)] ₆	4, 5	3.176 (av)	2.60(2)–2.72(2)	NA	NA	8
[K(L)(thf)SR']	8	3.197 (av)	2.722–2.845 (av)	NA	NA	8
[K(thf)SR'] _∞	4	3.136 (av)	2.682 (av)	NA	NA	8
[K(pmdta)SR'] _∞	5	3.177 (av)	2.876 (av)	NA	NA	8
[K(SR) ₂ (thf)] _∞	4 (+4)	3.159(1)–3.171(1)	2.676(3)	NA	NA	11
			2.920(2)–3.094(2)			

^a R = C₆H₃-2,6,-Tripp₂, R' = Trip, Rf = C₆H₂-2,4,6-(CF₃)₃. L = DB18C6. ^b This work.

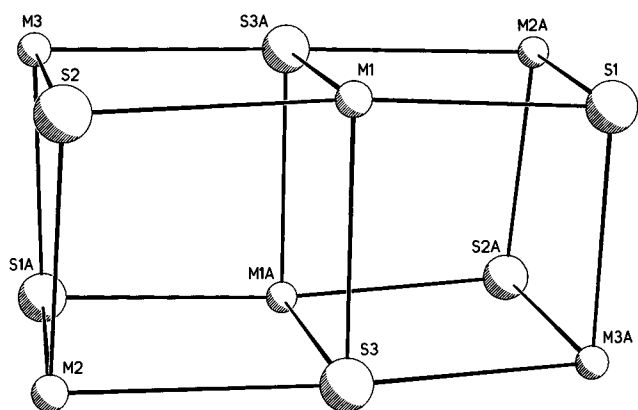


Figure 5. Computer-generated scheme of the M₆S₆ box aggregate for compounds **6–8** (M = Na, K).

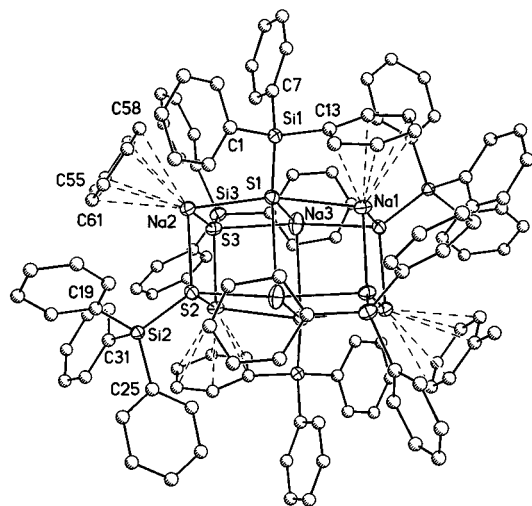


Figure 6. Computer-generated plot of **6** with anisotropic displacement parameters depicting 30% probability. Symmetry-related trityl groups and the coordinating solvent molecule are shown. The hydrogen atoms have been omitted for clarity.

the corner coordination site at Na(2) in compound **6** is capable of accommodating the steric presence of a toluene molecule such that strong η^6 -arene stabilization of the cation is possible. The corner coordination site is closely related to the radial extension of phenyl groups from the M₆S₆ core and to the size and donor strength of the coordinated molecule (*vide infra*).³⁰ Selected

Na–S and Na– π -arene bond distances between compound **6** and related sodium thiolates are summarized in Table 4.

The metathesis reaction of KH and HSCPh₃ in toluene, and in the absence of crown ether, results in the isolation of hexameric box-shaped potassium thiolate aggregates. In [(KSCPh₃)₆(hmpa)₂] (**7**) and [(KSCPh₃)₆(tol)₂] (**8**) the K₆S₆ core is assembled through K–S bonding and intramolecular arene coordination of the alkali-metal cations. Completing the overall ligand environment are two coordinated molecules of hmpa in **7** and toluene in **8**. Interestingly, the 1:1 KH–hmpa stoichiometry in the synthesis of **7** is not reflected in the solid-state structure, where only one-third of the amount of hmpa has been incorporated. Compounds **7** and **8** display similar M₆S₆ box frameworks (Figure 5) with nominal deviations between the K–S bond distances and intrabox angles. Further, the framework geometries for both boxes are similar to those in other potassium thiolate complexes (Table 3). Significant changes are observed, however, in the conformation of phenyl groups about the core structures for **7** and **8**, which are sensitive to the donor molecules ligating the corner cation positions of the box (Figures 7 and 9).

Remarkable in structures **7** and **8** is the degree of intramolecular arene solvation of the K₆S₆ core. As with [(NaSSiPh₃)₆(tol)₂], compounds **7** and **8** feature 18 aromatic rings disposed about the hexameric grid and 2 coordinating donor molecules, hmpa and toluene, respectively (Figures 8 and 10). In contrast to the sodium congener, however, the larger ionic radii of potassium (CN = 6: K at 1.52 Å versus Na at 1.16 Å) results in increased cation– π interactions.³¹ In compound **7**, phenyl groups C(21)–C(26) and C(52)–C(57) interact in an η^6 fashion with K(1) and K(2), respectively: the K(1) to C(21)–C(26) distances range from 3.104(2) to 3.491(2) Å with a K(1)–centroid distance of 2.999 Å, while K(2) to C(52)–C(57) distances are 3.127(2)–3.626(3) Å with a K(2)–centroid distance of 3.079 Å. The ligand environment about K(3) is satiated

(30) The reaction of NaH and HSSiPh₃ in toluene and the presence of 1 equiv of hmpa leads to the cubic [Na(hmpa)SSiPh₃]₄, which emphasizes the role a strong donor plays in stabilizing the putative solution aggregates. The structural refinement of this tetramer is still under investigation.

(31) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry*, 4th ed.; Harper Collins: New York, 1993.

Table 4. Bond Distances in 6 and Related Sodium Thiolates

compd	CN	Na–S (Å)	Na–donor (Å)	Na⋯arene (Å)	Na⋯centroid (Å)	ref
6	4	2.845 (av)				<i>b</i>
	3 (+6)			2.852(2)–3.664(3)	2.972	
	3 (+6)			2.896(4)–3.115(3)	2.665	
[(NaSR) ₆ (Et ₂ O) ₄]	4	2.867 (av)	2.305(3)–2.417(3)	NA	NA	8
[NaSR'] ₆	4	2.818 (av)	2.481(9)	NA	NA	10
[NaSR''] ₂	2 (+6)	2.710 (av)		3.016(5)–3.266(5)	2.701	4a
				2.839(5)–3.244(5)	2.720	
[Na(SR _f)(thf) ₂] ₆	4 (+2)	av. 2.833	2.263(4)–2.317(3)	NA	NA	11

^a R = Trip, R' = C₅H₂N-3,6-(SiMe₂Bu)₂, R'' = C₆H₃-2,6-Trip₂, R_f = C₆H₂-2,4,6-(CF₃)₃. ^b This work.

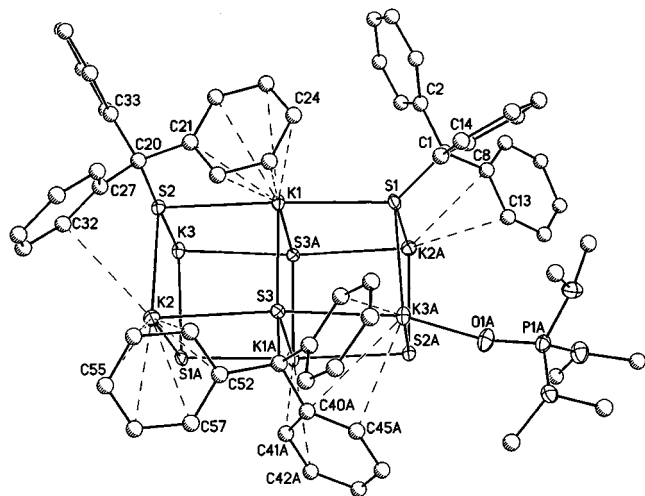


Figure 7. Computer-generated plot of **7** with anisotropic displacement parameters depicting 30% probability. Ligands corresponding to the asymmetric unit are shown; hydrogen atoms have been omitted for clarity.

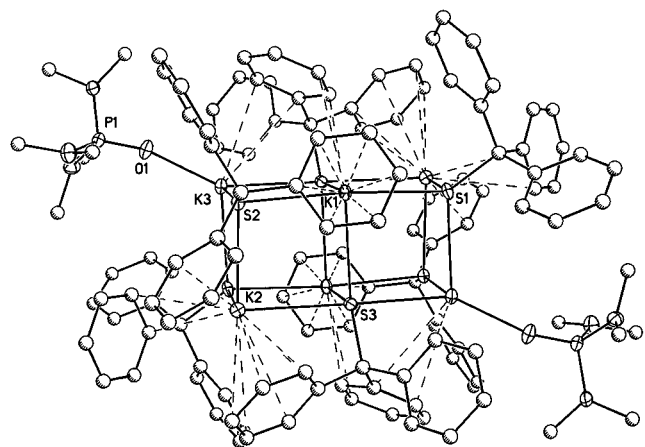


Figure 8. Computer-generated plot of **7** with anisotropic displacement parameters depicting 30% probability. All symmetry-related ligands are shown; hydrogen atoms have been omitted for clarity.

by a strongly coordinating hmpa donor; no η^6 -arene interactions are observed. A number of more distant, but nonetheless important, contacts occur between phenyl rings and each cation in the box. For example, the aromatic ring C(40)–C(45) is disposed over the [K(1)K(3)–S(2)S(3A)] face such that C(41) and C(42) approach K(1) at 3.225(2) and 3.546(3) Å, respectively, while C(40) and C(45) interact with K(3) at 3.532(2) and 3.367(3) Å. Completing the closest neighbor set about K(3) is C(47) at 3.307(3) Å, while all other K(1)– and K(3)–phenyl contacts are above 3.750 Å. In addition to the strong η^6 -arene solvation of K(2) from C(52)–C(57), phenyl carbons C(8A), C(13A), and C(32) have

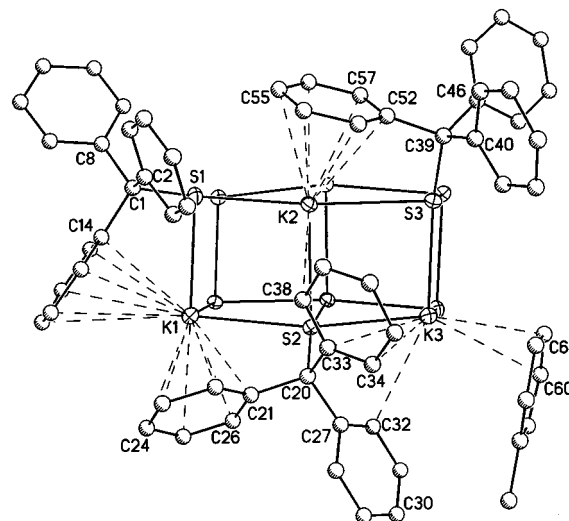


Figure 9. Computer-generated plot of **8** with anisotropic displacement parameters depicting 30% probability. Ligands corresponding to the asymmetric unit are shown; hydrogen atoms have been omitted for clarity.

contacts with this cation at 3.571(2), 3.556(3), and 3.398(2) Å, respectively. All other K(2)–arene interactions are above 3.80 Å. Taking into account only the strong η^6 -arene coordination in **7**, the phenyl groups corresponding to the trityl unit connected to S(1) are less active in cation solvation as compared to the phenyls from trityl S(2) and S(3), where one phenyl from each of the latter exhibits η^6 -arene coordination to separate cations.

In contrast to the molecular conformation about the organic periphery of **7**, coordination of toluene in **8** requires a reorganization of the phenyl rings such that all three trityl units exhibit one η^6 -arene interaction with nearby cations. Specifically, C(14)–C(19) coordinates rather weakly with K(1) over 3.275(5)–3.972(6) Å with a K(1)–centroid distance of 3.365 Å, while C(21)–C(26) is disposed more closely at 3.125(5)–3.675(7) Å with a K(1)–centroid distance of 3.121 Å. The ligand environment about K(2) features an η^6 -arene interaction from the third trityl unit; C(52)–C(57) contacts range from 3.116(5) to 3.449(6) Å with a K(2)–centroid distance of 2.988 Å. At one corner, K(3) does not interact strongly with any trityl phenyl groups. Instead, the coordination void is filled with a toluene solvent molecule. The steric presence of nearby phenyl groups associated with S(1A), S(2) and S(3) is such that only one edge of the toluene can access K(3). The K(3) to C(60)–C(61) distances are 3.205(7) and 3.270(8) Å, respectively, with next nearest contacts above 3.73 Å. Several further cation–arene interactions complete the coordination environment about K(2) and K(3). Partially covering the [K(2)K(3)–S(2)S(3)] face is phenyl

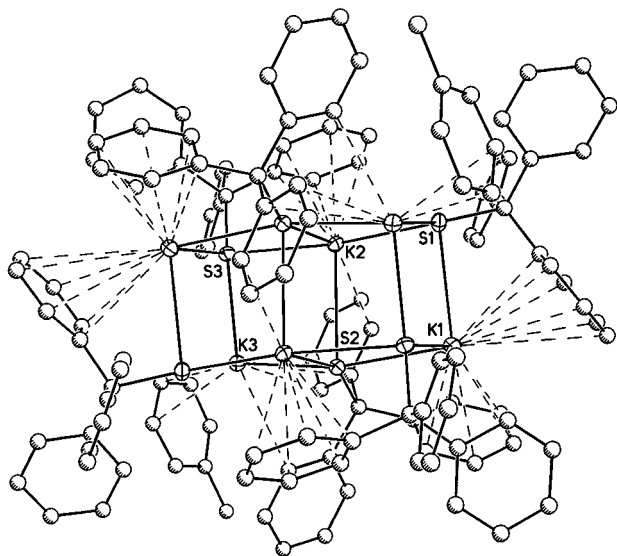


Figure 10. Computer-generated plot of **8** with anisotropic displacement parameters depicting 30% probability. All symmetry-related ligands are shown; hydrogen atoms have been omitted for clarity.

C(33)–C(38), with C(38) being 3.349(5) Å from K(2) and C(33) and C(34) being 3.286(5) and 3.173(5) Å from K(3), respectively. Also proximate to K(3) is C(32) at 3.338(5) Å. The potassium– η^6 -arene distances in **7** and **8** can be compared to those in the recently described $[\text{KSCPh}_3\text{-}2,6\text{-Trip}_2]_2$, where K–arene interactions lie in the range 3.279(5)–3.564(5) Å.^{4a} Further, potassium intercalated into graphite was shown to have a K–C interaction of 3.08 Å.³² Comparative data for these compounds and related potassium thiolates are summarized in Table 3.

The core hexameric frameworks of compounds **6–8** are roughly similar, with the exception of **6** being more compact due to the shorter Na–S bonding. Significant differences arise, however, in the interaction of the trityl phenyl groups with the core structures and coordinating ligand molecules. In the potassium thiolate boxes, an open corner coordination site is available for hmpa or toluene ligation: K(3)–hmpa in **7** and K(3)–toluene in **8**. Depending on the steric presence and coordinating ability of the donor, the organic periphery adopts a conformation accommodating hmpa in **7**, while reorganization in **8** is such that the more weakly coordinating toluene molecule cannot gain full access to the cation site. In contrast, the greater radial extension of SSiPh_3 versus SCPh_3 allows η^6 -arene coordination by toluene at the corner site Na(2), while the more compact Na_6S_6 skeleton precludes extensive intramolecular cation– π interactions. Indeed, in the analogous box structure of $[(\text{KSSiPh}_3)_6(\text{tol})_2]$, the larger coordination site at one corner metal position is occupied by toluene in an η^6 fashion.³³ Compounds **7** and **8** can also be compared to the dme-linked bis(cubane) complex $[\text{K}_8(\text{OSiPh}_3)\text{-}(\text{dme})_3]$.²¹ The short K–O bond distances and ethereal coordination result in cuboidal units exhibiting one close cation– π contact of 3.078(4) Å.

(32) Solin, S. S. *Adv. Chem. Phys.* **1982**, *49*, 455.

(33) The experimental protocol for $[(\text{KSSiPh}_3)_6(\text{tol})_2]$ was identical with the synthesis of compound **7**; however, the crystal quality of the compound did not suffice to allow for a satisfactory structural refinement.

When metathesis between potassium hydride and triphenylmethanethiol is run in the presence of stoichiometric pyridine, 1,4-dioxane, or pmdta, the sole isolated product is the toluene box $[(\text{KSCPh}_3)_6(\text{tol})_2]$. Clearly, then, toluene is an effective donor for potassium in this series, being displaced only by the strongly ligating hmpa. A similar observation was made in the synthesis of $[\text{K}\{\text{Sn}(\text{CH}_2\text{Bu}^t)_3\}(\text{tol})_3]$, where three η^6 -toluene interactions effectively displace thf about the cation.²⁹ⁱ

The cation–chalcogenolato bonding in compounds **1–8** is governed primarily by ionic contributions, which can be observed in the high cation coordination numbers in **1–5** and in the nondirectional metal–chalcogenolato and –ligand interactions throughout. Further, a complicated and subtle relationship exists between the core ionic metal–chalcogenolato interaction, metal–ligand association, ligand–ligand steric repulsion, and the overall molecular structure. For example, in the absence of an appropriate crown ether, the metal–triphenylmethanethiolate subunits oligomerize as a function of the metal and added donor, yielding $[\text{Li}(\text{thf})_2\text{-}(\text{SCPh}_3)_2]$,^{4c} $[(\text{NaSSiPh}_3)_6(\text{tol})_2]$, and $[(\text{KSCPh}_3)_6(\text{donor})_2]$. Truncation of the nascent oligomer during subunit association can, of course, be affected by donor and ligand, but as observed in compounds **6–8**, association can also be affected by inter-ligand–ligand steric repulsion. This is analogous to the ring-stacking principle observed in organolithium complexes and related systems: on the basis of an ionic bonding model, the cation maximizes anion contacts, the number of which are inherently limited due to the energy penalty incurred from ligand–ligand repulsion.³⁴

Conclusion

Crown ether complexation of lithium and potassium triphenylmethanethiolates allows the isolation of monomeric species. The resultant high coordination number about lithium in $[\text{Li}(15\text{C}5)\text{SCPh}_3]$ leads to a lengthening of the Li–S bonding distance in comparison to known, but lower coordinate, lithium thiolates. 18C6 or DB18C6 effectively preclude oligomerization in the KSCPh_3 series, where the balance between the coordinating ability of crown ether, cation displacement from the crown plane, and steric interaction of crown ether and triphenylmethanethiolate is reflected in the ligation of donor molecules. Indeed, thf coordination in $[\text{K}(18\text{C}6)\text{-}(\text{SCPh}_3)(\text{thf})_{0.5}]$ is quite weak, in part as a result of the cation displacement above the crown plane toward triphenylmethanethiolate. DB18C6 ligates potassium in a decidedly in-plane orientation, which facilitates donor interaction with the cation (*vis-à-vis* $[\text{K}(\text{DB18C}6)\text{-}(\text{SCPh}_3)(\text{hmpa})_{0.5}]$ and $[\text{K}(\text{DB18C}6)\text{SCPh}_3(\text{tol})]$). In the absence of crown ethers, however, aggregation behavior is observed for sodium and potassium thiolates, which is dependent on the specific combination of alkali-metal cation, thiolate, and adjunct donor ligand. Metathesis of HSSiPh_3 or HSCPh_3 with NaH or KH leads to the hexameric aggregates $[(\text{NaSSiPh}_3)_6(\text{tol})_2]$, $[(\text{KSCPh}_3)_6(\text{hmpa})_2]$, and $[(\text{KSCPh}_3)_6(\text{tol})_2]$. These compounds are based on a similar M_6S_6 hexameric grid, but significant

(34) Gregory, K.; Schleyer, P. v. R.; Snaith, R. *Adv. Inorg. Chem.* **1991**, *37*, 47.

differences arise in the degree of cation- π interaction about the core structures and the closely related donor ligation at corner positions on each box. The compact Na_6S_6 framework in compound **6** and greater radial extension of triphenylsilylthiolate prohibits extensive intramolecular cation- π interaction, while it simultaneously forms two coordination sites at corner metal positions such that toluene can interact in an η^6 fashion. In contrast, the larger K_6S_6 frame in compounds **7** and **8** requires extensive intramolecular cation- π interaction. As a result, the two open corner sites cannot accommodate η^6 -arene coordination from toluene in compound **8** (rather, there is a π -edge orientation), whereas the strongly coordinating hmpa occupies these sites in compound **7**, requiring a reorganization of the trityl periphery. In accord with the known propensity of potassium to sequester toluene to its coordination environment, competitive experiments in the reaction of KH and HSCPh_3 in toluene with stoichiometric

pyridine, 1,4-dioxane, or pmdta consistently result in the isolation of compound **8**.

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Supporting Information Available: Full tables of data collection parameters, atom coordinates, bond distances and angles, hydrogen coordinates, and anisotropic thermal parameters for **1-8** and additional ORTEP plots for **3-5** and **7** (98 pages). Ordering information is given on any current masthead page.

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