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Donor-Free Alkali Metal Thiolates: Synthesis and Structure of Dimeric, Trimeric, and Tetrameric Complexes with Sterically Encumbered Terphenyl Substituents

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The synthesis and characterization of the tetrameric lithium thiolate $(\mathrm{LiSC_6H_2\text{-}2,4,6\text{-}Ph_3})_4\cdot\mathrm{C_7H_8}$ (**1**), the trimeric lithium thiolate $(\mathrm{LiSC_6H_3\text{-}2,6\text{-}Mes_2})_3\cdot\mathrm{C_6H_{14}}$ (**2**) (Mes = 2,4,6-$\mathrm{Me_3C_6H_2}$), the thiol $\mathrm{HSC_6H_3\text{-}2,6\text{-}Trip_2}$ (**3**) (Trip = 2,4,6-*i*-$\mathrm{Pr_3C_6H_2}$), and the complete alkali metal series of dimeric thiolates $(\mathrm{MSC_6H_3\text{-}2,6\text{-}Trip_2})_2$ (M = Li (**4**, **5**), Na (**6**), K (**7**), Rb (**8**), Cs (**9**)) are described. The compounds were characterized by ^{1}H, ^{7}Li, and ^{13}C NMR and IR spectroscopy and by X-ray crystallography. The compounds **1** and **2** crystallize as four- and three-rung ladder framework structures. The compounds **4**−**9** crystallize as dimers with $\mathrm{M_2S_2}$ cores. In addition, the metal ions interact with the ortho aryl groups to varying degrees in all the structures. The extent of these interactions appears to be determined mainly by ionic sizes and geometric factors. The coordination geometry of the thiolato sulfurs also varies from pyramidal in **1**, **2**, **4**, **5**, and **6** and one planar and one slightly pyramidal sulfur geometry in **7** to both sulfurs being planar coordinated in **8** and **9**. Crystal data at 130 K are as follows: $(\mathrm{LiSC_6H_2\text{-}2,4,6\text{-}Ph_3})_4\cdot\mathrm{C_7H_8}$ (**1**), $a = 15.961(2)$ Å, $b = 16.243(3)$ Å, $c = 17.114(3)$ Å, $\alpha = 89.375(14)°$, $\beta = 85.334(14)°$, $\gamma = 63.343(12)°$, $V = 3950(1)$ Å^3, space group $P\bar{1}$, $Z = 2$, $R_1 = 0.082$; $(\mathrm{LiSC_6H_3\text{-}2,6\text{-}Mes_2})_3\cdot\mathrm{C_6H_{14}}$ (**2**), $a = 14.554(4)$ Å, $b = 14.010(4)$ Å, $c = 32.832(8)$ Å, $\beta = 95.20(2)°$, $V = 6667(2)$ Å^3, space group $P2_1/n$, $Z = 4$, $R_1 = 0.089$; $\mathrm{HSC_6H_3\text{-}2,6\text{-}Trip_2}$ (**3**), $a = 8.180(2)$ Å, $b = 25.437(5)$ Å, $c = 15.752(3)$ Å, $V = 3278(1)$ Å^3, space group *Pnma*, $Z = 4$, $R_1 = 0.045$; $(\mathrm{LiC_6H_3\text{-}2,6\text{-}Trip_2})_2$ (**4**), $a = 12.652(2)$ Å, $b = 14.218(1)$ Å, $c = 18.713(2)$ Å, $\alpha = 83.56(1)°$, $\beta = 84.36(1)°$, $\gamma = 73.82(1)°$, $V = 3205(1)$ Å^3, space group $P\bar{1}$, $Z = 2$, $R_1 = 0.055$; $(\mathrm{LiC_6H_3\text{-}2,6\text{-}Trip_2})_2\cdot\mathrm{C_7H_8}$ (**5**), $a = 15.383(3)$ Å, $b = 14.381(2)$ Å, $c = 16.524(2)$ Å, $\beta = 111.10(1)$, $V = 3410.3(9)$ Å^3, space group $P2_1/n$, $Z = 2$, $R_1 = 0.086$; $(\mathrm{NaSC_6H_3\text{-}2,6\text{-}Trip_2})_2\cdot 0.5\mathrm{C_7H_8}$ (**6**), $a = 13.952(2)$ Å, $b = 20.267(2)$ Å, $c = 24.475(3)$ Å, $\beta = 98.673(9)°$, $V = 6842(1)$ Å^3, space group $P2_1/n$, $Z = 4$, $R_1 = 0.068$; $(\mathrm{KSC_6H_3\text{-}2,6\text{-}Trip_2})_2\cdot\mathrm{C_7H_8}$ (**7**), $a = 13.683(4)$ Å, $b = 15.071(4)$ Å, $c = 17.824(5)$ Å, $\alpha = 82.73(2)$, $\beta = 86.09(2)$, $\gamma = 88.46(2)$, $V = 3637(2)$ Å^3, space group $P\bar{1}$, $Z = 2$, $R_1 = 0.072$; $(\mathrm{RbSC_6H_3\text{-}2,6\text{-}Trip_2})_2\cdot\mathrm{C_7H_8}$ (**8**), $a = 19.710(3)$ Å, $b = 20.892(3)$ Å, $c = 18.755(2)$ Å, $\beta = 106.900(9)°$, $V = 7389(2)$ Å^3, space group $P2_1/n$, $Z = 4$, $R_1 = 0.069$; $(\mathrm{CsSC_6H_3\text{-}2,6\text{-}Trip_2})_2$ (**9**), $a = 13.109(3)$ Å, $b = 15.941(3)$ Å, $c = 17.748(4)$ Å, $\alpha = 101.65(2)°$, $\beta = 100.76(2)°$, $\gamma = 104.25(2)°$, $V = 3410(1)$ Å^3, space group $P\bar{1}$, $Z = 2$, $R_1 = 0.048$.

Introduction

The structural aspects of the chemistry of alkali metal thiolates have received considerably less attention than those of their alkoxide or aryloxide counterparts.[1] In fact, the first structure of an alkali metal thiolate as a molecular species was reported as recently as 1985.[2] Currently, about a dozen structures of lithium thiolates have been described[1] and a number of lithium selenolato[1,3] and tellurolato[1,4] structures have also been published. The majority of the compounds studied are lithium salts, and reports for the heavier alkali metals are limited to the tris(trifluoromethyl)phenyl compounds $[\mathrm{Na(THF)_2SC_6H_2\text{-}2,4,6\text{-}(CF)_3}]_n$ and $[\mathrm{K(THF)SC_6H_2\text{-}2,4,6\text{-}(CF_3)_3}]_n$, which have polymeric structures,[5] and the recently reported[6] hexameric complexes $[(\mathrm{KSAr})_2\{\mathrm{K(THF)SAr}\}_2\{\mathrm{K(THF)_2SAr}\}_2]$ and $[(\mathrm{KSAr})_2\{\mathrm{K(THF)SAr}\}_2\{\mathrm{K(TMEDA)SAr}\}_2\cdot\mathrm{THF}]$ (Ar = 2,4,6-*i*-$\mathrm{Pr_3C_6H_2}$−; TMEDA = *N*,*N*,*N*′*N*′-tetramethylenediamine) which have stacked structures. Furthermore, all the thiolate structures reported to date involve solvation of some or all of the metal ions by classical Lewis bases,[1,7] e.g. $\mathrm{Et_2O}$, THF, or pyridine (py). Thus, apart from the powder diffraction studies of $(\mathrm{MSMe})_n$[8a] (M = Li, Na or K), there are no structural data for formally unsolvated alkali metal thiolates. In addition, it is not possible at present to compare a complete set of structures of molecular alkali metal chalcogenolates in which the substituent remains the same

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[3] For example: (a) du Mont, W.-W.; Kubiniok, S.; Lange, L.; Pohl, S.; Saak, W.; Wagner, I. *Chem.Ber*. **1991**, *124*, 1315. (b) Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem*. **1991**, *30*, 2633; (c) Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem*. **1993**, *32*, 4505.

[4] For example: (a) Bonasia, P. J.; Gindelberger, D. E.; Dabbousi, B. O.; Arnold, J. *J. Am. Chem. Soc*. **1992**, *114*, 5209. (b) Becker, G.; Klinkhammer, K. W.; Lartiges, S.; Böttcher, P.; Poll, W. *Z. Anorg. Allg. Chem*. **1992**, *613*, 7. (c) Bonasia, P. J.; Arnold, J. *J. Organomet. Chem*. **1993**, *449*, 147. (d) Becker, G.; Klinkhammer, K. W.; Massa, W. *Z. Anorg. Allg. Chem*. **1992**, *619*, 628.

[5] Brooker, S.; Edelmann, F. T.; Kottke, T.; Roesky, H. W.; Sheldrick, G. M.; Stalke, D.; Whitmire, K. H. *J. Chem. Soc., Chem. Commun*. **1991**, 144.

[6] Ruhlandt-Senge, K.; Englich, U. *J. Chem. Soc., Chem. Commun*. **1996**, 147.

[7] Some unsolvated lithium salts of other chalcogenolates have been characterized, however. Examples include the hexamer $[\mathrm{LiTeSi(SiMe_3)_3}]_6$ in ref 4d, the enolate $[\mathrm{LiOC(CH_2)C(CH_3)_3}]_6$[a] and the siloxide $[\mathrm{LiOSiMe_2(1\text{-}naphthyl)}]_6$[b] in: (a) Williard, P. G.; Carpenter, G. B. *J. Am. Chem. Soc*. **1985**, *107*, 3345. (b) Bazhenova, T. A.; Lobkovskaya, R. M.; Shibaeva, R. P.; Shilov, A. E.; Shilova, A. K. *J. Organomet. Chem*. **1987**, *330*, 9.

[8] (a) Weiss, E.; Joergens, U. *Chem. Ber*. **1972**, *105*, 481. The structure of a compound $(\mathrm{Cs_4(dibenzo\text{-}18\text{-}crown\text{-}6)_3(S_6)_2\cdot 2MeCN}$ (3.53(2) Å) involving Cs−S interactions is described in. (b) Schnock, M.; Böttcher, P. *Z. Naturforsch*. **1995**, *50b*, 721.

[9] This is mainly due to the fact that the heavier alkali metal derivatives have received less attention. This situation is rapidly changing, however. See ref. 1b and the following: (a) Schade, C.; Schleyer, P. v. R. *Adv. Organomet. Chem*. **1987**, *24*, 893. (b) Weiss, E. *Angew. Chem. Int. Ed. Engl*. **1993**, *32*, 1501.

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Table 1. Crystallographic Data for Compounds **1**−**9**[a]

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
formula	$C_{103}H_{76}Li_4S_4$	$C_{78}H_{89}Li_3S_3$	$C_{36}H_{49}S$	$C_{72}H_{98}Li_2S_2$	$C_{79}H_{106}Li_2S_2$	$C_{75.5}H_{102}Na_2S_2$	$C_{79}H_{106}K_2S_2$	$C_{79}H_{106}Rb_2S_2$	$C_{72}H_{98}Cs_2S_2$
fw	1469.6	1143.5	514.8	1041.5	1133.6	1119.7	1198.0	1290.7	1293.4
color, habit	colorless block	colorless plate	colorless plate	colorless plate	colorless block	colorless plate	colorless needle	colorless plate	colorless plate
cyst syst	triclinic	monoclinic	orthorhombic	triclinic	monoclinic	monoclinic	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/n$	Pnma	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a, Å	15.961(2)	14.554(4)	8.180(2)	12.652(2)	15.383(3)	13.952(2)	13.683(4)	19.710(3)	13.109(3)
b, Å	16.243(3)	14.010(4)	25.437(5)	14.218(1)	14.381(2)	20.267(2)	15.071(4)	20.892(3)	15.941(3)
c, Å	17.114(3)	32.832(8)	15.752(3)	18.713(2)	16.524(2)	24.475(3)	17.824(5)	18.755(2)	17.748(4)
α, deg	89.375(14)			83.56(1)			82.73(2)		101.65(2)
β, deg	85.334(14)	95.20(2)		84.36(1)	111.10(1)	98.673(9)	86.09(2)	106.900(9)	100.76(2)
γ, deg	63.343(12)			73.82(1)			88.46(2)		104.25(2)
V, Å^3	3950(1)	6667(1)	3278(1)	3205(1)	3410.3(9)	6842(1)	3637(2)	7389(2)	3410(1)
Z	2	4	4	2	2	4	2	4	2
d, g cm^{-3}	1.235	1.139	1.041	1.079	1.014	1.132	1.094	1.160	1.260
cryst dimsens, mm	0.20 × 0.08 × 0.04	0.25 × 0.25 × 0.05	0.24 × 0.20 × 0.04	0.60 × 0.50 × 0.10	0.10 × 0.06 × 0.03	0.47 × 0.20 × 0.04	0.60 × 0.16 × 0.08	0.26 × 0.16 × 0.04	0.52 × 0.50 × 0.12
μ, cm^{-1}	14.79	13.20	10.05	10.29	9.67	11.34	19.75	25.29	11.68
no. of unique data	8693	7149	2195	8718	4453	8917	9472	9594	13403
no. of data with ($I > 2\sigma(I)$)	5608	4089	1638	6829	2470	5314	6604	5368	9957
no. of params	1057	795	263	747	410	851	938	901	807
R_1 ($I > 2\sigma(I)$)	0.0816	0.0894	0.0454	0.0548	0.0860	0.0680	0.0724	0.0687	0.0482
wR$_2$ (all data)	0.2129	0.2407	0.0952	0.1357	0.2354	0.1790	0.2089	0.1397	0.1143

[a] All data were collected at 130 K using either Cu Kα (λ = 1.541 78 Å) (**1**−**8**) or Mo Kα (λ = 0.710 93 Å) (**9**) radiation.

through the series, since thiolato derivatives of rubidium and cesium are currently uncharacterized.[8b] In fact, a comparison of this type is rarely possible[9] for molecular alkali metal derivatives of any kind. In this paper the synthesis and structures of all members of such a series are now presented.

Experimental Section

Preparation of Compounds. All reactions were performed by using modified Schlenk techniques under an inert atmosphere of N_2 or a Vacuum Atmospheres HE43-2 drybox. Solvents were freshly distilled under N_2 from a Na/K alloy and degassed twice before use. The compounds HSC_6H_2-2,4,6-Ph_3,[10a] HSC_6H_3-2,6-Mes_2,[10b] and $Li(OEt_2)$-C_6H_3-2,6-$Trip_2$[11] were synthesized as previously described. Alkali metals were purchased from commercial suppliers and used as received. NMR spectra were recorded in C_6D_6 solution by using a General Electric QE-300 spectrometer; IR spectra (Nujol mull, CsI plates) were recorded in the range 4000−200 cm^{-1} with a Perkin-Elmer 1420 spectrometer.

($LiSC_6H_3$-2,4,6-Ph_3)$_4$·C_7H_8 (1). A solution of HSC_6H_3-2,4,6-Ph_3 (1.08 g, 3.19 mmol) in *ca*. 20 mL of toluene was treated dropwise with *n*-BuLi (2.0 mL of a 1.6 M solution in *n*-hexane), and the reaction was allowed to stir for 1 h. Removal of *ca*. half of the solvent under reduced pressure resulted in the formation of a white microcrystalline precipitate which could not be redissolved by heating or the addition of more toluene. Crystals, which were suitable for X-ray crystallographic studies, were grown by further cooling of the solution in a 0 °C freezer for 10 d. Total yield 0.98 g (89%). Mp: 380−385 °C dec. ^{1}H NMR (C_6D_6) δ 2.11 (s, C_7H_8), 6.97−7.32 (m, aryl-*H*). A satisfactory ^{13}C NMR spectrum could not be obtained due to the poor solubility of **1** in C_6D_6. ^{7}Li NMR (C_6D_6): δ −1.13. IR (Nujol, cm^{-1}): 1597 ms, 1571 w, 1545 w, 1489 s, 1402 s, 1341 m, 1305 w, 1238 w, 1175 vw, 1153 w, 1110 ms, 1069 m, 1041 ms, 1025 m, 996 w, 970 vw, 913 w, 886 ms, 850 vw, 837 w, 760 vs, 734 ms, 700 vs, 625 w, 555 ms.

($LiSC_6H_3$-2,6-Mes_2)$_3$·C_6H_{14} (2). HSC_6H_3-2,6-Mes_2 (0.81 g, 2.34 mmol) was dissolved in *ca*. 20 mL of toluene and treated dropwise with a solution of *n*-BuLi (1.5 mL of a 1.6 M solution in *n*-hexane). The reaction was allowed to stir for 2 h whereupon the solvent was removed under reduced pressure. The remaining yellow oil was treated with *ca*. 10 mL of *n*-hexane. Within *ca*. 1 min colorless crystals, which were suitable for X-ray crystallographic studies, began to precipitate. Cooling of the mother liquid in a −30 °C freezer afforded a further crop of crystals. Yield: 0.73 g (82%). Mp: 229−232 °C (110 °C desolvation). ^{1}H NMR (C_6D_6): δ 0.84−1.23 (m, C_6H_{14}), 2.02 (s, *o*-C*H*$_3$), 2.18 (s, *p*-C*H*$_3$), 6.81−6.94 (m, Aryl-*H*). ^{13}C NMR (C_6D_6): δ 21.2 (*o*-CH_3), 21.3 (*p*-CH_3), 122.6 (*p*-Ph), 127.9 (*m*-Ph), 129.2 (*m*-Mes), 135.7 (*o*-Mes), 136.2 (*o*-Mes), 141.8 (*i*-Mes), 143.2 (*p*-Ph), 143.6

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Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**−**9**[a]

Compound **1**							
Li(1)−S(1)	2.365(14)	Li(4)−S(3)	2.411(12)	Li(2)···C(60)	2.73(2)	Li(1)···Li(2)	3.12(2)
Li(1)−S(2)	2.431(13)	Li(4)−S(4)	2.428(13)	Li(3)···C(43)	2.695(14)	Li(2)···Li(3)	3.14(2)
Li(2)−S(1)	2.442(13)	av Li−S	2.454	Li(3)···C(48)	2.65(2)	Li(3)···Li(4)	3.05(2)
Li(2)−S(2)	2.62(2)	Li(1)···C(19)	2.66(2)	Li(4)···C(72)	2.453(14)	S(1)−C(1)	1.783(7)
Li(2)−S(3)	2.417(14)	Li(1)···C(24)	2.55(2)	Li(4)···C(91)	2.583(14)	S(2)−C(25)	1.766(7)
Li(3)−S(2)	2.444(11)	Li(1)···C(31)	2.73(2)	Li(4)···C(95)	2.59(2)	S(3)−C(49)	1.775(7)
Li(3)−S(3)	2.586(13)	Li(1)···C(36)	2.63(2)	Li(4)···C(96)	2.41(2)	S(4)−C(73)	1.763(7)
Li(3)−S(4)	2.392(11)	Li(2)···C(55)	2.73(2)				
S(1)−Li(1)−S(2)	105.1(5)	S(3)−Li(4)−S(4)	105.2(5)	Li(1)−S(2)−C(25)	110.1(4)	Li(2)−S(3)−C(49)	110.6(4)
S(1)−Li(2)−S(2)	97.7(5)	Li(1)−S(1)−Li(2)	80.8(5)	Li(2)−S(2)−C(25)	103.5(4)	Li(3)−S(3)−C(49)	109.0(4)
S(1)−Li(2)−S(3)	134.1(6)	Li(1)−S(1)−C(1)	106.2(4)	Li(3)−S(2)−C(25)	108.8(4)	Li(4)−S(3)−C(49)	115.5(4)
S(2)−Li(2)−S(3)	102.5(5)	Li(2)−S(1)−C(1)	101.7(4)	Li(2)−S(3)−Li(3)	77.8(4)	Li(3)−S(4)−Li(4)	78.5(4)
S(2)−Li(3)−S(3)	102.7(4)	Li(1)−S(2)−Li(2)	76.2(4)	Li(2)−S(3)−Li(4)	131.9(4)	Li(3)−S(4)−C(73)	106.6(4)
S(2)−Li(3)−S(4)	128.8(5)	Li(1)−S(2)−Li(3)	136.6(4)	Li(3)−S(3)−Li(4)	75.1(4)	Li(4)−S(4)−C(73)	106.1(4)
S(3)−Li(3)−S(4)	101.1(4)	Li(2)−S(2)−Li(3)	76.8(4)				
Compound **2**							
Li(1)−S(1)	2.37(2)	Li(3)−S(3)	2.33(2)	Li(3)···C(31)	2.38(2)	Li(3)···X	2.16(2)
Li(1)−S(2)	2.42(2)	av Li−S	2.45(2)	Li(3)···C(32)	2.50(2)	Li(1)···Li(2)	3.20(2)
Li(2)−S(1)	2.51(2)	Li(1)···C(7)	2.73(2)	Li(3)···C(33)	2.66(2)	Li(2)···Li(3)	3.16(2)
Li(2)−S(2)	2.65(2)	Li(1)···C(40)	2.66(2)	Li(3)···C(34)	2.77(2)	S(1)−C(1)	1.775(8)
Li(2)−S(3)	2.42(2)	Li(1)···C(45)	2.71(2)	Li(3)···C(35)	2.62(2)	S(2)−C(25)	1.771(8)
Li(3)−S(2)	2.44(2)	Li(2)···C(56)	2.58(2)	Li(3)···C(36)	2.47(2)	S(3)−C(49)	1.753(8)
S(1)−Li(1)−S(2)	104.2(6)	Li(1)−S(1)−C(1)	109.5(5)	Li(2)−S(2)−C(25)	141.9(4)	Li(2)−S(2)−Li(3)	76.5(5)
S(1)−Li(2)−S(2)	94.3(5)	Li(2)−S(1)−C(1)	126.9(5)	Li(3)−S(2)−C(25)	103.9(5)	Li(2)−S(3)−C(49)	113.8(5)
S(1)−Li(2)−S(3)	141.4(7)	Li(1)−S(1)−Li(2)	82.0(5)	Li(1)−S(2)−Li(2)	78.3(5)	Li(3)−S(3)−C(49)	128.6(5)
S(2)−Li(2)−S(3)	90.5(5)	Li(1)−S(2)−C(25)	109.3(5)	Li(1)−S(2)−Li(3)	146.7(5)	Li(2)−S(3)−Li(3)	83.4(5)
S(2)−Li(3)−S(3)	97.9(6)						
Compound **3**							
S(1)−C(1)	1.763(4)	av S(1)−H(1)	1.35				
C(2)−C(1)−S(1)	120.0(2)	C(2)−C(1)−C(2)′	120.0(3)				
Compound **4**							
Li(1)−S(1)	2.395(6)	Li(1)···C(7)	2.524(6)	Li(2)···C(45)	2.700(6)	Li(2)···X3	2.196(6)
Li(1)−S(2)	2.432(6)	Li(1)···C(8)	2.531(6)	Li(2)···C(46)	2.614(6)	Li(1)···Li(2)	2.880(7)
Li(2)−S(1)	2.375(5)	Li(1)···Li(2)	2.880(7)	Li(2)···C(47)	2.504(6)	S(1)−C(1)	1.769(3)
Li(2)−S(2)	2.383(5)	Li(2)···C(43)	2.571(6)	Li(2)···C(48)	2.520(6)	S(2)−C(37)	1.774(3)
av Li−S	2.396	Li(2)···C(44)	2.707(6)				
S(1)−Li(1)−S(2)	102.5(2)	Li(1)−S(1)−Li(2)	74.3(2)	Li(1)−S(1)−C(1)	98.7(2)	Li(2)−S(2)−C(37)	109.8(2)
S(1)−Li(2)−S(2)	104.6(2)	Li(1)−S(2)−Li(2)	73.5(2)	Li(2)−S(1)−C(1)	127.7(2)	Li(1)−S(2)−C(37)	123.2(2)
Compound **5**							
Li(1)−S(1)	2.461(10)	Li(1)···C(7)	2.412(13)	Li(1)···C(10)	2.898(13)	Li(1)···X1	2.249
Li(1)−S(1)′	2.401(11)	Li(1)···C(8)	2.576(13)	Li(1)···C(11)	2.699(13)	Li(1)···Li(1)′	2.72(2)
av Li−S	2.431	Li(1)···C(9)	2.819(13)	Li(1)···C(12)	2.445(13)	S(1)−C(1)	1.791(6)
S(1)−Li(1)−S(1)′	111.9(4)	Li(1)−S(1)−Li(1)′	68.1(4)	Li(1)−S(1)−C(1)	103.6(4)	Li(1)′−S(1)−C(1)	136.4(3)
Compound **6**							
Na(1)−S(1)	2.762(2)	Na(1)···C(9)	3.064(5)	Na(2)···C(44)	2.839(5)	Na(1)···X4	3.076
Na(1)−S(2)	2.695(2)	Na(1)···C(10)	3.079(5)	Na(2)···C(45)	2.856(5)	Na(2)···X2	4.163
Na(2)−S(1)	2.684(2)	Na(1)···C(11)	3.016(5)	Na(2)···C(46)	3.112(5)	Na(2)···X3	2.720
Na(2)−S(2)	2.697(2)	Na(1)···C(12)	3.028(5)	Na(2)···C(47)	3.244(5)	Na(1)···Na(2)	4.225(3)
av Na−S	2.710	Na(1)···C(58)	3.266(5)	Na(2)···C(48)	3.228(5)	S(1)−C(1)	1.765(4)
Na(1)···C(7)	3.023(5)	Na(1)···C(63)	3.108(5)	Na(1)···X1	2.701	S(2)−C(37)	1.746(5)
Na(1)···C(8)	3.043(5)	Na(2)···C(43)	3.038(5)				
S(1)−Na(1)−S(2)	76.80(6)	Na(1)−S(1)−Na(2)	101.73(7)	Na(1)−S(1)−C(1)	117.3(2)	Na(1)−S(2)−C(37)	121.5(2)
S(1)−Na(2)−S(2)	78.11(7)	Na(1)−S(2)−Na(2)	103.16(7)	Na(2)−S(1)−C(1)	127.1(2)	Na(2)−S(2)−C(37)	113.6(2)
Compound **7**							
K(1)−S(1)	3.093(2)	K(1)···C(12)	3.309(5)	K(2)···C(23)	3.376(5)	K(2)···C(47)	3.279(5)
K(1)−S(2)	3.039(2)	K(1)···C(21)	3.472(5)	K(2)···C(24)	3.326(5)	K(2)···C(48)	3.328(5)
K(2)−S(1)	3.045(2)	K(1)···C(58)	3.475(5)	K(2)···C(25)	3.340(5)	K(1)···X1	3.140
K(2)−S(2)	3.044(2)	K(1)···C(59)	3.501(5)	K(2)···C(26)	3.351(5)	K(1)···X4	3.152
av K−S	3.055	K(1)···C(60)	3.469(5)	K(2)···C(27)	3.412(5)	K(2)···X2	3.067
K(1)···C(7)	3.447(5)	K(1)···C(61)	3.456(5)	K(2)···C(43)	3.422(5)	K(2)···X3	3.093
K(1)···C(8)	3.564(5)	K(1)···C(62)	3.383(5)	K(2)···C(44)	3.501(5)	K(1)···K(2)	5.124(2)
K(1)···C(9)	3.535(6)	K(1)···C(63)	3.398(5)	K(2)···C(45)	3.453(5)	S(1)−C(1)	1.739(5)
K(1)···C(10)	3.447(5)	K(2)···C(22)	3.430(5)	K(2)···C(46)	3.378(5)	S(2)−C(37)	1.740(5)
K(1)···C(11)	3.304(5)						
S(1)−K(1)−S(2)	65.73(5)	K(1)−S(1)−K(2)	113.18(5)	K(1)−S(1)−C(1)	119.2(2)	K(1)−S(2)−C(37)	124.1(2)
S(1)−K(2)−S(2)	66.28(5)	K(1)−S(2)−K(2)	114.78(6)	K(2)−S(1)−C(1)	123.5(2)	K(2)−S(2)−C(37)	121.1(2)

Table 2. (Continued)

			Compound **8**				
Rb(1)−S(1)	3.166(2)	Rb(1)···C(12)	3.440(7)	Rb(2)···C(24)	3.427(7)	Rb(2)···C(47)	3.304(7)
Rb(1)−S(2)	3.157(2)	Rb(1)···C(58)	3.518(8)	Rb(2)···C(25)	3.560(6)	Rb(2)···C(48)	3.398(8)
Rb(2)−S(1)	3.159(2)	Rb(1)···C(59)	3.479(8)	Rb(2)···C(26)	3.588(6)	Rb(1)···X1	3.156
Rb(2)−S(2)	3.180(2)	Rb(1)···C(60)	3.470(7)	Rb(2)···C(27)	3.563(7)	Rb(1)···X4	3.170
av Rb−S	3.166	Rb(1)···C(61)	3.463(7)	Rb(2)···C(29)	3.675(7)	Rb(2)···X2	3.213
Rb(1)···C(7)	3.555(7)	Rb(1)···C(62)	3.410(8)	Rb(2)···C(43)	3.540(7)	Rb(2)···X3	3.166
Rb(1)···C(8)	3.538(7)	Rb(1)···C(63)	3.447(9)	Rb(2)···C(44)	3.596(7)	Rb(1)···Rb(2)	5.366(1)
Rb(1)···C(9)	3.434(7)	Rb(2)···C(22)	3.493(8)	Rb(2)···C(45)	3.517(7)	S(1)−C(1)	1.749(7)
Rb(1)···C(10)	3.384(7)	Rb(2)···C(23)	3.386(7)	Rb(2)···C(46)	3.393(6)	S(2)−C(37)	1.731(8)
Rb(1)···C(11)	3.344(7)						
S(1)−Rb(1)−S(2)	64.15(5)	Rb(1)−S(1)−Rb(2)	116.05(7)	Rb(1)−S(1)−C(1)	123.5(2)	Rb(1)−S(2)−C(37)	122.1(2)
S(1)−Rb(2)−S(2)	63.97(5)	Rb(1)−S(2)−Rb(2)	115.71(7)	Rb(2)−S(1)−C(1)	120.4(2)	Rb(2)−S(2)−C(37)	121.9(2)
			Compound **9**				
Cs(1)−S(2)	3.3041(13)	C(1)···C(12)	3.637(4)	Cs(2)···C(24)	3.614(4)	Cs(2)···C(48)	3.602(4)
Cs(1)−S(1)	3.3087(13)	Cs(1)···C(21)	3.828(4)	Cs(2)···C(25)	3.674(5)	Cs(2)···C(53)	3.753(5)
Cs(2)−S(1)	3.2870(13)	Cs(1)···C(58)	3.740(4)	Cs(2)···C(26)	3.693(5)	Cs(2)···C(56)	3.709(5)
Cs(2)−S(2)	3.3309(13)	Cs(1)···C(59)	3.684(4)	Cs(2)···C(27)	3.724(4)	Cs(1)···X1	3.353
av Cs−S	3.308	Cs(1)···C(60)	3.574(4)	Cs(2)···C(29)	3.819(5)	Cs(1)···X4	3.356
Cs(1)···C(7)	3.716(4)	Cs(1)···C(61)	3.564(4)	Cs(2)···C(43)	3.742(4)	Cs(2)···X2	3.401
Cs(1)···C(8)	3.724(4)	Cs(1)···C(62)	3.578(5)	Cs(2)···C(44)	3.828(4)	Cs(2)···X3	3.404
Cs(1)···C(9)	3.637(5)	Cs(1)···C(63)	3.668(4)	Cs(2)···C(45)	3.754(5)	Cs(1)···Cs(2)	5.424(1)
Cs(1)···C(10)	3.551(4)	Cs(2)···C(22)	3.712(4)	Cs(2)···C(46)	3.618(4)	S(1)−C(1)	1.747(4)
Cs(1)···C(11)	3.541(4)	Cs(2)···C(23)	3.650(4)	Cs(2)···C(47)	3.531(4)	S(2)−C(37)	1.752(4)
S(1)−Cs(1)−S(2)	68.15(3)	Cs(1)−S(1)−Cs(2)	110.65(4)	Cs(1)−S(1)−C(1)	124.49(14)	Cs(2)−S(1)−C(1)	124.74(14)
S(1)−Cs(2)−S(2)	68.09(3)	Cs(1)−S(2)−Cs(2)	109.67(4)	Cs(1)−S(2)−C(37)	126.4(2)	Cs(2)−S(2)−C(37)	123.4(2)

[a] X = centroid of the aromatic plane defined by positions C(31) to C(36) (**2**). X1, X2, X3, and X4 = centroids of the aromatic planes defined by positions C(7) to C(12), C(22) to C(27), C(43) to C(48), and C(58) to C(63) (**4**−**9**).

(*i*-Ph). IR (Nujol, cm^{-1}): 1608 ms, 1570 m, 1483 sh, 1451 vs, 1381 vs, 1241 w, 1178 vw, 1160 vw, 1112 w, 1086 w, 1044 s, 1012 m, 884 vw, 854 s, 847 sh, 796 s, 773 w, 742 vs, 729 s, 586 m, 545 vw, 464 m, 388 m, 349 w, 278 w.

HSC_6H_3-2,6-Trip$_2$ (3). Sulfur (0.40 g, 12.5 mmol) was added via a solids-addition tube to a solution of Li(OEt_2)C_6H_3-2,6-Trip$_2$ (2.59 g, 5 mmol) in *ca*. 20 mL of THF. After overnight stirring, the deep red solution was slowly added dropwise to a suspension of $LiAlH_4$ (1.2 g) in diethyl ether (10 mL) with cooling in an ice bath. After 1 h of stirring, the excess $LiAlH_4$ was destroyed with water and 30 mL of 10% hydrochloric acid was added. The organic layer was separated, and the aqueous solution was extracted with diethyl ether (2 × 30 mL). The combined phases were dried over K_2CO_3 and filtered. The solvent was removed under reduced pressure and the residue recrystallized from ethyl acetate. Crystals suitable for X-ray crystallography were grown from *n*-hexane. Yield: 1.75 g (68%). Mp: 203−205 °C. ^{1}H NMR (C_6D_6): δ 1.18 (d, *o/p*-CH(C*H*$_3$)$_2$), 1.24 (d, *o/p*-CH(C*H*$_3$)$_2$), 1.39 (d, *o/p*-CH(C*H*$_3$)$_2$), 2.88 (m, *o*+*p*-C*H*(CH$_3$)$_2$), 3.19 (s, S*H*), 6.95−7.24 (m, aryl-*H*). ^{13}C NMR (C_6D_6) δ 24.1 (*o*-CH(*C*H$_3$)$_2$), 24.3 (*o*-CH(*C*H$_3$)$_2$), 25.0 (*p*-CH(*C*H$_3$)$_2$), 31.2 (*o*-*C*H(CH$_3$)$_2$), 34.8 (*p*-*C*H(CH$_3$)$_2$), 121.5 (*m*-Trip), 124.3 (*p*-Ph), 129.3 (*m*-Ph), 135.9 (*i*-Trip), 136.1 (*i*-Ph), 138.7 (*o*-Ph), 147.2 (*o*-Trip), 149.3 (*p*-Trip). IR (Nujol, cm^{-1}): 2550 m, 1758 vw, 1738 w, 1602 ms, 1564 ms, 1390 s, 1358 vs, 1334 m, 1312 ms, 1255 w, 1235 m, 1168 m, 1149 w, 1101 m, 1057 m, 1047 m, 942 m, 918 w, 876 s, 794 s, 774 w, 754 w, 741 ms, 727 m, 648 m.

($LiSC_6H_3$-2,6-Trip$_2$)$_2$ (4) and **($LiSC_6H_3$-2,6-Trip$_2$)$_2$·C_7H_8 (5)**. *n*-BuLi (0.75 mL of a 1.6 M solution in *n*-hexane) was added dropwise to a stirred solution HSC_6H_3-2,6-Trip$_2$ (0.62 g, 1.20 mmol) in *ca*. 15 mL toluene. The reaction was allowed to stir for another 2 h whereupon the solvent was removed under reduced pressure. The colorless residue was redissolved in *ca*. 5 mL of *n*-hexane. Cooling in a 0 °C freezer afforded colorless crystals suitable for X-ray crystallographic studies. The synthesis of the solvate-free compound **4** was accomplished in a similar manner with use of HSC_6H_3-2,6-Trip$_2$ (0.35 g, 0.68 mmol) and *n*-BuLi (0.42 mL) in *n*-hexane. Yield: *ca*. 60%. Mp: 215−218 °C. ^{1}H NMR (C_6D_6): δ 1.12 (d, *o/p*-CH(C*H*$_3$)$_2$), 1.29 (d, *o/p*-CH(C*H*$_3$)$_2$), 1.31 (d, *o/p*-CH(C*H*$_3$)$_2$), 2.10 (s, C$_7$*H*$_8$), 2.90 (m, *o/p*-C*H*(CH$_3$)$_2$), 6.89−7.24 (m, aryl-*H*). ^{13}C NMR (C_6D_6) δ 24.2 (*o*-CH(*C*H$_3$)$_2$), 24.3 (*o*-CH(*C*H$_3$)$_2$), 24.9 (*p*-CH(*C*H$_3$)$_2$), 30.9 (*o*-*C*H(CH$_3$)$_2$), 34.0 (*p*-*C*H(CH$_3$)$_2$), 121.3 (*p*-Ph), 121.4 (*m*-Trip), 128.8 (*m*-Ph), 140.5 (*i*-Trip), 142.5 (*o*-Ph), 146.6 (*o*-Trip), 146.8 (*i*-Ph), 148.0 (*p*-Trip). ^{7}Li NMR (C_6D_6): δ −1.72. IR (Nujol, cm^{-1}): 1600 ms, 1563 m, 1499 w, 1358 s, 1315 m, 1249 w, 1237 vw, 1166 m, 1149 w, 1104 m, 1077 w, 1066 w, 1045 m, 1000 vw, 953 vw, 939 m, 919 vw, 884 m, 873 ms, 795 ms, 774 w, 742 ms, 730 s, 697 w, 650 w, 599 m br, 460 w, 416 w, 360 m br, 244 w.

($NaSC_6H_3$-2,6-Trip$_2$)$_2$·0.5C_7H_8 (6). Sodium (0.046 g, 2 mmol) was added via a solids-addition tube to a solution of HSC_6H_3-2,6-Trip$_2$ (0.50 g, 0.97 mmol) in *ca*. 15 mL of toluene. The mixture was warmed to *ca*. 50 °C and stirred overnight. The supernatant liquid was separated from the excess of alkali metal via a cannula. The volume was reduced to incipient crystallization, and the solution was cooled for 2 d in a 0 °C freezer to give **6** as colorless crystals. Removal of the solvent afforded more compound in nearly quantitative yield. Mp: 214−216 °C. ^{1}H NMR (C_6D_6): δ 1.14 (d, *o/p*-CH(C*H*$_3$)$_2$), 1.24 (d, *o/p*-CH(C*H*$_3$)$_2$), 1.35 (d, *o/p*-CH(C*H*$_3$)$_2$), 2.10 (s, C$_7$*H*$_8$), 2.99 (m, *o* + *p*-C*H*(CH$_3$)$_2$), 6.89−7.14 (m, aryl-*H*). ^{13}C NMR (C_6D_6): δ 24.4 (*o*-CH(*C*H$_3$)$_2$), 24.5 (*o*-CH(*C*H$_3$)$_2$), 24.7 (*p*-CH(*C*H$_3$)$_2$), 30.8 (*o*-*C*H(CH$_3$)$_2$), 34.2 (*p*-*C*H(CH$_3$)$_2$), 119.5 (*p*-Ph), 120.1 (*m*-Trip), 128.0 (*m*-Ph), 141.6 (*o*-Ph), 142.3 (*i*-Trip), 147.1 (*p*-Trip), 147.6 (*o*-Trip), 151.2 (*i*-Ph). IR (Nujol, cm^{-1}): 1600 m, 1564 m, 1358 s, 1334 w, 1314 m, 1250 m, 1166 m, 1148 w, 1105 m, 1078 w, 1066 w, 1047 ms, 1028 ms, 1004 w, 958 m, 939 m 918 vw, 875 s, 846 vw, 796 m, 786 sh, 774 w, 753 w, 734 s, 693 vw, 648 m, 517 w, 462 w.

(KSC_6H_3-2,6-Trip$_2$)$_2$·C_7H_8 (7). The synthesis was accomplished in almost quantitative yield in a manner similar to the preparation of **6** with use of HSC_6H_3-2,6-Trip$_2$ (0.50 g, 0.97 mmol) and potassium (0.08 g, 2.1 mmol). Mp: 283−285 °C. ^{1}H NMR (C_6D_6): δ 1.17 (d, *o/p*-CH(C*H*$_3$)$_2$), 1.27 (d, *o/p*-CH(C*H*$_3$)$_2$), 1.31 (d, *o/p*-CH(C*H*$_3$)$_2$), 2.10 (s, C$_7$*H*$_8$), 2.89 (sep, *p*-C*H*(CH$_3$)$_2$), 3.14 (sep, *o*-C*H*(CH$_3$)$_2$), 6.86−7.12 (m, aryl-*H*). ^{13}C NMR (C_6D_6): δ 24.4 (*o*-CH(*C*H$_3$)$_2$), 24.4 (*o*-CH(*C*H$_3$)$_2$), 24.8 (*p*-CH(*C*H$_3$)$_2$), 30.8 (*o*-*C*H(CH$_3$)$_2$), 34.6 (*p*-*C*H(CH$_3$)$_2$), 118.3 (*p*-Ph), 119.9 (*m*-Trip), 127.7 (*m*-Ph), 141.4 (*o*-Ph), 144.2 (*i*-Trip), 146.7 (*p*-Trip), 148.5 (*o*-Trip), 157.0 (*i*-Ph). IR (Nujol, cm^{-1}): 1594 w, 1563 m, 1354 s, 1334 w, 1314 m, 1254 m, 1233 w, 1160 w, 1148 vw, 1112 m, 1078 w, 1067 vw, 1049 ms, 1000 w, 937 m, 917 w, 878 s, 846 vw, 795 vw, 782 m, 754 w, 736 s, 690 vw, 651 m, 516 w.

($RbSC_6H_3$-2,6-Trip$_2$)$_2$·C_7H_8 (8). The synthesis was accomplished in almost quantitative yield in a manner similar to the preparation of **6** with use of HSC_6H_3-2,6-Trip$_2$ (0.50 g, 0.97 mmol) and rubidium (0.14 g, 1.6 mmol). Mp: 295−297 °C. ^{1}H NMR (C_6D_6): δ 1.17 (d, *o/p*-CH(C*H*$_3$)$_2$), 1.27 (d, *o/p*-CH(C*H*$_3$)$_2$), 1.28 (d, *o/p*-CH(C*H*$_3$)$_2$), 2.10 (s,

C_7*H*$_8$), 2.82 (sep, *p*-C*H*$(CH_3)_2$), 3.17 (sep, *o*-C*H*$(CH_3)_2$), 6.88−7.11 (m, aryl-*H*). ^{13}C NMR (C_6D_6): δ 24.3 (*o*-CH(*C*H$_3$)$_2$), 24.4 (*o*-CH(*C*H$_3$)$_2$), 24.8 (*p*-CH(*C*H$_3$)$_2$), 30.9 (*o*-*C*H$(CH_3)_2$), 34.7 (*p*-*C*H$(CH_3)_2$), 118.2 (*p*-Ph), 120.2 (*m*-Trip), 127.8 (*m*-Ph), 141.6 (*o*-Ph), 144.7 (*i*-Trip), 146.6 (*p*-Trip), 148.7 (*o*-Trip), 158.0 (*i*-Ph). IR (Nujol, cm^{-1}): 1766 w, 1595 m, 1562 s, 1380 vs, 1356 s, 1237 m, 1312 s, 1257 s, 1246 sh, 1233 m, 1167 m, 1150 w, 1117 s, 1099 m, 1078 m, 1066 m, 1051 s, 1002 w, 939 m, 918 w, 881 vs, 848 w, 796 m, 783 s, 755 w, 738 vs, 727 s, 692 m, 652 s, 607 vw, 520 w br, 459 vw, 405 vw, 368 vw.

($CsSC_6H_3$-2,6-Trip$_2$)$_2$ (9). The synthesis of **9** was accomplished in a similar manner to the preparation of **6** with use of HSC_6H_3-2,6-Trip$_2$ (0.50 g, 0.97 mmol) and cesium (0.18 g, 1.4 mmol) in *n*-hexane. Mp: 263−265 °C. ^{1}H NMR (C_6D_6): δ 1.17 (d, *o*/*p*-CH(C*H*$_3$)$_2$), 1.24 (d, *o*/*p*-CH(C*H*$_3$)$_2$), 1.30 (d, *o*/*p*-CH(C*H*$_3$)$_2$), 2.80 (sep, *p*-C*H*$(CH_3)_2$), 3.22 (sep, *o*-C*H*$(CH_3)_2$), 6.86−7.05 (m, aryl-*H*). ^{13}C NMR (C_6D_6): δ 24.4 (*p*-CH(*C*H$_3$)$_2$), 24.6 (*o*-CH(*C*H$_3$)$_2$), 24.7 (*o*-CH(*C*H$_3$)$_2$), 30.9 (*o*-*C*H$(CH_3)_2$), 34.6 (*p*-*C*H$(CH_3)_2$), 118.4 (*p*-Ph), 120.6 (*m*-Trip), 128.1 (*m*-Ph), 141.9 (*o*-Ph), 145.2 (*i*-Trip), 146.5 (*p*-Trip), 148.6 (*o*-Trip), 158.0 (*i*-Ph). IR (Nujol, cm^{-1}): 1575 w, 1560 ms, 1373 vs, 1354 s, 1333 w, 1310 m, 1248 m, 1242 m, 1230 w, 1164 w, 1147 vw, 1108 m, 1075 w, 1065 w, 1045 ms, 998 w, 938 w, 918 vw, 873 s, 845 vw, 793 w, 781 w, 773 w, 751 vw, 735 s, 649 m, 604 vw, 513 w br, 408 vw.

X-ray Crystallographic Studies. X-ray-quality crystals were obtained as described in the Experimental Section. Crystals were removed from Schlenk tubes and immediately covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and immediately placed in a low-temperature N_2-stream, as previously described.[12] All data were collected at 130 K using either a Siemens P4/RA (**1**-**3**, **5**−8), a Syntex P2$_1$ (**4**), or a Siemens R3 (**9**) diffractometer. Selected crystal data are given in Table 1. Calculations were carried out with the SHELXTL-PLUS and SHELXL-93 program system installed on a UNIX workstation or PCs. Scattering factors and the correction for anomalous scattering were taken from common sources.[13a] The structures were solved by direct or Patterson (**3, 5, 7**) methods and refined by blocked-diagonal least-squares refinement. An absorption correction was applied by using the program XABS2.[13b] Anisotropic thermal parameters were included for all non-hydrogen atoms, excluding all C atoms of the solvate hexane molecule in **2** and three C atoms in **5**. The solvate toluene molecules in **5**, **6**, and **8** are disordered and were refined as rigid hexagons. Positions and isotropic thermal parameter for most H atoms in **3** and **7** were allowed to refine. All other H atoms were included by use of a riding model with fixed C−H distances and refined or fixed isotropic thermal parameters equal to 1.2 or 1.5 times that of the bonded carbon. The S-bound hydrogen in **3** is disordered over three crystallographically independent positions which were taken from a difference map and were fixed during refinement with S−H in the range 1.34−1.39 Å and $U_H = 0.06$. Three *i*-Pr groups in **4** and **5** showed disorder and were successfully modeled as described in the Supporting Information. Final *R* factors are listed in Table 1. Important bond distances and angles are given in Table 2. Further details are provided in the Supporting Information.

Discussion

Synthesis. The thiol, HSC_6H_3-2,6-Trip$_2$ (**3**) was synthesized in a manner similar to that previously reported for HSC_6H_3-2,6-Mes$_2$[10b] or HSC_6H_3-2,6(2,6-$Me_2C_6H_3$)$_2$.[10c] The reaction involved the addition of elemental sulfur to LiC_6H_3-2,6-Trip$_2$, followed by hydrolysis to afford the product in good yield. The lithium derivatives ($LiSC_6H_2$-2,4,6-Ph$_3$)$_4$·C_7H_8 (**1**), ($LiSC_6H_3$-2,6-Mes$_2$)$_3$·C_6H_{14} (**2**), ($LiSC_6H_3$-2,6-Trip$_2$)$_2$ (**4**), and ($LiSC_6H_3$-2,6-Trip$_2$)$_2$·C_7H_8 (**5**) were then obtained in virtually quantitative yield by the treatment of the respective thiols with *n*-BuLi in *n*-hexane or toluene. The heavier element derivatives **6**−**9** were synthesized by the direct reaction of the metal with the thiol in toluene or *n*-hexane. It is noteworthy that the compounds **6**−**9** all possess good solubility in *n*-hexane. The ^{13}C NMR signals of the ipso-carbon show a characteristic downfield shift (146.8−158.0 ppm) which becomes more positive with increasing atomic numbers of the alkali metals. The chemical shifts of the Trip ring carbons of compounds **5**−**9** (Table 3) show a similar trend in the case of *i*, *o*, and *m* ring atoms although the *p*-carbons show a slight (*ca*. 1.5 ppm overall) shift in the opposite direction. This trend for the majority of the Trip ring carbons is consistent with increasingly effective metal−ring π-interactions (vide infra).

Table 3. Selected ^{13}C NMR Chemical Shifts (ppm) for the Trip(2,4,6-*i*-Pr-C_6H_2) Substituents in Compounds **5**−**9**

	i-Trip	*o*-Trip	*m*-Trip	*p*-Trip
5	140.5	146.6	121.4	148.0
6	142.3	147.6	120.1	147.1
7	144.2	148.5	119.9	146.7
8	144.7	148.7	120.2	146.6
9	145.2	148.6	120.6	146.5

The new thiol **3** was synthesized in order to explore the steric effects of the more crowding $-C_6H_3$-2,6-Trip$_2$ substituent. Its structure, which has a crystallographically imposed mirror plane along the S−C vector, displayed no unusual features. The S−C distance is 1.763(4) Å and is similar to what is observed in the other complexes. The sulfur hydrogen, which has an average S−H distance of 1.35(5) Å, is disordered over three crystallographically independent positions.

The steric effectiveness of the less bulky $-SC_6H_3$-2,6-Mes$_2$ thiolate ligand has already been demonstrated in the case of the neutral iron(II) thiolate Fe(SC_6H_3-2,6-Mes$_2$)$_2$ where a two-coordinate, monomeric structure was observed.[10b] In contrast the corresponding {Fe(SMes*)$_2$}$_2$[14] (Mes* = 2,4,6-*t*-Bu$_3C_6H_2$) complex has a dimeric structure. Nonetheless, attempts to structurally characterize Na-Cs derivatives of the $-SC_6H_3$-2,6-Mes$_2$ thiolate ligand in order to compare their structures with those of the Li−Cs derivatives (**4**−**9**) of the ligand -SC_6H_3-2,6-Trip$_2$ were unsuccessful owing to their insolubility in nondonor solvents.

Lithium Thiolate Structures. A comparison of the structures of the lithium derivatives **1**, **2**, **4**, and **5** clearly demonstrates the greater steric requirements of the $-SC_6H_3$-2,6-Trip$_2$ ligand. The structure of **1** is tetrameric, **2** is trimeric, whereas both **4** and **5** are dimers. A trimeric structure has not been previously observed for thiolates, although a trimeric arrangement has been observed in the solvated selenolate species {Li(THF)SeMes*}$_3$ which has an almost planar six-membered Li_3Se_3 ring.[3c] The structures of **1** (Figure 1) and **2** (Figure 2) are in effect four- and three-rung ladders and are related to the infinite ladder structure seen in [$PhCH_2SLi$·NC_5H_5]$_n$.[15] In the structures of **1** and **2** the ladders are terminated at the tetrameric and trimeric stage for steric reasons. The four Li_2S_2 rings in **1** are almost planar with fold angles in the range 175.3−177.7° along the Li---Li axes. Fold angles of 142.7 and 137.9° are observed along the common Li(2)−S(2) and Li(3)−S(3) edges. The resulting boat-shaped Li_4S_4 core resembles a fragment of a, so far unknown, hexagonal Li_6S_6 heteroprismane structural type. The Li−S distances have an average value of 2.45 Å and vary between 2.365(14) and 2.62(2) Å. The longest Li−S distances are observed for the internal Li(2)−S(2) (2.62(2) Å)

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(12) This method is described by: Hope, H. A Practicum in Synthesis and Characterization. In *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington DC, 1987; Chapter 10.

(13) (a) *International Tables for Crystallography*; D. Reidel Publishing Co.: Dordrecht, The Netherlands, 1993; Vol. C. (b) Parkin, S.; Moezzi, B.; Hope, H. *J. Appl. Crystallogr.* **1995**, *28*, 53.

(14) Shoner, S. C.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 330.

(15) Banister, A. J.; Clegg, W.; Gill, W. R. *J. Chem. Soc., Chem. Commun.* **1987**, 850.

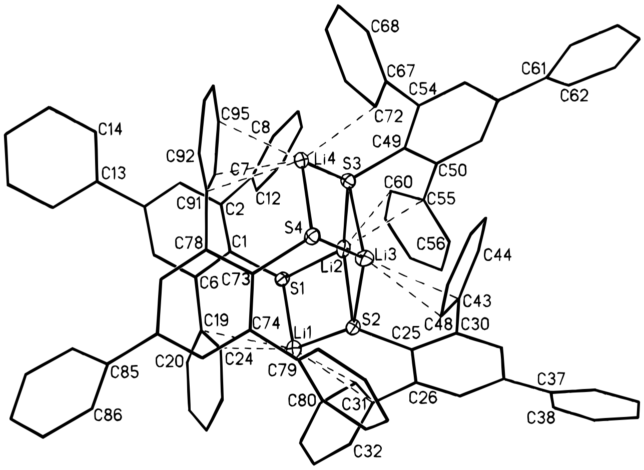

Figure 1. Structure of **1**, showing 30% thermal ellipsoids for lithium and sulfur and the atom-labeling scheme. H atoms have been omitted, and C atoms were indicated by lines for clarity.

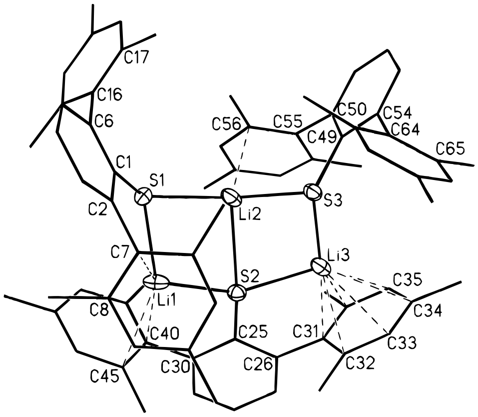

Figure 2. Structure of **2**, showing 30% thermal ellipsoids for lithium and sulfur and the atom-labeling scheme. H atoms have been omitted, and C atoms were indicated by lines for clarity.

and Li(3)−S(3) (2.586(13) Å) bonds. All four lithium ions have relatively close contacts with one or more carbons from a phenyl ring as indicated by dashed lines in Figure 1. The Li−C distances fall in the range 2.41(2)−2.73(2) Å and are comparable to known values for lithium six-membered aromatic ring interactions in other systems.[16]

The three-rung ladder structural arrangement in **2** (Figure 2) bears a resemblance to that seen for the lithium halide−lithium amide complexes [LiCl{Li(TMEDA)NR$_2$}$_2$] (R = *i*-Pr[17a] or SiMe$_3$[17b]). In **2** each Li$_2$S$_2$ ring deviates from planarity and there is a considerable fold angle (147.7°) along the common LiS edge. The Li−S distances vary from 2.33(2) to 2.65(2) Å with the longest distance being observed for the Li(2)−S(2) bond at the common edge. The shortest Li−S bond lengths are observed for the outer Li(1)−S(1) and Li(3)−S(3) bonds which involve nominally two-coordinate lithiums and the doubly bridging thiolates. The mean distance for all Li−S bonds is 2.45(7) Å, which is near the average value seen in a range of other lithium thiolates.[1] The lithium atoms also display close interactions with some of the carbon atoms from an *o*-mesityl group. The strongest interactions involve Li(3) where Li−C approaches as close as 2.38(2) Å (to C(31)). This distance is comparable to that seen in other compounds where lithium interacts with a neutral six-membered ring π-system.[16] For Li(1) and Li(2) the shortest approaches are 2.66(2) Å to C(40) and 2.58(2) Å to C(56), respectively. There does not appear to be any strong correlation between the Li−S bond lengths and the Li---C distances although the S(2)−Li(3)−S(3) angle (97.9(6)°) is smaller than the corresponding angle S(1)−Li(1)−S(2) 104.2(6)° in the adjacent ring. This suggests that Li(3) is more strongly attracted by the C(31) mesityl ring. The trimeric nature of **2** may be contrasted to its behavior when complexed to ether. In this case its structure becomes dimeric, having the formula {LiSC$_6$H$_3$-2,6-Mes$_2$}$_2$(Et$_2$O)$_2$,[18] in which one of the Li$^+$ ions is solvated by two thiolate sulfurs and two ethers; the other being solvated by two thiolate sulfurs and ortho aryl ring carbons. The Li−S distances involving the ether solvated Li$^+$ ion are *ca.* 2.50(2) Å whereas the aryl ring solvated Li$^+$ ions have much shorter Li−S distances near 2.37(1) Å with long Li---C interactions in the range 2.637(7)−2.801(7) Å.

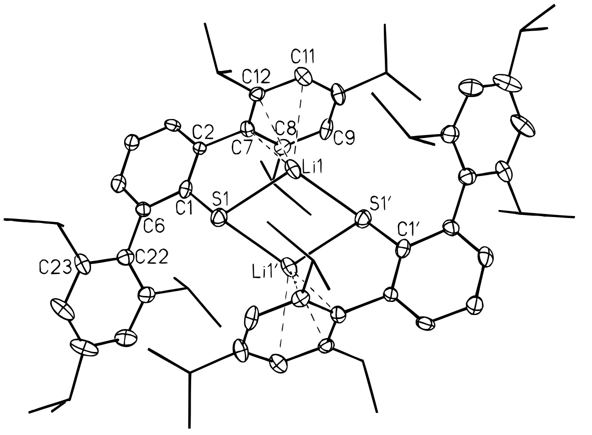

Figure 3. Structure of **5**, showing 50% thermal ellipsoids and the atom-labeling scheme. H atoms have been omitted, and isopropyl groups were indicated by lines for clarity.

The compound LiSC$_6$H$_3$-2,6-Trip$_2$ may be crystallized from either hexane as the solvent free species **4** or from toluene as the solvate **5** (Figure 3) whose crystals include a toluene of crystallization. In contrast to **1** and **2**, both compounds crystallize as dimers which is presumably due to larger steric requirements of the organo substituent. The main difference between **4** and **5** is the arrangement of the thiolate ligands with respect to each other. The phenyl rings bound to sulfur in **5** are parallel to each other as crystallographically required whereas the corresponding rings in **4** have an interplanar angle of 53°. The structure of **5** is simpler since it has a crystallographically required center of symmetry and a planar Li$_2$S$_2$ core and just two independent Li−S distances of 2.40(1) and 2.46(1) Å. The internal Li$_2$S$_2$ ring angles at lithium and sulfur are 111.9(4) and 68.1(4)°. The sulfur atom is pyramidally coordinated with $\sum°S = 308.1(4)°$. The lithium also interacts with the C(7) ortho Trip ring which involves a Li−centroid distance of 2.25 Å. The Li−C distances vary from 2.412(13) to 2.699(13) Å. There is no close interaction between the toluene of crystallization and the thiolate dimer.

The structure of **4** (not illustrated but the Li$_2$S$_2$ core geometry is shown in Figure 8, vide infra) is similar to **5** but there is no symmetry requirement and the sums of the interligand angles ($\sum°$) at S(1) and S(2) are 300.7(2) and 306.5(2)°, respectively. The Li$_2$S$_2$ core is folded (158.8°) along the Li---Li axis. The

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(16) (a) Pilz, M.; Allwohn, J.; Willershausen, P.; Massa, W.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1030. (b) Chen, H.; Bartlett, R. A.; Dias, H. V. R.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1991**, *30*, 2487.

(17) (a) Mair, F. S.; Clegg, W.; O'Neil, P. A. *J. Am. Chem. Soc.* **1993**, *115*, 3388. (b) Henderson, K. W.; Dorigo, A. E.; Liu, Q.-Y.; Williard, P. G.; Schleyer, P. v. R.; Bernstein, P. R. *J. Am. Chem. Soc.* **1996**, *118*, 1339.

(18) Ellison, J. J.; Power, P. P. *Inorg. Chem.* **1994**, *33*, 4231.

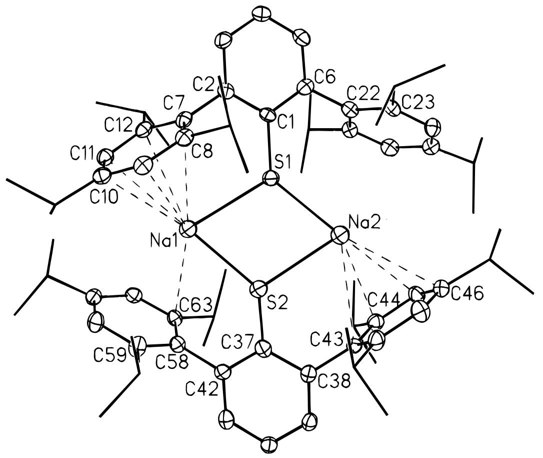

Figure 4. Structure of **6**, showing 30% thermal ellipsoids and the atom-labeling scheme. H atoms have been omitted, and isopropyl groups were indicated by lines for clarity.

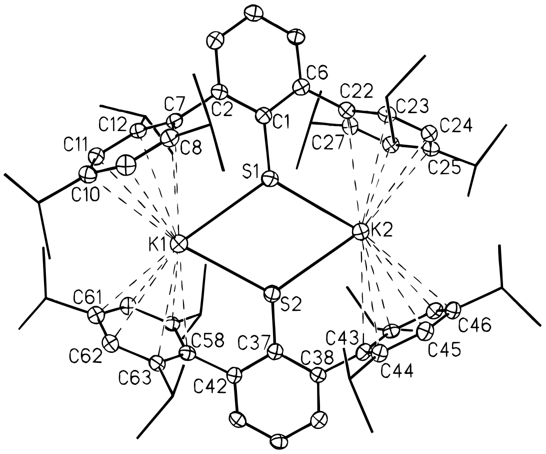

Figure 5. Structure of **7**, showing 30% thermal ellipsoids and the atom-labeling scheme. H atoms have been omitted, and isopropyl groups were indicated by lines for clarity.

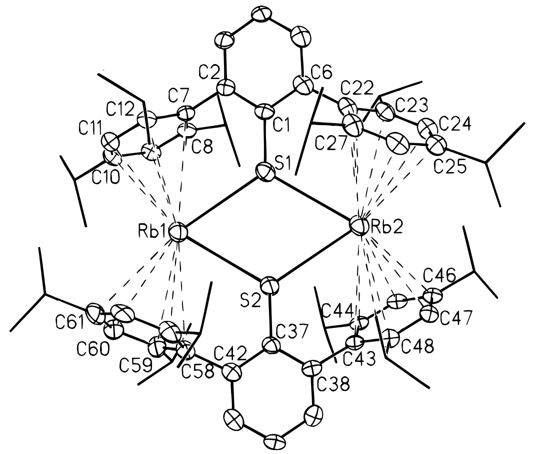

Figure 6. Structures of **8**, showing 30% thermal ellipsoids and the atom-labeling scheme. H atoms have been omitted, and isopropyl groups were indicated by lines for clarity.

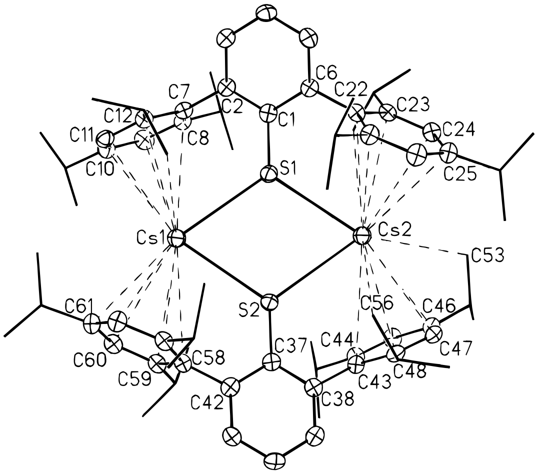

Figure 7. Structure of **9**, showing 50% thermal ellipsoids and the atom-labeling scheme. H atoms have been omitted, and isopropyl groups were indicated by lines for clarity.

Li−S distances have a mean value of 2.396(17) Å, and the internal Li_2S_2 ring angles are near 74° for sulfur and 104° at lithium. The Li(1) atom interacts weakly with C(7) and C(8) (Li−C distances near 2.53 Å) and the Li−centroid distance for the C(7) ring is 2.649(6) Å. In contrast the Li(2)−centroid distance for the C(43) ring is 2.196(6) Å and the Li(2)---C(43)−C(48) Å interactions vary from 2.520(6) to 2.707(6) Å with the Li(2) atom located much more symmetrically with respect to the Trip ring.

In essence **5** has weaker Li−S and stronger Li---C interactions than the corresponding interactions in **4**. It is notable that in the two structures each lithium interacts with just one Trip substituent. The other minor differences between the two structures which involve, inter alia, arrangement of the ligands, folding of the Li_2S_2 ring, and different angles surrounding sulfur and lithium, are indicative of a significant amount of flexibility in the basic structure which can be relatively easily distorted by secondary bonding interactions and/or crystal packing effects.

Heavier Alkali Metal Structures. The structures of the heavier alkali metal derivatives **6**−**9** (Figure 4−7) are also dimeric and display varying degrees of interaction between the metal and the *o*-Trip aromatic rings. The M_2S_2 cores of **6**−**8** are almost planar with fold angles in the range 174.6−178.1°, whereas for **9** a fold angle of 156.1° is observed along the Cs---Cs axis. Further trends in the structures may be discerned in Table 4, which lists important interplanar angles. In general, the angle between the M_2S_2 core (plane A) and the phenyl rings bound to sulfur, i.e. B or E, is lower for the heavier elements **7**−**9**. In contrast, the angles between the ortho Trip substituents and the phenyl ring, i.e. B/C, B/D, E/F and E/G (Table 4) remain relatively high and are in the range 73.0−89.6° for the series **4**−**9**. This permits the *o*-Trip groups to maintain a face-on interaction with the metal. In effect, the most favorable M---C interactions are maintained primarily through rotation around the C−S bonds rather than by adjustment of the interplanar angles involving the ortho Trip group and the phenyl ring.

Although the structures of **4**−**9** seem broadly similar since they are all dimers, the structure of the sodium derivative **6** (Figure 4) shows certain differences in structural features from its lithium counterpart that become more prominent upon proceeding further down the group. First, the sulfur coordination in the thiolate ligand becomes less pyramidal (Σ° S(1) = 346.1°; Σ°S(2) = 338.2°), and one of the sodiums (i.e. Na(1)) displays interaction to a second Trip substituent. These changes can be attributed to the larger size of the sodium vis a vis the lithium ion.[19] In addition to these features, a more symmetric interaction with the ring carbon Trip ring is observed. Thus, Na(1) interacts essentially equally with the six ring carbons of the C(7) Trip group and has Na---C distances in the very narrow range 3.016(5)−3.108(5) Å and an Na(1)−C(7) ring centroid distance of 2.701 Å. The Na(2) atom interacts strongly with

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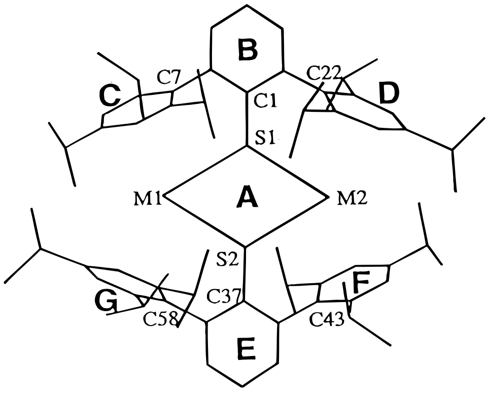
[19] Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr.* **1969**, *B25*, 925.

Table 4. Fold Angles (deg) in M_2S_2 Rings along the M···M Vector in **1**−**9** and Angles (deg) between Normals of Least-Square Planes (A-G) for **4**−**9**[a]

1	2	4	5	6	7	8	9
175.3	169.6	158.8	180.0	174.6	178.1	175.3	156.1
175.5	146.1						
177.7							

	4	5	6	7	8	9
A/B	61.8	37.1	39.5	21.7	15.6	16.5
A/E	59.7		39.8	13.5	19.8	21.8
B/E	53.3	0.0	36.9	32.5	34.7	37.9
B/C	76.4	84.6	80.2	78.5	78.9	76.3
B/D	84.3	73.0	77.0	87.7	81.0	82.5
E/F	86.3		89.6	80.7	76.0	75.4
E/G	74.9		83.9	84.5	81.5	88.5
A/C	60.1	50.1	42.4	88.2	73.7	8.22
A/D	23.4	39.2	84.6	66.5	74.0	67.5
A/F	34.0		61.8	75.8	77.2	88.3
A/G	75.9		45.8	78.0	66.0	66.9

[a] Structure:



the C(43) Trip ring but here the Na(2)−C distances have a wider range, 2.839(5)−3.249(5) Å, and the Na(2)−C(43) ring centroid distance is 2.720 Å. A weaker Na(1)−C(58) ring interaction is also discernible although here the Na(1)−C(58) ring centroid distance is 3.076 Å and the closest Na(1)−C carbon distances involve Na(1)−C(63) = 3.108(5) Å and Na(1)−C(58) = 3.266(5) Å. The Na−C interactions in **6** may be compared with those in other compounds displaying Na^+ ion interaction to neutral six-membered aromatic rings.[20] The effects of the sodium ring interactions are also noticeable in the Na−S−C angles which differ by *ca.* 8−10°; the smaller angle being observed at the side at which the Na−ring interaction occurs.

The Na_2S_2 core (Figure 8) is almost planar (fold angle 174.6° along the Na---Na axis), and the Na(1)−S(1) bond, 2.762(2) Å, is longer than the other three, which have an average value of 2.692(5) Å. It is notable that the longer Na−S distance involves Na(1) which interacts most strongly with the Trip substituents. The Na−S distances may be compared with the 2.8 Å observed for $(NaSMe)_n$[8a] or the average value of 2.933(3) Å in $[Na(THF)_2SC_6H_2\text{-}2,4,6\text{-}(CF_3)_3]_n$.[5] The shorter distances observed in **6** are a consequence of the lower formal coordination number of the sodiums.

The structural trends observed in the sodium derivative **6** are continued in the corresponding potassium derivative **7** (Figure 5). The K_2S_2 (Figure 8) core is essentially planar. The K−S bond lengths average 3.055(8) Å, which may be compared to the average 3.165(4) Å observed in the compound $[K(THF)\text{-}SC_6H_2\text{-}2,4,6\text{-}(CF_3)_3]_n$[5] (ladder K−S framework structure) or the range 3.10−3.28 Å found[6] in $[(KSAr)_2\{K(THF)SAr\}_2\{K(THF)_2\text{-}SAr\}_2]$ and $[(KSAr)_2\{K(THF)SAr_2\{K(TMEDA)SAr\}_2]$ (Ar = 2,4,6-*i*-$Pr_2C_6H_3$−) which have a stacked or box-type structure with four-coordinate potassium and sulfur atoms. A similar average K−S distance of 3.15 Å has also been observed in $(KSMe)_n$.[8] The longer distances in these compounds are due to the higher effective potassium and sulfur coordination numbers. The coordination at potassium in **7** is characterized by interactions of each metal with two Trip substituents. These interactions are quite symmetric and the differences in the K−S−C angles are *ca.* 3−4°. Thus, for the first time in the series of compounds **4**−**9** the four Trip substituents interact essentially equally with the two metals in the dimeric structure. The K---C distances are in the range 3.304(5)−3.564(5) Å with an average distance of 3.42(2) Å. The K−centroid distances in **7** range from 3.067−3.152 Å. These are longer than the 2.97 Å in $[K(C_6H_6)][K\{C(SiMe_3)_2SiMe_2Ph\}_2]$.[21a] The K---C distances are also somewhat longer than those observed in the salt $KPMe_2(CHPh)_2$.[21b] The geometry at S(2) is planar (Σ°S = 360.0(2)°) whereas that of S(1) is just slightly distorted from planarity (Σ°S(1) = 355.9(2)°).

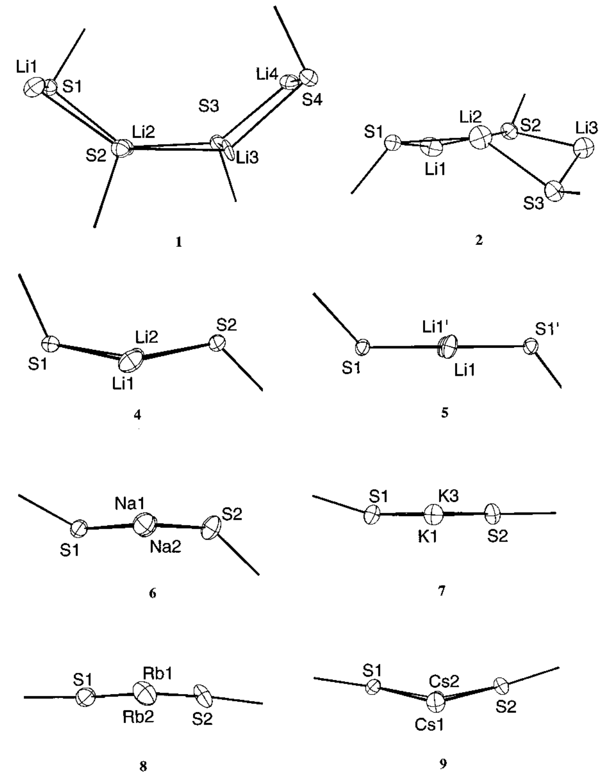


Figure 8. Views of the metal and sulfur core atoms in the structures of **1**, **2**, and **4**−**9**.

The rubidium and cesium thiolates **8** (Figure 6) and **9** (Figure 7) represent the first structural characterization of thiolate derivatives of these metals. In the rubidium compound **8**, the Rb_2S_2 core has a fold angle of 175.3° and the Rb−S distances average 3.166(8) Å. This bond length is slightly less than what is expected on the basis of the potassium−sulfur distance (K−S = 3.06(2) Å) since the ionic radius of Rb^+ is 0.14 Å greater than that of K^+.[19] The four Rb−centroid distances indicate similar interactions between the four Trip rings and the two rubidiums. This is borne out by the Rb---C distances which are in the relatively narrow range 3.344(7)−3.596(7) Å. These

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(20) For example: (a) Bock, H.; Ruppert, K.; Havlas, Z.; Fenske, D. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1042. (b) Corbelin, S.; Kopf, J.; Lorenzen, N. P.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 825. (c) Al-Juaid, S. S.; Eaborn, C.; Hitchcock, P. B.; Izod, K.; Mallien, M.; Smith, J. D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1268.

(21) (a) Eaborn, C.; Hitchcock, P. B.; Izod, K.; Smith, J. D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2679. (b) Schmidbaur, H.; Deschler, U.; Milewski-Mahrla, B.; Zimmer-Gasser, B. *Chem. Ber.* **1981**, *114*, 608.

distances are significantly shorter than the Rb---C carbon interactions in $\{RbSi(SiMe_3)_3\}_2 \cdot PhMe$[22] which are 3.42(3)−3.91(3) Å. Overall, the interactions between the rubidium ions and the ligand result in a quite symmetric structure and the molecule almost has a 2-fold axis of symmetry along the S---S vector.

The Cs_2S_2 core in **9** displays a similar fold angle (i.e. 156.1° along the Cs---Cs vector) (Figure 8) to that observed in the lithium compound **4**. The cause of this folding is difficult to discern and may be just a consequence of packing effects. The average Cs−S distance is 3.308(4) Å, which is *ca*. 0.14 Å greater than the average Rb−S bond length. This difference is in almost exact agreement with the difference in ionic radii (0.15 Å) between the rubidium and cesium ions.[19] However, the Cs−S distance is significantly shorter than the 3.4 Å observed in Cs_2S[23] or the 3.52(2) Å in $Cs_4(\text{dibenzo-18-crown-6})_3(S_6)_2 \cdot 2MeCN$.[8b] As with the rubidiums in **8**, each cesium also interacts with two Trip rings and has Cs---C distances that are in the range 3.531(4)−3.928(4) Å with an average value of 3.66 Å. These distances are comparable to those observed in complexes between Cs^+ and neutral six-membered aromatic rings.[22,24] In addition, in the structure of **9** there are relatively close approaches between the C(53) (3.753(5) Å) and C(56) (3.709(5) Å) methyl groups and Cs(2).

Conclusion. The use of *o*-terphenyl-substituted thiolate ligands has permitted the synthesis of a range of new Lewis base free lithium thiolates which have novel structures. The large $-SC_6H_3$-2,6-$Trip_2$ group imposes low aggregate dimeric structures for all its metal derivatives, even in the case of the large cations Rb^+ and Cs^+. The smaller, but still crowding, ligand $-SC_6H_3$-2,6-Mes_2 affords only insoluble products which probably have polymeric structures in the case of the $Na^+ \rightarrow Cs^+$ salts. With the Li^+ derivative, however, an unique trimeric structure is observed, and a tetrameric structure is observed for the less crowded $(LiSC_6H_2\text{-}2,4,6\text{-}Ph_3)_4$. Although all compounds are Lewis base-free, the metal ions are “solvated” to varying degrees by interactions with the *o*-aryl substituents. The preservation of the dimeric structural motif in **4** → **9** is, in some respects, is surprising since heavier and larger alkali metal salts of organic and related ligands are usually more ionic than the lithium counterparts and therefore more prone to aggregation. Apparently, the $-C_6H_3$-2,6-$Trip_2$ substituent is sufficiently large and lipophilic (as well as being capable of solvating a wide range of metal ions through π-interactions) that solubility and a dimeric structural motif is preserved throughout the group 1 metals.

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Supporting Information Available: Tables giving full details of the crystallographic data and data collection parameters, atom coordinates, bond distances, bond angles, anisotropic thermal parameters, and hydrogen coordinates for **1**−**9**. (126 pages). Ordering information is given on any current masthead page.

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