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Synthesis and Structural Characterization of Lithium Thiolates: Dependence of Association and Aggregation on Donor Hapticity and Ligand Size and Synthesis of the First Trimeric Lithium Thiolate [Li(THF)SR]$_3$ and the Solvent-Separated Ion Pair [Li(12-crown-4)$_2$][SR] (R = 2,4,6-tBu$_3$C$_6$H$_2$)[1]

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The synthesis and structural characterization of several lithium thiolates are reported. Formation of discrete species can be achieved by careful variation of ligand size and donor hapticity, as exemplified by the monomeric formulation of Li(PMDTA)STrityl (PMDTA = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine, Trityl = CPh$_3$), **1**, and Li(PMDTA)STrip, **2** (Trip = 2,4,6-iPr$_3$C$_6$H$_2$), versus the dimeric species [Li(THF)$_2$STrityl]$_2$, **3**, and [Li(TMEDA)STrip]$_2$, **4** (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine). By control of the stoichiometry of the donor, the first trimeric lithium thiolate [Li(THF)SMes*]$_3$, **5** (Mes* = 2,4,6-tBu$_3$C$_6$H$_2$), exhibiting a six-membered ring system and rare three-coordinate lithium centers, becomes available. In contrast, use of a crown ether leads to the isolation of the monomeric contact ion pair Li(12-crown-4)STrityl, **6**, while employing the cumbersome −SMes* ligand allows for the isolation of the first solvent-separated lithium thiolate [Li(12-crown-4)$_2$][SMes*], **7**. All compounds were prepared by reacting the respective thiols with nBuLi in the presence of various donor adjuncts. The target molecules were characterized using ^{1}H NMR and IR spectroscopy and melting point criteria. Crystal structure analysis was employed to determine solid state structures. Crystal data are as follows. **1**: Cu Kα (λ = 1.541 78 Å) at 130 K, a = 12.152(3) Å, b = 15.260(3) Å, c = 14.764(5) Å, β = 106.90(2)°, V = 2619.6(12) Å^3, Z = 4, monoclinic, space group $P2_1/c$, 2526 reflections ($I > 2\sigma(I)$), R = 0.064. **2**: Cu Kα (λ = 1.541 78 Å) at 228 K, a = 15.805(7) Å, b = 9.206(4) Å, c = 18.923(7) Å, β = 99.74(3)°, V = 2714(2) Å^3, Z = 4, monoclinic, space group $P2_1/n$, 2047 reflections ($I > 2\sigma(I)$), R = 0.085. **3**: Mo Kα (λ = 0.710 73 Å) at 213 K, a = 13.141(3) Å, b = 12.381(2) Å, c = 14.664(3) Å, β = 94.84(3)°, V = 2377.3(8) Å^3, Z = 2, monoclinic, space group $P2_1/n$, 2622 reflections ($I > 2\sigma(I)$), R = 0.052. **4**: Cu Kα (λ = 1.541 78 Å) at 130 K, a = 18.906(4) Å, b = 9.516(2) Å, c = 25.617(5) Å, β = 92.75(3)°, V = 4603(2) Å^3, Z = 4, monoclinic, space group $I2/a$, 2390 reflections ($I > 2\sigma(I)$), R = 0.067. **5**: Mo Kα (λ = 0.710 73 Å) at 213 K, a = 9.991(2) Å, b = 17.934(4) Å, c = 20.314(4) Å, α = 83.36(3)°, β = 76.74(3)°, γ = 76.72(3)°, V = 3440.4(12) Å^3, Z = 2, triclinic, space group $P1$, 6397 reflections ($I > 2.5\sigma(I)$), R = 0.063. **6**: Mo Kα (λ = 0.710 73 Å) at 213 K, a = 10.542(2) Å, b = 12.821(3) Å, c = 18.729(4) Å, β = 102.22(3)°, V = 2474.0(9) Å^3, Z = 4, monoclinic, space group $P2_1/c$, 4206 reflections ($I > 2\sigma(I)$), R = 0.086. **7**: Mo Kα (λ = 0.710 73 Å) at 213 K, a = 10.134(2) Å, b = 19.800(4) Å, c = 18.423(4) Å, β = 93.15(3)°, V = 3691.0(13) Å^3, Z = 4, monoclinic, space group $P2_1/n$, 4088 reflections ($I > 2\sigma(I)$), R = 0.092.

Introduction

Lithium organochalcogenolates are important reagents for the synthesis of a large variety of metal chalcogenolato complexes; numerous reports indicate their central role in synthetic chemistry.[2−10] Despite the importance of lithium organochalcogenolates, only a relatively small number of structural reports have appeared in the literature. As a result of this paucity in comparative structural data, a concise study of aggregation and association behavior with respect to chalcogeno atom, nature of the R group, and donor atoms has not yet been possible.

The most common structural motifs observed in lithium thiolates, selenolates, and tellurolates are the monomeric[11−16] and dimeric formulations.[17−24] Only one trimeric species has been reported, [Li(THF)SeMes*]$_3$, exhibiting a six-membered

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(1) This work is dedicated to Professor Kurt Dehnicke on the occasion of his 65th birthday.

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ring composed of alternating metal and selenium atoms and rare, three-coordinate metal centers.[25] Higher aggregates include the unusual hexameric, donor-free tellurolate $[LiTeSi(SiMe_3)_3]_6$,[26] while use of a mono-ortho-amino-substituted arenethiol led to the isolation of a compound exhibiting a hexameric cage structure $[Li\{S\text{-}2\text{-}((R)CH(Me)NMe_2)C_6H_4\}]_6$. The formation of a planar hexameric structure $[LiS\text{-}2,6\text{-}(CH_2NMe_2)_2C_6H_3]_6$ was observed when the related bis-ortho-amino-substituted ligand was used.[27] A small number of polymeric thiolates have been structurally characterized; examples include $[Li(py)_2SPh]_n$ and $[Li(py)SCH_2Ph]_n$.[16] Solvent-separated alkali metal organochalcogenolates are extremely rare, and only one has been reported: the recently described tellurolate $[Li(12\text{-crown-}4)_2][TeSi(SiMe_3)_3]$.[21] The corresponding thiolato or selenolato derivatives are unknown.

By preparing a family of lithium thiolates with systematic, independent variation of ligand and donor, we plan to elucidate the factors affecting the aggregation behavior of these compounds. Further, we wish to develop an understanding of the relationship between coordinative saturation of the metal center resulting from metal−donor interaction and steric saturation achieved *via* steric bulk of the ligand.

In this paper, we report the synthesis and characterization of a variety of lithium thiolates exhibiting various degrees of association and aggregation. The synthetic outcome for the desired metal complexes can be directed by careful ligand and donor selection. The monomeric species Li(PMDTA)STrityl, **1**, and Li(PMDTA)STrip, **2**, are synthesized in high yield by employing the η^3 donor PMDTA. The corresponding dimeric species $[Li(THF)_2STrityl]_2$, **3**, and $[Li(TMEDA)STrip]_2$, **4**, are obtained if the η^1 and η^2 donors THF and TMEDA, respectively, are used. If the amount of donor is limited to 1 equiv, the first trimeric lithium thiolate $[Li(THF)SMes^*]_3$, **5**, exhibiting a six-membered ring system and rare three-coordinated lithium centers is observed. Use of the multihapto donor 12-crown-4 leads to the isolation of monomeric species whose association is governed by the thiolate ligand. The contact ion pair [Li(12-crown-4)STrityl], **6**, is formed with the sterically less demanding triphenylmethanethiolate, while the solvent-separated ion pair $[Li(12\text{-crown-}4)_2][SMes^*]$, **7**, is formed when the cumbersome −SMes* ligand is employed.

Experimental Section

All reactions were performed under purified nitrogen atmosphere by using either modified Schlenk techniques or a Braun Labmaster 100 drybox. *n*-Hexane, toluene, and THF were freshly distilled from a Na/K alloy and degassed twice before use. Commercially available nBuLi (1.6 M solution in hexanes) was used as received. The compounds HSMes*[27] and HStrip[28] were synthesized by following literature procedures. TMEDA and PMDTA were refluxed over CaH_2 and distilled under vacuum. Commercially available 12-crown-4 was dried over molecular sieves (4 Å) and distilled prior to use. $HSCPh_3$ was recrystallized from diethyl ether. Melting points were determined on a Mel-Temp melting point apparatus and are uncorrected. ^1H NMR spectra were obtained at 300 MHz using a GE QE-300 spectrometer. Infrared spectra were recorded on Nujol mulls between KBr or NaCl plates, using a Perkin-Elmer Paragon 1000 FT-IR spectrometer.

Synthesis of Li(PMDTA)STrityl, 1. A 0.83 g sample of HSTrityl (3 mmol) was dissolved in 20 mL of THF, and the solution was treated with 1.9 mL of nBuLi (3.04 mmol) and 0.65 mL of PMDTA. The clear, pale yellow solution was stirred for 18 h and filtered over a Celite-padded filter frit. After reduction of the volume to 15 mL and storage at −30 °C, clear, colorless crystals, suitable for X-ray analysis, were obtained in 83% yield (1.13 g, 2.5 mmol). Mp: 144−146 °C. ^1H NMR ($CDCl_3$): δ 7.05−7.66 (m, 15H, Trityl), 2.44 (s, 3H, CH_3 of PMDTA), 2.38 (m, 8H, CH_2 of PMDTA), 2.11 (s, 12H, CH_3 of PMDTA), IR (cm^{-1}) (Nujol mull): 1300 s, 1168 m, 1152 m, 1110 w, 1056 m, 1028 w, 968 w, 936 w, 899 w, 788 s, 764 w, 701 mw, 669 s, 616 m.

Synthesis of Li(PMDTA)STrip, 2. A 3 mmol sample of HSTrip (0.71 g) was dissolved in 20 mL of THF, and 1.9 mL of nBuLi (3.04 mmol) and 0.65 mL of PMDTA were added to afford a pale yellow, clear solution. The solution was stirred for 18 h and afforded, after filtration, reduction of the volume to 10 mL, and storage at −30 °C, 0.96 g (2.31 mmol, 77%) of colorless crystals, suitable for crystallographic studies. Mp: 171−173 °C. ^1H NMR (C_6D_6): δ 6.77 (s, 2H, *m*-H), 4.35 (sep, 2H, *o*-CH of iPr), 2.79 (sep, 1H, *p*-CH of iPr), 2.50 (s, 3H, CH_3 of PMDTA), 2.32−2.48 (m, 8H, CH_2 of PMDTA), 2.10 (s, 12H, CH_3 of PMDTA), 1.18−1.23 (2 d, 18H, *o*- and *p*-iPr). IR (cm^{-1}) (Nujol mull): 1302 s, 1251 m, 1152 m, 1128 w, 1108 w, 1058 m, 1035 m, 1020 w, 982 w, 933 w, 898 w, 870 w, 789 w, 772 w, 643 w.

Synthesis of $[Li(THF)_2STrityl]_2$, 3. A 1.3 mL portion of nBuLi (2.1 mmol) was added to a flask containing 0.55 g of HSTrityl (2.0 mmol) dissolved in 30 mL of THF. Upon addition, the reaction mixture turned blood-red and remained so while it was stirred for 1 h at room temperature. The solution was then filtered through a Celite-padded filter frit, followed by removal of ca. 10 mL of the solvent under vacuum. After storage of the solution at 0 °C pale yellow plates, suitable for crystallographic analysis, were obtained in 80% yield (0.68 g). Mp: dec >180 °C. ^1H NMR (C_6D_6): δ 7.72 (d, 6H, Trityl, 7.58 Hz), 7.13 (t, 6H, Trityl, 7.68 Hz), 6.97 (t, 3H, Trityl, 7.26 Hz), 3.25 (br m, 8 Hz, THF), 1.26 (br m, 8H, THF). IR (cm^{-1}) (Nujol mull): 2923 s, 1590 m, 1462 s, 1376 s, 1048 s, 1032 m, 756 s, 741 s, 701 s, 670 w, 616 m.

Synthesis of $[Li(TMEDA)STrip]_2$, 4. A 0.71 g sample of HSTrip (3 mmol) was dissolved in 20 mL of toluene, and the solution was cooled in an ice bath and treated with 1.9 mL of nBuLi (3.04 mmol). The resulting, slightly turbid, pale yellow solution was stirred for 0.5 h, after which 0.5 mL of TMEDA was added via syringe. The cloudy solution was stirred for a further 6 h, followed by filtration. The volume of the resulting pale yellow solution was reduced to 15 mL, the solution was stored at −30 °C, and pale yellow crystals were formed within 1 week in 69% yield (0.74 g, 1.04 mmol). Mp: dec >320 °C. ^1H NMR ($CDCl_3$): δ 6.81 (s, 2H, *m*-H), 4.29 (sept, 2H, *o*-CH of iPr), 2.80 (sept, 1H, *p*-CH of iPr), 2.33 (s, 4H, CH_2 of TMEDA), 2.17 (s, 12H, CH_3 of TMEDA), 1.19−1.24 (2 d, 18H, CH_3 of Trip). IR (cm^{-1}) (Nujol mull): 1354 m, 1290 m, 1255 m, 1182 w, 1129 m, 1101 m, 1069 m, 1035 m, 1017 m, 977 w, 945 m, 871 m, 792 m, 744 w, 757 w, 642 w, 587 w, 522 w, 437 m.

Synthesis of $[Li(THF)SMes^*]_3$, 5. A 1.39 g sample of HSMes* (5 mmol) was dissolved in 30 mL of toluene, and the solution was treated with 3.13 mL of nBuLi (5 mmol) to afford a cloudy solution. Upon addition of 0.4 mL (0.36 g, 5 mmol) of THF *via* syringe, an

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almost colorless solution was obtained. The solution was filtered over a Celite-padded filter frit, its volume was reduced to 15 mL, and the concentrate was stored in the freezer (−30 °C). A 1.66 g quantity of **5** (1.55 mmol, 93% yield) was obtained. Mp: 198−203 °C. ^{1}H NMR (C_6D_6): δ 7.53 (s, 2H, *m*-H), 3.02 (m, 4H, THF), 2.02 (s, *o*-tBu, 18H), 1.34 (s, *p*-tBu, 9H), 1.06 (m, 4H, THF). IR (cm^{-1}) (Nujol mull): 1348 m, 1283 m, 1260 m, 1240 m, 1212 m, 1175 m, 1159 m, 1041 m, 918 w, 877 m, 800 w, 775 w, 757 w, 674 w, 644 w, 611 w.

Synthesis of [Li(12-crown-4)STrityl], 6. A 0.55 g sample of HSTrityl (2 mmol) was dissolved in 20 mL of toluene, and 1.25 mL of nBuLi (2 mmol) and 0.35 g of 12-crown-4 (2 mmol) were added. The pale yellow solution was stirred overnight at room temperature. Filtration over a Celite-padded filter frit, addition of 5 mL of hexane, and reduction of the volume resulted in the isolation of 0.82 g (1.78 mmol), 89% yield) of large, colorless single crystals. Mp: slow dec >100 °C. ^{1}H NMR ($CDCl_3$): δ 7.07−7.58 (m, 15H, Trityl), 3.55−3.73 (br s, CH_2, 12-crown-4). IR (cm^{-1}) (Nujol mull): 1133 w, 1086 m, 1021 m, 967 w, 925 w, 860 w, 770 w, 698 w, 672 w, 616 w, 558 w.

Synthesis of [Li(12-crown-4)$_2$][SMes*], 7. A 2 mmol sample of HSMes* (0.557 g), dissolved in 20 mL of hexane, was treated with 1.25 mL of nBuLi (2 mmol) and 0.704 g (4 mmol) of 12-crown-4. The resulting pale yellow solution was stirred at room temperature for 18 h. A 1.27 g quantity (1.74 mmol, 87% yield) of colorless crystals was obtained after filtration, addition of 5 mL of hexane, reduction of the volume, and storage at −30 °C. Mp: 180−182 °C. ^{1}H NMR (C_6D_6): δ 7.53 (s, 2H, *m*-H), 3.47 (s, 32H, CH_2 of 12-crown-4), 2.05 (s, 18H, *o*-tBu), 1.41 (s, 9H, *p*-tBu). IR (cm^{-1}) (Nujol mull): 1303 s, 1142 m, 1097 m, 1023 m, 968 m, 919 m, 874 m, 853 m, 772 m, 634 w, 613 w, 554 w, 487 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. A suitable crystal was selected, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream of the diffractometer.[30] Data sets for compounds **1**, **2**, and **4** were collected with Cu Kα radiation (λ = 1.541 78 Å), using a Siemens P2$_1$ diffractometer for compounds **1** and **2** and a Siemens P4RA rotating-anode system for **4**. The P2$_1$ diffractometer was equipped with a graphite monochromator, and the P4RA, with a Ni filter. Both instruments used a locally modified Siemens LT2 low-temperature apparatus. The intensity data sets of compounds **1** and **4** were collected at 130 K; the data for compound **2** were gathered at 228 K, due to cracking of the crystal below 210 K, presumably caused by irreversible phase transition. Intensity data sets for compounds **3**, **5**, **6**, and **7** were collected with a Rigaku AFC5S diffractometer at 213 K using Mo Kα radiation (λ = 0.710 73 Å). The diffractometer was equipped with a graphite monochromator and a Molecular Structure Corp. low-temperature device for low-temperature work. Standard reflections were measured; in all cases, only statistical variations (<1.5%) were observed. The intensities for all data sets were corrected for Lorentz and polarization effects. Extinction effects were corrected for compounds **4** and **5**, and an empirical absorption correction (XABS2)[31] was applied for compounds **1** and **2**. All structures were solved using SHELXS 86.[32] Structures of compounds **1**−**4**, **6**, and **7** were refined by full-matrix least-squares techniques on F^2 (SHELXL 93);[33] that of compound **5** was refined by full-matrix least-squares calculations on $|F_o|$ (SHELX 76).[32] All non-hydrogen atoms were refined anisotropically. Neutral-atom scattering factors and anomalous dispersion corrections were taken from common sources.[34−36]

For compounds **1** and **3**, hydrogen atoms were included in the refinement using a riding model with C−H distances of 0.96 Å and isotropic thermal parameters of 1.2 times the values of the equivalent isotropic thermal parameters of the carrier C atoms. Compound **2** shows positional disorder in the iPr methyl positions of the Trip ligand; the affected carbon atoms were refined using half-occupied split positions. Hydrogen atoms were included with fixed isotropic thermal parameters of 1.2 times the values of the equivalent isotropic thermal parameters of the carrier C atoms. Compound **4** exhibits a partly disordered TMEDA molecule; the occupancies of the two positions were refined to 0.79 and 0.21, and hydrogen atoms were included in all positions with isotropic thermal parameters of 1.2 times the equivalent isotropc thermal parameters of the corresponding phenyl and methine atoms and 1.5 times those of the methyl carbons. For compound **5**, hydrogen atoms were included using fixed isotropic thermal parameters of 0.08 Å^2. Compounds **6** and **7** show severely disordered crown ether units. For compound **6**, the crown ether was modeled using two independent positions with refined occupancies of 0.63 and 0.37, respectively; neighboring positions in the crown ether molecules were refined using identical anisotropic displacement parameters. Hydrogen atoms were included in the STrityl ligand with isotropic thermal parameters of 1.2 times those of the corresponding carbon atoms. In compound **7** each of the two crown ether molecules is disordered over two positions, which can be converted into each other by an inversion center located in the center of the crown ether molecule, resulting in fully occupied C21, C23, C25, C27, C31, C33, C35, and C37 positions; all other positions are half-occupied. Hydrogen atoms were included in the SMes* ligand, using isotropic thermal parameters of 1.2 times those of the corresponding carbon atoms.

Some details of the data collections and refinements are given in Table 1, atomic coordinates of selected atoms are provided in Table 2, and important bond lengths and angles are given in Tables 3−6. Further details are provided in the Supporting Information.

Results

Structural Descriptions. Li(PMDTA)STrityl, 1. The crystal structure of **1**, depicted in Figure 1, clearly shows the monomeric formulation of the target compound. The lithium atom is surrounded in a distorted tetrahedral fashion by three PMDTA nitrogen atoms and the sulfur atom from the thiolato ligand, with angles about lithium from 86.0(3) up to 125.5(3)°; the smallest angles are observed between the PMDTA nitrogen atoms. The Li−S distance is found to be 2.412(7) Å, the average Li−N distances being 2.12(1) Å. The S−C bond length is 1.866(4) Å, and the Li−S−C angle is 112.1(2)°. The lithium atom also interacts with a hydrogen atom located on one of the phenyl groups (H3A) with a distance of 2.52 Å, resulting in a pseudo-five-coordinate lithium center.

Li(PMDTA)STrip, 2. Compound **2**, which is pictured in Figure 2, exhibits a rare, monomeric structure. The lithium atom is bound in a distorted tetrahedral fashion to three PMDTA nitrogen atoms and one thiolate sulfur atom, with angles ranging from 84.7(3) to 128.1(3)°. As in **1**, the narrowest angle is found between the nitrogen atoms in the PMDTA donor. The Li−S distance is 2.366(7) Å, and the S−C bond length, 1.760(4) Å. The average Li−N distance is 3.14(2) Å, and the Li−S−C angle is 101.4(2)°.

[Li(THF)$_2$STrityl]$_2$, 3. Compound **3**, pictured in Figure 3, exhibits a dimeric structure containing a central rhombus composed of two S and two Li atoms. Each asymmetric unit contains half of the [Li(THF)$_2$STrityl]$_2$ molecule, the second half of which is generated by an inversion center located in the center of the Li_2S_2 unit, resulting in a planar arrangement of the four-membered ring. The lithium atoms exhibit a distorted tetrahedral environment, with angles between 99.1(3) and

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Table 1. Summary of Data Collection and Structure Refinement Details for Li(PMDTA)STrityl, **1**, Li(PMDTA)STrip, **2**, [Li(THF)$_2$STrityl]$_2$, **3**, [Li(TMEDA)STrip]$_2$, **4**, [Li(THF)SMes*]$_3$, **5**, [Li(12-crown-4)STrityl], **6**, and [Li(12-crown-4)$_2$][SMes*], **7**

	1	**2**	**3**	**4**
formula	$C_{28}H_{38}LiN_3S$	$C_{24}H_{46}LiN_3S$	$C_{54}H_{62}Li_2O_4S_2$	$C_{42}H_{78}Li_2N_4S_2$
fw	455.6	415.6	853.0	717.1
crystal descripn	colorl plate	colorl parallelep	pale yellow plate	colorl plate
crystal dimens (mm)	0.35 × 0.35 × 0.12	0.6 × 0.6 × 0.2	0.35 × 0.33 × 0.1	0.4 × 0.3 × 0.08
a (Å)	12.152(3)	15.805(7)	13.141(3)	18.906(4)
b (Å)	15.260(3)	9.206(4)	12.381(2)	9.516(2)
c (Å)	14.764(5)	18.923(7)	14.664(3)	25.617(5)
α (deg)	90	90	90	90
β (deg)	106.90(2)	99.74(3)	94.84(3)	92.75(3)
γ (deg)	90	90	90	90
V (Å^3)	2619(12)	2714(2)	2377.3(8)	4603(2)
Z	4	4	2	4
space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$I2/a$
d_{calc} (g/cm^3)	1.155	1.017	1.192	1.035
lin abs coeff	1.227	1.132	1.156	1.257
diffractometer	Siemens P2$_1$	Siemens P2$_1$	Rigaku AFC5S	Siemens P4/RA
radiation	Cu Kα	Cu Kα	Mo Kα	Cu Kα
T (K)	130	228	213	130
θ range (deg)	4−57	3−53	2−25	3−56
no. of independ refl	3531	3092	4192	3015
no. of variables	298	281	280	258
R1^a	0.064 ($I > 2\sigma(I)$)	0.085 ($I > 2\sigma(I)$)	0.052 ($I > 2\sigma(I)$)	0.067 ($I > 2\sigma(I)$)
wR2^b	0.143 ($I > 2\sigma(I)$)	0.202 ($I > 2\sigma(I)$)	0.114 ($I > 2\sigma(I)$)	0.171 ($I > 2\sigma(I)$)
R1^a (all data)	0.099	0.130	0.118	0.084
wR2^b (all data)	0.162	0.24	0.141	0.189

	5	**6**	**7**
formula	$C_{66}H_{111}Li_3O_3S_3$	$C_{27}H_{31}LiO_4S$	$C_{34}H_{61}LiO_8S$
fw	1069.5	458.5	636.8
crystal descripn	colorl needle	colorl rod	colorl plate
crystal dimens (mm)	0.4 × 0.15 × 0.15	0.5 × 0.35 × 0.05	0.4 × 0.4 × 0.05
a (Å)	9.991(2)	10.542(2)	10.134(2)
b (Å)	17.934(4)	12.821(3)	19.800(4)
c (Å)	20.314(4)	18.729(4)	18.423(4)
α (deg)	83.36(3)	90	90
β (deg)	76.74(3)	102.22(3)	93.15(3)
γ (deg)	76.72(3)	90	90
V (Å^3)	3440.4(12)	2474.0(9)	3691.0(13)
Z	2	4	4
space group	$P1$	$P2_1/c$	$P2_1/n$
d_{calc} (g/cm^3)	1.032	1.231	1.146
lin abs coeff	1.47	1.61	1.33
diffractometer	Rigaku AFC5S	Rigaku AFC5S	Rigaku AFC5S
radiation	Mo Kα	Mo Kα	Mo Kα
T (K)	213	213	213
θ range (deg)	0−27.5	2−30	1.5−27
no. of independ refl	9967	7203	6511
no. of obs refl	6397 ($I > 2.5\sigma(I)$)	4206 ($I > 2\sigma(I)$)	4088 ($I > 2\sigma(I)$)
no. of variables	677	337	445
R1^a	0.063 ($I > 2.5\sigma(I)$)	0.086 ($I > 2\sigma(I)$)	0.092 ($I > 2\sigma(I)$)
wR2^b	0.071 ($I > 2.5\sigma(I)$)^c	0.232 ($I > 2\sigma(I)$)	0.247 ($I > 2\sigma(I)$)
R1^a (all data)	0.099	0.153	0.148
wR2^b (all data)	0.079^c	0.292	0.284

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] $wR = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$.

125.8(3)°. The geometry at sulfur is pyramidal, the sum of angles being 317.7(8)°. The lithium−sulfur distances are 2.466(5) and 2.494(5) Å, while the S−C distance is 1.869(3) Å. Short lithium−hydrogen interactions are observed at 2.83 and 3.14 Å, with one hydrogen atom interacting with two lithium centers, resulting in a two-sided capping of the Li_2S_2 rhombus and pseudo-six-coordinate lithium atoms.

[Li(TMEDA)STrip]$_2$, 4. Compound **4**, shown in Figure 4, exhibits a dimeric solid state structure. The halves of the dimer are transformed into each other by a center of symmetry located in the center of the Li_2S_2 rhombus, resulting in a planar four-membered ring of alternating Li and S atoms. Each lithium atom is surrounded in a distorted tetrahedral fashion by two sulfur atoms and two TMEDA nitrogen atoms, with angles ranging from 84.5(2) to 149.9(2)°. The smallest angles are observed between the nitrogen donors, while the largest is between the donors and the thiolato function. The lithium sulfur distances are 2.429(5) and 2.463(4) Å, and the sulfur−carbon distance is 1.778(2) Å. The sulfur atoms are only slightly pyramidal, with the sum of angles being 340.6°.

[Li(THF)SMes*]$_3$, 5. Compound **5**, pictured in Figures 5 and 6, consists of neutral, well-separated trimeric units with no crystallographically imposed symmetry. The core exhibits a slightly nonplanar six-membered ring composed of alternating lithium and sulfur atoms; ring configuration and respective deviations from planarity are shown in Figure 6. The lithium atoms are surrounded in an almost undistorted trigonal planar arrangement by two sulfur atoms and one THF oxygen atom, with angles ranging between 115.5(3) and 127.4(3)°. The sulfur atoms exhibit a distorted trigonal planar environment, with

Table 2. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (Å^2 $\times$ 10^3) for Significant Atoms in Li(PMDTA)STrityl, **1**, Li(PMDTA)STrip, **2**, [Li(THF)$_2$STrityl]$_2$, **3**, [Li(TMEDA)STrip]$_2$, **4**, [Li(THF)SMes*]$_3$, **5**, [Li(12-crown-4)STrityl], **6**, and [Li(12-crown-4)$_2$][SMes*], **7**

atom	*x*	*y*	*z*	*U*, Å^2
		Compound **1**		
Li1	7767(6)	1750(5)	1454(5)	18(2)
S1	7756(1)	1249(1)	3000(1)	14(1)
C1	6868(3)	240(3)	2935(3)	13(1)
N1	9209(3)	1345(2)	1012(2)	17(1)
N2	8464(3)	3012(2)	1622(2)	18(1)
N3	6330(3)	2318(2)	408(2)	16(1)
		Compound **2**		
Li1	6857(5)	−1096(8)	10001(4)	46(2)
S1	6414(1)	1343(1)	9794(1)	53(1)
C1	7240(3)	2035(4)	9372(2)	39(1)
N1	6786(2)	−1687(4)	11086(2)	51(1)
N2	6137(2)	−2995(4)	9732(2)	50(1)
N3	7812(2)	−2073(4)	9440(2)	53(1)
		Compound **3**		
Li1	−407(4)	495(5)	908(3)	36(1)
S1	1321(1)	569(1)	325(1)	32(1)
C1	1867(2)	1900(2)	14(2)	28(1)
O1	−1261(2)	1792(2)	1022(2)	46(1)
O2	−215(2)	85(2)	2191(1)	43(1)
		Compound **4**		
Li1	8285(2)	1348(5)	5384(2)	37(1)
S1	7961(1)	1611(1)	4446(1)	55(1)
C1	8309(1)	768(3)	3895(1)	31(1)
N1	8958(1)	397(2)	6014(1)	39(1)
N2	8894(1)	3167(2)	5544(1)	45(1)
		Compound **5**		
Li1	2022(8)	1449(4)	3443(4)	63(4)
Li2	4325(8)	2959(4)	2188(4)	57(3)
Li3	5059(8)	677(5)	1709(4)	63(4)
S1	2587(1)	2654(1)	3107(1)	42(1)
S2	5548(1)	1910(1)	1556(1)	42(1)
S3	3141(1)	527(1)	2625(1)	48(1)
C1	2112(4)	3534(2)	3522(2)	32(2)
C19	6645(4)	2326(2)	857(2)	34(2)
C37	3917(4)	−454(2)	2825(2)	34(2)
O1	522(3)	1291(2)	4180(2)	63(1)
O2	4760(3)	3950(2)	1958(2)	62(1)
O3	6246(3)	−86(2)	1157(2)	67(2)
		Compound **6**		
Li1	5774(4)	2198(3)	2337(3)	60(1)
S1	6183(1)	3748(1)	1704(1)	33(1)
C1	7756(2)	3735(1)	1409(1)	27(1)
O1	3900(3)	2422(2)	2606(1)	66(1)
O1′	3552(3)	1871(2)	1664(2)	66(1)
O2	4684(2)	1123(2)	1672(2)	70(1)
O2′	5516(3)	672(3)	1654(3)	70(1)
O3	6992(3)	954(2)	2580(1)	94(1)
O3′	7127(5)	1208(2)	2919(2)	94(1)
O4	6134(2)	2184(2)	3545(2)	81(1)
O4′	4789(3)	2227(3)	3074(2)	81(1)
		Compound **7**		
Li1	2924(5)	10693(2)	3144(2)	49(1)
S1	993(1)	8201(1)	4450(1)	50(1)
C1	−126(2)	7535(1)	4573(1)	29(1)
O1	742(4)	10320(2)	2593(2)	63(1)
O1′	560(4)	10547(2)	3016(2)	63(1)
O2	3150(4)	9613(2)	2566(2)	56(1)
O2′	2438(4)	9756(2)	2393(2)	56(1)
O3	3916(4)	9875(2)	4011(2)	62(1)
O3′	4048(4)	9701(2)	3640(3)	62(1)
O4	1537(4)	10575(2)	3995(2)	59(1)
O4′	2138(4)	10479(2)	4233(2)	59(1)
O5	2976(5)	11106(3)	1944(3)	82(1)
O5′	2474(6)	11266(3)	2018(3)	82(1)
O6	2048(6)	11790(2)	3095(3)	97(1)
O6′	2109(6)	11783(3)	3307(4)	97(1)
O7	4103(6)	11393(3)	4014(3)	105(1)
O7′	4405(7)	11289(3)	3895(3)	105(1)
O8	5124(4)	10771(2)	2863(3)	67(1)
O8′	4838(4)	10724(2)	2535(3)	67(1)

Table 3. Important Bond Lengths (Å) and Angles (deg) in the Monomeric Lithium Thiolates Li(PMDTA)STrityl, **1**, Li(PMDTA)STrip, **2**, Li(THF)$_3$SMEs*, **8**, and Li(THF)$_3$STriph, **9**, and Li(py)$_3$S-2-MePh, **10** (D = Donor)

	1	**2**	**8**	**9**	**10**
Li−S	2.412(7)	2.366(7)	2.44(1), 2.46(1)	2.43(1)	2.412(6)
S−C	1.866(4)	1.760(4)	1.788(4), 1.785(4)	1.762(4)	1.751(3)
Li−D	2.131(8)	2.145(8)	1.95(1), 1.99(1)	1.908(4)	2.081(7)
	2.090(8)	2.101(8)	1.97(1), 1.94(1)	2.004(4)	2.083(6)
	2.149(7)	2.181(8)	1.95(1), 1.99(1)	1.943(4)	2.081(7)
Li−S−C	112.1(2)	101.4(2)	103.1(3), 104.5(1)	99.1(1)	114.0(2)
D−Li−D	87.9(3)	84.7(3)	97.9(4), 114.1(6)	111.2(2)	112.6(3)
D−Li−D	86.0(3)	86.0(3)	97.0(4), 99.6(5)	105.0(2)	101.7(3)
D−Li−D	117.8(3)	120.9(4)	104.4(6), 102.7(5)	100.0(2)	104.5(3)
D−Li−S	107.0(3)	128.1(3)	104.3(5), 127.5(5)	108.7(1)	117.4(2)
D−Li−S	115.4(3)	109.7(3)	118.5(5), 113.7(4)	122.5(2)	104.8(3)
D−Li−S	125.5(3)	121.4(3)	116.9(4), 113.9(5)	109.2(1)	115.4(3)
shortest Li−H	2.52	>4	>4	>4	>4

Table 4. Important Bond Lengths (Å) and Angles (deg) in the Dimeric Lithium Thiolates [Li(THF)$_2$STrityl]$_2$, **3**, and [Li(TMEDA)Strip]$_2$, **4** (D = Donor)

	3	**4**
Li−S	2.466(5)	2.429(5)
	2.494(5)	2.463(4)
S−C	1.869(3)	1.778(2)
Li−D	1.945(5)	2.107(5)
Li−D	1.974(6)	2.201(5)
Li−S−C	117.7(2)	130.10(14)
Li−S−C	119.7(2)	119.69(13)
Li−S−Li	80.3(2)	90.8(2)
D−Li−D	99.1(3)	84.5(2)
D−Li−S	125.8(3), 104.6(2)	114.0(2), 116.3(2)
	107.0(2), 122.7(3)	102.4(2), 149.9(2)
S−Li−S	99.7(2)	88.0(2)

Table 5. Important Bond Lengths (Å) and Angles (deg) in the Trimeric Lithium Thiolates and Selenolates [Li(THF)SMes*]$_3$, **5**, and [Li(THF)SeMes*]$_3$ (E = S, Se)

	5	[Li(THF)SeMes*]$_3$
Li−E	2.346(8), 2.348(7)	2.473(9), 2.476(12)
Li−E	2.337(7), 2.343(9)	2.462(13), 2.478(14)
Li−E	2.383(8), 2.385(7)	2.463(14), 2.478(14)
E−C	1.789(4), 1.786(4)	1.972(9), 1.974(6)
E−C	1.794(4)	1.972(7)
Li−O	1.906(8), 1.907(9)	1.902(16), 1.888(14)
Li−O	1.881(8)	1.903(16)
Li−E−C	132.0(2), 99.8(2)	126.7(4), 94.1(4)
Li−E−C	103.5(2), 129.1(2)	99.6(4), 127.3(5)
Li−E−C	124.5(2), 93.1(2)	123.2(4), 90.6(3)
Li−E−Li	127.4(3), 126.3(3)	127.4(4), 126.1(4)
Li−E−Li	124.6(3)	119.4(5)
E−Li−E	112.5(3), 113.5(3)	111.8(5), 108.5(5)
E−Li−E	114.1(3)	116.7(6)
E−Li−O	123.0(4), 123.0(4)	115.5(5), 127.7(6)
E−Li−O	125.1(4), 121.4(3)	128.1(7), 123.4(6)
E−Li−O	118.4(4), 127.3(4)	114.0(7), 128.6(7)

Table 6. Important Bond Lengths (Å) and Angles (deg) in the Lithium Thiolates [Li(12-crown-4)STrityl], **6**, and [Li(12-crown-4)$_2$][SMes*]

	6	**7**
Li−S	2.399(4)	5.87
Li−O (range)	1.895(6)−2.450(5)	2.176(6)−2.493(6)
S−C	1.855(2)	1.761(2)
Li−S−C	113.96(12)	

angles between 93.1(2) and 132.0(2)° and angle sums of 359.2 (S1), 358.9 (S2), and 342.2° (S3). The mean deviation from the least-squares plane of the Li$_3$S$_3$ ring is 0.012 Å, as illustrated in Figure 6. The Li−S bond lengths are very similar and range from 2.337(7) to 2.385(7) Å, the average S−C bond length is 1.79(1) Å, and Li−O distances range from 1.881(8) to 1.907(9) Å.

[Li(12-crown-4)STrityl], 6. The structure of **6** is presented in Figure 7; the molecule consists of neutral, discrete, mono-

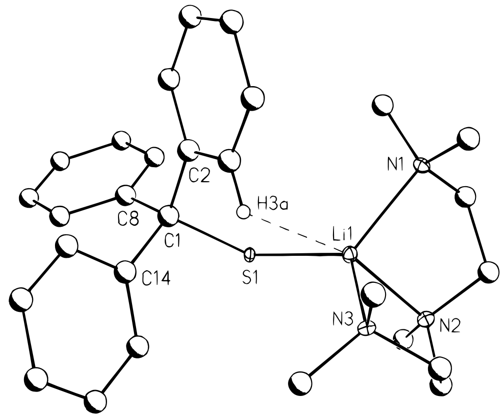

Figure 1. Computer-generated plot of **1** (25% ellipsoids). Hydrogen atoms except H3a have been omitted for clarity.

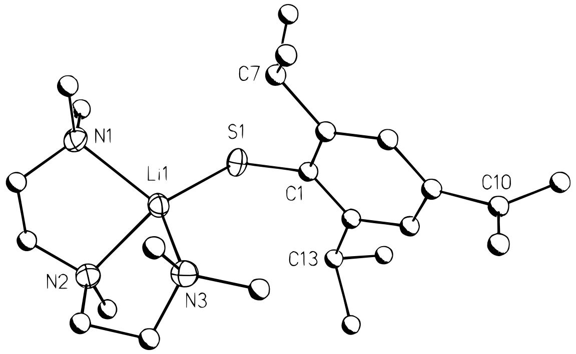

Figure 2. Computer-generated plot of **2** (25% ellipsoids). Hydrogen atoms have been omitted for clarity.

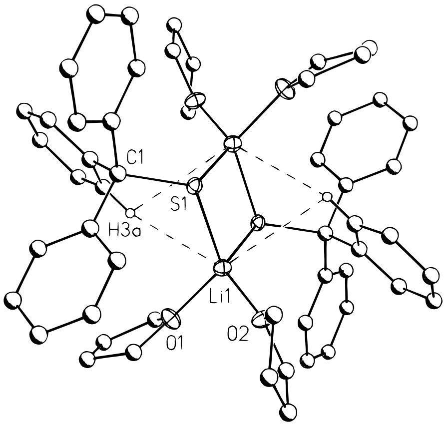

Figure 3. Computer-generated plot of **3** (25% ellipsoids). Hydrogen atoms except the bridging H3a have been omitted for clarity.

meric units with no crystallographically imposed symmetry. The lithium atom is five-coordinate and is bound to four oxygen atoms in the 12-crown-4 molecule with average Li—O distances of 2.27(2) Å. The lithium atom is also attached to the thiolato sulfur atom, the Li—S distance being 2.399(4) Å. The angle at sulfur is found to be 113.96(12)°.

[Li(12-crown-4)$_2$][SMes*], 7. Compound **7**, presented in Figure 8, displays solvent-separated ion pairs. The lithium cation is coordinated in a sandwich-like fashion to eight oxygen atoms in two 12-crown-4 molecules, resulting in a coordination number of 8 at the metal center. The crown ether molecules are disordered over two positions, resulting in 16 Li—O contacts with a fairly large range of Li—O distances, the average being 2.36 Å. The anion, consisting of a naked SR— unit, displays a one-coordinate sulfur atom, which is bound to the Mes* ligand. The S—C distance is 1.761(2) Å; cation and anion are separated by 5.87 Å.

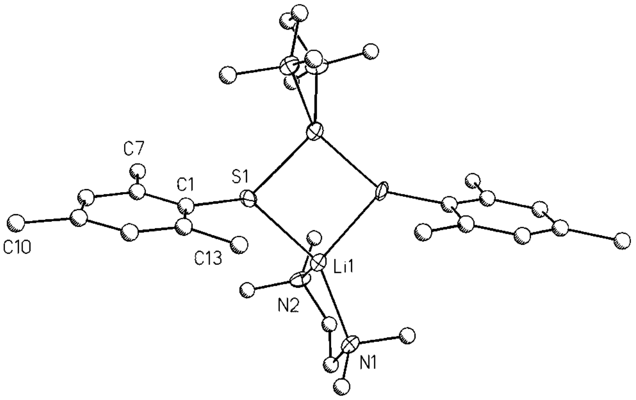

Figure 4. Computer-generated plot of **4** (25% ellipsoids). Hydrogen atoms and the iPr methyl groups have been omitted for clarity.

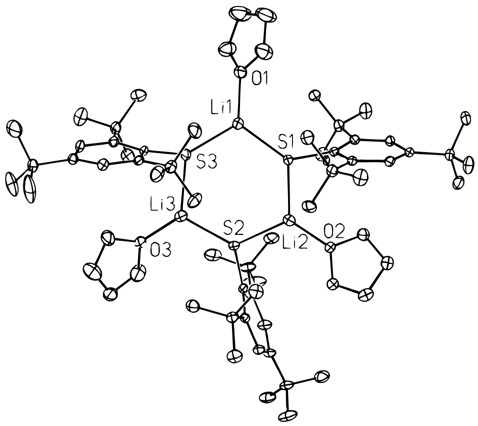

Figure 5. Computer-generated plot of **5** (25% ellipsoids). Hydrogen atoms have been omitted for clarity.

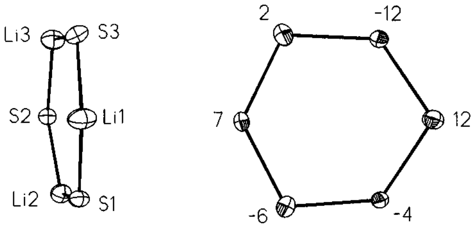

Figure 6. Computer-generated plot of the ring framework of **5** showing deviations from planarity relative to the least-squares plane (in 0.01 Å).

Discussion

All compounds presented in this paper were synthesized in a straightforward manner by reacting the corresponding thiols with nBuLi. The addition of multidentate donor molecules such as PMDTA led to the isolation of the monomeric species Li(PMDTA)STrityl, **1** (Figure 1), and Li(PMDTA)STrip, **2** (Figure 2). If an identical set of ligands was used in combination with the mono- and bidentate donors THF and TMEDA, the dimeric species [Li(THF)$_2$STrityl]$_2$, **3** (Figure 3), and [Li(TMEDA)-STrip]$_2$, **4** (Figure 4), became available. By limiting the amount of THF to 1 equiv, we obtained the first trimeric lithium thiolate [Li(THF)SMes*]$_3$, **5** (Figures 5 and 6). Use of a crown ether led to the isolation of the monomeric contact ion pair [Li(12-crown-4)STrityl], **6** (Figure 7), while employment of the sterically demanding —SMes* ligand in combination with a crown ether allowed the preparation of the first solvent-separated lithium thiolate [Li(12-crown-4)$_2$][SMes*], **7** (Figure 8). Compounds **1**—**7** are colorless or pale yellow, air-sensitive materials that are quite stable if stored under inert gas atmosphere.

The most notable feature of **1** and **2** is their monomeric formulation, in both the solid state and solution, as evidenced

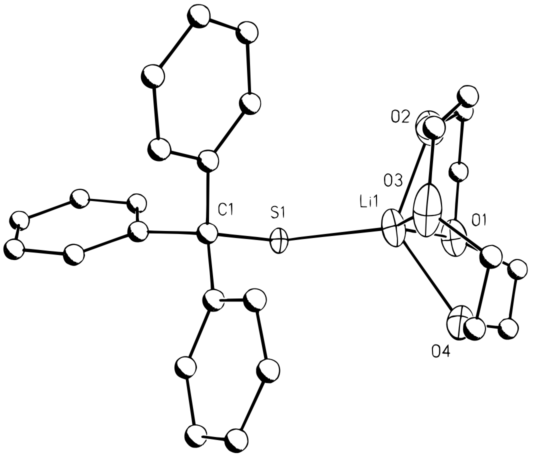

Figure 7. Computer-generated plot of **6** (25% ellipsoids). Hydrogen atoms have been omitted for clarity.

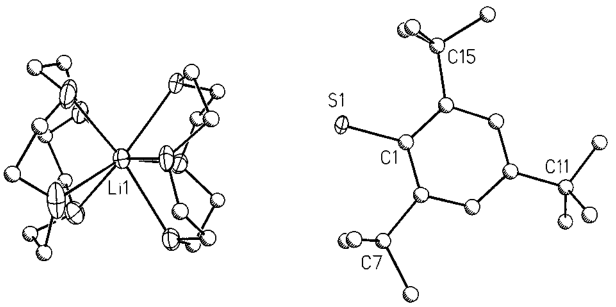

Figure 8. Computer-generated plot of **7** (25% ellipsoids). Hydrogen atoms have been omitted for clarity.

by crystallographic and NMR studies; each lithium atom is surrounded in a distorted tetrahedral fashion by three nitrogens of a PMDTA donor and one sulfur atom. Compound **1** also displays a short lithium−hydrogen interaction. The overall structural features observed for **1** and **2** are very similar; and the compounds are closely related to other monomeric thiolates, such as Li(THF)$_3$SMes*, **8**,[11] Li(THF)$_3$STriph, **9**[15] (Triph = 2,4,6-Ph$_3$C$_6$H$_2$), and Li(py)$_3$S-2-MePh, **10**[16] (see Table 3). The lithium−sulfur distances are fairly uniform, with 2.412(7) Å for **1**, 2.366(7) Å for **2**, 2.45(1) Å (average) for **8**, 2.43(1) Å for **9**, and 2.412(6) Å for **10**. The slightly shorter Li−S distance observed in **2** can be explained by the attenuated steric bulk of the Trip ligand. An overall comparison of structural data in monomeric lithium thiolates is provided in Table 3.

The monomeric formulation of **1** and **2** is obtained only if the tridentate donor PMDTA is employed. If the same thiolate ligands are utilized in combination with mono- or bidentate THF or TMEDA, the dimeric compounds **3** and **4** are formed. The monomeric formulation of compounds **8**[11] and **9**,[15] which were crystallized from an excess of THF, is ensured by the use of the sterically very cumbersome ligands Mes* and Triph which provide steric shielding at the metal center and thereby disfavor dimerization. The ligands Trityl and Trip are less sterically demanding, and if used in combination with the donors THF and TMEDA, yield the dimeric species **3** and **4**, respectively. Reduction of steric bulk in the ligand usually results in the formation of dimeric species; however, this tendency can be suppressed by employment of multidentate donors, which limit structural flexibility and preclude dimerization.

Compounds **3** and **4** display four-membered rings composed of alternating lithium and sulfur atoms. The Li−S distances are very uniform with 2.48(1) Å (average) for **3** and 2.45(1) Å (average) for **4**. The metal−sulfur bond lengths are slightly longer than in the monomeric species; an explanation is provided by the bridging nature of the thiolato ligands. The bond lengths are in good accord with the closely related dimers [Li(THF)$_2$-{SCH(SiMe$_3$)$_2$}]$_2$ and [Li(THF)$_{1.75}${SC(SiMe$_3$)$_3$}]$_2$.[17] Compound **3** exhibits short lithium−hydrogen interactions. One hydrogen atom is asymmetrically bridging each face of the Li$_2$S$_2$ rhombus. Each lithium atom is also bound to two donors and two sulfur atoms, resulting in pseudo-six-coordinate lithium centers with angles ranging between 99.1(3) and 125.8(3)°. In compound **4**, the lithium atoms display a distorted tetrahedral environment with two donor and two sulfur contacts; the respective angles range from 84.5(2) to 149.9(2)°. The greater degree of distortion around the lithium atom as observed in **4** can partly be explained by the geometric requirements implemented into the system by the bidentate TMEDA. The geometry at sulfur indicates the steric bulk of the ligand: observed are a pyramidal environment for compound **3** (sum of angles 317.7°) and a significantly more planar sulfur atom in **4** (sum of angles 340.6°), indicating the increased steric bulk of the Trip ligand in comparison to Trityl. Closely related dimeric species have also been observed for the heavier organochalcogenolates; examples include the selenolate [Li-(DME)SeSi(SiMe$_3$)$_3$]$_2$[18] and the tellurolates [Li(THF)$_2$TeSi-(SiMe$_3$)$_3$]$_2$[21] and [Li(DME)TeSi(SiMe$_3$)$_3$]$_2$.[19]

In contrast to the monomeric Li(THF)$_3$SMes*, **8**,[11] which is obtained by using excess THF, the trimeric [Li(THF)$_3$SMes*]$_3$, **5**, is isolated in excellent yield if the amount of THF is limited to 1 equiv. Exposing monomeric **8** to vacuum, even at elevated temperatures, does not result in loss of donor solvent; therefore, the trimeric **5** is only available if a stoichiometric amount of donor is used. Compound **5** is the first example of a trimeric lithium thiolate. The compound displays an almost planar six-membered ring system composed of alternating lithium and sulfur atoms (see Figures 5 and 6). Each lithium atom is surrounded in a distorted trigonal planar fashion by one THF oxygen atom and two sulfur atoms. The structure of **5** is isomorphous with that of the selenolate [Li(THF)SeMes*]$_3$,[25] and comparative structural data are summarized in Table 5. A comparison of Li−S bond lengths shows significantly shorter bonds in **5** (average 2.36(1) Å) than those observed for compounds displaying four-coordinate metal centers, **1**−**4** and **8**−**9** (2.46 Å (average) for **8**). Consequently, the short Li−S bond length in **5** can be directly related to the lower coordination number at lithium. A similar trend was observed for the corresponding monomeric Li(THF)$_3$SeMes* (2.57 Å (average))[12,13] and the trimeric [Li(THF)SeMes*]$_3$ (2.47 Å (average)).[25] In both the thiolates and selenolates, the differences in bond length between the four-coordinate monomer and the three-coordinate trimer are about 0.1 Å, further supporting the explanation that the short bond length observed in **5** is a result of the lower coordination number. A similar effect was observed in comparing the three-coordinate dimeric tellurolate [Li(THF)TeSi(SiMe$_3$)$_3$]$_2$[20] with the four-coordinate [Li(THF)$_2$-TeSi(SiMe$_3$)$_3$]$_2$.[19]

Very few examples of lithium organochalcogenolates displaying three-coordinate metal centers have been described. Examples are limited to the trimeric lithium thiolate, **5**, the isomorphous selenolate [Li(THF)SeMes*]$_3$,[25] the hexameric tellurolate [LiTeSi(SiMe$_3$)$_3$]$_6$,[26] and the dimeric compound [Li-(THF)TeSi(SiMe$_3$)$_3$]$_2$.[19] In all cases, sterically cumbersome ligands made possible the isolation of the low-coordinate compounds.

Trimeric species stabilized by intramolecular coordination have been observed previously for lithium aryloxides. In these compounds, a coordination number of 4 at lithium was observed.[37] The trimeric species **5** is structurally related to the hexameric cage species [Li{S-2-((R)CH(Me)NMe$_2$)C$_6$H$_4$}]$_6$[27] and [C$_5$Me$_5$Ta$_2$Li$_4$(THF)$_4$S$_6$].[38] In both derivatives, the lithium atoms exhibit a coordination number of 4; the lithium atoms in [Li{S-2-((R)CH(Me)NMe$_2$)C$_6$H$_4$}]$_6$ are solvated in an intramolecular fashion by the ortho-amino function of the arenethiolate ligand; in [C$_5$Me$_5$Ta$_2$Li$_4$(THF)$_4$S$_6$], each lithium atom is bound to a THF atom. The structural flexibility of lithium thiolates is further underscored by the hexameric open ring structure observed in [LiS-2,6-(CH$_2$NMe$_2$)$_2$C$_6$H$_3$]$_6$, obtained by using a bis-ortho-amino-substituted arenethiol. The lithium centers are connected to two sulfur atoms and are additionally solvated by two amino donors.[27]

Employment of the crown ether 12-crown-4 led to the isolation of monomeric [Li(12-crown-4)STrityl], **6**, displaying structural features very similar to those of the monomers **1**, **2**, **8**, **9**, and **10**. The lithium atom is solvated by 12-crown-4 and bound to the sulfur atom in the ligand, resulting in a coordination number of 5. As a result, the Li−S bond length is slightly elongated (2.399(4) Å) in comparison with that in the monomeric Li(PMDTA)STrityl (2.366(7) Å). The S−C distance in **6** is almost identical to that in **1**.

If the sterically more demanding thiol HSMes* is reacted with nBuLi under addition of 2 equiv of 12-crown-4, the first solvent-separated lithium thiolate, [Li(12-crown-4)$_2$][SMes*], **7**, is obtained in high yield. Attempts to synthesize a solvent-separated [Li(12-crown-4)$_2$][STrityl] were not successful; instead, the contact ion pair **6** was observed.

Solvent-separated alkali organochalcogenolates are extremely rare, and other examples are limited to the tellurolate [Li(12-crown-4)$_2$][TeSi(SiMe$_3$)$_3$][20] and the recently prepared solvent-separated potassium thiolates and selenolates [K(18-crown-6)(THF)$_2$][EMes*] (E = S, Se), both highly reactive organochalcogenolato reagents.[39]

Compound **7**, [Li(12-crown-4)$_2$][TeSi(SiMe$_3$)$_3$], and the potassium salts [K(18-crown-6)(THF)$_2$][EMes*] exhibit very similar structural features; in each, the alkali cation and organochalcogeno anion are separated by more than 4 Å, resulting in a naked anion with the sulfur, selenium, or tellurium atom only bound to the Mes* or the Si(SiMe$_3$)$_3$ ligand. Accordingly, the S−C and Te−Si distances are remarkably short with 1.761(2) Å for **7**, 1.741(1) Å for [K(18-crown-6)(THF)$_2$][SMes*],[39] 1.929(1) Å for [K(18-crown-6)(THF)$_2$][SeMes*],[39] and 2.468(3) Å for the tellurolate [Li(12-crown-4)$_2$][TeSi(SiMe$_3$)$_3$].[20]

In compound **7** and the tellurolate [Li(12-crown-4)$_2$][TeSi(SiMe$_3$)$_3$], the lithium cation is solvated by two 12-crown-4 molecules, leading to a sandwich-like arrangement of the cation (see Figure 8). This motif has been previously observed in a number of solvent-separated ion pairs, for example the lithium amide [Li(12-crown-4)$_2$][N(SiPh$_3$)$_2$]·THF[40] or the phosphide [Li(12-crown-4)$_2$][PPh$_2$].[41] Crown ethers have been exploited previously to provide the necessary solvation energy to allow for the isolation of solvent-separated species as observed in the tellurolate,[21] several cuprates, carbanions, phosphides, and amides.[42] The formation of the solvent-separated ion pair can be explained on the basis of a weak metal−sulfur interaction, as well as the enhanced stabilization provided by the crown ether−lithium interactions.

Conclusions

We synthesized a variety of lithium thiolates and related their aggregation and association behavior to the ligands and donors employed. Many different factors affect the formation of monomeric *versus* oligomeric compounds. For example, the strength of the metal−chalcogen interactions decreases by descending group 6, resulting in an enhanced influence of solvation. As a consequence, monomeric structures are more likely to be observed for the heavier analogues because the formation of oligomeric species is not necessarily favored in lieu of energetically advantageous solvation. Further, the size and electronic nature of chalcogenolate ligands play an important role. The effect of solvation is essential, immediately affecting the shape of the molecule. Slight changes in ligand or donor result in the formation of different aggregates; a complex pattern exists between oligomerization and aggregate formation, as can be visualized by the monomeric formulation of **8** in contrast to the trimeric **5**; ligand influence is demonstrated by the monomeric formulation of **8** and **9**, both carrying extremely bulky ligands, in contrast to the dimeric **3** and **4**.

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Supporting Information Available: Full tables of data collection parameters, atom coordinates, bond distances and angles, hydrogen coordinates, and anisotropic thermal parameters (63 pages). Ordering information is given on any current masthead page.

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