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Syntheses and Structure Determinations of Calcium Thiolates

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The exploration of synthetic methodologies toward heavy alkaline-earth chalcogenolates resulted in the preparation and structural characterization of a family of calcium thiolates, including $[Ca(SC_6F_5)_2(py)_4]$, **1** (py = pyridine), the separated ion-triple $[Ca(18\text{-crown-}6)(NH_3)_3)][SMes^*]_2\cdot 2THF$, **2** (Mes* = 2,4,6-tBu$_3$C$_6$H$_2$), and the contact triple $[Ca(18\text{-crown-}6)(SMes^*)_2]\cdot THF$, **3**. Compound **1** was prepared by treating $[Ca(N(SiMe_3)_2)_2]_2$ with 4 equiv of HSC_6F_5 under addition of pyridine. The thiolates **2** and **3** were synthesized by treatment of calcium metal dissolved in dry, liquid NH_3 under addition of 2 equiv of HSMes* and crown ether or, alternatively, by the reduction of Mes*SSMes* with calcium metal in dry, liquid ammonia. We also report two reaction products isolated during attempted calcium thiolate syntheses: $[CaBr_4(THF)_2(\mu^2\text{-}Li)_2(THF)_4]$, **4**, isolated as the product of a salt elimination reaction between $CaBr_2$ and 2 equiv of $[Li(THF)_nS\text{-}2,4,6\text{-}{}^iPr_3C_6H_2]_m$. $[(NH_4)(py)(SC_6F_5)]$, **5**, was obtained as the sole product in the reaction of metallic calcium with HSC_6F_5 in liquid ammonia under addition of pyridine. All compounds were characterized by single-crystal X-ray crystallography in addition to IR and NMR spectroscopy.

Introduction

The discovery of superconducting ceramics and ferroelectric materials containing alkaline-earth ions such as $BaTiO_3$, $K_{0.4}Ba_{0.6}BiO_3$, $YBa_2Cu_3O_{7-x}$, $BaMg_{0.33}Ta_{0.66}O_3$, $Cu_3O_xM_2Tl$ (M = Ca, Ba), $CuO_4La_{1-x}Sr_x$, or $CuO_xSr_yCa_n$ has revived research interest in the area of alkaline-earth chemistry.[1−3] This work resulted in the preparation of a tableau of strontium and barium aryloxides, alkoxides, and siloxides,[4] as well as a small number of structurally characterized calcium analogues, such as $[Ca(BHT)_2(THF)_3]$ (BHT = O-2,6-tBu$_2$-4-MeC$_6$H$_2$,[5] $[Ca_9(OCH_2CH_2OMe)_{18}(HOCH_2CH_2OMe)_2]$,[6] $[Ca(\mu\text{-Oclox})(Oclox)(THF)]_2\cdot 2C_7H_8$ (clox = $C(C_6H_5)_2CH_2\text{-}4\text{-}ClC_6H_4$),[7] $[Ca_2(OSiPh_3)_3(NH_3)_4]\cdot 0.5C_7H_8$,[8] and the triangular cation $[Ca_3(OPh)_5(OP(NMe_2)_3)_6]^+$.[9] Other examples include $[Ca(O\text{-}2,4,6\text{-}(CF_3)_3C_6H_2)_2]_n$,[10] $[Ca_3(OSiPh_3)_6(THF)_2]$,[11] the presumably dimeric $[Ca(OMes^*)_2]_2$[4f] (Mes* = 2,4,6-tBu$_3$C$_6$H$_2$), and the monomers $[Ca(OMes^*)_2(THF)_3]$[4f] and $[Ca(Oclox)_2(THF)_3]$.[7]

In marked contrast, considerably less attention has been paid to the exploration of the calcium−sulfur bond, and accordingly, no solid state investigations into calcium thiolate structural chemistry have been undertaken. In addition, only two compounds displaying calcium−sulfur interactions, namely $[Ca\{(OCS)OMe\}_2(MeOH)_3]_2$[12] and $[Ca(SOCMe)_2(15\text{-crown-}5)]$,[13] have been structurally characterized. Moreover, the presence of a sulfur atom in a ligand system does not necessarily result in a Ca−S interaction, as shown in $[Ca\{S_2CC(CN)_2\}]\cdot 5H_2O$[14] and $[Ca(C_{10}H_8N_2)_2(SCN)_2(H_2O)]$[15] where no Ca−S interactions are observed to the resonance delocalized anions.

However, a small selection of calcium thiolates have been reported, but no information is available regarding their solid-state structure. Examples include the presumably polymeric $[Ca(SC_6H_5)Cl]_\infty$,[16] $[Ca(SAd)_2]_\infty$, (Ad = adamantyl), $[Ca(SCMe_3)_2]_\infty$, and $[Ca(SCEt_3)_2]_\infty$.[17] A few calcium selenolates and

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tellurolates have been mentioned, although the only structurally characterized example is that of the monomer $[Ca(TeSi(SiMe_3)_3)_2(THF)_4]$,[18,19] while the related $[Ca(SeSi(SiMe_3)_3)_2(TMEDA)_2]$[20] (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) and $[Ca(TeSi(SiMe_3)_3)_2(py)_4]$[20] have been mentioned, but structural data are not available.

This lack of data is in sharp contrast to the potential use of calcium chalcogenolates in a variety of technically important applications such as the production of two-color IR optical windows[21] or phosphor materials.[22] Moreover, the target molecules are potential dopants in the production of wide band-gap chalcogen-based semiconductors.[23]

Our work is geared toward the exploration of synthetic methodologies to allow for a facile, clean, high yield production of the target molecules. This will enable a systematic investigation of calcium−chalcogen bond characteristics and improve the understanding of the nature of the metal−ligand interaction in addition to the association and aggregation behavior in dependence of chalcogen atoms, ligands, and donors. Difficulties associated with heavy alkaline-earth chemistry are the electropositive character of the metals, their large radii, and the low solubility of the dihalide precursors in organic solvents.[24,25] Moreover, the high sensitivity of many molecular alkaline-earth derivatives toward hydrolysis paired with their low solubility, especially if small groups are attached to the metal center, makes spectroscopic or crystallographic analysis of the target molecules difficult. Accordingly, any progress in heavy alkaline-earth chemistry depends on the development of practical synthetic routes and the systematic investigation of ligand and donor systems. In this paper, we describe the exploration of synthetic methods toward calcium chalcogenolates and present eminent structural features in the target molecules.

Experimental Section

General Procedures. All reactions were performed under purified nitrogen atmosphere by using either modified Schlenk techniques or a Braun Labmaster 100 drybox. *n*-Hexane, toluene, tetrahydrofuran (THF), and diethyl ether (Et_2O) were freshly distilled from a Na/K alloy and degassed twice before use. Ammonia was predried over sodium metal and condensed into the reaction vessel. Commercially available ^nBuLi was used as received. HSC_6F_5 and pyridine (py) were stirred over CaH_2 and distilled prior to use. 18-Crown-6 was dissolved in hexanes, refluxed over freshly cut sodium, filtered, and crystallized at −30 °C. $[Ca(N(SiMe_3)_2)_2]_2$,[26] HSMes*,[27] Mes*SSMes*,[27] and HSTrip[28] (Trip = 2,4,6-i-$Pr_3C_6H_2$) were synthesized using literature procedures. ^1H (300 MHz) and ^{13}C (100 MHz) NMR spectra were obtained utilizing a Bruker DPX-300 spectrometer. Infrared spectra were recorded as a Nujol mull between KBr plates using a Perkin-Elmer PE 1600 FT-IR spectrometer. Reliable elemental analyses could not be obtained, even when glovebox handling was attempted, due to the high thermal and moisture sensitivity of all compounds reported, which is a well-known problem in alkaline-earth chemistry.[29] In addition, thiolates tend to give notoriously unreliable elemental analyses due to the formation of nonvolatile metal sulfides.

$[Ca(SC_6F_5)_2(py)_4]$, 1. To a 100 mL Schlenk flask was added 0.28 g (0.2 mmol) of $[Ca(N(SiMe_3)_2)_2]_2$ and 20 mL of toluene. With vigorous stirring, 0.2 mL (1.6 mmol) of HSC_6F_5 was added dropwise, resulting in a cloudy yellow/green solution. Approximately 0.75 mL of pyridine was added to the reaction followed by brief heating to reflux temperature. This resulted in a homogeneous yellow solution, which was immediately filtered through a Celite-padded frit. After cooling to room temperature, clear crystals formed in 16% isolated yield (0.12 g). Mp: the white powder melted slightly and then quickly decomposed to a yellow/brown solid above 120 °C. ^1H NMR (THF-d_8): δ 8.53 (d, 8H), 7.67 (t, 4H), 7.26 (t, 8H). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 150.84, 136.51, 124.51 (resonances for $^-SC_6F_5$ were not apparent). IR (cm^{-1}) (Nujol): 3039 w, 2923 s, 2853 s, 1616 w, 1593 w, 1504 w, 1464 m, 1377 m, 1263 w, 1150 w, 1077 w, 1004 w, 959 m, 865 m, 817 w, 748 w, 700 m, 618 w.

$[Ca(NH_3)_3(18\text{-crown-}6)][SMes^*]_2\cdot 2THF$, 2, and $[Ca(18\text{-crown-}6)(SMes^*)_2]\cdot THF$, 3. To a 100 mL Schlenk flask was added 0.04 g (1.0 mmol) of calcium metal powder, 0.26 g (1.0 mmol) of 18-crown-6, and 0.56 g (2.0 mmol) of HSMes*. Approximately 20 mL of $NH_{3(l)}$ was condensed onto the mixture at −78 °C followed by stirring at low temperature for 1 h. The reaction was then warmed to room temperature causing the NH_3 to evaporate, and then 20 mL of THF was added. Heating the reaction for approximately 5 min allows the isolation of the contact triple $[Ca(18\text{-crown-}6)(SMes^*)_2]\cdot THF$, **3**, while stirring at room temperature without application of heat leads to $[Ca(NH_3)_3(18\text{-crown-}6)][SMes^*]_2\cdot 2THF$, **2**. The resultant gray-white reaction mixtures were filtered through a Celite-padded filter frit. Colorless crystals formed out of the hazy filtrates on storage at 0 °C for several days in 61% isolated yield (0.57 g) for **3** and in 29% isolated yield (0.31 g) for **2**. Any coordinated ammonia in **2** appears to be stripped away, under vacuum, even for a very brief period, verified by NMR and IR spectroscopic analyses. Accordingly, the following experimental data apply to the exclusive product 3, obtained after brief (3 min) drying of **2** or **3** in a vacuum. Mp: decomposition to a brown oil >235 °C. ^1H NMR (THF-d_8): δ 7.05 (s, 4H), 3.76 (s, 24H), 1.72 (s, 36H), 1.23 (s, 18H). $^{13}C\{^1H\}$ NMR was precluded due to marginal solubility even in donor solvents such as THF-d_8. IR (cm^{-1}) (Nujol): 2918 s, 1588 w, 1494 w, 1466 s, 1381 s, 1354 s, 1285 m, 1242 m, 1213 w, 1095 s, 1041 s, 971 s, 877 m, 845 m, 750 m, 729 s, 694 w, 615 m, 492 w, 464 w, 414w.

An alternative route to compounds **2** and **3** involves the combination of activated calcium, 18-crown-6 and Mes*SSMes* followed by solvation with approximately 20 mL of dry ammonia at −78 °C. The reaction mixture is stirred at the low temperature for 2 h and then allowed to reflux at −33 °C for 4 h. The mixture is then allowed to warm gradually to room temperature while stirring vigorously. The resulting powder is dark gray, indicating the metal has not fully reduced the disulfide to the thiolate. Accordingly, a second treatment with liquid ammonia, analogous as described above, was undertaken, followed by an identical workup. After the second ammonia treatment products with identical physical data as those observed for **2** and **3** were isolated.

$[CaBr_4(THF)_2(\mu^2\text{-}Li)_2(THF)_4]$, 4. To a 100 mL flask was added 0.4 g of $CaBr_2$ (2 mmol) which was subsequently dissolved in 20 mL of THF. A solution containing 4 mmol of $Li(THF)_nSTrip$, prepared from the reaction of 0.95 g of HSTrip (4 mmol) dissolved in 20 mL of

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Table 1. Summary of Data Collection, Structure Solution and Refinement of [Ca(SC_6F_5)$_2$(py)$_4$], 1, [Ca(18-crown-6)(NH_3)$_3$)][SMes*]$_2$•2THF, **2**, [Ca(18-crown-6)(SMes*)$_2$]•THF, **3**, [$CaBr_4$(THF)$_2$(μ^2-Li)$_2$(THF)$_4$], **4**, and [(NH_4)(py)(SC_6F_5)], **5**[a]

	1	**2**	**3**	**4**	**5**
empirical formula	$C_{32}H_{20}CaF_{10}N_4S_2$	$C_{56}H_{107}CaN_3O_8S_2$	$C_{52}H_{90}CaO_7S_2$	$C_{24}H_{48}Br_4CaLi_2O_6$	$C_{22}H_{18}F_{10}N_4S_2$
fw	754.72	1054.65	931.44	806.22	592.52
a [Å]	7.9597(3)	20.3908(2)	18.1457(3)	8.731(2)	6.1230(4)
b [Å]	9.7792(4)	18.1902(2)	16.9937(3)	13.659(3)	28.543(2)
c [Å]	10.8684(4)	18.9865(2)	35.2183(1)	15.687(3)	7.2894(5)
α [deg]	103.916(1)	90	90	90	90
β [deg]	93.138(1)	116.053(1)	90	105.87(3)	94.261(2)
γ [deg]	99.278(1)	90	90	90	90
V [Å^3]	806.55(5)	6326.75(11)	10860.0(3)	1799.5(7)	1270.45(14)
Z	1	4	8	2	2
space group	$P\bar{1}$	$P2_1/c$	$Pbca$	$P2_1/n$	$P2_1/n$
$d_{calc.}$ [g/cm^3]	1.554	1.107	1.139	1.488	1.549
linear abs. coeff. [mm^{-1}]	0.413	0.214	0.238	4.645	0.303
T [K]	156	150	150	213	150
2θ range, [deg]	4−57	2−57	2−45	4−50	3−57
no. of indep. reflns	3800	14754	7020	1370	2982
no. of parameter	223	712	552	164	188
R1, wR2 (all data)[b]	0.0490, 0.1095	0.1916, 0.2384	0.1824, 0.1862	0.1347, 0.1777	0.1186, 0.1215
R1, wR2 ($>2\sigma$)[b]	0.0394, 0.1009	0.0985, 0.1965	0.1238, 0.1667	0.0633, 0.1435	0.0628, 0.0987

[a] All data sets except **4** were collected on a Siemens SMART system; data for compound **4** were collected on a Rigaku AFC5S system. All data sets were collected utilizing Mo Kα radiation (λ = 0.710 73 Å). [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \sqrt{\sum w\{(F_o)^2-(F_c)^2\}^2/\sum w\{(F_o)^2\}^2}$.

THF and 2.5 mL of ^{n}BuLi (4 mmol), was added slowly utilizing a cannula. The initially cloudy solution became clear after the addition of the lithium thiolate but developed some cloudiness after 15 min. The solution was stirred a further 18 h at room temperature, after which it was filtered over a Celite-padded filter frit. After storage at −20 °C, colorless crystals suitable for X-ray crystallography were isolated in 12% yield (0.097 g). Mp: >405 °C. ^{1}H and ^{13}C NMR studies was precluded due to marginal solubility even in donor solvents such as THF-d_8. IR (cm^{-1}) (Nujol): 1464 s, 1375 m, 1259 m, 1108 m, 806 w, 726 w, 483 w.

[(NH_4)(py)(SC_6F_5)], 5. To a 100 mL Schlenk flask was added 0.3 mL (2.3 mmol) of HSC_6F_5 and 20 mL of toluene. This was cooled to −78 °C followed by the condensation of approximately 10 mL of $NH_{3(l)}$. Initially a thick white solid formed, which cleared slightly as more ammonia was added. Pyridine, 0.2 mL (2.8 mmol), was added at −78 °C, causing the reaction to clear somewhat. This was stirred at low temperature for 30 min, warmed to room temperature, and filtered at reflux temperature through a Celite-padded frit. Clear crystals grew from the colorless filtrate on cooling to room temperature in 27% isolated yield (0.08 g). Mp: the yellow/white powder started to shrink above 104 °C and melted irreversibly to a yellow oil at 119−122 °C. ^{1}H NMR (THF-d_8): δ 8.54 (broad s, 2H), 7.64 (broad s, 2H), 7.26 (t, 2H). ^{13}C{^{1}H} NMR (THF-d_8): δ 150.91, 136.49, 124.53 (resonances for $^-SC_6F_5$ were not apparent). IR (cm^{-1}) (Nujol): 3350−2600 broad s, 1672 w, 1462 broad s, 1377 m, 1263 m, 1116 w, 1027 w, 958 m, 867 m, 800 w, 749 m, 699 m, 618 w.

X-ray Crystallographic Studies. X-ray-quality crystals for all compounds were grown as described above in the Experimental Section. The crystals were removed from the Schlenk flask under a stream of N_2 and immediately covered with a layer of viscous hydrocarbon oil (Paratone N, Exxon). A suitable crystal was selected under the microscope, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream of the diffractometer.[30] The data set for compound **4**, [$CaBr_4$(THF)$_2$(μ^2-Li)$_2$(THF)$_4$], was collected at −60 °C using a Rigaku AFC5S diffractometer equipped with a Molecular Structure Corporation low-temperature device and graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Three standard reflections were measured every 150 reflections and showed in all cases only statistical variation of the intensity (<1.5%). The intensities were corrected for Lorentz and polarization effects, extinction was disregarded. An absorption correction was applied using semiempirical ψ scans. The intensity data sets for all other compounds were collected using a Siemens SMART system, complete with three-circle goniometer and CCD detector operating at −54 °C. The data sets for compounds **2**, **3**, and **5** were collected at −123 °C, and the compound **1** data set was collected at −117 °C, utilizing either a Cryojet low-temperature device from Oxford Instruments (compounds **2**, **3**, and **5**) or a Siemens LT-2 (compound **1**). In all cases graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) was employed. The data collections nominally covered a hemisphere of reciprocal space utilizing a combination of three sets of exposures, each with a different ϕ angle, and each exposure covering 0.3° in ω. Crystal decay was monitored by repeating the initial frames at the end of the data collection and analyzing the duplicate reflections. In all cases, no decay was observed. An absorption correction for compounds **2**, **3**, and **5** was applied utilizing the program SADABS.[31] The crystal structures of all compounds were solved by Direct Methods, as included in the SHELX program package.[32] Missing atoms were located in subsequent difference Fourier maps and included in the refinement. The structures of all compounds were refined by full-matrix least-squares refinement on F^2 (SHELX-93).[33] Hydrogen atoms were placed geometrically and refined using a riding model, including free rotation about C−C bonds for methyl groups with U_{iso} constrained at 1.2 for nonmethyl groups and at 1.5 for methyl groups times U_{eq} of the carrier C atom. The crystallographic programs used for structure refinement and solution were installed on a Silicon Graphics Indigo^2 R10000 Solid Impact or a PC clone. Scattering factors were those provided with the SHELX program system. All non-hydrogen atoms, with the exception of some disordered or restrained positions were refined anisotropically. Disorder was typically handled by including split positions for the affected groups and included the refinement of the respective occupancies. Generally, a set of restraints was applied to aid in modeling the disorder.[33] Crystals of **3**, even after repeated synthetic attempts and consequent recrystallization efforts, tended to be small and only weakly diffracting. Accordingly, the data set for **3** was cut at a 2θ value of 45°. The low intensity of the data set and severe disorder, paired with the large volume of the unit cell, resulted in a comparably high R value. Further details about the refinements and how disorder was handled are outlined in the Supporting Information. Selected details of the data collections and refinements are given in Table 1, and important bond lengths and angles are given in Tables 2−4.

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Table 2. Synthetic Routes to Alkaline-Earth Chalcogenolates[a]

type of reaction	equation	used for	ref
transamination	$Ae(N(SiMe_3)_2)_2 + 2HSR \rightarrow Ae(SR)_2 + 2HN(SiMe_3)_2$	Be, Mg, Ca, Sr, Ba 17−20	17−20 33, *
salt elimination	$AeX_2 + 2ASR \rightarrow Ae(SR)_2 + 2AX$	Be, Mg, Sr	20, 33, 38, 48
alkane elimination	$(C_4H_9)_2Mg + 2HSR \rightarrow Mg(SR)_2 + 2C_4H_{10}$	Mg	18, 20, 33, 36
metalation	$Ae_{act.} + 2HSR \rightarrow Ae(SR)_2 + H_2$	Ca, Sr, Ba	*
insertion	$Ae_{act.} + RSSR \rightarrow Ae(SR)_2$	Ca, Sr, Ba	*
transmetalation	$Mg + Hg(SR)_2 \rightarrow Mg(SR)_2 + Hg$	Mg	20
chalcogen insertion	$R_2Mg + {}^{2}/_{8}S_8 \rightarrow Mg(SR)_2$	Mg	49

[a] Ae = Be, Mg, Ca, Sr, Ba; R = alkyl, aryl, silyl; X = Br, I; A = alkali metal; "*", this work.

Results and Discussion

Syntheses. Synthetic access to alkaline-earth chalcogenolates is possible by a variety of methodologies, as summarized in Table 2. Synthetic limitations in the synthesis of the heavier alklaine-earth derivatives are due to difficulties with specific starting materials, for example, alkane elimination, which has been applied extensively in the synthesis of magnesium thiolates,[34] is not applicable since the organometallic starting materials are not readily available. Three reaction schemes, metalation, salt elimination and chalcogenolysis, are based on available alkaline-earth sources and have therefore been applied toward the synthesis of calcium thiolates.

Metalation. These reactions depend critically on the use highly activated calcium metal and suitable donors. Lappert et al. reported the synthesis of $[Ca(BHT)_2(THF)_3]$ by reacting co-condensed calcium with HBHT (HBHT = HO-2,6-tBu$_2$-4-MeC$_6$H$_2$) in THF.[5] Interestingly, the reaction failed if hydrocarbon solvents were employed. As shown with the synthesis of heavier alkaline-earth alkoxides, siloxides, and aryloxides,[4b,e,f,h,i,8] and now with the preparation of compounds **2** and **3**, the addition of anhydrous ammonia to the reaction mixture allows the isolation of the target molecules in acceptable yields and purity (eq 1).

$$Ca_{act.} + 2HSMes^* + NH_{3(exc.)} + donor \rightarrow [Ca(donor)_n(SMes^*)_2] + H_2 \quad (1)$$

An alternative synthetic scheme involves the reaction of calcium metal dissolved in liquid ammonia with disulfide (eq 2). Here, a quantitative alkaline-earth insertion and reduction of sulfur is observed and compounds **2** and **3** are isolated in good yield and purity.

$$Ca_{act.} + Mes^*SSMes^* + 18\text{-crown-6} \rightarrow [Ca(18\text{-crown-6})(SMes^*)2] \quad (2)$$

However, the relatively low reactivity of calcium paired with a strong sulfur−sulfur bond requires extended treatment in ammonia at reflux temperature (−33 °C) to result in a complete reduction. In analogous reactions with strontium and barium more facile reactions are observed, reflecting the higher reactivity of the heavier alkaline-earth metals.[35] The insertion route is most applicable for the preparation of the selenolate and tellurolate derivatives, since the reduction of diselenides or -tellurides to the highly air-sensitive selenols or tellurols can be avoided.[36] Metal insertion into selenium−selenium or tellurium-tellurium bonds has been observed previously in lanthanide chemistry.[37]

Disadvantages of the metalation route involve limitations with respect to potential ligand systems. Exposure of the highly acidic arylthiols HSC_6H_5 or HSC_6F_5 to liquid ammonia results in acid−base chemistry and consequent deprotonation of the thiol under formation of ammonium salts, as shown with the two-dimensional network polymer $[(NH_4)(py)(SC_6F_5)]$, **5**.

Chalcogenolysis. This has been the method of choice for the preparation of a variety of alkaline-earth derivatives, such as $[Mg(S\text{-}2,4,6\text{-}Ph_3C_6H_2)_2]_2$,[34] $[Mg(15\text{-crown-}5)(SCPh_3)_2]$,[38] $[Mg(SeMes^*)_2(THF)_2]$,[34] $[Ca(TeSi(SiMe_3)_3)_2(THF)_4]$,[18,19] $[(Sr(\mu\text{-}SCEt_3)_2(NH_3)py]_\infty$,[17] $[Sr(SeSi(SiMe_3)_3)_2(TMEDA)_2]$,[20] $[Ba(TeSi(SiMe_3)_3)_2(py)_5]$,[20] and others. The reaction involves the treatment of alkaline-earth amides $Ae(NR_2)_2$ (R = SiMe$_3$, H) with 2 equiv of chalcogenol (eq 3). The resulting amine is either gaseous at room temperature (NH$_3$) or can be removed in a vacuum (HN(SiMe$_3$)$_2$). This reaction route allowed the preparation of compound **1**.

$$Ca(N(SiMe_3)_2)_2 + 2HSR \rightarrow Ca(SR)_2 + 2HN(SiMe_3)_2 \quad (3)$$

A common element in successful, high-yield chalcogenolysis reactions seems to be the employment of sterically demanding chalcogenols. Recent results in our laboratory have shown that the utilization of small, highly acidic arylthiols such as HSC_6H_5 or HSC_6F_5 in conjunction with alkaline-earth bis(trimethylsilyl)amides result in a competitive reaction: unreacted arylthiol protonates $HN(SiMe_3)_2$ leading to the formation of silylthioether and primary amine. The primary amine can then be protonated again, generating a second equivalent silylthioether and NH$_3$. The consequent deprotonation of the thiol with the NH$_3$ results in the formation of an ammonium salt, as observed in $[(NH_4)(py)(SC_6F_5)]$, **5** (eq 4). Very similar chemistry has been observed in the reaction of lanthanide or actinide bistrimethylsilylamides with excess perfluorinated alkyl alcohols.[39,40]

$$\begin{gathered} HSR + HN(SiMe_3)_2 \rightarrow RSSiMe_3 + H_2NSiMe_3 \qquad (4) \\ HSR + H_2NSiMe_3 \rightarrow RSSiMe_3 + NH_3 \\ NH_3 + HSR \rightarrow [NH_4][SR] \\ (R = C_6H_5,\ C_6F_5) \end{gathered}$$

Structural proof for this competitive side reaction came from the identification of reaction products displaying H_2NSiMe_3 and/or NH$_3$ donor coordination.[41] This reaction path is currently

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(34) Ruhlandt-Senge, K. *Inorg. Chem.* **1995**, *34*, 3499.

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(36) (a) Ruhlandt-Senge, K., Power, P. P. *Inorg. Chem.* **1991**, *30*, 3683. (b) Du Mont, W. W.; Kubinock, S.; Lange, L.; Pohl, S.; Saak, W.; Wagner, I. *Chem. Ber.* **1991**, *124*, 1315.

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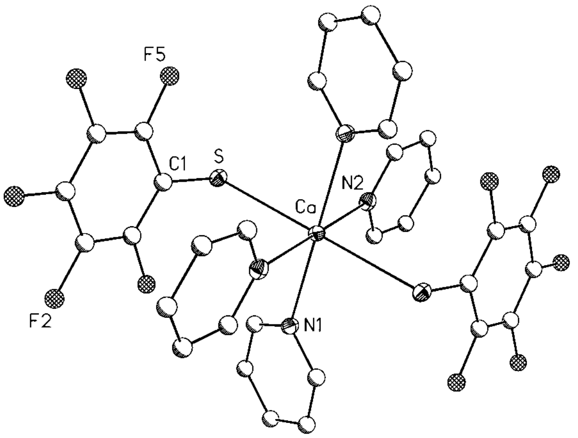

Figure 1. Computer-generated plot of **1**. Hydrogen atoms are omitted for clarity.

under investigation and does, in part, explain the low yield observed for compound **1**.

Salt Elimination. These reactions involve the treatment of alkaline-earth halides with alkali chalcogenolates (eq 5). The low solubility of alkaline-earth chlorides even in etheral solvents makes the use of the corresponding bromides or iodides necessary. Even so, limited solubility is observed, and etheral solvents are required.

$$\mathrm{CaBr_2 + 2LiSR \rightarrow Ca(SR)_2 + 2LiBr} \qquad (5)$$

To date only few alkaline-earth chalcogenolates have been prepared via salt elimination. Arnold and Gindelberger describe the reaction between lithium tellurolate and magnesium bromide as resulting only in intractable mixtures,[20] an observation commonly shared in our group. For example, the reaction of $MgBr_2$ with 2 equiv of $[Li(THF)_3EMes^*]$ (E = S, Se) results in the formation of the projected compounds,[34] whereas an analogous reaction scheme involving the treatment of $CaBr_2$ with 2 equiv of $[Li(THF)_nSTrip]_m$ (Trip = 2,4,6-$^iPr_3C_6H_2$) leads to the isolation of an adduct between unreacted $CaBr_2$ and LiBr, $[CaBr_4(THF)_2(\mu^2\text{-}Li)_2(THF)_4]$, **4**. Apparently, the reaction takes place to some degree, as indicated by the formation of LiBr. Interestingly, the reaction of SrI_2 with 2 equiv of lithium thiolate or selenolate led only to the isolation of starting materials, while the employment of the potassium reagents led to the isolation of $[Sr(EMes^*)_2(THF)_4]$ (E = S, Se) in high yields and purity.[42]

Structural Chemistry. $[Ca(SC_6F_5)_2(py)_4]$, 1. Compound **1**, depicted in Figure 1, displays a six-coordinate calcium center complete with two thiolate sulfur bonds in addition to four pyridine nitrogen contacts. The two thiolate ligands are arranged in the trans or axial positions, while the four pyridine donors are located in the equatorial plane. A center of inversion at calcium generates the second thiolate ligand and two of the four pyridine donors. The calcium−sulfur bond length is observed at 2.893(4) Å, while the calcium−nitrogen contacts are 2.502(2) and 2.534(2) Å. The calcium−sulfur−carbon angle is found at 101.22(6)°, and the carbon−sulfur bond length is observed at 1.752(2) Å.

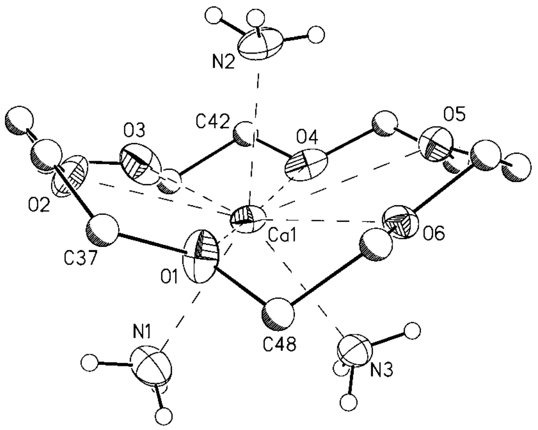

Figure 2. Computer-generated plot of **2**. Only the cation is shown, disordered positions and hydrogen atoms are omitted for clarity.

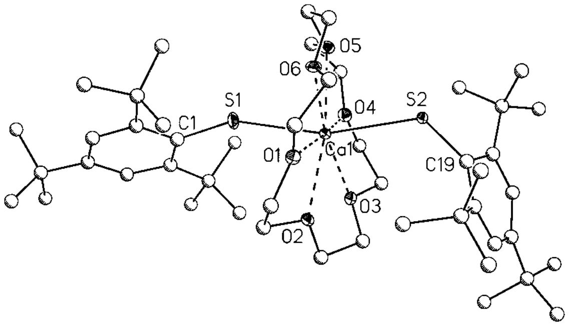

Figure 3. Computer-generated plot of **3**. Disordered positions and hydrogen atoms are omitted for clarity.

$[Ca(NH_3)_3(18\text{-crown-}6)][SMes^*]_2\cdot THF$, 2. Compound **2** crystallizes as separated ion-triples containing isolated $[Ca(NH_3)_3(18\text{-crown-}6)]^{2+}$ cations (shown in Figure 2) in addition to two $[SMes^*]^-$ anions. No close contacts (<5 Å) between cations and anions are observed. The closest intermolecular interactions observed at the cation are to N−H groups in neighboring cations (~3.8 Å). The calcium cation is nine coordinate with three NH_3 interactions and additional ligation by 18-crown-6. Two of the three NH_3 donors are located on one face of the crown ether, while the third NH_3 molecule is located at the opposite face. Accordingly, the crown ether is slightly distorted toward the crown ether face carrying only one NH_3 donor, resulting in a slight bowl-shaped arrangement. Small differences in the calcium−nitrogen distances are observed: the two NH_3 donors located on one face of the crown display slightly longer Ca−N interactions (2.523(3) and 2.541(2) Å) whereas the single NH_3 exhibits a slightly shorter Ca−N contact (2.469(3) Å). The calcium−oxygen distances within the crown ether range between 2.421(3) and 2.964(3) Å, indicating significant asymmetric placement of the calcium within the crown ether. The isolated $[SMes^*]^-$ anions display sulfur−carbon distances of 1.761(4) and 1.775(4) Å.

$[Ca(18\text{-crown-}6)(SMes^*)_2]\cdot THF$, 3. Compound **3**, shown in Figure 3, displays monomeric, neutral molecules with no crystallographically imposed symmetry. Calcium is ligated by six crown ether oxygen donors, in addition to two calcium−sulfur bonds resulting in an overall coordination number of eight. The thiolate groups are located in trans positions to one another and display remarkably different calcium−sulfur bond lengths (2.775(3) and 2.851(2) Å) and calcium−sulfur−carbon angles (119.1(2) and 154.0(3)°). The calcium−oxygen bond lengths within the crown ether are observed in the range of 2.516(5) to 2.624(5) Å. The sulfur−carbon bond lengths in the SMes* ligands are displayed at 1.785(7) and 1.764(7) Å.

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Table 3. Important Bond Lengths (Å) and Angles (deg) in Calcium Thiolates and Related Compounds[a]

compound	Ca−S (Å)	Ca−donor (Å)	S−C$_{ipso}$ (Å)	Ca−S−C	CN	ref
[Ca(SC_6F_5)$_2$(py)$_4$]	2.8493(4)	2.502(2), 2.534(2)[a]	1.752(2)	101.22(6)	6	*
[Ca(18C6)(NH_3)$_3$][SMes*]$_2$	−	2.421(3)−2.964(4)[b] 2.469(3),[a] 2.523(3)[a] 2.541(2)[a]	1.775(4), 1.761(4)	−	9	*
[Ca(18C6)(SMes*)$_2$]	2.775(3), 2.851(2)	2.516(5)−2.624(5)[b]	1.785(7), 1.764(7)	119.1(2), 154.0(3)	8	*
[Ca({OCS}OMe)$_2$(MeOH)$_3$]$_2$ 2.961(2)	2.961(2)	2.357(2)−2.521(2)[b]	*b*	*b*	8	12
[Ca(SOCMe)$_2$(15C5)]	2.92(5)	2.357(2)−2.461(2)[b]	*b*	*b*	8	13

[a] Mes* = 2,4,6-tBu$_3$C$_6$H$_2$; py = pyridine; a = Ca−N; b = Ca−O (crown); 18C6 = 18-crown-6; 15C5 = 15-crown-5. [b] S−C$_{ipso}$ distances and Ca−S−C angles not given due to the nonthiolato nature of the ligands; "*", this work.

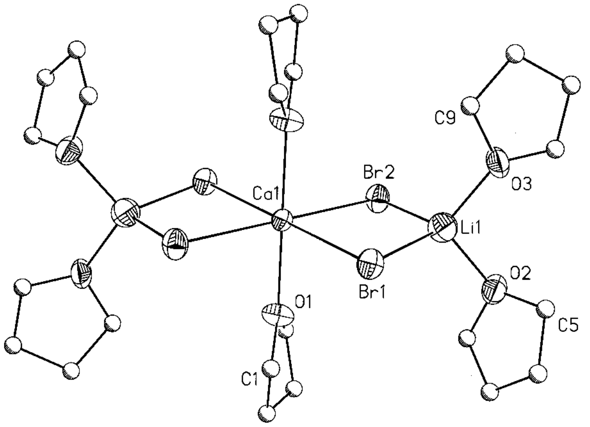

Figure 4. Computer-generated plot of **4**. Hydrogen atoms are omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for [CaBr$_4$(THF)$_2$(μ^2-Li)$_2$(THF)$_4$], 4

Ca(1)−Br(1)	2.895(2)	Ca(1)−Br(2)	2.883(2)
Ca(1)−O(1)	2.368(10)		
Li(1)−O(2)	1.93(3)	Li(1)−O(3)	1.95(3)
Li(1)−Br(1)	2.50(3)	Li(1)−Br(2)	2.50(3)
O(1)−Ca(1)−O(1)#1	180.0	O(1)−Ca(1)−Br(2)	89.7(3)
O(1)−Ca(1)−Br(1)	88.0(3)	Br(2)−Ca(1)−Br(1)	86.31(5)
O(1)#1−Ca(1)−Br(2)	90.3(3)	O(1)#1−Ca(1)−Br(1)	92.0(3)
O(2)−Li(1)−O(3)	104(2)	O(2)−Li(1)−Br(2)	11(2)
O(3)−Li(1)−Br(2)	112.7(14)	O(2)−Li(1)−Br(1)	112(2)
O(3)−Li(1)−Br(1)	113(2)	Br(2)−Li(1)−Br(1)	104.6(11)
Li(1)−Br(1)−Ba(1)	84.2(8)	Li(1)−Br(2)−Ca(1)	84.4(7)

[CaBr$_4$(THF)$_2$(μ^2-Li)$_2$(THF)$_4$], 4. Compound **4**, depicted in Figure 4, displays an octahedrally coordinate calcium center ligated by four bromine atoms and two THF oxygen atoms. The THF molecules are located in trans or axial positions, while the four bromine atoms are placed in the equatorial positions. An inversion center at calcium generates two of four bromine atoms in addition to the second THF molecule. Two neighboring bromine atoms are doubly bridging to a lithium atom, such that a four-membered ring composed of calcium, two bromine, and one lithium atom is formed. In addition to being connected to two bromine atoms, each lithium atom is connected to two THF molecules. This results in a distorted tetrahedral coordination sphere at lithium, with angles ranging from 104(2) to 130.7(14)°. The calcium−bromine contacts are observed at 2.883(2) and 2.895(2) Å, while the calcium THF−oxygen distance is observed at 2.368(10) Å. The Li−Br bond lengths are exhibited at 2.50(3) Å, while the Li−O distances are observed at 1.93(3) and 1.95(3) Å.

[(NH$_4$)(py)(SC$_6$F$_5$)], 5. Compound **5**, shown in Figures 5 and 6 (see also Table 5), displays a two-dimensional infinite-sheetlike structure based on strong intramolecular interactions between [NH$_4$]$^+$ cations, [SC$_6$F$_5$]$^-$ anions, and pyridine donors. The four [NH$_4$]$^+$ hydrogen atoms, which have been located in difference Fourier maps, are hydrogen-bonded to three [SC$_6$F$_5$]$^-$ anions and one pyridine donor. Each [SC$_6$F$_5$]$^-$ anion is connected to three [NH$_4$]$^+$ cations. This arrangement results in a 1:1:1 stoichiometry of [NH$_4$]$^+$, [SC$_6$F$_5$]$^-$, and pyridine. N−H distances are observed in the range of 0.91(3)−1.00(4) Å, S−H contacts are found at 2.33(3)−2.38(3) Å, while the pyridine−hydrogen interaction is observed at 1.86(4) Å.

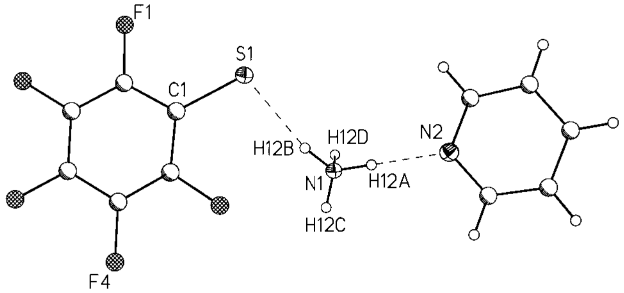

Figure 5. Computer-generated plot of the framework displayed in **5**, indicating hydrogen bonding.

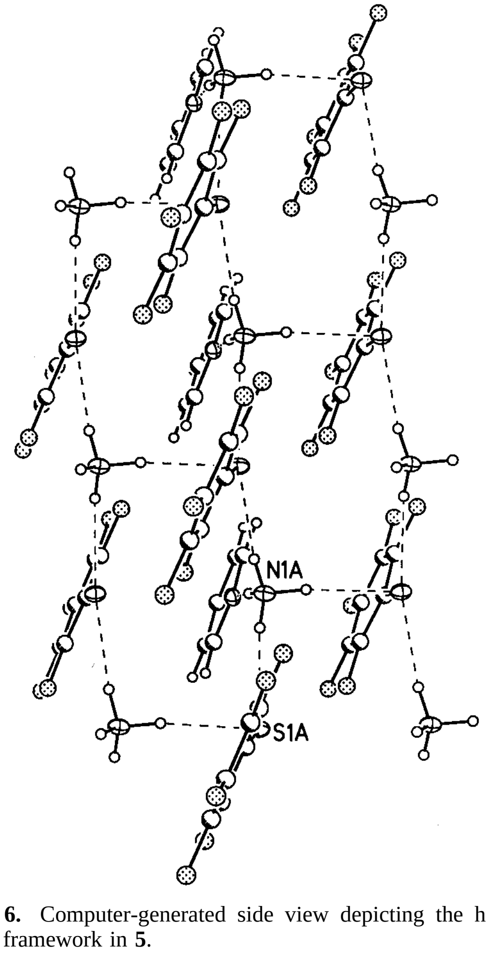

Figure 6. Computer-generated side view depicting the hydrogen-bonded framework in **5**.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $[(NH_4)(py)(SC_6F_5)]$, **5**

S(1)−C(1)	1.744(3)	N(1)−H(12C)	0.91(3)
N(1)−H(12B)	0.97(3)	N(1)−H(12A)	1.00(4)
N(1)−H(12D)	0.99(4)	N(2)−H(12A)	1.86(4)
S(1)−H(12B)	2.33(3)	S(1A)−H(12C)	2.38(3)
H(12C)−N(1)−H(12C)	118(3)	H(12C)−N(1)−H(12A)	113(3)
H(12B)−N(1)−H(12A)	111(3)	H(12C)−N(1)−H(12D)	104(3)
H(12B)−N(1)−H(12D)	102(3)	H(12A)−N(1)−H(12D)	109(3)

The commonly observed coordination geometry in calcium chalcogenolates seems to contain six or more ligands as observed in the monomeric octahedral pyridine adduct $[Ca(SC_6F_5)_2(py)_4]$, **1** (Figure 1), the previously described $[Ca(TeSi(SiMe_3)_3)_2(THF)_4]$,[18,19] the eight-coordinate [Ca(18-crown-6)(SMes*)$_2$]·2THF, **3** (Figure 3), and the nine-coordinate separate ion-triple [Ca(18-crown-6)$(NH_3)_3$][SMes*]$_2$·THF, **2** (Figure 2).

$[Ca(SC_6F_5)_2(py)_4]$ displays an octahedral coordination sphere. Two calcium−sulfur bonds (2.8493(4) Å) are observed in addition to four calcium−nitrogen linkages (2.502(2) and 2.534(2) Å). The Ca−S bond length is significantly shorter than in the previously mentioned calcium thiocarboxylates [Ca{(OCS)OMe}$_2$(MeOH)$_3$]$_2$,[13] and [Ca(SOCMe)$_2$(15-crown-5)][14] (2.92(5) and 2.961(2) Å), whose longer bonds are due to the higher coordination number of the metal center. As a lower limit for calcium thiolato bonding, the linear, two coordinate gas-phase species $[Ca(SH)_2]$ has a calculated Ca−S interaction of 2.650 Å.[43] This is a considerably shorter value than seen in the solid-state structure of **1**, however, it should be kept in mind that the calculated bond length reflects a two-coordinate metal center. The calcium−nitrogen distances in **1** compare favorably with the Ca−TMEDA nitrogen contacts in the metallocene [Ca(TMEDA){$(C_5H_4)C(Me)_2C(Me)_2(C_5H_4)$}] (2.503(6) and 2.564(6) Å).[44] The calcium−nitrogen and −sulfur interactions in **1** also compare well with the six-coordinate [Ca(OH)(SMes*)(PMDTA)]$_2$ (PMDTA = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine), available by chalcogenolysis of $[Ca(N(SiMe_3)_2)_2]_2$ with HSMes* in the presence of PMDTA followed by protonolysis with trace H_2O.[45] A comparison of structural features of **1** with those in the magnesium analogues $[Mg(SPh)_2(py)_4]$ and $[Mg(SC_6F_5)_2(py)_3]$[46] clearly indicates that the larger size of calcium allows for the accommodation of two pentafluorothiolate ligands in addition to four pyridine donors.

Use of 18-crown-6 in conjunction with the sterically demanding ligand SMes* leads to the isolation of [Ca(18-crown-6)(SMes*)$_2$], **3**, displaying an eight-coordinate calcium center with Ca−S distances of 2.775(3) and 2.851(2) Å. These interactions are quite comparable to the values seen in **1** and also with those in [Ca(OH)(SMes*)(PMDTA)]$_2$.[45] The calcium−oxygen (crown ether) bonds in **3** are observed over a fairly tight range (2.516(5)−2.624(5) Å) with the crown adopting a slightly ruffled orientation with maximum Ca−O displacements from the mean crown ether-calcium plane of −0.220 to +0.304 Å. Comparison of these values with free 18-crown-6 (−0.20 to +0.20 Å)[47] reveals an only modest distortion of the crown ether. The small deviations from planarity are due to steric interactions between the crown and the ortho *tert*-butyl substituents on the ligand. The correlation of Ca−S−C angles with Ca−S bond lengths supports this argument, since the wider Ca−S−C angle (154.0(3)°) coincides with the shorter Ca−S bond, and the narrower Ca−S−C angle (119.1(2)°) is associated with the longer Ca−S distance. The relatively short Ca−S bonds in **3** might be explained on the basis of relatively weak Ca−O crown ether interactions resulting in a reduced coordinative presence of the donor. This interpretation is supported by structural data observed for the thiocarboxylate [Ca(SOCMe)$_2$(15-crown-5)][13] where shorter Ca−O crown contacts (2.49(3) Å average) and, consequently, longer Ca−S bonds (2.92(5) and 2.961(2) Å) are observed. The calcium−sulfur bond lengths in compounds **1** and **3** agree well with the sum of ionic radii for six- or eight-coordinate Ca^{2+} and six-coordinate S^{2-} (2.84 and 2.96 Å).[48] The slightly longer experimental values may be explained by discrepancies in the coordination number for the S^{2-} ion and the thiolate ligands.

The separated ion-triple $[Ca(NH_3)_3$(18-crown-6)][SMes*]$_2$, **2**, was prepared analogous to **3**, with the exception that a room-temperature THF extraction was performed after the thiol reduction. Compound **2** features fully separated (more than 5 Å) cations and thiolate anions. The cation exhibits a nine-coordinate calcium center ligated by 18-crown-6, in addition to three NH_3 donors. The tight calcium−nitrogen distances (2.469(3)−2.541(2) Å) are in the same range as those observed for the lower coordinate **1**. Ammonia solvation of alkaline-earth metal cations is only now being described in the solid state, although it has been known for some time that solvent separated ammoniate complexes can form in analogy to alkaline-earth hydrates.[49] Recently, $[Mg(NH_3)_6][Mg(NH_3)_2(SC_6H_5)_3][Mg(NH_3)(SC_6H_5)_3]$[38] and $[Sr(NH_3)_8][HP_{11}]$[50] have been identified crystallographically, and the calcium derivative $[Ca(NH_3)_8][PH_2]_2$ was also mentioned, although no detailed information was given.[50] The NH_3 donors can be removed by a short exposure of **2** to vacuum, or by extraction in hot solvent, as evidenced by IR and NMR spectroscopic analyses. An equilibrium between **2** and **3** is apparent: exposure of **3** to anhydrous NH_3 yields **2**, which again can be transformed into **3** by vacuum or hot extraction.

The calcium−oxygen crown ether distances in compound **2** vary significantly from 2.421(3) to 2.964(3) Å, indicating an asymmetric location of calcium within the crown ether. Much tighter Ca−O distances are observed in $[Ca(OH_2)_3$(15-crown-5)]$[UO_2Cl_4]$,[51] with the smaller size of the crown resulting in the placement of calcium above the plane of the crown oxygen atoms, and Ca−O distances between 2.45(1) and 2.57(1) Å. Three water molecules located on the opposite face of the crown complete the coordination sphere at calcium.

The comparison of carbon−sulfur bond lengths in **2** (1.761(4) and 1.775(4) Å) and **3** (1.785(7) and 1.764(7) Å) indicates no trend indicating an increased bond order between carbon and sulfur in the separated species **2**. In addition, no indication of delocalization of electron density into the phenyl ligand is observed. The slightly shorter C−S distances in **2** seems to be solely due to the reduced coordination number at sulfur.

The facile formation of separated ion triples underscores the high ionic character and weak nature of the Ca−S bond. This argument is further supported by calculation by Pappas,[43]

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experimental work by Mingos et al. and results presented herein, generally indicating long, weak calcium−sulfur bonds.[12]

Conclusions

The evaluation of synthetic protocols for the synthesis of alkaline-earth chalcogenolates allowed the preparation and structural characterization of the first calcium thiolates. The three main synthetic routes, metalation, chalcogenolysis, and salt elimination offer advantages, as well as drawbacks which have to be considered in each individual case. For example, use of a highly acidic arylthiol is problematic in both metalation and chalcogenolysis, since either protonation of the resulting amine and the subsequent formation of thioether, or protonation of the solvent NH_3 and consequent formation of ammonium salts are likely. If, however, sterically demanding ligands are employed, protonation of the resulting amine seems not to be a significant factor. Salt elimination is difficult in any case, partly caused by the insufficient solubility of the alkaline-earth chlorides and bromides and the necessity to use the iodides, often causing difficulties in regard to alkali halide precipitation.

The coordination about calcium seems to favor a coordination environment of six or more, even if sterically demanding ligands are utilized. The good agreement of calcium−sulfur bond lengths with the sum of ionic radii and the facile formation of separated ion complexes supports our view that the calcium−sulfur bonds are weak and predominantly ionic, explaining in part the synthetic difficulties encountered in calcium thiolate chemistry.

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Supporting Information Available: X-ray crystallographic files, in CIF, format for the structure determinations of **1**−**5** are available on the Internet only. Access information is given on any current masthead page.

Note Added in Proof

After submission of this manuscript we became aware of two structurally characterized calcium dithiocarbamates displaying Ca−S bonds.[52]

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(52) Purdy, A. P.; George, C. F. *Main Group Chem.* **1996**, *1*, 229.