Communication
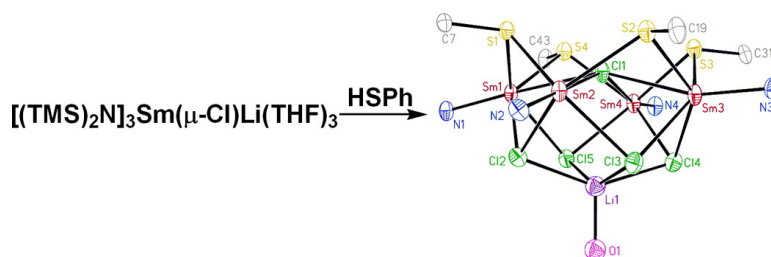
Construction of Polymeric and Oligomeric Lanthanide(III) Thiolates from Preformed Complexes [(TMS)N]Ln(☐-Cl)Li(THF) (Ln = Pr, Nd, Sm; (TMS)N = Bis(trimethylsilyl)amide)

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Construction of Polymeric and Oligomeric Lanthanide(III) Thiolates from Preformed Complexes [(TMS)₂N]₃Ln(μ-Cl)Li(THF)₃ (Ln = Pr, Nd, Sm; (TMS)₂N = Bis(trimethylsilyl)amide)

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As in past decades, much interest in lanthanide thiolates continues to be motivated by their chemistry[1] and their potential applications in advanced materials[2] and catalysis.[3] Several synthetic approaches to lanthanide thiolates, including metathesis of a lanthanide halide with an alkali metal thiolate,[4] oxidative addition of organic disulfide RSSR to lanthanide(II) complexes[5] or lanthanide metals under the presence of catalyst,[6] and the reactions of lanthanide thiolates with elemental sulfur,[7] have been developed. However, an additional approach, protonolysis of preformed lanthanide complexes with thiols,[8] has been less explored for synthesizing polymeric or oligomeric lanthanide thiolate complexes. Lanthanide tri(dimethylsilyl)amide complexes, [Ln(N(TMS)₂)₃], could serve as suitable precursors for such a protonolysis since thiol has an acidity stronger than that of HN(TMS)₂ and may protonate and remove the (TMS)₂N⁻ anion ligated on Ln centers.[8] For example, the rare earth complex [Yb(N(TMS)₂)₂] can be acidified with 2 equiv of HSC₆H₂-Buᵗ₃-2,4,6 to form [Yb(SC₆H₂Buᵗ₃-2,4,6)₂].[8b] Intriguingly, treatment of [Ln(N(TMS)₂)₃] with high concentrations of BuᵗSH (3 equiv) led to the rapid formation of insoluble lanthanide thiolate polymeric material.[8d] Previously, the ways to tackle this problem were to use a low concentration of BuᵗSH (1 equiv) at lower temperature,[4a] to dissolve the insoluble material into strong donor solvents,[8d] to directly use very bulky thiol (e.g., HSC₆H₂Buᵗ₃-2,4,6[8b] or HESi-(TMS)₃ (E = Se, Te)),[9a,b] or to use slightly excess thiol plus noncoordinating tertiary amine in aprotic solvents.[9c]

During the process of the construction of oligomeric and polymeric metal sulfide compounds from preformed metal clusters, we found that added lithium chloride may play a critical role in the construction of aggregated clusters.[10] The incorporation of Li⁺ or Cl⁻ ions into the resulting compound may change its charge and thus enhance its solubility in solution. Therefore, it may produce new soluble lanthanide thiolate compounds if LiCl is also introduced into [Ln(N(TMS)₂)₃]. In this context, we deliberately chose the known lanthanide amide complexes containing a bridging Cl⁻ and a [Li(THF)₃]⁺ unit, [(TMS)₂N]₃Ln(μ-Cl)Li(THF)₃ (Ln = Pr (**1**), Nd (**2**), and Sm (**3**)) for their protonolysis via thiol. When **1**−**3** were treated with equimolar benzenthiol, three different soluble Ln−thiolate complexes, [{(TMS)₂N}₂(μ-SPh)Pr(μ-SPh)Li(THF)₂]∞ (**4**), Li[{(TMS)₂N}₄(μ₄-Cl)Nd₄(μ-SPh)₈]·C₆H₆ (**5·C₆H₆**), and [{(TMS)₂N}₄-(μ₄-Cl)Sm₄(μ-SPh)₄(μ₃-Cl)₄Li(THF)] (**6**), were successfully isolated. In this communication, we report their synthesis, characterization, and catalytic property for the ring-opening polymerization (ROP) of ε-caprolactone.

Treatment of **1** in THF with equimolar HSPh in *n*-hexane resulted in a clear solution, from which a standard workup produced colorless crystals of **4** in 23% yield along with a byproduct, [{((Me₃-
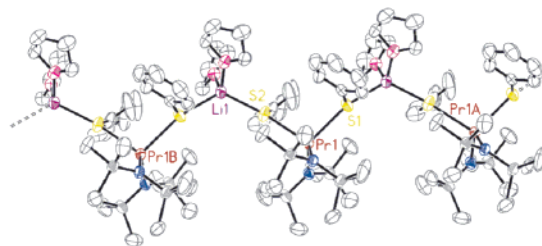
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Figure 1. Perspective view of a section of the polymeric chain of **4** with labeling scheme and 50% probability. All hydrogen atoms are omitted for clarity.

Si)₂N)₂Pr(μ′-Cl)Li(THF)₃}(μ-Cl)]₂ (**7**), in 11% yield. The similar reaction of **2** with equimolar HSPh, followed by a similar workup, gave rise to an anionic tetranuclear cluster, **5·C₆H₆** (39% yield), mixed with the unreacted precursor **2**. Intriguingly, the analogous reaction of **3** with equimolar HSPh generated a neutral tetranuclear cluster **6** in 30% yield coupled with a side-product, [{(((TMS)₂N)₂Sm-(μ′-Cl)Li(THF)₂}(μ₃-Cl)]₂ (**8**) (9% yield)[11] (see Supporting Information). As discussed below in this paper, the Li⁺ and/or Cl⁻ were incorporated into the polymeric backbone or cluster frameworks, which guarantee the formation of the soluble compounds **4**−**6**. However, when **1**−**3** were treated with 2 equiv of HSPh, the unidentified oily materials were always observed. Attempts to synthesize late lanthanide (e.g., Yb) thiolate complexes from the [{(TMS)₂N}₃Yb(μ-Cl)Li(THF)₃]/HSPh reaction system always led to the formation of an unidentified red oily material, which may be due to the smaller ionic radii of Yb³⁺. Fortunately, **4**−**6** were successfully characterized by elemental, IR, and X-ray single-crystal analysis.

An X-ray analysis[11a] revealed that **4** has an interesting 1D wavelike chain structure in which the two ((TMS)₂N)₂Pr⁺ and Li-(THF)₂⁺ units are alternatively bridged by SPh groups along the crystallographic *a* axis (Figure 1). There are no other apparent interactions between the chains. In the structure of **4**, each Pr atom is tetrahedrally coordinated by two S and two N atoms, while Li ions also show a normal tetrahedral coordination geometry with two μ-SPh and two THF molecules. On the other hand, the structure of the cluster anion of **5** can be viewed as a cyclic tetramer of a square array of Nd(III) ions with a Cl⁻ ligand capping slightly above the Nd₄ plane (Figure 2).[11b] Alternatively, the anion is composed of a starlike {((TMS)N)₂Nd}₄(μ-Cl) unit connected by four pairs of bridging SPh groups, forming a "four-flier pinwheel" structure with an approximate S₄ symmetry. Each Nd atom in **5** is coordinated by one Cl atom, one N atom, and four S atoms, forming a distorted octahedral coordination geometry. The structure of the square Nd₄ array resembles that of (THF)₆Yb₄I₂(μ-η²:η²-S₂)₄(μ₄-S),[7a] which contains a square array of seven coordinate Yb(III) ions connected
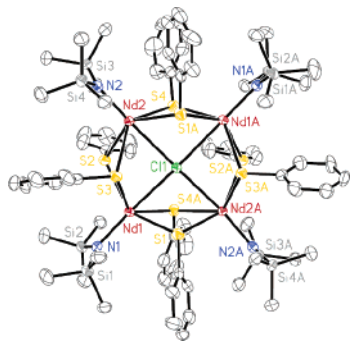
Figure 2. Perspective view of the anion of **5** with labeling scheme and 50% probability. All hydrogen atoms are omitted for clarity.
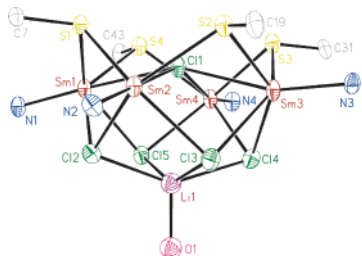

Figure 3. Molecular structure of **6** with labeling scheme and 50% probability. The TMS, Ph groups, and all hydrogen atoms are omitted for clarity.

to adjacent metals by a μ-η^2:η^2-S_2 ligand, with a single S^{2-} ligand capping the Yb_4 plane.

As shown in Figure 3, **6** may be viewed as having a wine-cup-shaped structure in which a $\{(TMS)_2NSm\}_4(\mu_4\text{-Cl})(\mu\text{-SPh})_4$ unit and Li atom are bridged by four μ_3-Cl bridges.[11c] The five metals may form a Sm_4Li square pyramidal framework in which the four Sm atoms occupy the four basal sites and one Li atom locates at the apical position. A four-fold crystallographic axis passes through the apical lithium atom and the center of the square pyramid base. Each basal Sm atom in **6** is octahedrally bound by a μ_4-Cl, two μ_3-Cl, one N(TMS)$_2$, and two μ-SPh ligands, while the apical Li atom is square-pyramidally coordinated by four μ_3-Cl and one O atom from a THF molecule. The μ_4-Cl atom occupies a position in which it interacts with all four Sm atoms over the Sm_4 plane, while each μ_3-Cl spans one of four triangular $LiSm_2$ faces of the Sm_4Li square pyramidal core.

It is noted that weak coordination of soft base sulfur at a hard acidic Ln center may influence the catalytic behavior of lanthanide thiolate complexes.[3a] In this regard, the catalytic properties of **4**–**6** deserve comment. It was found that compounds **4**–**6** initiated the ROP of ϵ-caprolactone at room temperature to give relatively high molecular weight polymers ($M_n > 22\,000$) with narrow molecular weight distributions ($M_w/M_n = 1.34$–1.53) in good yields within a few minutes, and that the activity of **5** or **6** was higher than that of **4** (see Supporting Information). Comparative runs with **1**–**3** and their mono- or disubstituted silylamido complexes of lanthanides[12] showed that **4**–**6** initiated faster polymerization and produced poly-(ϵ-caprolactone) with narrower molecular weight distribution. The reason may be ascribed to the clusterings and the more facile dissociation of SPh$^-$ from the Ln centers.[3]

In conclusion, the present work demonstrates that the introduction of Li$^+$ and Cl$^-$ ions into lanthanide amide complexes (**1**–**3**) afforded three unprecedented Ln–thiolate compounds (**4**–**6**) when treated with a low concentration of benzenthiol. It is anticipated that the synthetic methodology may be applied to other Ln–amide compounds to yield previously unknown species with better catalytic activities. Studies on these respects are underway in our laboratory.

Supporting Information Available: Crystallographic data for **4**–**8** (CIF); synthesis and polymerization details (PDF). This material is available free of charge via the Internet at http:// pubs.acs.org.

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(11) Crystal data for **4**: triclinic, space group $P\bar{1}$, $a = 8.693(2)$ Å, $b = 11.595$-(3) Å, $c = 22.719(6)$ Å, $\alpha = 103.694(6)°$, $\beta = 95.940(6)°$, $\gamma = 90.653$-(5)°, $V = 2211.4(10)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.248$ g/cm^3, μ(Mo Kα) = 1.331 cm^{-1}, $T = 193$ K, $R = 0.065$, $R_w = 0.078$, GOF = 1.007. (b) Crystal data for **5**: monoclinic, space group $C2/c$, $a = 18.305(2)$ Å, $b = 24.227$-(2) Å, $c = 24.326(3)$ Å, $\beta = 98.520(3)°$, $V = 10669.3(19)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.337$ g/cm^3, μ(Mo Kα) = 2.221 cm^{-1}, $T = 193$ K, $R = 0.052$, $R_w = 0.056$, GOF = 1.003. (c) Crystal data for **6**: triclinic, space group $P1$, $a = 13.7062(11)$ Å, $b = 17.0964(13)$ Å, $c = 19.882(2)$ Å, $\alpha = 75.817$-(4)°, $\beta = 83.698(5)°$, $\gamma = 77.496(4)°$, $V = 4401.8(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.461$ g/cm^3, μ(Mo Kα) = 3.016 cm^{-1}, $T = 193$ K, $R = 0.050$, $R_w = 0.065$, GOF = 1.055.

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