

Cubic lanthanide sulfido clusters: $\text{Ln}_8\text{S}_6(\text{SPh})_{12}(\text{thf})_8$ ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Gd}$)

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Lanthanide thiolates react with elemental sulfur to give $\text{Ln}_8\text{S}_6(\text{SPh})_{12}(\text{thf})_8$ clusters in high yield.

Lanthanide thiolates $[\text{Ln}(\text{SPh})_3; \text{Ln} = \text{Pr}, \text{Nd}, \text{Gd}]$ react with elemental sulfur to give crystalline octametallic $\text{Ln}_8\text{S}_6(\text{SPh})_{12}(\text{thf})_8$ clusters in high yield.

Inorganic clusters are important synthetic targets because their unique physical properties provide insight into the relationships between molecular and solid state properties. Lanthanide (Ln)¹ clusters are scarcer than main group² or transition metal clusters,³ primarily because no general synthetic approach to such materials has as yet been identified. The recent explosion of interest in determining the properties of Ln thiolates (SR), selenolates (SeR), and tellurolates (TeR) has in effect created a wide variety of potential starting materials for cluster syntheses.^{1a,4} Relative to more conventional O, N, or C based anions, these singly charged, electropositive chalcogenolate ligands should be considerably more susceptible to displacement from Ln coordination spheres. Here we present an extremely general approach to the synthesis of lanthanide sulfido cluster materials: $\text{Ln}(\text{SPh})_3$ reacts with elemental sulfur to form thiolate capped lanthanide sulfide clusters in 40–60% isolated yields.

Addition of sulfur to a suspension of $\text{Ln}(\text{SPh})_3$ in thf results in the formation of a homogeneous solution that can be saturated by layering with hexane to give crystals of $\text{Ln}_8\text{S}_6(\text{SPh})_{12}(\text{thf})_8$ ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Gd}$) [eqn. (1)].[†]



The compounds were characterized by conventional methods and the Gd derivative (1) was also characterized by low

temperature single crystal X-ray diffraction.[‡] Unit cell data for the Pr and Nd compounds indicated that all three clusters are isostructural. The clusters (Fig. 1) contain a cube of Ln^{III} ions, with the six faces of the cube all capped with S^{2-} , and the 12 edges of the cube all spanned by μ -SPh. The cubic structure appears to be particularly stable: thus far, $\text{Ln}_8\text{S}_6(\text{SPh})_{12}(\text{thf})_8$ clusters[§] have crystallized in three distinct phases which differ in the amount of lattice thf present, and the related selenido cluster $\text{Sm}_8\text{Se}_6(\text{SePh})_{12}$ can be isolated in low yield from the thermal decomposition of $\text{Sm}(\text{SePh})_2$.^{1c} The isolation of a neutral cluster compound is an additional benefit of $\text{Ln}(\text{SR})_3$ starting materials: whereas in $\text{Ln}(\text{SeR})_3$ chemistry SeR abstraction by excess $\text{Hg}(\text{SeR})_2$ is a complicating side reaction,^{1c,5} in related thiolate work Ln–S bonds have yet to be cleaved by the addition of excess $\text{M}(\text{ER})_2$ ($\text{M} = \text{Zn}, \text{Cd}, \text{Hg}$),⁶ and so more rational syntheses are possible.

Thiolate displacement is clearly a general reaction that does not require a redox active metal. The reactivity can be understood in terms of ‘hard’, ionic metals preferentially binding harder, highly charged bases. The ability of S^{2-} to bridge four metals must also contribute significantly to the stability of the final product. To date, only the middle of the Ln series (Pr–Tb) have yielded crystalline sulfido clusters from thf solution. The earlier (La, Ce) and later (Dy–Yb) lanthanides also react with elemental sulfur, as judged by the solubilization of $\text{Ln}(\text{SPh})_3$, but these reactions precipitate microcrystalline materials from saturated thf solutions. Clusters of redox active Eu have also proven elusive. Solutions of europium(II) chalcogenoates in thf are colorless,^{4f,g} and so the dark red solution color that results from the addition of S to a suspension of $\text{Eu}(\text{SPh})_2$ in thf leads us to suggest that some form of Eu^{III} , with a visible $\text{S} \rightarrow \text{Eu}$ charge transfer absorption, is present in solution.

The facility with which lanthanide thiolates react with S–S bonds to form sulfido anions and PhSSPh at room temp. suggests the possibility that $\text{Ln}(\text{SR})_3$ compounds may be valuable reagents for doping Ln into sulfide matrices.^{7,8} Preliminary experiments indicate that reactions of $\text{Ln}(\text{ER})_3$ ($\text{E} = \text{S}, \text{Se}$) with elemental Se proceed similarly, and thus this is an extremely general synthetic route to lanthanide chalcogenide cluster compounds.

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Footnotes and References

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[†] Cluster synthesis: under nitrogen, Ln (2.42 mmol), PhSSPh (0.791 g, 3.62 mmol), and Hg (0.06 g, 0.3 mmol) were combined in thf (35 ml). The lightly colored solution was stirred for 1 d. Elemental sulfur was added (0.058 g, 1.8 mmol, 0.75 equiv. to Ln), and after 3 d the solution [yellow green (Gd), blue (Nd), blue green (Pr)] was filtered to remove a trace of black solid, and the filtrate was layered with hexane. Colorless (Gd), light blue (Nd), or light green (Pr) crystals of $\text{Ln}_8\text{S}_6(\text{SPh})_{12}(\text{thf})_8 \cdot 2.9\text{thf}$ were collected (0.44–0.57 g, yields range from 42 to 57% with longer saturation times giving larger yields). The compounds do not melt but begin turning yellow between 165 °C (Pr) and 175 °C (Gd). Upon isolation, the crystals lose thf and become amorphous within hours. Elemental analyses are consistent with the structure (less lattice thf) if the compound is analyzed immediately after isolation [e.g. Calc. for $\text{Pr}_8\text{S}_6(\text{SPh})_{12}(\text{thf})_8 \cdot \text{C}, 38.9; \text{H}, 3.90$. Found: C, 37.1; H, 3.80%], but the materials continue to lose coordinated thf upon standing

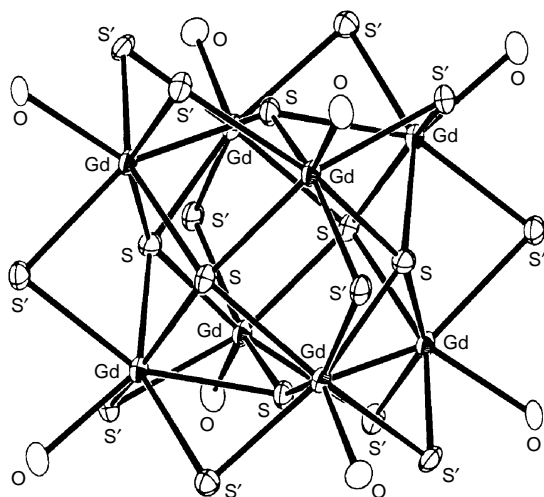


Fig. 1 Molecular structure of $\text{Gd}_8\text{S}_6(\text{SPh})_{12}(\text{thf})_8$ 1, with H and C atoms omitted for clarity. The unit cell contains two independent ‘half’ molecules that differ primarily in the orientation of the phenyl groups. The Gd– S^{2-} bond lengths range from 2.746(4) to 2.835(4) Å and average 2.80 Å, while the Gd–S(Ph) (labeled S’) bond lengths range from 2.794(4) to 2.881(4) Å, and average 2.84 Å. Thermal ellipsoids are shown at the 50% probability level. The analogous Pr and Nd clusters are isostructural with the Gd cluster.

at room temp. The IR and NMR spectra are essentially identical for all three compounds. ^1H NMR ($[\text{D}_2\text{H}_6]\text{thf}$) revealed only peaks due to displaced thf at δ 1.754(t) and 3.604(m). IR (KBr, Nujol): 3151w, 2923s, 2854s, 2724w, 2672w, 2199w, 2036w, 1947w, 1874w, 1813w, 1571m, 1461s, 1377s, 1305w, 1262w, 1169m, 1154m, 1113w, 1075m, 1022m, 973w, 917w, 863w, 803w, 736m, 724m, 691m, 662w, 481m cm^{-1} . Unit cell data (-120°C): Pr; triclinic space group $P\bar{1}$, $a = 17.661(5)$, $b = 18.297(5)$, $c = 20.490(5)$ Å, $\alpha = 102.84(2)$, $\beta = 94.56(2)$, $\gamma = 94.17(2)^\circ$, $U = 6407(3)$ Å³. Nd; triclinic space group $P\bar{1}$, $a = 17.632(4)$, $b = 18.236(3)$, $c = 20.441(2)$ Å, $\alpha = 102.92(1)$, $\beta = 94.65(2)$, $\gamma = 94.21(2)^\circ$; $U = 6357(2)$ Å³.

‡ Complex **1** crystallizes in the triclinic space group $P\bar{1}$, with $a = 17.513(4)$, $b = 18.136(4)$, $c = 20.382(4)$ Å, $\alpha = 102.94(2)$, $\beta = 94.39(2)^\circ$, $\gamma = 93.72(2)^\circ$, $U = 6268(3)$ Å³, $Z = 2$, $D_c = 1.878$ g cm^{-3} , (Mo-K α radiation at -120°C). Full-matrix least-squares refinement [8486 observations with $I > 2\sigma(I)$] gave $R(F) = 0.054$, $wR(F^2) = 0.115$. CCDC 182/621.

§ The terbium complex crystallizes in the monoclinic space group $C2/c$, with $a = 26.706(8)$, $b = 20.751(5)$, $c = 46.95(1)$ Å, $\beta = 90.21(2)^\circ$, $U = 26020(11)$ Å³. The Sm compound crystallizes from thf-dme in the tetragonal space group $I4/m$, with $a = 18.256(6)$, $c = 21.478(7)$ Å, and $U = 7158(4)$ Å³.

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