Experimental Section

[Mn(cth)Cl$_2$] was prepared from [(NEt$_4$)$_2$MnCl$_4$] (5 mmol) and cth (6 mmol) in acetonitrile (30 mL). The reaction between dtbcat (1 mmol) and [Mn(cth)Cl$_2$] (1 equiv) in basic methanol (30 mL) under inert atmosphere gave [Mn(cth)(dtbcat)]. Crystals of **1** were obtained by adding an aereated solution of NaBPh$_4$ in methanol, and **2** by adding an aqueous solution of NaClO$_4$. The inert atmosphere was removed and the resulting suspensions were stirred for 1 h at room temperature. Complexes **1** and **2** were obtained in 80 and 70 % yield, respectively.

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[6] Crystal data for **1**: $MnBC_{55.5}H_{72}N_4O_{3.5}$, $M_r = 916.92$, $Mo_{K\alpha}$ radiation $\lambda = 0.71069$ Å, crystal dimensions 0.3 × 0.2 × 0.5 mm, triclinic, space group $P\bar{1}$ (no. 2), $a = 11.225(2)$, $b = 11.545(1)$, $c = 21.800(2)$ Å, $\alpha = 83.64(1)$, $\beta = 77.78(1)$, $\gamma = 76.99(1)°$, $Z = 2$, $V = 2684(2)$ Å^3, $\rho_{calcd} = 1.134$ g cm^{-3}. Of 5346 reflections collected at 293 K, 5021 were unique and observed. Final R values ($I > 2\sigma I$): $R1 = 0.0663$, $wR2 = 0.1715$. Hydrogen atoms were treated as fixed contributions in calculated positions with isotropic thermal parameters $B(H) = 1.2\, B_{eq}(C)$. An absorption correction based on a ψ scan was performed, and no decay was observed. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100691. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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A Novel Beryllium Thiolate Resulting from N–Si Bond Cleavage: Liberation of Ammonia in the Reaction of Be[N(SiMe$_3$)$_2$]$_2$ with HSPh[**]

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In the course of our investigations into the synthesis and solid-state structures of alkaline earth metal thiolates, we have used the bis(trimethylsilyl)amides of beryllium, magnesium, and calcium as hydrocarbon-soluble metalating agents.[1] We anticipated clean metathesis reactions between the metal amide and arenethiols with formation of the amine HN(SiMe$_3$)$_2$. Here we present results that indicate competitive acid/base reactions between hexamethyldisilazane and unchanged thiol in the reaction of [Be{N(SiMe$_3$)$_2$}$_2$] with stoichiometric amounts of HSPh in the presence of Lewis bases.

The chemistry of the beryllium–oxygen bond is by far the most extensively studied interaction between beryllium and another element.[2] In contrast, information on beryllium thiolates is scarce. In the only crystallographically characterized homoleptic beryllium thiolate, the sterically demanding SMes* ligand (SMes* = S-2,4,6-*t*Bu$_3$C$_6$H$_2$) afforded the three-coordinate monomer [Be(thf)(SMes*)$_2$].[3] A three-coordinate monomeric structure was also identified in the mixed alkylberyllium thiolate [Be(2,6-Mes$_2$C$_6$H$_3$)(SMes*)(Et$_2$O)] (Mes = 2,4,6-Me$_3$C$_6$H$_2$), in which the metal center is also stabilized by bulky ligands.[4] A four-coordinate beryllium center was found in [Be(S$_2$CN*i*Pr$_2$)$_2$], in which both dithiocarbamato ligands chelate the cation through the two thiolato groups.[5] Finally, a small family of alkylberyllium thiolate compounds have been shown by ^{1}H NMR spectroscopy and cryoscopic measurements to exist as monomeric or oligomeric complexes, depending on the combination of ligands and donor, although detailed structural data are not available.[6] Here we report the synthesis and characterization of the novel, ammonia-coordinated, crown ether templated beryllium thiolate [{Be(SPh)$_2$(py)(NH$_3$)}$_2${[18]crown-6}] · 2 C$_7$H$_8$ (**1**; py = pyridine), which is formed by a sequence of acid-promoted N–Si bond cleavage reactions and in situ trapping of the liberated ammonia.

The reaction of [Be{N(SiMe$_3$)$_2$}$_2$][7] with two equivalents of HSPh in toluene in the presence of [18]crown-6 gave a thick, white suspension; addition of one equivalent of pyridine generated a homogenous solution,[8] from which **1** was obtained as colorless crystals, which were analyzed by single-crystal X-ray diffraction. The identity of **1** was also

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confirmed by NMR and IR spectroscopy. The NH stretching frequency of 3302 cm^{-1} in the IR spectrum is similar to those of [Be{OC(CF$_3$)$_3$}$_2$(NH$_3$)$_2$].[9] Compound **1** consists of two beryllium thiolate moieties that are associated with an [18]crown-6 molecule through ammonia molecules (Figure 1). The {Be(SPh)$_2$(py)(NH$_3$)} units are located on opposite faces of the crown ether, each with three N–H ⋯ O hydrogen bonds to alternate oxygen atoms. The H ⋯ O distances lie in the range of 2.20(1) – 2.31(1) Å, in agreement with data for related transition metal complexes.[10] The coordination environment at each beryllium center is distorted tetrahedral with bond angles from 99.7(2) to 125.2(3)°. The Be–S distances range between 2.086(3) and 2.103(3) Å. These are somewhat longer than those at the three-coordinate Be centers in [Be(thf)(SMes*)$_2$] (1.987(8) and 1.991(7) Å), which can be attributed to the higher coordination number of Be in **1**. Regarding the Be–N distances, the cation – ammonia bonds (1.724(4) and 1.731(4) Å) are marginally shorter than the cation – pyridine interactions (1.779(4) and 1.778(4) Å).

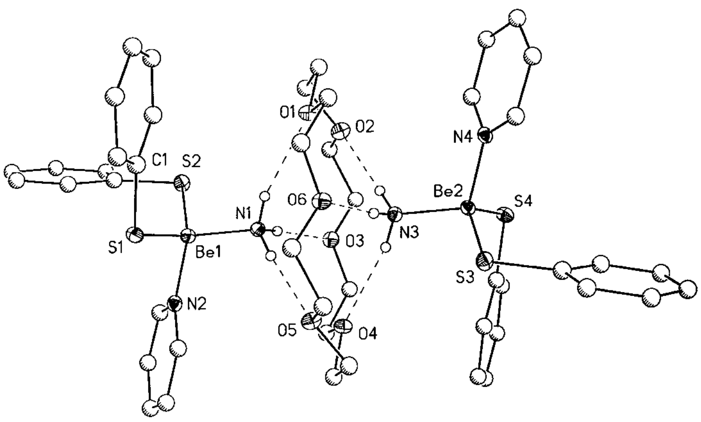
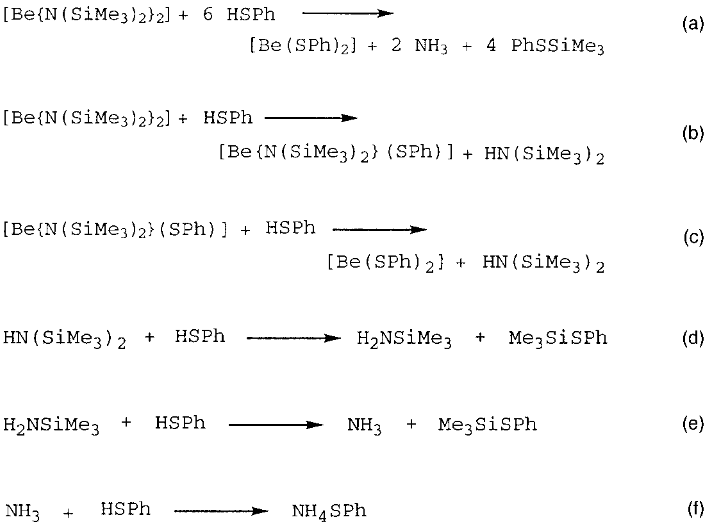


Figure 1. Structure of **1** (30 % probability ellipsoids). For clarity, hydrogen atoms other than those of the two ammonia moieties have been omitted. Selected bond lengths [Å] and angles [°]: Be1–S1 2.103(3), Be1–S2 2.095(3), Be1–N1 1.724(4), Be1–N2 1.779(4), Be2–S3 2.086(3), Be2–S4 2.100(3), Be2–N3 1.731(4), Be2–N4 1.778(4), S1–C1 1.770(2), S2–C7 1.771(3), S3–C18 1.764(3), S4–C24 1.768(2); S1-Be1-S2 124.6(2), N1-Be1-N2 108.8(2), S3-Be2-S4 125.2(2), N3-Be2-N4 107.9(2).

Completely unexpected in the reaction of [Be{N(SiMe$_3$)$_2$}$_2$] with two molar equivalents of HSPh was the formation and trapping of one NH$_3$ molecule per cationic center. The coordination of nascent donors has been observed in [Zn{Se-2,4,6-(CF$_3$)$_3$C$_6$H$_2$}{HN(SiMe$_3$)$_2$}], [Sr(μ-SCEt$_3$)(NH$_3$)(py)]$_\infty$, and [Li$_6$(HNMe$_2$)$_6${Sb(PCy)$_3$}$_2$] · 2 C$_7$H$_8$ (Cy = cyclohexyl).[11–13] Here the in situ coordination of gaseous nitrogen compounds in the strontium thiolate (ammonia) and the lithium complex (dimethylamine) is noteworthy.

Protonolysis products, such as ammonia-coordinated lanthanides [M{OCH(CF$_3$)$_2$}$_3$(NH$_3$)$_2$] (M = Sc, Pr)[14] were identified in metathesis reactions of lanthanide bis(trimethylsilyl)amide with a large excess of acid. In contrast, if stoichiometric amounts of reagents are utilized, protonolysis of the liberated amine with formation of NH$_3$ is generally not observed. In many cases, the NH$_3$ complexes were initially regarded as accidental hydrolysis products.[15] We now have conclusive evidence for a competitive protonolysis reaction that occurs when stoichiometric amounts of acid and base are combined and the initially formed HN(SiMe$_3$)$_2$ reacts competitively with remaining thiol (Scheme 1).



Scheme 1. Reaction of [Be{N(SiMe$_3$)$_2$}$_2$] with HSPh [Eq. (a)]. The individual reacions (b) – (f) emphasize the acid-promoted cleavage of the N–Si bond in HN(SiMe$_3$)$_2$.

In the first protonation step, [Be{N(SiMe$_3$)$_2$}$_2$] and HSPh react to form the mixed beryllium amide thiolate [Be{N(SiMe$_3$)$_2$}(SPh)]. This intermediate can react with a second equivalent of thiol or disproportionate to produce the dithiolate [Be(SPh)$_2$]. The primary amine H$_2$NSiMe$_3$, NH$_3$, and the ammonium salt [(NH$_4$)(SPh)]$_\infty$ are thought to form by sequential protonation reactions between the initially liberated hexamethyldisilazane and thiol. Further evidence for this sequence is provided by the isolation of [Be(SC$_6$F$_5$)$_2$(NH$_3$)(NH$_2$SiMe$_3$)] from the reaction of [Be{N(SiMe$_3$)$_2$}$_2$] with two equivalents of HSC$_6$F$_5$ in toluene. Remarkably, two protonolysis products, H$_2$NSiMe$_3$ and NH$_3$ are coordinated to the beryllium center.[16] If an excess of thiol in pyridine is used, quantitative formation of the ammonium salt [(NH$_4$)(SC$_6$F$_5$)py]$_\infty$ is observed.[1c] We therefore assume that protonolysis competes with the desired metathesis reaction of beryllium bis(trimethylsilyl)amide and benzenethiol. It is noteworthy that **1** crystallizes reproducibly from the complex mixture of [Be{(SiMe$_3$)$_2$}$_2$], [Be{N(SiMe$_3$)$_2$}(SPh)], [Be(SPh)$_2$], PhSSiMe$_3$, HN(SiMe$_3$)$_2$, H$_2$NSiMe$_3$, NH$_3$, and [(NH$_4$)(SPh)]$_\infty$.[17]

The identification of **1** provides evidence for acid-promoted N–Si bond cleavage in the reaction of [Be{N(SiMe$_3$)$_2$}$_2$] with HSPh. In light of the widespread use of metal bis(trimethylsilyl)amides, this protonolysis is of general interest. For example, we have gathered preliminary evidence that a competitive protonolysis of the N–Si bond also occurs in the reaction of heavier alkaline earth metal bis(trimethylsilyl)amides with arenethiols.

Experimental Section

All reactions were performed under a purified nitrogen atmosphere by modified Schlenk techniques or in a dry box (Braun Labmaster 150).

Toluene was distilled from a Na/K alloy and degassed. [Be{N(SiMe$_3$)$_2$}$_2$] was prepared according to a known procedure.[7] **Caution**: [Be{N(SiMe$_3$)$_2$}$_2$] is a known carcinogen and should be handled only in a well-ventilated fume hood with proper precautions. Benzenethiol was dried over activated 4-Å molecular sieves. [18]Crown-6 was dissolved in hexane, and freshly cut potassium was added. The mixture was briefly heated to reflux, and the remaining potassium removed by filtration. The dried crown ether was isolated by crystallization from hexane.

1: HSPh (0.21 mL, 2.0 mmol) was added dropwise to [Be{N(SiMe$_3$)$_2$}$_2$] (0.33 g, 1.0 mmol) and [18]crown-6 (0.26 g, 1.0 mmol) in toluene (20 mL) at room temperature. A heavy white precipitate formed after stirring for several minutes. Pyridine (0.1 mL, 1.2 mmol) was added dropwise, and a homogeneous light yellow solution was obtained. After the mixture had been stirred at room temperature for 30 min, it was filtered through a Celite-loaded frit and stored at 0 °C. Colorless plates gradually grew over several days, and 0.20 g (55 % yield) were collected from the first crystallization.[17] The white powder shrank slightly when heated above 80 °C and then irreversibly melted to a yellow oil in the range of 145 – 153 °C. ^{1}H NMR (300 MHz, 25 °C, [D$_8$]THF): $\delta = 8.54 - 6.71$ (broad overlapping signals, 40 H), 3.52 (s, 24 H), 2.31 (s, 6 H); IR (Nujol): $\tilde{\nu} = 3302$ m, 3197 m, 3043 w, 2926 s, 1643 m, 1610 m, 1576 s, 1463 s, 1377 m, 1352 m, 1317 s, 1286 m, 1216 m, 1137 m, 1105 s, 1070 m, 1050 m, 956 s, 837 m, 785 m, 743 s, 696 s, 648 w, 580 m, 478 cm^{-1} m.

Crystal structure data for **1**: $C_{60}H_{76}Be_2N_4O_6S_4$, $M_r = 1095.51$, triclinic, space group $P\bar{1}$, $a = 10.432(2)$, $b = 13.5950(3)$, $c = 22.0275(4)$ Å, $\alpha = 79.374(1)$, $\beta = 77.760(1)$, $\gamma = 87.160°$, $V = 3000.5(1)$ Å^3, $T = 150$ K, $Z = 2$, $\mu(\mathrm{Mo_{K\alpha}}) = 0.210$, crystal dimensions $0.42 \times 0.20 \times 0.20$ mm. Of 12886 independent reflections collected ($2.56 \leq 2\theta \leq 56.00°$) on a Siemens SMART system with a three-circle goniometer and a CCD detector operating at −54 °C, 8176 were observed ($I > 2\sigma(I)$). Crystal decay was monitored by repeating a set of initial frames at the end of data collection and comparing the duplicate reflections; no decay was observed. An absorption correction was applied with the program SADABS.[18] The crystal structure was solved by direct methods with SHELXTL. Missing atoms were located in subsequent difference Fourier maps and included in the refinement. The structure of **1** was refined by full-matrix least-squares refinement on F^2.[19] Hydrogen atoms with the exception of the NH protons were placed geometrically and refined by using a riding model with U_{iso} constrained at 1.2 U_{eq} of the carrier C atom. All non-hydrogen atoms were refined anisotropically. NH$_3$ hydrogen atoms were located in difference maps and included in the refinement by using distance restraints. A center of symmetry, suspected in the center of the crown ether molecule could not be confirmed even after various symmetry checks and transformation of the suspected inversion center to the origin of the unit cell. The absence of significant correlations also confirms the correct symmetry. $R_1 = 0.0575$ for data with $I > 2\sigma(I)$, and $wR_2 = 0.1234$ for all data. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101292. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[16] [Be(SC$_6$F$_5$)$_2$(NH$_3$)(H$_2$NSiMe$_3$)] was synthesized by treatment of [Be{N(SiMe$_3$)$_2$}$_2$] with two equivalents of HSC$_6$F$_5$ in toluene. The resulting colorless crystals were analyzed crystallographically. However, further spectroscopic analysis was not possible due to rapid decomposition of the sample. We were unable, even after several attempts, to trap the intermediate and obtain spectroscopic data. S. Chadwick, K. Ruhlandt-Senge, unpublished results.

[17] The maximum theoretical yield of this reaction is 66 % taking into account the 1:1 ratio of [Be(SC$_6$H$_5$)$_2$] and NH$_3$ in the final product. Accordingly, the experimental yield was 55 %. Since the limiting reagent in this reaction is HSC$_6$H$_5$, the reaction was repeated with six equivalents of HSC$_6$H$_5$, as indicated in Scheme 1. Instead of isolating an increased amount of **1**, only $[(NH_4)(SC_6H_5)(py)]_\infty$ was identified in the solid state.

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First Synthetic Carbohydrates with the Full Anticoagulant Properties of Heparin[**]

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Heparin, a major drug for the prevention and treatment of cardiovascular diseases, exerts its activity through activation of the serine proteinase inhibitor antithrombin III (AT III), the main physiological inhibitor of blood coagulation.[1, 2] A unique pentasaccharide sequence[3] in the polysaccharide binds to the protein in a highly specific way, inducing a

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