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Sodium and Potassium Triisopropylbenzenethiolates: Influence on Solid-State Structure by Metal and Donor

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The synthesis and characterization of a family of sodium and potassium thiolates [A(donor)S(Trip)]$_n$ (A = Na, K; Trip = 2,4,6-i-Pr$_3$C$_6$H$_2$, n = 1−∞) is described. [Na(PMDTA)S(Trip)]$_2$, **1** (PMDTA = *N*,*N*,*N*′,*N*′′,*N*′′-pentamethyldiethylenetriamine), [(NaS(Trip))$_2$(Na(Et$_2$O)S(Trip))$_4$]·0.5 solvent, **2**, [Na(TMEDA)S(Trip)]$_\infty$, **3** (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine), [Na(THF)S(Trip)]$_n$, **4** (n = 6 or ∞), [K(dibenzo-18-crown-6)(THF)S(Trip)]·THF, **5**, [(KS(Trip))$_2$(K(THF)S(Trip))$_2$(K(THF)$_2$S(Trip))$_2$], **6**, [K(THF)S(Trip)]$_\infty$, **7**, [(K(THF)S-(Trip))$_2$(K(TMEDA)S(Trip))$_2$(KS(Trip))$_2$]·THF, **8**, and [K(PMDTA)S(Trip)]$_\infty$, **9**, were synthesized by treatment of HS(Trip) with NaH or KH along with the addition of various donors. The target molecules were characterized by IR, ^{1}H NMR, and depending on solubility, ^{13}C NMR spectroscopy and melting point. Compounds **1**−**3** and **5**−**9** were also characterized by single-crystal X-ray crystallography. Analysis of structural data clearly indicates that the structural chemistry of the target molecules can be influenced by donor choice, as exemplified by the large structural diversity observed in the target molecules: the use of a crown ether allowed the isolation of the monomeric species **5**, whereas the use of a monodentate donor, such as THF, led to the isolation of the ladder-type polymer **7** or the discrete hexameric compounds **2** and **6**. Addition of the bidentate donor TMEDA to a solution of [NaS(Trip)]$_\infty$ resulted in the formation of the one-dimensional zigzag polymer **3**, whereas utilization of the tridentate donor PMDTA allowed the isolation of the dimer **1**. Changing from sodium to potassium and utilization of the tridentate donor PMDTA yielded the one-dimensional zigzag polymer **9**, while employment of a mixture of mono- and bidentate donors (THF and TMEDA) resulted in the asymmetrically coordinate hexamer **8**. Crystal data with Mo Kα (λ = 0.710 73 Å) at 150 K are as follows: **1**, a = 13.2300(1) Å, b = 10.6176(1) Å, c = 19.6262(3) Å, β = 100.449(1)°, V = 2711.19(5) Å^3, Z = 4, monoclinic, space group $P2_1/n$, 6309 independent reflections, R1 (all data) = 0.1004; **2**, a = 14.4178(3) Å, b = 17.6498(4) Å, c = 26.2052(6) Å, α = 89.847(1)°, β = 77.475(1)°, γ = 70.189(1)°, V = 6106.3(2) Å^3, Z = 2, triclinic, space group $P\bar{1}$, 25 722 independent reflections, R1 (all data) = 0.1311; **3**, a = 9.2702(1) Å, b = 20.1017(2) Å, c = 25.9256(4) Å, V = 4831.15(10) Å^3, Z = 8, orthorhombic, space group *Pbca*, 5032 independent reflections, R1 (all data) = 0.1125; **5**, a = 14.196(3) Å, b = 15.429(3) Å, c = 22.562(5) Å, α = 101.92(2)°, β = 97.31(3)°, γ = 114.19(3)°, V = 4313(2) Å^3, Z = 4, triclinic, space group $P\bar{1}$, 6592 ($I > 2\sigma(I)$) data, R = 0.074; **6**, a = 15.071(3) Å, b = 25.301 (5) Å, c = 17.866(4) Å, β = 113.01(3)°, V = 6270(3) Å^3, Z = 2, monoclinic, space group $P2_1/n$, 2332 ($I > 2\sigma(I)$) data, R = 0.103; **7**, a = 11.9079(2) Å, b = 14.7672(2) Å, c = 24.0448(1) Å, β = 98.220(1)°, V = 4184.75(9) Å^3, Z = 4, monoclinic, space group $P2_1/c$, 9693 independent reflections, R1 (all data) = 0.1324; **8**, a = 18.324(4) Å, b = 14.323(3), c = 26.300(5) Å, β = 106.39(3)°, V = 6622(3) Å^3, Z = 2, monoclinic, space group $P2_1/c$, 4511 ($I > 3\sigma(I)$) data, R = 0.105; **9**, a = 10.4903(2) Å, b = 20.1551(5) Å, c = 26.4295(4) Å, V = 5588.1(2) Å^3, Z = 8, orthorhombic, space group *Pbca*, 6649 independent reflections, R1 (all data) = 0.146.

Introduction

The structural chemistry of lithium, sodium, and potassium alkoxides and aryloxides has been fairly well explored,[1−3] but the heavier chalcogen congeners have not received detailed attention.[4] The first structural characterization of a lithium thiolate was reported in 1985.[5] Since then a number of publications pertaining to lithium thiolates, selenolates, and tellurolates have appeared in the literature,[4−21] resulting in about 30 structural reports concerned with lithium chalcogenolates.

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Recent results emphasizing the structural diversity in lithium chalcogenolates describe the first trimeric,[20] hexameric,[21] and solvent-separated[20] lithium thiolates. In contrast, the heavier alkali analogs have received much less attention. So far only a handful of sodium, potassium, rubidium, and cesium chalcogenolates have been investigated in the solid state. This lack of knowledge is in sharp contrast to the importance of sodium and potassium chalcogenolates in synthetic chemistry: their increased reactivity makes them powerful and versatile reagents.[22] Examples of structurally characterized heavier alkali thiolates include sodium and potassium tris(trifluoromethyl)benzenethiolates;[3a] the sodium derivative crystallizes in the presence of THF as a one-dimensional zigzag polymer $[Na(THF)_2SR_f]_\infty$ ($R_f = 2,4,6\text{-}(CF_3)_3C_6H_2$), while the potassium species forms a ladder-type polymer $[K(THF)SR_f]_\infty$. The polymeric motif in the donor-free $[ASMe]_\infty$ (A = Li, Na, K) was shown utilizing powder diffraction techniques.[23] Recently, a series of donor-free dimeric species $[AS\text{-}2,6\text{-}Trip_2C_6H_3]_2$ (A = Li, Na, K, Rb, Cs; Trip = 2,4,6-i-$Pr_3C_6H_2$) was reported. Clearly, their nonpolymeric structures were made possible by utilization of the very bulky terphenyl ligand.[24] Only one hexameric sodium derivative, the hexagonal prismatic intramolecularly stabilized sodium 2-pyridinethiolate, has been published previously.[25] The hexameric, discrete, double-ladder derivatives $[(KSR)_2(K(THF)SR)_2(K(THF)_2SR)_2]$ and $[(K(THF)SR)_2(K(TMEDA)SR)_2(KSR)_2]$ (R = Trip) have been mentioned in a preliminary communication;[26] a full account of their chemistry is included in this paper. A few sodium and potassium tellurolates are known, such as the monomeric compounds $Na(TMEDA)_2Te\text{-}2,4,6\text{-}Me_3C_6H_2$[4b,27] and K(18-crown-6)TeTrip [4b,27] and the ladder-type polymer $[K(THF)_{1.33}TeTrip]_\infty$.[4b,15]

The large structural variety observed in the small group of structurally characterized alkali chalcogenolates indicates a rich structural chemistry, as also shown with the preparation and structural characterization of the first anionic sodium thiolate $[Na(12\text{-}crown\text{-}4)_2]_4\,[Na(THF)(S\text{-}2\text{-}NC_5H_4)_2][Na_2(S\text{-}2\text{-}NC_5H_4)_4]_2$.[28] This unusual “ate” complex crystallizes with two coordinatively distinct anions in each asymmetric unit. Utilizing one system and varying the metal and donor resulted in the polymeric derivative $[K_2(15\text{-}crown\text{-}5)(S\text{-}2\text{-}NC_5H_4)_2]_\infty$, where the crown ether serves as connecting unit and bridging template between KS-2-NC_5H_4 units.[28] A significantly different coordination chemistry was observed in a series of sodium and potassium trityl thiolates where extensive π-type interaction between the alkali metals and the phenyl rings of the ligands made possible the isolation of discrete hexameric species.[29]

In this paper we report the synthesis and structural characterization of a family of sodium and potassium triisopropylbenzenethiolates. The influence on their solid-state structures in dependence of steric bulk, hapticity of the donor and nature of the metal will be analyzed and discussed.

Experimental Section

General Procedures. All reactions were performed under a purified nitrogen atmosphere by using either modified Schlenk techniques or a Braun Labmaster 100 drybox. *n*-Hexane, tetrahydrofuran, and diethyl ether were freshly distilled from a Na/K alloy under a nitrogen atmosphere and subjected to several freeze−evacuate−thaw cycles prior to use. TMEDA and PMDTA were dried over CaH_2 and distilled prior to use. Commercially available dibenzo-18-crown-6 was used as received. Commercial NaH and KH, available as suspensions in mineral oil, were washed several times with *n*-hexane and dried in a vacuum. HS(Trip) was synthesized according to published procedures.[30] ^{1}H and ^{13}C NMR spectra were obtained utilizing either a General Electric QE-300 or a Bruker DPX-300 spectrometer. Infrared spectra were recorded as Nujol mulls between KBr plates, using a Perkin-Elmer PE 1600 FT-IR spectrometer.

Synthesis of $[Na(PMDTA)S(Trip)]_2$, 1. HS(Trip) (0.71 g, 3.00 mmol) was dissolved in 25 mL of hexane and slowly added to a mixture of 0.08 g of NaH (3.10 mmol) in 10 mL of hexane and 0.7 mL (3.30 mmol) of PMDTA. The solution was stirred overnight while slowly developing hydrogen gas, as indicated by the formation of gas bubbles. The resulting cloudy solution was warmed up to reflux temperature, upon which it became clear. After cooling to room temperature, 0.95 g of colorless needle-shaped crystals, suitable for X-ray crystallography, was obtained in 74% yield. Mp: 141 °C.

^{1}H NMR (C_6D_6) isotropic shifts at 25 °C: δ 1.34−1.36 (d, 6H *p*-CH_3 iPr), 1.50−1.51 (d, 12H *o*-CH_3 iPr), 1.79 (s, 3H), 1.84−1.93 (2 br d, 8H, PMDTA), 2.10 (s, 12H, PMDTA), 2.93 (sept, 1H, *p*-CH iPr), 4.81 (sept, 2H *o*-CH iPr), 7.15 (s, 2 *m*-H).

^{13}C{^{1}H} NMR (C_6D_6) isotropic shifts at 25 °C: δ 24.44 (*o*-CH_3 iPr), 24.83 (*p*-CH_3 iPr), 31.90 (*o*-CH iPr), 34.65 (*p*-CH iPr), 43.60 (NCH_3 PMDTA), 45.49 [$N(CH_3)_2$ PMDTA], 54.72 (CH_2 PMDTA), 57.29 (CH_2 PMDTA), 119.57 (*m*-Ph), 139.43 (*o*-Ph), 148.96 (*p*-Ph), ipso carbon atom unobserved.

IR (Nujol) ν (cm^{-1}): 1543 m, 1304 s, 1113 m, 1058 m, 1037 m, 970 m, 933 m, 903 m, 869 m, 770 m, 636 w, 582 w, 564 w, 525 w.

Synthesis of $[(NaS(Trip))_2(Na(Et_2O)S(Trip))_4]\cdot 0.5(solvent)$, 2. A solution of 0.71 g (3.00 mmol) of HS(Trip) in 30 mL of Et_2O was added to 0.07 g (3.00 mmol) of NaH, whereupon hydrogen gas production started immediately. The resulting pale yellow solution was stirred for 5 min until all NaH had reacted, and the solution became pale yellow and clear. Upon removal of the solvent and redissolving of the solid in 20 mL of a 5:1 mixture of hexane and diethyl ether, pale yellow needles suitable for crystallographic analysis were obtained in 77% yield (0.72 g).

Mp: >400 °C.

^{1}H NMR (C_6D_6) isotropic shifts at 25 °C: δ 1.28−1.36 (m, 18H, *o*- and *p*-CH_3 iPr), 2.88 (m, 1H, *p*-CH iPr), 4.22 (sept, 2H, *o*-CH iPr), 7.12 (s, 2 H, *m*-H).

^{13}C NMR: not available due to very limited solubility of the compound in nondonor solvents.

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IR (Nujol) ν (cm^{-1}): 1599 w, 1553 m, 1424 s, 1360 s, 1302 m, 1260 m, 1161 m, 1098 m, 1036 m, 934 m, 874 m, 804 m, 753 m, 635 m, 522 w.

Synthesis of [Na(TMEDA)S(Trip)]$_\infty$, 3. Compound **3** was synthesized by donor-exchange reaction utilizing compound **4** or by direct reaction between NaH and thiol: 0.50 g (1.51 mmol) of [Na(THF)S(Trip)]$_\infty$, **4,** was dissolved in 20 mL of toluene along with the addition of 2 mL of TMEDA. The resulting slightly turbid reaction mixture was stirred for 16 h followed by removal of most of the solvent and storage of the solution in the freezer at −15 °C. After 1 week, 0.50 g of a microcrystalline colorless product was obtained in 88% yield. An identical product was obtained by stirring equimolar amounts of NaH and HS(Trip) dissolved in THF along with the addition of TMEDA. Crystals suitable for crystallographic analysis became available after recrystallization from 10 mL of a 5:1 mixture of hexane and TMEDA.

Mp: 409 °C.

^{1}H NMR (C_6D_6) isotropic shifts at 25 °C: δ 1.32−1.34 (d, 6H *p*-CH_3 iPr), 1.50−1.51 (d, 12H *o*-CH_3 iPr), 1.82 (s, 4H, TMEDA), 1.87 (s, 12H, TMEDA), 2.91 (sept, 1H, *p*-CH iPr), 4.64 (br sept, 2H, *o*-CH iPr), 7.15 (s, 2 *m*-H).

^{13}C{^{1}H} NMR (C_6D_6) isotropic shifts at 25 °C: δ 24.05 (*o*-CH_3 iPr), 24.74 (*p*-CH_3 iPr), 32.25 (*o*-CH iPr), 34.63 (*p*-CH iPr), 45.51 [$N(CH_3)_2$ TMEDA], 57.16 (bridging-CH_2 TMEDA), 120.09 (*m*-Ph), 148.74 (*p*-Ph), ortho and ipso carbon unobserved.

IR (Nujol) ν (cm^{-1}): 1552 w, 1422 m, 1300 m, 1162 w, 1132 w, 1058 m, 1035 m, 1016 w, 934 w, 872 m, 834 w, 752 w, 639 w.

Synthesis of [Na(THF)S(Trip)]$_n$, 4. A 4.73-g sample of HS(Trip) (20.00 mmol) was dissolved in 40 mL of THF and the solution added to 0.48 g of NaH (20.00 mmol), whereupon an immediate evolution of hydrogen gas was observed. The solution was stirred for 2 h, followed by a reduction of volume to 10 mL to yield 5.62 g of a white powder (85%). Small, needle-shaped crystals were obtained by redissolving the powder in a small amount of THF followed by dropwise addition of hexane to initialize crystallization. The crystal quality did not allow for a crystallographic analysis.

Mp: 402 °C.

^{1}H NMR (C_6D_6) isotropic shifts at 25 °C: δ 1.28−1.33 (m, 10H, *p*-CH_3 iPr and THF), 1.42 (d, 12H, *o*-CH_3 iPr), 2.85 (sept, 1H, *p*-CH iPr), 3.39 (br m, 4H, THF), 4.29 (sept, 2H, *o*-CH iPr), 7.11 (s, 2 H, *m*-H).

^{13}C{^{1}H} NMR (C_6D_6) isotropic shifts at 25 °C: δ 23.96 (*o*-CH_3 iPr), 24.67 (*p*-CH_3 iPr), 25.42 (CH_2 THF), 32.57 (*o*-CH iPr), 34.59 (*p*-CH iPr), 67.96 (CH_2 THF), 120.36 (*m*-Ph), 141.81 (*o*-Ph), 148.74 (*p*-Ph), ipso carbon unobserved.

IR (Nujol) ν (cm^{-1}): 1599 w, 1553 m, 1424 s, 1360 s, 1302 m, 1260 m, 1161 m, 1098 m, 1036 m, 934 m, 874 m, 804 m, 753 m, 635 m, 522 w.

Synthesis of [K(dibenzo-18-crown-6)(THF)(S(Trip))]·THF, 5. KH (0.44 g, 1.10 mmol) and 0.40 g (1.10 mmol) of dibenzo-18-crown-6 were combined in a drybox and transferred into a Schlenk flask. Approximately 30 mL of THF was added, followed by brief heating of the reaction mixture with a heat gun to dissolve the crown ether. HS(Trip) (0.23 g, 1.00 mmol) dissolved in 10 mL of THF was added slowly to the hot KH/crown ether solution utilizing a cannula. The evolution of hydrogen gas was instantaneous, followed by the formation of a homogeneous pale yellow solution. After being stirred for 1 h, the solution was filtered through a Celite-padded filter frit and the volume was reduced by approximately 5 mL by applying vacuum. Upon cooling to 0 °C, colorless plates suitable for X-ray diffraction studies gradually formed in 30.8% yield (0.24 g).

Mp: decomposes >185 °C, yielding a yellow oil.

^{1}H NMR (THF-d_8) isotropic shifts at 25 °C: δ 6.87 (m, 8H, crown), 6.60 (s, 2H, *m*-Trip), 4.56 (sep, 2H, *o*-C*H*(CH_3)$_2$), 4.11 (br s, 16H, −CH_2−), 2.68 (sept, 1H, *p*-C*H*(CH_3)$_2$)), 1.16 (d, 6H, *p*-CH(C*H*$_3$)$_2$), 1.04 (d, 12H, *o*-CH(C*H*$_3$)$_2$)).

^{13}C{^{1}H} NMR (THF-d_8) isotropic shifts at 25 °C: δ 148.99, 148.57, 136.37, 121.59, 118.72, 111.59, 69.53, 68.37, 35.21, 32.13, 25.18, 24.04.

IR (Nujol) ν (cm^{-1}): 1596 m, 1505 m, 1465 s, 1377 s, 1253 m, 1216 w, 1126 s, 1061 m, 946 m, 740 m.

Syntheses of [(KS(Trip))$_2$(K(THF)S(Trip))$_2$(K(THF)$_2$S(Trip))$_2$], 6, and [K(THF)S(Trip)]$_\infty$, 7. To a suspension of 0.15 g of KH (3.67 mmol) in a mixture of 20 mL of hexane and 5 mL of THF was added a solution of 0.87 g of HS(Trip) (3.68 mmol) in 20 mL of hexane slowly via cannula. The reaction started immediately, recognizable by the formation of hydrogen gas. The mixture was stirred for 2 h. The resulting slightly cloudy, colorless solution was then filtered over a Celite-padded filter frit and stored for 24 h at −30 °C to yield 72% or 0.91 g of clear, colorless crystals. Upon examination of the crystals under the microscope it became obvious that a mixture of needle- and plate-shaped crystals had formed. The needles were very thermally sensitive, and rapid decay of the crystal quality, rendering X-ray analysis extremely difficult, was observed. In contrast, the plates were much more robust. X-ray analysis made possible the assignment of the crystals: the needle-shaped crystals were identified as the hexamer **6**, while the plates proved to be the ladder-type polymer **7**. The mechanical separation of needles and plates was not possible, due to the fragile and highly sensitive nature of the needles. The NMR spectra of the needles and plates shows only one set of signals for the combined fractions of **6** and **7**, whose overall chemical composition is identical, suggesting an identical solution structure or rapid equilibrium for the two compounds.

Mp: for the mixed species >350 °C.

^{1}H NMR (C_6D_6) isotropic shifts at 25 °C: δ 7.13 (s, 12H, *m*-H), 4.16 (sept, 12H, *o*-CH), 3.42 (m, 24H, THF), 2.91 (sept, 6H, *p*-CH), 1.45 (d, 72H, *o*-*i*-Pr), 1.35 (d, 36H, *p*-*i*-Pr).

^{13}C{^{1}H} NMR (C_6D_6) isotropic shifts at 25 °C: δ 148.61 (Ph), 144.46 (Ph), 141.47 (Ph), 120.70 (Ph), 68.16 (THF), 35.16 (*p*-CH), 32.93 (*o*-CH) 26.18 (THF), 25.27 (*p*-CH_3), 24.29 (*o*-CH_3).

IR (Nujol) ν (cm^{-1}): 1300.0 s, 1238.4 m, 1221.2 w, 1160.5 w, 1129.7 w, 1102.0 w, 1054.8 s, 932.5 w, 897.7 w, 871.8 m, 754.7 w, 722.3 w, 635.9 w, 521.9 w.

Synthesis of [(K(THF)S(Trip))$_2$(K(TMEDA)S(Trip))$_2$(KS(Trip))$_2$]·THF, 8. A solution of 0.47 g of HS(Trip) (2.00 mmol) in 20 mL of THF was added dropwise to a suspension of 0.08 g of KH (2.00 mmol) in 10 mL of THF. The colorless, slightly turbid reaction mixture was stirred for 1 h, after which 5 mL of TMEDA was added via syringe. This mixture was stirred for another 18 h, after which it was filtered through a Celite-padded filter frit. The volume of the solution was reduced to 10 mL. After storage at −30 °C for several days, 0.38 g (55% yield) colorless crystals was obtained.

Mp: >350 °C.

^{1}H NMR (C_6D_6) isotropic shifts at 25 °C: δ 7.35 (s, 12H, *m*-H), 4.07 (sept, 12H, *o*-CH), 3.55 (m, 8H, THF), 2.93 (sept, 6H, *o*-CH), 2.34 (s, 8 H, TMEDA), 2.12 (s, 24H, TMEDA), 1.57−1.43 (m, 80H, o-*i*-Pr, THF), 1.41 (d, 36H, p-*i*-Pr).

^{13}C NMR: not available due to limited solubility of the compound in nondonor solvents.

IR (Nujol) ν (cm^{-1}): 1546 w, 1300 m, 1238 w, 1160 m, 1130 m, 1102 m, 1056 s, 917 m, 872 m, 754 m, 722 s, 636 w, 522 m, 482 w.

Synthesis of [K(PMDTA)S(Trip)]$_\infty$, 9. HS(Trip) (0.71 g, 3.00 mmol) was dissolved in 50 mL of hexane and added to a slurry of 0.12 g KH in 10 mL of hexane, upon which hydrogen gas bubbles started to form immediately. PMDTA (0.70 mL, 3.30 mmol) was added slowly via syringe, and the solution was stirred overnight at room temperature, during which a white precipitate was formed. After isolation of the white powder and recrystallization from 20 mL of a toluene/hexane mixture, 0.88 g of long colorless needles, suitable for crystallographic analysis, was obtained in 66% yield.

Mp: 405 °C.

^{1}H NMR (C_6D_6) isotropic shifts at 25 °C: δ 1.35−1.38 (d, 6H, *p*-CH_3 iPr), 1.45−1.47 (d, 12H, *o*-CH_3 iPr), 2.08 (s, 3H), 2.09 (s, 12H), 2.21−2.33 (2 br m, 8H), 2.94 (sept, 1H, *p*-CH iPr), 4.87 (sept, 2H *o*-CH iPr), 7.15 (s, 2H, *m*-H).

^{13}C{^{1}H} NMR (C_6D_6) isotropic shifts at 25 °C: δ 24.36 (*o*-CH_3 iPr), 25.23 (*p*-CH_3 iPr), 32.63 (*o*-CH iPr), 35.11 (*p*-CH iPr), 42.70 (center CH_3 PMDTA), 45.99 (terminal CH_3 PMDTA), 56.67 (CH_2 PMDTA), 58.15 (CH_2 PMDTA), 120.40 (*m*-Ph), 140.73 (*o*-Ph), 145.50 (br, ipso carbon Ph), 148.69 (*p*-Ph).

IR (Nujol) ν (cm^{-1}): 1596 w, 1559 w, 1542 m, 1420 s, 1351 s, 1307 s, 1256 m, 1163m, 1128 m, 1098 m, 1083 m, 1070 m, 1060 m, 1041 m, 969 m, 944 m, 932 m, 901 m, 870 m, 784 m, 775 m, 754 m, 646 m, 593 m, 572 w, 523 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 N_2 and immediately covered with a layer of viscous hydrocarbon oil (Paratone N, Exxon). A suitable crystal was selected under the microscope, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream of the diffractometer.[31] Data sets for compounds [K(dibenzo-18-crown-6)S(Trip)]·THF, **5**, $[(KS(Trip))_2(K(THF)S(Trip))_2(K(THF)_2S(Trip))_2]$, **6**, and $[(K(THF)S(Trip))_2(K(TMEDA)S(Trip))_2(KS(Trip))_2]$·THF, **8,** were collected at −60 °C using a Rigaku AFC5S diffractometer equipped with a Molecular Structure Corporation low-temperature device and graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Three standard reflections were measured every 150 reflections and showed in all cases only statistical variation of the intensity (<1.5%). The intensities were corrected for Lorentz and polarization effects, and extinction was disregarded. An absorption correction was applied using semiempirical ψ-scans. The intensity data sets for compounds **1**−**3**, **7**, and **9** were collected using a Siemens SMART system, complete with a three-circle goniometer and a CCD detector operating at −54 °C. The data sets were collected at −123 °C using a Cryojet low-temperature device from Oxford Instruments by employing graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The data collections nominally covered a hemisphere of reciprocal space utilizing a combination of three sets of exposures, each with a different ϕ angle, and each exposure covering 0.3° in ω. Crystal decay was monitored by repeating the initial frames at the end of the data collection and analyzing the duplicate reflections. In all cases, no decay was observed. An absorption correction was applied utilizing the program SADABS.[32] The crystal structures of all compounds were solved by direct methods, as included in the SHELX program package.[33,34] Missing atoms were located in subsequent difference Fourier maps and included in the refinement. The structures of compounds **1**−**3**, **7**, and **9** were refined by full-matrix least-squares refinement on F^2 (SHELX-93),[33] and those of compounds **5**, **6**, and **8** were refined by full-matrix least-squares calculations on $|F_o|$ (SHELX-76).[34] Hydrogen atoms were placed geometrically and refined using a riding model, including free rotation about C−C bonds for methyl groups. Compounds **1**−**3**, **7**, and **9** 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 compound **5** were constrained at $U_{iso} = 0.06$ for non-methyl and $U_{iso} = 0.08$ for methyl groups. In compounds **6** and **8** all hydrogen atoms were included using $U_{iso} = 0.08$. The crystallographic programs used for structure refinement and solution were installed on a PC clone (SHELX-76) or a Silicon Graphics Indigo² R10000 solid impact (SHELX-93). Scattering factors were those provided with the SHELX program system. 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 the disorder.[33] In compound **2**, a highly disordered solvent molecule was identified. Since both diethyl ether and hexane had been used in the synthesis and can fill the void in the elementary cell, no distinction between the two different solvent molecules could be made. The remaining electron density of the solvent molecule was treated using SQUEEZE (Platon),[35] resulting in a symmetrical difference Fourier map. A comparative refinement, where 12 maxima were included in the refinement as half-occupied carbon atoms, resulted, however, in an asymmetric difference Fourier map. Very comparable *R* values were obtained using the two strategies, and no significant differences were detected in the main molecule. Further details about the refinements and how disorder was handled are outlined in the Supporting Information. Selected details of the data collections and refinements are given in Table 1. Important bond lengths and angles are given in Tables 2 and 3.

Results and Discussion

Structural Descriptions. $[Na(PMDTA)S(Trip)]_2$, 1. The structure of compound **1** is presented in Figure 1, and important bond lengths and angles are summarized in Table 2. Compound **1** consists of neutral, well-separated dimeric molecules. The two halves of the dimer are related by a center of symmetry located in the center of the four-membered Na_2S_2 ring, requiring the ring to be planar. Each sodium atom is surrounded in a distorted trigonal bipyramidal fashion by two sulfur atoms and three PMDTA nitrogen donors, with an S−Na−S angle of 91.82(3)°. The N−Na−S angles are 91.62(5)°, 99.30(5)°, 103.83(6)°, 113.87(5)°, 131.07(6)°, and 161.86(6)°. The neighboring N−Na−N angles within the chelating PMDTA are very acute with 71.22(7)° and 73.09(6)°, while the N(1)−Na−N(3) angle is 123.30(7)°. Sodium−sulfur distances are 2.807(1) and 2.843(1) Å, while the sodium−nitrogen distances are 2.508(2), 2.534(2), and 2.567(2) Å. The carbon−sulfur bond length is 1.781(2) Å with Na−S−C angles of 121.83(7)° and 139.87(7)°.

$[(NaS(Trip))_2(Na(Et_2O)S(Trip))_4]$·0.5(solvent), 2. The structure of **2** is depicted in Figure 2, crystallographic parameters are summarized in Table 1, and selected structural data are provided in Table 2. Two halves of two crystallographically independent molecules are contained in each asymmetric unit, together with one solvent molecule. Solvents employed in the synthesis were *n*-hexane and diethyl ether; however, due to the highly disordered nature of the solvent molecules, no clear distinction between the two could be made. The second half of each $[(NaS(Trip))_2(Na(Et_2O)S(Trip))_4]$ molecule is symmetry-generated via a center of symmetry located in the central Na_2S_2 ring. The overall structural features of the two independent molecules are fairly similar and can be described as dimerized discrete ladder structures, displaying a box-shaped or face-fused cuboidal geometry. The geometry of the molecule can also be understood in terms of a trimer of dimers, with the two outer dimers exhibiting diethyl ether coordination at the sodium atoms in addition to three sodium−sulfur contacts. The sodium ions in the central ring are ligated to four sulfur atoms, but do not display any diethyl ether coordination. This asymmetric ether coordination results in a sodium:dietylether stoichiometry of 6:4 and a coordination number of 4 for all sodium centers. The position of the sodium atoms in the outer rings as corner atoms in the box-shaped or face-fused cuboidal motif also determines their coordination geometry, and angles close to 90° are

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[34] Sheldrick, G. M. *SHELXTL-Plus. A program package for crystal structure solution and refinement*; University of Göttingen: Göttingen, Germany, 1990.

[35] Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

Table 1. Summary of Data Collection, Structure Solution, and Refinement of [Na(PMDTA)S(Trip)]$_2$, **1**, [(NaS(Trip))$_2$(Na(Et$_2$O)S(Trip))$_4$]·0.5(solvent), **2**, [Na(TMEDA)S(Trip)]$_\infty$, **3**, [K(dibenzo-crown-6)S(Trip)]·THF, **5**, [(KS(Trip))$_2$(K(THF)S(Trip))$_2$(K(THF)$_2$Trip)$_2$], **6**, [K(THF)S(Trip)]$_\infty$, **7**, [(K(THF)S(Trip))$_2$(K(TMEDA)S(Trip))$_2$(KS(Trip))$_2$]·THF, **8**, and K(PMDTA)S(Trip)]$_\infty$, **9**[a]

	1	**2**	**3**	**5**	**6**
formula	$C_{24}H_{46}N_3NaS$	$C_{106}H_{178}Na_6O_4S_6$	$C_{21}H_{39}N_2NaS$	$C_{43}H_{63}KO_8S$	$K_6S_6C_{114}H_{186}O_6$
fw	431.69	1846.90	374.59	779.13	2079.7
a (Å)	13.2300(1)	14.4178(3)	9.2702(1)	14.196(3)	15.071(3)
b (Å)	10.6176(1)	17.6498(4)	20.1017(2)	15.429(3)	25.301(5)
c (Å)	19.6262(3)	26.2052(6)	25.9256(4)	22.562(5)	17.866(4)
α (deg)	90	89.847(1)	90	101.92(3)	90
β (deg)	100.449(1)	77.475(1)	89	97.31(3)	113.01(3)
γ (deg)	90	70.189(1)	90	114.19(3)	90
V (Å^3)	2711.19(5)	6106.3(2)	4831.2(1)	4285(2)	6270(3)
Z	4	2	8	4	2
space group	$P2_1/n$	$P\bar{1}$	$Pbca$	$P\bar{1}$	$P2_1/n$
d_{calc} (g/cm^3)	1.058	1.004	1.030	1.208	1.102
linear abs coeff (mm^{-1})	0.149	0.175	0.158	0.218	0.354
T (K)	150	150	150	213	213
2θ range, deg	3−57	3−57	3−57	0−50	0−45
indep reflns	6309	25722	5032	11249	4758
obs reflns ($>2\sigma$)	4403	15172	3292	6592	2332
no. of params	263	1111	227	942	385
R1, wR2 (all data)	0.1004, 0.1297	0.1311, 0.1904	0.1125, 0.1350	b	b
R1, wR2 ($>2\sigma$)	0.0625, 0.1153	0.0772, 0.1664	0.0637, 0.1171	0.0743, 0.0628	0.103, 0.11

	7	**8**	**9**
formula	$C_{38}H_{62}K_2O_2S_2$	$K_6S_6C_{114}H_{194}N_4O_3$	$C_{24}H_{46}KN_3S$
fw	693.23	2095.8	447.80
cryst shape	colorless plate	colorless needle	colorless plate
cryst size (mm)	0.6 × 0.2 × 0.05	0.2 × 0.15 × 0.6	0.7 × 0.12 × 0.06
α (Å)	11.9079(2)	18.324(4)	10.4903(2)
b (Å)	14.7672(2)	14.323(3)	20.1551(5)
c (Å)	24.0448(1)	26.300(5)	26.4295(4)
α (deg)	90	90	90
β (deg)	98.220(1)	106.39(3)	90
γ (deg)	90	90	90
V (Å^3)	4184.75(9)	6622(3)	5588.1(2)
Z	4	2	8
space group	$P2_1/c$	$P2_1/c$	$Pbca$
d_{calc} (g/cm^3)	1.100	1.051	1.065
linear abs coeff (mm^{-1})	0.354	0.336	0.279
T (K)	150	213	150
2θ range, deg	3−56	0−50	3−57
indep reflns	9693	11617	6649
obs reflns ($>2\sigma$)	6151	4511 ($>3\sigma$)	3835
no. of params	398	588	263
R1, wR2 (all data)	0.1324, 0.1485	c	0.1460, 0.1683
R1, wR2 ($>2\sigma$)	0.0786, 0.1328	0.105, 0.123	0.0760, 0.1432

[a] All data sets were collected utilizing Mo Kα radiation ($\lambda = 0.710\,73$ Å). $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = \sqrt{\sum w\{(F_o)^2 - (F_c)^2\}^2/\sum w\{(F_o)^2\}^2}$, $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = \sqrt{\sum w||F_o| - |F_c||^2/\sum w|F_o|^2}$. [b] Refined on $|F_o|$ with $F > 4.0\sigma(F)$ (SHELX-76); listed are R and R_w. [c] Refined on $|F_o|$ with $F > 6.0\sigma(F)$ (SHELX-76); listed are R and R_w.

displayed throughout. The sodium atoms located in the central dimer are ligated to four thiolato sulfur atoms, resulting in a distinct seesaw coordination with angles close to 90° and 180°. Sodium−sulfur contacts are found in the range 2.822(2)−2.98(1) Å, with no apparent pattern regarding Na−S contacts in inner or outer rings. The sodium−oxygen distances are 2.305(3), 2.345(3), 2.384(2) and 2.417(3) Å, while the sulfur−carbon distances are observed between 1.782(3) and 1.802(3) Å.

[Na(TMEDA)S(Trip)]$_\infty$, 3. The structure of a short fragment of the polymeric compound **3** is displayed in Figure 3, while Figure 4 exhibits an extended view of the zigzag chains. The most striking feature of the molecule is its one-dimensional polymeric shape. The Na(TMEDA)S(Trip) units are arranged in an infinite zigzag chain, composed of alternating sodium and sulfur atoms. Each sodium atom is connected to two sulfur atoms and two TMEDA nitrogens, resulting in a distorted tetrahedral geometry with an S−Na−S angle of 138.64(3)°, an N−Na−N angle of 76.86(7)°, and N−Na−S angles of 91.61(6)°, 104.79(6)°, 112.26(6)°, and 113.76(6)°. The sodium−sulfur distances are very consistent with 2.770(1) and 2.773(1) Å. The sulfur−carbon bond lengths are observed at 1.795(2) Å. The sodium−nitrogen distances fall in a narrow range with 2.481(2) and 2.509(2) Å.

[K(dibenzo-18-crown-6)(S(Trip))(THF)]·THF, 5. The most important feature of compound **5** is its monomeric nature, as shown in Figure 5. Two independent, THF-solvated monomers and two independent solvent THF molecules are contained in each asymmetric unit. The structures of the two independent molecules are quite similar. The potassium atoms are linked to six oxygen atoms in the crown ether molecule, in addition to one THF oxygen contact in a trans position to the sulfur atom of the S(Trip) anion, resulting in a coordination number of 8 at potassium. K(1)−O distances are quite similar and range from 2.701(4) to 2.792(4) Å for the crown ether. The K−O (THF) bond distances in the two independent molecules differ signifi-

Table 2. Important Bond Lengths (Å) and Angles (deg) in the Sodium Thiolates **1**−**3** and Some Related Compounds

compound[a]	Na−S (Å)	Na−donor (Å)	S−C (Å)	S−Na−S (deg)	Na−S−C (deg)	CN	ref
$[Na(PMDTA)SR]_2$, **1**	2.808(1), 2.843(1)	2.508(2),[b] 2.534(2)[b] 2.567(2)[b]	1.781(2)	91.82(3)	121.83(7), 139.87(7)	5	*d*
$[(Na(D)_{2/3}SR)_6$, **2**	2.822(2), 2.824(2) 2.831(2), 2.831(2) 2.834(2), 2.847(1) 2.855(2), 2.857(2) 2.860(2), 2.864(2) 2.870(2), 2.872(1) 2.876(2), 2.883(2) 2.886(2), 2.902(2) 2.896(2), 2.903(2) 2.912(2), 2.918(1)	2.305(3),[c] 2.384(2)[c] 2.345(3),[c] 2.417(3)[c]	1.782(3), 1.795(3) 1.797(3), 1.797(3) 1.799(3), 1.802(3)	81.09(4), 82.71(4) 87.15(4), 87.93(5) 88.30(4), 88.42(5) 88.98(4), 89.00(4) 89.01(4), 89.29(4) 89.71(4), 90.34(4) 90.75(4), 90.99(4) 93.41(4), 94.26(5) 94.29(5), 95.47(5) 97.74(4), 99.77(5) 100.56(5), 101.08(5) 173.94(6), 175.73(5)	87.3(1), 89.1(1) 93.4(1), 94.8(1) 110.7(1), 118.9(1) 119.1(1), 119.3(1) 124.2(1), 125.2(1) 125.8(1), 126.7(1) 128.1(1), 128.9(1) 130.5(1), 133.0(1) 135.6(1), 136.9(1) 138.8(1), 140.6(1)	4	*d*
$[Na(TMEDA)SR]_\infty$, **3**	2.770(1), 2.773(1)	2.481(2),[b] 2.509(2)[b]	1.795(2)	138.64(3)	108.51(8), 121.48(9)	4	*d*
$[NaS2,6R_2C_6H_3]_2$	2.684(2), 2.695(2) 2.697(2), 2.762(2)	2.839(5)−3.266(5)	1.746(5), 1.765(4)	101.73(7), 103.16(7)	113.6(2), 117.3(2) 121.5(2), 127.1(2)	3(+6)	24
$[Na(THF)_2SR_f]_\infty$	2.825(2), 2.833(2) 2.835(2), 2.838(2)	2.263(4),[c] 2.277(3)[c] 2.312(3),[c] 2.317(3)[c]	1.732(4), 1.732(4)	140.4(1), 160.4(1)	95.9(1), 97.5(1) 113.2(1), 114.1(1)	4(+2)	3a
$[Na(SR')]_6$	2.785(4)−2.857(5)	2.461(7)[c]−2.518(8)[b]	1.756(9), 1.759(9) 1.771(6) 101.6(1), 102.5(1) 103.0(1), 103.3(1)	94.1(1), 95.8(1) 100.5(1), 101.5(1)	na[e]	4	25
$Na(15\text{-crown-}5)]_2S_6$	2.77(1), 2.82(1)	2.39(1)[c]−2.56(1)[c]				6	35

[a] R = 2,4,6-$iPr_3C_6H_2$ (=Trip), R′ = C_5H_2N-3,6-($SiMe_2$-tBu)$_2$, D = Et_2O. [b] Sodium−nitrogen interaction. [c] Sodium−oxygen interaction. [d] This work. [e] na, not analyzed.

Table 3. Important Bond Lengths (Å) and Angles (deg) in the Potassium Thiolates **5**−**9** and Some Related Compounds

compound[a]	K−S (Å)	K−donor (Å)	S−C (Å)	S−K−S (deg)	K−S−C (deg)	CN	ref
[K(dbc)(THF)SR], **5**	3.191(3), 3.202(3)	2.700(5),[b] 2.821(4)[b] 2.744(8),[c] 2.868(7)[c]	1.765(6), 1.779(9)		130.6(2), 139.1(3)	8	*f*
$(K(THF)SR)_6$, **6**	3.072(7), 3.081(8) 3.128(6), 3.133(7) 3.154(8), 3.169(7) 3.193(7), 3.229(7) 3.273(9), 3.324(6)	2.60(2),[c] 2.66(5)[c] 2.72(2)[c]	1.784(9), 1.789(11) 1.806(11)	76.3(2), 86.1(2) 86.8(2), 87.2(2) 87.9(2), 88.4(2) 88.4(2), 91.1(2) 92.7(2), 176.9(3)	84.2(4), 89.7(4) 102.3(4), 121.5(3) 126.1(5), 128.5(5) 128.6(4), 130.1(5) 131.6(4), 135.0(4)	4, 5	26
$K_6(D)_2(D')_2(SR)_6$, **8**	3.119(4), 3.137(4) 3.179(4), 3.181(4) 3.186(4), 3.230(4) 3.233(5), 3.235(4) 3.273(6), 3.297(4)	2.66(1)[c] 2.94(1),[d] 3.00(1)[d]	1.730(11), 1.805(9) 1.782(1)	78.9(1), 82.3(1) 83.9(1), 84.0(1) 86.4(1), 86.8(1) 86.7(1), 92.9(1) 95.5(1), 97.5(1) 98.4(1), 172.2(1)	75.6(3), 98.3(3) 111.8(4), 113.4(5) 125.4(3), 125.8(4) 129.0(3), 129.9(4) 131.9(3), 133.1(3)	4, 5	26
$[K(THF)SR]_\infty$, **7**	3.077(1), 3.082(1) 3.089(1), 3.091(1) 3.222(1), 3.252(1)	2.677(3)[c], 2.687(3)[c]	1.784(3), 1.789(3)	85.81(3), 86.43(3) 92.23(3), 94.16(3) 143.95(4), 157.22(4)	82.0(1), 90.2(1) 98.4(1), 101.9(1) 124.9(1), 126.2(1)	4	*f*
$[K(PMDTA)SR]_\infty$, **9**	3.164(1), 3.190(1)	2.820(3),[d] 2.889(2)[d] 2.919(2)[d]	1.768(3)	133.21(2)	111.7(1), 112.5(1)	5	*f*
$[KS\text{-}2,6\text{-}R_2C_6H_3]_2$	3.039(2), 3.044(2) 3.045(2), 3.093(2)	3.304(5)[e]−3.564(5)[e]	1.739(5), 1.740(5)	65.73(5), 66.28(5)	119.2(2), 121.1(2) 123.5(2), 124.1(2)	2(+12)	24
$[K(THF)SR_f]_\infty$	3.159(1), 3.166(1) 3.171(1)	2.676(3)[c]	1.729(3)	78.1(1), 78.2(1) 99.9(1)	88.4(1), 124.4(1) 130.2(1)	4(+4)	3a
$[K(18\text{-crown-}6)_2]S_6$	3.075(2)	2.745(3)[b]−3.005(4)[b]				7	38

[a] R = 2,4,6-$iPr_3C_6H_2$ (=Trip), dbc = dibenzo-18-crown-6, D = THF, D′ = TMEDA. [b] Crown ether distances. [c] THF−potassium contacts. [d] Potassium−nitrogen interactions. [e] Potassium−carbon contacts. [f] This work.

cantly with 2.744(8) and 2.859(5) Å. The K−S distances are 3.203(2) and 3.194(2) Å. K(1) is nominally displaced from the mean crown ether oxygen plane by 0.124 Å, while K(2) exhibits a greater deviation from its crown ether oxygen plane at 0.443 Å. Each S(Trip) unit is oriented similarly with respect to the dibenzo crown moiety. In the Trip unit, a C(1)−S(1)−K(1) angle of 138.6(2)° disposes the C(13) *o*-isopropyl group proximate to O(4) and O(5) of the crown ether. A C(40)−S(2)−K(2) angle of 130.3(2)° in the second molecule also places an *o*-isopropyl group [C(46)] proximate to one side of the crown ether [O(9) and O(10)]. In both molecules, no significant electrostatic interactions are apparent between the crown and the *o*-isopropyl groups.

[(KS(Trip))$_2$(K(THF)S(Trip))$_2$(K(THF)$_2$S(Trip))$_2$], 6. Com-

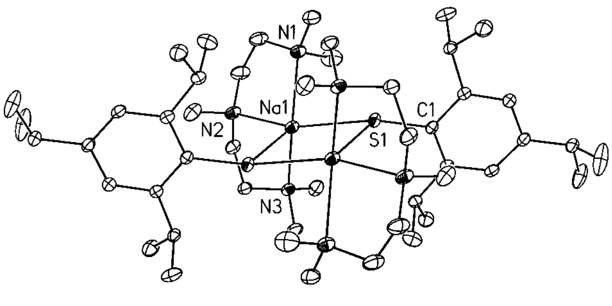

Figure 1. Computer-generated plot of **1** with anisotropic displacement parameters depicting 30% probability. The hydrogen atoms have been omitted for clarity.

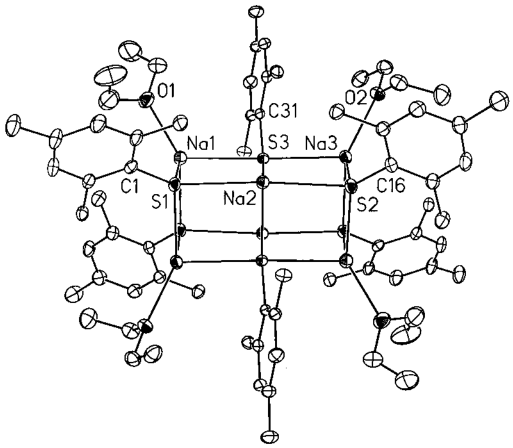

Figure 2. Computer-generated plot of **2** with anisotropic displacement parameters depicting 30% probability. Only one of the two independent molecules is shown. Solvent molecule, the methyl groups on the isopropyl substituents on the ligand, and hydrogen atoms have been omitted for clarity.

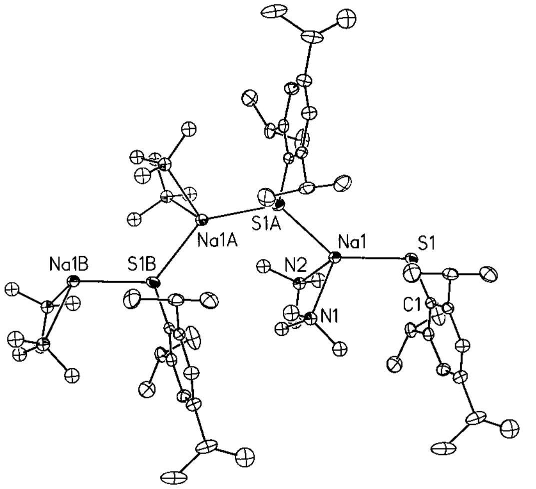

Figure 3. Computer-generated plot of **3** with anisotropic displacement parameters depicting 30% probability showing one part of the polymeric chain structure. Hydrogen atoms have been omitted for clarity.

pound **6** crystallizes as a hexameric molecule. Each asymmetric unit contains half of the hexameric unit; the second half of the hexamer is generated by a center of symmetry located in the central K_2S_2 ring. The overall structural motif in **6** can be described as a dimerized finite double ladder, where two separate ladders are associated. The structure can therefore be described as a dimer of trimers with the appearance of a box-shaped or face-fused cuboidal framework. The coordination geometry of the three independent potassium atoms is asymmetric in the respect that the potassium atom in the central ring is ligated by four sulfur atoms. The metal atoms in the outer rings coordinate to three sulfur atoms; in addition, two of the four potassium atoms coordinate to one THF oxygen atom, while the other two are ligated by two THF molecules, resulting in coordination numbers of 4 and 5. The geometry of the potassium atoms in the outer rings is defined by their position as “corner” atoms in the hexamer; therefore S−K−S angles close to 90° are observed. The central potassium atoms are linked to four sulfur units, but are not ligated by THF. Due to their position in the central K_2S_2 ring S−K−S angles are found closely at 90° or 180°, resulting in an unusual seesaw coordination. The potassium−sulfur bonds are on average slightly longer for the five-coordinate (3.275 Å) than for the four-coordinate (3.117 Å) potassium centers. Accordingly, longer potassium−oxygen (THF) bonds [2.69(1) Å average] are observed for the five-coordinate than for the four-coordinate [2.60(2) average] potassium atoms. The sulfur−carbon distances are in a close range with 1.784(9), 1.789(11), and 1.806(11) Å.

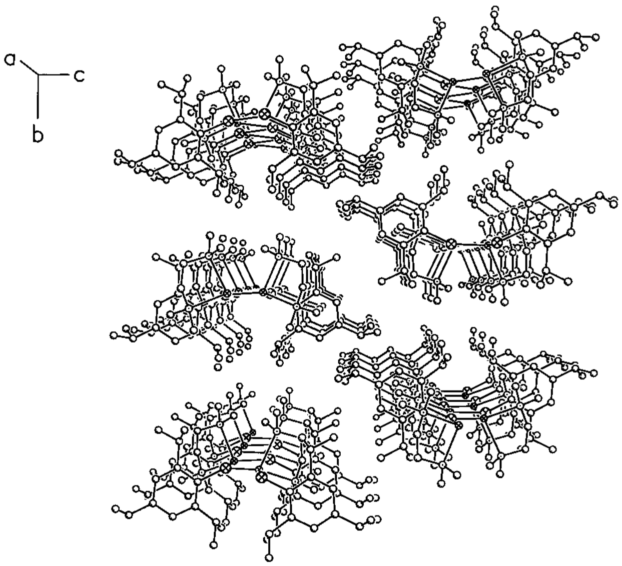

Figure 4. Computer-generated plot of **3** looking down the *a* axis illustrating the zigzag chains. Hydrogen atoms have been omitted for clarity.

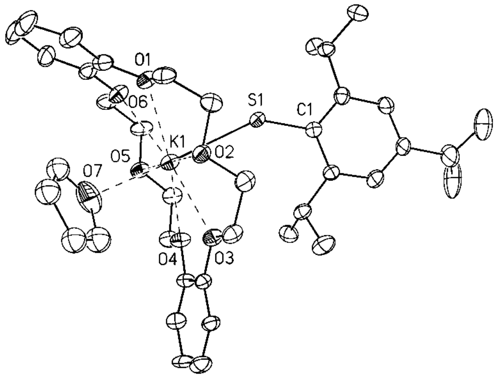

Figure 5. Computer-generated plot of **5** with anisotropic displacement parameters depicting 30% probability. Only one of the two independent molecules is shown. Solvent molecules, disordered positions, and hydrogen atoms have been omitted for clarity.

$[K(THF)S(Trip)]_\infty$, 7. Compound **7** is shown in Figure 6; important crystallographic data are summarized in Table 1, while selected structural parameters are listed in Table 3. Compound **7** exhibits a two-dimensional, polymeric, puckered, ladder-type structure with alternating potassium and sodium atoms arranged in nearly square planar K_2S_2 arrangements. Each potassium atom is four-coordinate, exhibiting three sulfur bonds and one oxygen bond with a coordination geometry intermediate between distorted-tetrahedral and square-planar. Accordingly, the angles at potassium range between 86.45(3)° and 175.48(4)°. Significantly different potassium−sulfur distances are observed within the K−S rung [3.077(1) and 3.091(1) Å] and between the K−S rungs [3.222(1) and 3.252(1) Å]. The potassium−oxygen distances are 2.677(3) and 2.687(3) Å, while sulfur−carbon distances are found at 1.787(6) Å (average).

$[(K(THF)S(Trip))_2(K(TMEDA)S(Trip))_2(KS(Trip))_2]\cdot$THF, 8. The structural motif of compound **8** (shown in Figure 7) resembles closely that of compound **6**. The overall geometry may be described as a finite dimerized ladder structure with a

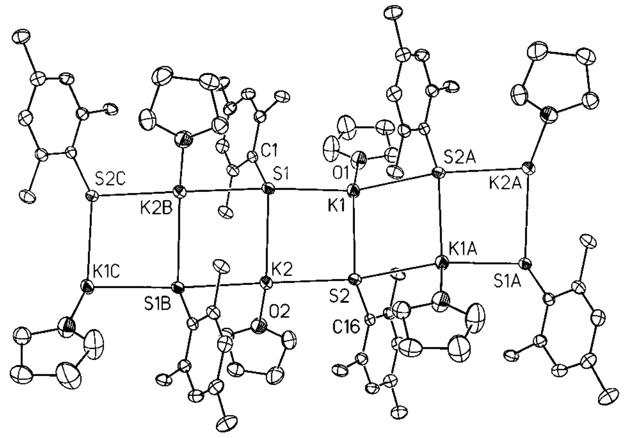

Figure 6. Computer-generated plot of **7** showing part of the ladder-type polymer with anisotropic displacement parameters depicting 30% probability. The methyl groups on the isopropyl substituents on the ligands and hydrogen atoms have been omitted for clarity.

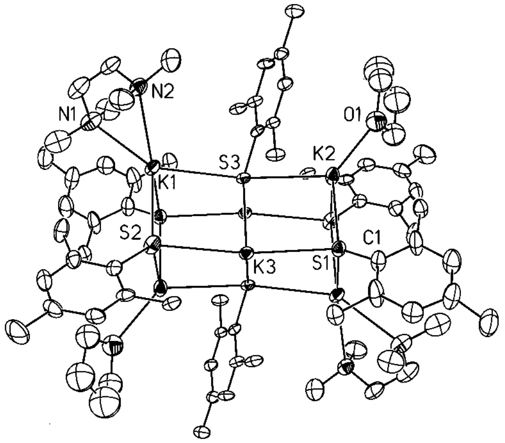

Figure 7. Computer-generated plot of **8** with anisotropic displacement parameters depicting 20% probability. The solvent molecule, methyl groups on the isopropyl substituents on the ligands. and hydrogen atoms have been omitted for clarity.

box-shaped or face-fused cuboidal geometry. Each asymmetric unit contains one half of the hexamer, while the second half is symmetry-generated by a center of symmetry located in the central K_2S_2 ring. In addition, one THF solvent molecule is identified in each asymmetric unit. The major structural difference between compounds **8** and **6** is the replacement of the two THF units in the outer K_2S_2 unit of **6** by one bidentate TMEDA donor in **8**. This results in two potassium atoms ligated by three sulfur atoms and one THF oxygen atom, and two potassium atoms connected to three sulfur atoms in addition to two TMEDA nitrogen atoms. The geometry in the central K_2S_2 rings remains largely unaffected, and each potassium atom is connected to four sulfur centers displaying angles of 90° and 180°. The replacement of the two THF units, as observed in compound **6**, by one TMEDA donor has almost no effect on the overall geometry in the central framework. The K−S distances for the three different potassium centers are found in a fairly close range, with a longer K−S bond for the five coordinate potassium centers (3.255 Å average) and slightly shorter metal−sulfur contacts for the four-coordinate ones (3.186 Å average). The K−N distances are 2.97(1) Å on average, while the potassium−oxygen distance is found at 2.659(11) Å. The sulfur carbon interactions range between 1.730(11) and 1.805(9) Å.

[K(PMDTA)S(Trip)]$_\infty$, 9. A part of the polymeric one-dimensional zigzag chain displayed in compound **9** is shown

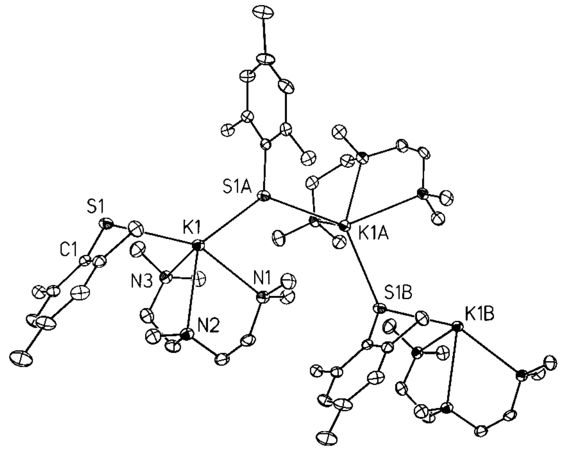

Figure 8. Computer-generated plot of **9** with anisotropic displacement parameters depicting 30% occupancy showing one part of the polymeric structure. The methyl groups on the isopropyl substituents on the ligands and hydrogen atoms have been omitted for clarity.

in Figure 8, while selected structural data are contained in Table 3. The polymeric chain is composed of alternating potassium and sulfur units. Each sulfur atom is connected to one Trip group and two potassium centers. Each potassium atom is ligated by two sulfur atoms and three nitrogen atoms from the PMDTA donor. The coordination at potassium can be described as severely distorted trigonal bipyramidal. Due to the chelating nature of the donor, fairly narrow N−K−N angles are observed for the neighboring nitrogen atoms with values of 61.80(7)° and 62.63(7)°, and the N(1)−K−N(3) angle is 112.46(7)°. The S−K−S angle is 133.21(2)°, while the N−K−S angles are 89.92(5)°, 90.07(6)°, 93.47(6)°, 96.70(6)°, 125.99(6)°, and 131.06(6)°. The K−S distances are found between 3.164(1) and 3.190(1) Å, while the K−N contacts are observed at 2.820(3), 2.889(2), and 2.191(2) Å. The K−S−C angle is found at 111.67(10)°.

Discussion

Synthesis. All compounds were synthesized in a straightforward manner by hydrogen elimination reaction between HS(Trip) and NaH or KH. If not mentioned otherwise, the reactions were carried out in ethereal solutions and, in the case of compounds **1**, **3**, **5**, **8**, and **9**, additional donors such as dibenzo-18-crown-6, PMDTA, or TMEDA were included in the reaction mixture. The reactions afforded the target compounds in good yield and high purity:

$$n\mathrm{AH} + n\mathrm{HS(Trip)} \xrightarrow{\text{donor}} [\mathrm{A(donor)S(Trip)}]_n + n\mathrm{H}_2$$

$$(\mathrm{A} = \mathrm{Na, K};\ n = 1 - \infty)$$

All compounds are oxygen- and moisture-sensitive colorless species but are quite stable if stored under an inert gas atmosphere. As shown in this publication, the formation of monomeric, dimeric, hexameric, and polymeric compounds can be influenced by careful donor choice: application of the multidentate donor dibenzo-18-crown-6 allowed the isolation of the monomeric **5**, while utilization of monodentate donors such as diethyl ether or THF resulted in the hexameric species **2** and **6** or the polymeric **7**. In addition to donor influence on the structural parameters, the nature of the metal has a significant impact on the coordination chemistry, as shown with the formation of the dimeric sodium thiolate [Na(PMDTA)S(Trip)]$_2$, **1**, versus the one-dimensional polymeric structure of the potassium thiolate [K(PMDTA)S(Trip)]$_\infty$, **9**.

Sodium Thiolates. The comparison of structural parameters in sodium thiolates nicely demonstrates the influence of donor molecules on structural chemistry: utilization of the tridentate donor PMDTA results in the formation of the dimeric $[Na(PMDTA)S(Trip)]_2$, **1** (Figure 1). Compound **1** exhibits a distorted trigonal bipyramidal environment at sodium with two sodium−sulfur and three sodium−nitrogen contacts. The sodium−sulfur bond lengths are observed at 2.818(1) and 2.843(1) Å. In contrast, diethyl ether ligation afforded the discrete hexameric species $[(NaS(Trip))_2(Na(Et_2O)S(Trip))_4]\cdot 0.5(solvent)$, **2**, illustrated in Figure 2. The higher degree of association displayed in compound **2** can be accredited to the reduced coordinative saturation provided by the monodentate diethyl ether in comparison with the tridentate PMDTA. Compound **2**, described as a discrete double-ladder array, displays a box-shaped or face-fused cuboidal geometry with a coordination number of 4 at all metal centers. The sodium atoms in the central Na_2S_2 ring are connected to four sulfur atoms; those in the outer rings display three sulfur and one diethyl ether coordination. A range of sodium−sulfur distances [2.822(2)−2.980(2) Å] is observed, with no apparent pattern regarding the position of the sodium atoms in the hexamer. The framework structure observed in compound **2** closely resembles that of the intramolecularly stabilized hexameric sodium aryloxide $[NaO(2\text{-}CH_2NMe_2C_6H_4)]_6$, published by van Koten et al.[2] In addition to three (in the outer Na_2O_2 rings) and four (in the central Na_2O_2 ring) Na−O contacts, each sodium atom is ligated by a $RNMe_2$ donor from the intramolecularly stabilizing $O(2\text{-}CH_2NMe_2C_6H_4)$ ligand, resulting in coordination numbers of 4 and 5 at the metal. The different coordination numbers cause significantly different Na−O distances in the central and outer rings.

Compound **3,** $[Na(TMEDA)S(Trip)]_\infty$, available by employment of the bidentate donor TMEDA, exhibits one-dimensional zigzag chains with four-coordinate sodium and three-coordinate sulfur atoms (Figure 3). The three-dimensional arrangement of the chains in the crystal is illustrated in Figure 4. Due to the low coordination number at the metal, rather short sodium−sulfur distances [2.779(2) and 2.772(1) Å] are observed. These contacts are very comparable with those observed for the dimeric, donor-free $[NaS\text{-}2,6\text{-}Trip_2C_6H_3)]_2$.[24] Here, sodium is connected to two sulfur atoms, and additional coordinate stabilization is provided by several π-type interactions with the ortho substituents of the ligand. The structural parameters observed in compound **3** may also be compared with the one-dimensional zigzag polymer $[Na(THF)_2SR_f]_\infty$.[3a] Despite the structural similarities, significantly different sodium−sulfur bond lengths are observed for compounds **3** [2.770(1) and 2.773(1) Å], and $[Na(THF)_2SR_f]_\infty$ [2.933(3) Å],[3a] indicating the larger steric requirements of the R_f ligand. Moreover, strong secondary interactions between the fluorine atoms in the *o*-CF_3 groups of the ligand and the sodium cation contribute significantly to the elongation of the Na−S bond. The sodium−sulfur bond lengths in **3** are found at the lower end of the range typically observed for the target molecules (see Table 2). Commonly observed values center around 2.785(4)−2.857(5) Å as found in the polymeric $[NaSMe]_\infty$[23] or 2.785(4)−2.857(5) as seen in the hexagonal-prismatic $[Na(SC_5H_2N\text{-}3,6\text{-}(SiMe_2\text{-}tBu)_2)]_6$.[25] These distances also agree well with the Na−S contacts in $[Na(15\text{-}crown\text{-}5)]_2S_6$ [2.77(1) and 2.81(1) Å], where sodium atoms are ligated by five oxygen atoms from the crown ether in addition to contacts with the terminal sulfur atoms in the hexasulfide chain.[36] However, a significant disagreement between experimental sodium−sulfur distances and calculated contacts in a hypothetical, monomeric NaSH (2.500 Å) is apparent.[37] This significantly shorter value may be explained on the basis of increased coordination numbers at sodium and sulfur in the target molecules. The sum of ionic radii for a sodium cation and sulfide anion ranges from 2.83 Å for a four-coordinate sodium up to 3.02 Å for a coordination number of eight at sodium.[38] These values are slightly longer than the experimental Na−S thiolate distances but generally agree with the overall trends observed for the target compounds. The slightly larger values may in part be explained by the differences in the coordination number of the S^{2-} anion since only a value for a coordination number of 6 (in the thiolates coordination numbers of 3 or 4 are observed) was available in the literature. The overall trend and fairly close fit between the sum of ionic radii and experimental values indicate a high ionic character in the sodium−sulfur bond, a view further supported by ab initio calculations by Pappas.[37]

Compound **4**, $[Na(THF)S(Trip)]_\infty$, has not been structurally characterized due to insufficient crystal quality. NMR analyses suggest a metal:ligand:donor ratio of 1:1:1. The crystals are very sensitive to air and moisture and decompose rapidly, indicating a rather open framework structure. NMR data are consistent with the existence of a ladder-type polymer, as observed in compound **7**, or a discrete hexameric arrangement as observed for compound **6**. A clear distinction between the two conformations could not be made, since NMR evidence indicates that the solid-state structure observed in compound **6** is not retained in solution. The existence of a hexamer, analogous to compound **2**, can be excluded on the basis of the ligand:donor ratio. Also, the formation of a one-dimensional zigzag polymer as observed in compound **3** or **9** seems unlikely on the basis of steric saturation arguments. With a donor:ligand ratio of 1:1, a one-dimensional zigzag chain would result in the unusual coordination number 3 at sodium.

Potassium Thiolates. A small family of potassium thiolates has been prepared and structurally characterized, enabling the comparison of geometrical and structural features in the target compounds. The monomeric species $[K(dibenzo\text{-}18\text{-}crown\text{-}6)(THF)S(Trip)]\cdot THF$, **5**, shown in Figure 5, consists of the first example of a structurally characterized monomeric potassium thiolate. The compound exhibits six potassium−crown ether oxygen contacts in addition to one THF oxygen−thiolato sulfur interaction in a trans position to one another. This results in a coordination number of 8 at potassium with K−S distances of 3.202(3) and 3.191(3) Å. Clearly, the multidentate nature of the crown ether makes possible the monomeric nature of compound **5**. Reduction of donor hapticity results in increased association, as observed in the hexameric molecules $[(KS(Trip))_2(K(THF)S(Trip))_2(K(THF)_2S(Trip))_2]$, **6** and $[(K(THF)S(Trip))_2(K(TMEDA)S(Trip))_2(KS(Trip))_2]\cdot THF$, **8**, the ladder-type polymer $K(THF)S(Trip)]_\infty$, **7**, and the one-dimensional polymer $[K(PMDTA)S(Trip)]_\infty$, **9**.

The hexameric compounds **6** and **8** display very similar structural features. Both have an asymmetric coordination geometry at the three independent potassium centers: the metal atoms in the central K_2S_2 ring are connected in a seesaw geometry to four thiolato sulfur atoms, and no donor contacts are observed. Two different coordination geometries are

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exhibited for the independent metal atoms in the outer K_2S_2 rings: each corner potassium atom is ligated by three sulfur atoms, while two potassium atoms are connected to one THF molecule, with the other two bound to either two THF molecules or one bidentate TMEDA donor, resulting in a coordination number of 4 at two potassium and 5 at the other two potassium centers. Accordingly, significantly different K−S bond lengths are observed for the four- and the five-coordinate metal centers. Interestingly, this effect is less pronounced in compound **8**; apparently the longer weaker K−N contacts (2.967 Å), as compared to the shorter K−O interactions (2.693 Å average), reduce the effect of the increased coordination number. The asymmetric coordination chemistry in compounds **6** and **8** in combination with their unusual coordination geometry indicates the low degree of covalency in the target compounds. Clearly, significant orbital control does not take place and the K−S interactions can be viewed as mainly electrostatic ones. This view is further supported by ab initio calculations by Pappas,[37] indicating that the metal−chalcogen interaction is a primary ionic one with little covalent character. Related asymmetric coordination architectures have been observed previously for a family of hexameric sodium and potassium thiolates $[(NaSSiPh_3)_6(C_7H_8)_2]$, $[(KSCPh_3)_6(HMPA)_2]\cdot 2C_7H_8$ (HMPA = hexamethylphosphoramide), and $[(KSCPh_3)_6(C_7H_8)_2]$, where the M_6S_6 hexameric core is stabilized through numerous cation−π interactions with several of the 18 phenyl groups comprising the organic periphery in addition to two donor molecules.[29] Interestingly, the arene interactions are distributed quite asymmetrically throughout the polyhedron. Asymmetric coordination geometry is also observed for a potassium siloxide $[K_4(\mu_3\text{-}OSiPh_3)_3\{\mu_3\text{-}OSiPh_2(\eta^1\text{-}Ph)\}(\eta^2\text{-}DME)](\mu\text{-}DME)$.[3b] Here, four triply bridging $OSiPh_3$ groups and four potassium atoms form the framework of the cuboidal structure. The metal centers are asymmetrically coordinated by donor molecules: one DME molecule ligates two neighboring cubes, and another DME molecule connects in a η^2 fashion with one potassium center. Another potassium atom exhibits fairly close interactions to one phenyl ipso carbon atom of the ligand, while the fourth potassium atom remains three-coordinate. The ability of predominantly ionic species to form compounds displaying a variety of coordination numbers and geometries is further demonstrated with compound **7**, which cocrystallizes with compound **6**. Physical separation of the two crystals was not possible. The needle-shaped crystals, assigned to the hexamer **6**, are very thin and break easily upon handling, in addition to being very sensitive to oxygen and moisture. NMR analysis of the crystal mixture resulted, however, in only one set of signals for the THF and Trip groups, indicating that the asymmetric hexameric structure, as observed in the solid state for compound **6**, is not retained in solution. If the hexameric array would have stayed intact, sets of signals for the anisochronous Trip groups and THF donors were expected. In contrast, the existence of only one set of THF and Trip signals indicates equivalent functionalities. A possible common solution structure could be the ladder-type polymer, as identified in the solid state for $[K(THF)S(Trip)]_\infty$, **7**.

The ladder-type polymer **7** shares many structural similarities with the potassium thiolate $[K(THF)R_f]_\infty$[3a] and the tellurolate $[K(THF)_{1.33}TeTrip]_\infty$.[4b,15] An interesting structural feature in compound **7** shows significantly different K−S bond lengths between [3.237(2) Å (average)] and within [3.09(1) Å (average)] the rungs of the ladder. These significantly different K−S distances suggest that the ladder-type structure can also be interpreted as the result of the dimerization of two one-dimensional chains resulting in an arrangement with slightly weaker interactions between the rungs. A comparison of K−S bond lengths between **7** and $[K(THF)R_f]_\infty$ shows significantly longer bond lengths for the R_f derivative, most likely due to significant secondary interaction between the fluorine atoms in the *o*-CF_3 groups and the metal, in addition to the larger steric requirement of the ligand. An identical trend was observed in the sodium analogs (vide supra). The potassium−sulfur distances within the rungs [3.09(1) Å (average)] in **7** are among the shortest observed and are comparable to those found in the dimeric donor-free $[KS\text{-}2,6\text{-}Trip_2C_6H_3]_2$ [3.055 Å (average)].[24] Compound **7** exhibits a coordination number of 4 at potassium, whereas $[KS\text{-}2,6\text{-}Trip_2C_6H_3]_2$ exhibits two potassium−sulfur bonds in addition to 12 potassium−arene interactions. As expected, the increase in coordination number at potassium results in an increase in K−S bond lengths, as observed for the five-coordinate one-dimensional polymer $[K(PMDTA)S(Trip)]_\infty$, **9** [3.177Å (average)], or the hexamers **6** and **8** with K−S distances of 3.10 (**6**) and 3.19 Å (**8**) for the four-coordinate metals, and 3.28 (**6**) and 3.26 Å (**8**) for the five-coordinate metal centers. These numbers agree well with the K−S contacts in the monomeric **5** (3.191(3) and 3.203(3) Å) and the hexasulfide $[K(18\text{-crown-}6)]_2S_6$ [3.075(2) Å].[39] Pappas calculated the potassium−sulfur distances in a hypothetical, monomeric KSH to be 2.867 Å,[37] a number significantly shorter than the experimental values observed. This trend is identical to the sodium analogs and might be explained on the basis of a reduced coordination number at the metal and sulfur atoms. The sum of ionic radii for a potassium cation and a sulfide anion in potassium sulfides ranges from 3.21 Å for four-coordinate potassium up to 3.35 Å for an eight-coordinate metal center. These values are longer than those observed in the target compounds, but might be explained on the basis of a higher coordination number (CN = 6) for S^{2-} utilized in the calculation.[38] However, the overall trends agree well with the experimental data.

General Comments

A comparison of structural features between sodium and potassium thiolates clearly shows the influence of the metal ionic radii: a pronounced tendency for an increased degree of association with increasing metal radius. A comparison of the one-dimensional zigzag polymers **3**, **9**, $[Na(THF)_2R_f]_\infty$,[3a] and $[Li(py)_2SPh]_\infty$[6] with the ladder polymers **7**, $[K(THF)R_f]_\infty$,[3a] and $[Li(py)SCH_2Ph]_\infty$[6] shows that either the increase of the ionic radius of the metal center or the decrease of ligand bulk yields higher associated species. These examples clearly demonstrate the direct influence of donor, metal, and ligand bulk on the structural outcome. The association and aggregation tendencies observed in the thiolates are closely related to those observed in the isoelectronic alkali phosphides. Often, ladder-type one-dimensional zigzag chains are observed,[40] such as in $[Li(OEt_2)PPh_2]_\infty$ or $[Li(THF)_2PPh_2]_\infty$.[41] Addition of the bidentate donor TMEDA yields the dimeric $[Li(TMEDA)PPh_2]_2$,[42] while utilization of PMDTA results in the monomer $Li(PMDTA)PPh_2$,[42] structural trends closely related to those reported in this paper.

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The synthesis and structural characterization of a series of sodium and potassium triisopropylbenzenethiolates clearly illustrates that structural parameters and association tendencies can be influenced by the nature of the metal, the spatial requirements of ligands and donors, and the ratio of metal to donor.

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Supporting Information Available: Tables listing data collection parameters, bond lengths and angles, atomic coordinates, anisotropic displacement coefficients, and hydrogen atoms for the X-ray structure of **5** (17 pages). X-ray crystallographic files, in CIF format, for the structure determinations of **1**, **2**, **3**, **7**, and **9** are available on the Internet only. Ordering and access information is given on any current masthead page.

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