

Dithiocarbamate Precursors for Rare-Earth Sulfides

Michelle D. Regulacio, Neil Tomson, and Sarah L. Stoll*

Department of Chemistry, Georgetown University, Washington, DC 20057

Received December 15, 2004. Revised Manuscript Received March 22, 2005

We have synthesized a series of lanthanide dithiocarbamate precursors for the synthesis of lanthanide sulfide materials and nanoparticles. Three dithiocarbamate complexes with europium, $[\text{Eu}(\text{S}_2\text{CNR}'\text{L})_3]$, where L = 1,10-phenanthroline, and R = methyl, R' = ethyl (**1**), R = R' = *n*-Propyl (**2**), and R = R' = *i*-Butyl (**3**), as well as the lanthanide complexes, $[\text{Ln}(\text{S}_2\text{CNR}_2)_3 \text{L}]$, where R = ethyl, L = 1, 10-phenanthroline, and Ln = Nd (**4**), Sm (**5**), Gd (**6**), Ho (**7**), and Er (**8**), were synthesized and characterized by single-crystal X-ray diffraction, infrared, NMR, and UV–visible spectroscopy. We have used thermal analysis coupled with GC–MS and X-ray powder diffraction to determine the mechanism of decomposition. With R = Et, smaller Ln ions give lower precursor decomposition temperatures, consistent with the higher lattice energies of the product Ln sulfides. Because they are monomeric, and water- and air-stable, these compounds should be ideal precursors for forming LnS as nanoparticles and bulk materials.

Introduction

Recently, dithiocarbamate and xanthate metal complexes have been used to prepare nanoparticles and nanowires¹ of a variety of semiconducting materials including CdS and ZnS,² PbS,³ as well as Bi₂S₃.⁴ These complexes serve as air-stable, single-source precursors that can undergo solution thermolysis to form metal sulfide nanoparticles under mild conditions. This is in contrast to the more hazardous reagents commonly used to prepare nanoparticles (highly toxic, flammable precursors such as CdMe₂).⁵ In addition, the phase and morphology of the resultant materials are often influenced by the precursor (as well as by the solvent and thermolysis temperature).⁶

We are interested in determining the general utility of rare-earth (RE) dithiocarbamate precursors in the synthesis of RE sulfide materials and nanoparticles. To our knowledge, the only LnE (Ln = lanthanide, and E = O, S, Se, or Te) nanoparticles that have been prepared are of EuO and EuS. For example, by using europium metal dissolved in liquid ammonia, in the presence of either oxygen to form EuO or hydrogen sulfide to form EuS, uncapped nanoparticles have been synthesized.^{7,8} Alternatively, by using an unusual solution photoreduction of Eu(III), EuO nanoparticles with polyurea modified surfaces have also been synthesized.

Surface modification substantially influenced the luminescence and magneto-optical properties of these nanoparticles.⁹ We desire a more general route to preparing monodisperse, nonaggregated, capped lanthanide sulfide (LnS) nanoparticles from single-source precursors.

The europium chalcogenides EuE form one of the major classes of magnetic semiconductors.^{10,11} These binary europium chalcogenides have the rocksalt structure type, exhibit a variety of magnetic ordering, and have often served as model Heisenberg magnets.¹² These compounds were considered “thoroughly investigated” in a review over 30 years ago,¹³ yet, the europium chalcogenides continue to be of theoretical^{14–16} as well as experimental^{17–20} interest. In part, this is due to advances in theory and computation,²¹ but also because of the potential for EuS to act as a spin filter^{22–24}

* Corresponding author. Phone: (202) 687-5839. Fax: (202) 687-6209. E-mail: sls55@georgetown.edu.

- (1) Koh, Y. W.; Lai, C. S.; Du, A. Y.; Tiekink, E. R. T.; Loh, K. P. *Chem. Mater.* **2003**, *15*, 4544–4554.
- (2) Pradhan, N.; Efrima, S. *J. Am. Chem. Soc.* **2003**, *125*, 2050.
- (3) Trindade, T.; O'Brien, P.; Zhang, X.-M.; Motevalli, M. *J. Mater. Chem.* **1997**, *7*, 1011.
- (4) Monteiro, O. C.; Trindade, T.; Park, J.-H.; O'Brien, P. *Chem. Vap. Deposition* **2000**, *6*, 230.
- (5) Murray, C. B.; Norris, D. J.; Bwendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706.
- (6) Monteiro, O. C.; Nogueira, H. I. S.; Trindade, T. *Chem. Mater.* **2001**, *13*, 2103–2111.
- (7) Thongchant, S.; Hasegawa, Y.; Wada, Y.; Yanagida, S. *Chem. Lett.* **2001**, 1274.
- (8) Thongchant, S.; Hasegawa, Y.; Wada, Y.; Yanagida, S. *J. Phys. Chem. B* **2003**, *107*, 2193.

- (9) Hasegawa, Y.; Thongchant, S.; Wada, Y.; Tanaka, H.; Kawai, T.; Sakata, T.; Mori, H.; Yanagida, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2073.
- (10) Sato, K. In *Advances in Crystal Growth*; Sato, K., Furukawa, Y., Nakajima, K., Eds.; Elsevier: New York, 2001; Chapter 17, pp 303–320.
- (11) Wernick, J. H. In *Treatise on Solid State Chemistry, the Chemical Structure of Solids*; Hannay, N. B., Ed.; Plenum Press: New York, 1974; Vol. 1, pp 175–272.
- (12) Nolting, W. *J. Phys. C: Solid State Phys.* **1982**, *15*, 733–745.
- (13) Wachter, P. *Crit. Rev. Solid State Sci.* **1972**, *3*, 189–238.
- (14) Horn, M.; Strange, P.; Temmerman, W. M.; Szotek, Z.; Svane, A.; Winter, H. *Los Alamos National Laboratory, Preprint Archive, Condensed Matter*, 2004; pp 1–7.
- (15) Dietl, T. *Los Alamos National Laboratory, Preprint Archive, Condensed Matter*, 2004; pp 1–7.
- (16) Aripnammal, S.; Natarajan, S. *Mod. Phys. Lett. B* **2000**, *14*, 843–848.
- (17) Goncharenko, I. N.; Mirebeau, I.; Ochiai, A. *Hyperfine Interact.* **2000**, *128*, 225–244.
- (18) Sakalle, U. K.; Jha, P. K.; Sanyal, S. P. *Bull. Mater. Sci.* **2000**, *23*, 233–235.
- (19) Kasuya, T. *J. Magn. Magn. Mater.* **1999**, *195*, 141–147.
- (20) Gortitz, D.; Kotzler, J. *Eur. Phys. J. B* **1998**, *5*, 37–43.
- (21) Luo, Y.; Wan, X.; Ito, Y.; Takami, S.; Kubo, M.; Miyamoto, A. *Chem. Phys.* **2002**, *282*, 197–206.
- (22) Hao, X.; Moodera, J. S.; Meservey, R. *Phys. Rev. B* **1990**, *42*, 8235–8243.
- (23) Metzke, R.; Nolting, W. *Phys. Rev. B: Condens. Matter* **1998**, *58*, 8579–8589.

important in “spintronics”, devices that use the property of electron spin and charge.^{25,26} It is quite interesting to consider the effect of particle size on the magnetic properties of the europium chalcogenides. Pressure studies have shown that the Curie temperature (T_c) is very sensitive to both the Eu–Eu distance and the band gap energy,^{27,28} which should also be affected by particle size.

The LnE series of compounds have a variety of novel solid-state properties, which are governed by partial delocalization of f electrons, which are likely to be influenced by band gap tuning using particle size. The relative position of the 4f electrons varies for each lanthanide, resulting in a number of electronic and magnetic properties. Many of the compounds, particularly SmE, TmE, and YbE, have electronic properties that have been modeled theoretically^{29,30} and studied experimentally for the relationship between the electronic structure and the magnetic ordering and the question of valency in these compounds.^{31,32} These properties are very sensitive to band gap changes as a function of pressure,³³ but none have been studied as a function of particle size.

Previously, the series of complexes of general formula $\text{Ln}(\text{S}_2\text{CNEt}_2)_3\text{L}$ (L = 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen)) have been synthesized, and two structures ($\text{Eu}(\text{S}_2\text{CNEt}_2)_3\text{phen}$ and $\text{Eu}(\text{S}_2\text{CNMe}_2)_3\text{bpy}$) were reported.³⁴ The structures of the lanthanide dithiocarbamate complexes generally have very similar structure types, independent of the lanthanide or alkyl group,³⁵ or whether the tris ($[\text{Ln}(\text{S}_2\text{CNR}_2)_3]^-$) or tetrakis ($[\text{Ln}(\text{S}_2\text{CNR}_2)_4]^-$) compounds are formed.³⁶ In principle, these complexes may be of interest for thermal formation of nanoparticles; however, the tris complexes hydrolyze easily,³⁷ and we anticipate the ionic salts will be insoluble in the high boiling tri-octyl phosphine (TOP) solvents used in nanoparticle synthesis. These complexes have also been utilized for forming thin films of europium-doped II–VI materials of interest for electroluminescent devices; however, their utility for this purpose is

limited by the volatility of the complexes.^{38,39} While there are drawbacks to these precursors for use in CVD, the concept of a single-source precursor is easily adapted from this work. The lanthanide dithiocarbamates contain a core of the elements of interest for the materials synthesis, and the alkyl group is easily tailored for solubility. The main advantage of these complexes includes: simple structures and facile synthesis. Here, we describe a series of lanthanide dithiocarbamate complexes of general formula, $\text{Ln}(\text{S}_2\text{CNR}_2)_3\text{-phen}$, for Ln = Eu with R = a variety of alkyl groups and for R = ethyl for representative lanthanides across the series (Ln = Nd, Sm, Gd, Ho, Er). Our goal is to couple information regarding structure and bonding in these complexes (using single-crystal X-ray diffraction, infrared, UV–visible, and NMR spectroscopy) with the mechanism of thermolysis using X-ray powder diffraction and GC–MS. This information will be of importance in establishing the utility of these precursors for materials and nanoparticle synthesis.

Experimental Section

Carbon disulfide, tetramethylammonium hydroxide, 1,10-phenanthroline, diethylammonium diethyldithiocarbamate, ethylmethylamine, di-*n*-propylamine, di-*n*-butylamine, and the rare-earth salts (mostly nitrates) were purchased from Aldrich Chemical Co. and used as received. The dithiocarbamate ligands were prepared according to published procedures.⁴⁰ NMR spectra were recorded using a 300 MHz Bruker spectrometer, calibrated internally to residual solvent for ^1H in CDCl_3 . Infrared spectra were measured in the range 450–4000 cm^{-1} as pressed pellets in KBr on a Nicolet FTIR. UV–visible spectroscopy was recorded from 200 to 800 nm in acetonitrile on an HP UV–visible spectrometer in quartz cuvettes. X-ray powder diffraction patterns were obtained using a Rigaku RAPID Curved IP X-ray powder diffractometer with $\text{Cu K}\alpha$ radiation and an image plate detector. Thermal analysis was performed on a SDT Q600 TA instrument. Simultaneous TGA-DTA data were studied from samples in an aluminum pan, from 20–1000 °C with a heating rate of 10 °C/min. GC–MS data were obtained on a Fisons model 8000/800. The column was a DB5, 15 m \times 0.25 mm. The injection temperature was 220 °C, the column temperature was 30–300 °C, and the detector was 250 °C. Samples were injected in dichloromethane.

[Eu(S₂CNMeEt)₃phen], 1. A solution of tetramethylammonium ethylmethyldithiocarbamate (0.63 g, 3 mmol) and 1,10-phenanthroline (0.18 g, 1 mmol) in 5:1 acetonitrile:CH₃OH (18 cm³) was added to a solution of europium nitrate pentahydrate (0.43 g, 1 mmol) in acetonitrile (5 cm³). A small amount of white solid came out and was immediately filtered out of the mixture. The red filtrate was left to stand for several minutes, after which red-orange crystals appeared. The crystals were collected by filtration and air-dried. Bright red crystals were obtained upon recrystallization from hot acetonitrile. ^1H NMR: δ 0.03 (s, 9H), δ 0.36 (t, $J = 7.1$ Hz, 9H), δ 1.46 (q, $J = 7.2$ Hz, 6H), δ 7.05 (s, 4H), δ 7.72 (d, $J = 7.8$ Hz, 2H), δ 12.82 (s, 2H). IR (KBr, cm^{-1}): $\nu_{\text{C-N}} = 1490(\text{s})$,

- (24) Horn, M.; Strange, P.; Temmerman, W. M.; Szotek, Z.; Svane, A.; Winter, H. *Los Alamos National Laboratory, Preprint Archive, Condensed Matter*, 2004; pp 1–7.
 (25) Oestreich, M. *Nature* **1999**, *402*, 735–736.
 (26) Awschalom, D. D.; Kawakami, R. K. *Nature* **2000**, *408*, 923–924.
 (27) Goncharenko, I. N.; Mirebeau, I. *Phys. Rev. Lett.* **1998**, *80*, 1082–1085.
 (28) Goncharenko, I. N.; Mirebeau, I. *Phys. Rev. Lett.* **1998**, *80*, 1082–1085.
 (29) Aripnammal, S.; Natarajan, S. *Mod. Phys. Lett. B* **2000**, *14*, 843–848.
 (30) Luo, Y.; Wan, X.; Ito, Y.; Takami, S.; Kubo, M.; Miyamoto, A. *Chem. Phys.* **2002**, *282*, 197–206.
 (31) Wachter, P. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, K., Eyring, L., Lander, G., Choppin, G. R., Eds.; Elsevier: New York, 1994; Vol. 19, Chapter 132, p 252.
 (32) Kaldis, E.; Fritzler, B.; Spychiger, H. *Solid State Chemistry 1982, Proceedings of the 2nd European Conference*; Elsevier: Amsterdam, 1983.
 (33) Chatterjee, A.; Singh, A. K.; Jayaraman, A. *Phys. Rev. B* **1972**, *6*, 2285–2291.
 (34) Su, C.; Tan, M.; Tang, N.; Gan, X.; Liu, W.; Wang, X. *J. Coord. Chem.* **1996**, *38*, 207.
 (35) Su, C.-Y.; Tan, M.-Y.; Ze-Fu; Tang, N.; Cai, L.-P.; Xue, Q.-J. *Synth. React. Inorg. Met.-Org. Chem.* **1999**, *29*, 35–51.
 (36) Su, C.; Tan, M.; Tang, N.; Gan, X.; Zhang, Z.; Xue, Q.; Yu, K. *Polyhedron* **1997**, *16*, 1643–1650.
 (37) Gorshkov, N. I.; Sidorenko, G. V.; Suglobov, D. N. *Radiokhimiya* **1994**, *36*, 154.

- (38) Bessergenev, V. G.; Ivanova, E. N.; Kovalevskaya, Y. A.; Vasilieva, I. G.; Varand, V. L.; Zemska, S. M.; Larionov, S. V.; Kolesov, B. A.; Ayupov, B. M.; Logvinenko, V. A. *Mater. Res. Bull.* **1997**, *32*, 1403–1410.
 (39) Kuzimina, N. P.; Ivanov, R. A.; Paramonov, S. E.; Martynenko, L. I. *Proc. Electrochem. Soc.* **1997**, 97-25 (*Chem. Vap. Deposition*), 880–885.
 (40) Brewer, M.; Khasnis, D.; Buretea, M.; Berardini, M.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1994**, *33*, 2743–2747.

$\nu_{C-S} = 962(\text{m})$. λ_{max} (acetonitrile, nm): 230, 265, 394, 434, 467, 580, 658. Anal. Calcd for $\text{C}_{26}\text{H}_{35}\text{N}_5\text{S}_6\text{Eu}$: C, 40.24; H, 4.55; N, 10.83; S, 24.80; Found: C, 39.93; H, 4.84, N, 10.66; S, 24.76. Percent yield 71%.

[Eu(S₂CNⁿPr₂)₃phen], 2. A solution of sodium di-*n*-propyldithiocarbamate (0.60 g, 3 mmol) and 1,10-phenanthroline (0.18 g, 1 mmol) in methanol (20 cm³) was added to a solution of europium nitrate pentahydrate (0.43 g, 1 mmol) in H₂O (10 cm³). Yellow-orange solid appeared immediately. The mixture was stirred for 1 h wherein the color of the mixture changed to red-orange. The solid obtained after filtration was washed with water and air-dried. Red crystals were obtained upon recrystallization from acetonitrile. ¹H NMR: δ 0.37 (t, $J = 7.2$ Hz, 18H), δ 0.83 (m, $J = 7.2$ Hz, 12H), δ 1.04 (t, $J = 7.7$ Hz, 12H), δ 7.04 (d, $J = 7.8$ Hz, 2H), δ 7.17 (s, 2H), δ 7.79 (d, $J = 8.1$ Hz, 2H), δ 12.38 (s, 2H). IR (KBr, cm⁻¹): $\nu_{C-N} = 1476(\text{s})$, $\nu_{C-S} = 982(\text{m})$. λ_{max} (acetonitrile, nm): 225, 265, 394, 434, 467, 580, 658. Anal. Calcd for $\text{C}_{33}\text{H}_{50}\text{N}_5\text{S}_6\text{Eu}$: C, 46.03; H, 5.85; N, 8.13; S, 22.35; Found: C, 46.12; H, 6.14; N, 8.16; S, 22.07. Percent yield 77%.

[Eu(S₂CNⁿButyl)₃phen], 3. A solution of tetramethylammonium di-*n*-butyldithiocarbamate (0.84 g, 3 mmol) and 1,10-phenanthroline (0.18 g, 1 mmol) in 5:1 acetonitrile:CH₃OH (18 cm³) was added to a 10 cm³ aqueous solution of europium nitrate pentahydrate (0.43 g, 1 mmol). This resulted in a mixture of red liquid and small amounts of white solid, which was immediately filtered out and discarded. Red-orange crystals came out upon standing the filtrate for several minutes. Recrystallization using hot acetonitrile gave red crystals. ¹H NMR: δ 0.27 (d, $J = 6.6$ Hz, 36H), δ 0.72 (m, $J = 6.9$ Hz, 6H), δ 0.97 (d, $J = 6.9$ Hz, 12H), δ 7.04 (d, $J = 7.8$ Hz, 2H), δ 7.37 (s, 2H), δ 7.93 (d, $J = 7.8$ Hz, 2H), δ 11.97 (s, 2H). IR (KBr, cm⁻¹): $\nu_{C-N} = 1466(\text{s})$, $\nu_{C-S} = 992(\text{m})$. λ_{max} (acetonitrile, nm): 227, 267, 394, 435, 467, 580, 655. Anal. Calcd for $\text{C}_{39}\text{H}_{60}\text{N}_5\text{S}_6\text{Eu}$: C, 49.55; H, 6.61; N, 7.41; S, 20.36. Found: C, 49.51; H, 6.83; N, 7.45; S, 20.09. Percent yield 83%.

[Nd(S₂CNEt₂)₃phen], 4. A solution of diethylammonium diethyldithiocarbamate (0.33 g, 1.5 mmol) and 1,10-phenanthroline (0.09 g, 0.5 mmol) in acetonitrile (5 cm³) was added to a solution of neodymium nitrate hexahydrate (0.22 g, 0.5 mmol) in acetonitrile (5 cm³). Light blue crystals appeared upon stirring. The solid was isolated and then recrystallized from hot acetonitrile. ¹H NMR (CDCl₃, ppm): δ 1.65 (t, $J = 6.6$ Hz, 18H), δ 5.55 (q, $J = 6.6$ Hz, 12H), δ 6.18 (s, 2H), δ 7.68 (d, $J = 8.4$ Hz, 2H), δ 8.38 (s, 2H), δ 8.95 (d, $J = 8.4$ Hz, 2H). IR (KBr, cm⁻¹): $\nu_{C-N} = 1481(\text{s})$, $\nu_{C-S} = 997(\text{m})$. λ_{max} (acetonitrile, nm): 230, 263, 521, 533, 585, 595, 755. Anal. Calcd for $\text{C}_{27}\text{H}_{38}\text{N}_5\text{S}_6\text{Nd}$: C, 42.16; H, 4.98; N, 9.11; S, 25.01. Found: C, 42.22; H, 5.33; N, 9.39; S, 24.86. Percent yield 84%.

[Sm(S₂CNEt₂)₃phen], 5. A solution of diethylammonium diethyldithiocarbamate (0.33 g, 1.5 mmol) and 1,10-phenanthroline (0.09 g, 0.5 mmol) in acetonitrile (10 cm³) was added to a solution of samarium chloride (0.13 g, 0.5 mmol) in H₂O (3 cm³). Light yellow crystals came out upon stirring. The solid was isolated and then recrystallized from hot acetonitrile. ¹H NMR: δ 1.19 (t, $J = 7.1$ Hz, 18H), δ 3.92 (q, $J = 7.0$ Hz, 12H), δ 7.41 (m, 2H), δ 7.85 (s, 2H), δ 8.29 (m, 4H). IR (KBr, cm⁻¹): $\nu_{C-N} = 1482(\text{s})$, $\nu_{C-S} = 999(\text{m})$. λ_{max} (acetonitrile, nm): 230, 264, 417, 429, 467. Anal. Calcd for $\text{C}_{27}\text{H}_{38}\text{N}_5\text{S}_6\text{Sm}$: C, 41.82; H, 4.94; N, 9.03; S, 24.82. Found: C, 40.04; H, 5.02; N, 8.71; S, 23.35. Percent yield 82%.

[Gd(S₂CNEt₂)₃phen], 6. A solution of diethylammonium diethyldithiocarbamate (0.68 g, 3 mmol) and 1,10-phenanthroline (0.18 g, 1 mmol) in acetonitrile (15 cm³) was added to a solution of gadolinium nitrate hexahydrate (0.45 g, 1 mmol) in acetonitrile (5 cm³). Fine white crystals appeared upon stirring. The solid was isolated and then recrystallized from hot acetonitrile. IR (KBr,

cm⁻¹): $\nu_{C-N} = 1482(\text{s})$, $\nu_{C-S} = 1001(\text{m})$. λ_{max} (acetonitrile, nm): 230, 264. Anal. Calcd for $\text{C}_{27}\text{H}_{38}\text{N}_5\text{S}_6\text{Gd}$: C, 41.45; H, 4.90; N, 8.96; S, 24.60. Found: C, 41.34; H, 5.10; N, 9.14; S, 23.48. Percent yield 84%.

[Ho(S₂CNEt₂)₃phen], 7. A solution of diethylammonium diethyldithiocarbamate (0.34 g, 1.5 mmol) and 1,10-phenanthroline (0.09 g, 0.5 mmol) in acetonitrile (5 cm³) was added to a solution of holmium nitrate pentahydrate (0.22 g, 0.5 mmol) in acetonitrile (5 cm³). Pink crystals came out upon stirring. The color of the crystals appears yellow with intense light. The solid was isolated and then recrystallized from 5:1 acetonitrile:CHCl₃. IR (KBr, cm⁻¹): $\nu_{C-N} = 1482(\text{s})$, $\nu_{C-S} = 1004(\text{m})$. λ_{max} (acetonitrile, nm): 230, 263, 420, 452, 485, 539. Anal. Calcd for $\text{C}_{27}\text{H}_{38}\text{N}_5\text{S}_6\text{Ho}$: C, 41.05; H, 4.85; N, 8.87; S, 24.36. Found: C, 40.55; H, 4.97; N, 9.18; S, 23.07. Percent yield 84%.

[Er(S₂CNEt₂)₃phen], 8. A solution of diethylammonium diethyldithiocarbamate (0.67 g, 3 mmol) and 1,10-phenanthroline (0.18 g, 1 mmol) in acetonitrile (20 cm³) was added to a solution of erbium nitrate pentahydrate (0.44 g, 1 mmol) in acetonitrile (5 cm³). Peach crystals appeared upon stirring. The solid was isolated and then recrystallized from 5:1 acetonitrile:CHCl₃. IR (KBr, cm⁻¹): $\nu_{C-N} = 1482(\text{s})$, $\nu_{C-S} = 1005(\text{m})$. λ_{max} (acetonitrile, nm): 230, 263, 490, 526, 655. Anal. Calcd for $\text{C}_{27}\text{H}_{38}\text{N}_5\text{S}_6\text{Er}$: C, 40.93; H, 4.83; N, 8.84; S, 24.29. Found: C, 40.88; H, 5.08; N, 8.97; S, 23.49. Percent yield 84%.

Precursor Thermolysis. The [Eu(S₂CNEt₂)₃phen] precursor was heated to 900 °C under vacuum, and the organic side products were collected in a trap and identified using GC-MS. The black solid material isolated from the thermolysis was characterized by X-ray powder diffraction.

X-ray Crystallography. Intensity data were collected on a Bruker SMART 1000 CCD diffractometer using Mo K α radiation. Structures 1–8 were solved and refined using the SHELX-97 packages. The structures were solved using direct methods and refined by full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were located in calculated positions and refined isotropically. The SADABS program was used for absorption correction calculations. The experimental details of the data collections are summarized in Tables 1 and 2. Complete crystallographic details are provided in the Supporting Information.

Results and Discussion

The largest class of potential precursor molecules that could be used for lanthanide chalcogenide materials is comprised of the lanthanide thiolates, which has greatly expanded in number over the past decade. Prototypical examples of lanthanide thiolates include the aryl thiolates (Ln(SPh)₂,^{41,42} and Ln(SPh)₃),^{43,44} pyridine thiolates ([PEt₄]-[Ln(SPy)₄] and (pyridine)₄Eu(SPy)₂, where SPy = S-2-NC₅H₄),^{45,46} as well as sterically encumbered thiolates such as the (tris-(trimethyl)silyl)silyl sulfide complexes (LnSSi-(SiMe₃)₃)⁴⁷ or mesityl sulfides Ln(SMes)₂thf_x (Mes = 2,4,

(41) Freedman, D.; Kornienko, A.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **2000**, *39*, 2168–2171.

(42) Lee, J.; Brewer, M.; Berardini, M.; Brennan, J. G. *Inorg. Chem.* **1995**, *34*, 3215–3219.

(43) Lee, J.; Freedman, D.; Melman, J.; Brewer, M.; Sun, L.; Emge, T. J.; Long, F. H.; Brennan, J. G. *Inorg. Chem.* **1998**, *37*, 2512–2519.

(44) Berardini, M.; Lee, J.; Freedman, D.; Lee, J.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1997**, *36*, 5772–5776.

(45) Berardini, M.; Brennan, J. *Inorg. Chem.* **1995**, *34*, 6179–6185.

(46) Cary, D.; Arnold, J. *J. Am. Chem. Soc.* **1993**, *115*, 2520–2521.

Table 1. Summary of Crystallographic Data for [Eu(S₂CNRR')₃phen]

	(1) R = Me; R' = Et	(2) R = R' = ⁿ Propyl	(3) R = R' = ^t Butyl
molecular formula	EuS ₆ N ₅ C ₂₄ H ₃₂ , C ₂ H ₃ N	EuS ₆ N ₅ C ₃₃ H ₅₀ , 2(C ₂ H ₃ N)	EuS ₆ N ₅ C ₃₉ H ₆₂
formula weight	775.92	943.21	945.26
T/K	183(2)	183(2)	183(2)
λ/Å	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	monoclinic
space group	P2 ₁ /n	P2 ₁ /c	P2 ₁ /c
a/Å	10.434(3)	19.366(3)	24.164 (3)
b/Å	18.192(5)	13.427(2)	10.9935(14)
c/Å	17.156(4)	18.757(3)	17.829(2)
β/deg	101.587(4)	110.744(2)	105.602(2)
V/Å ³	3190.0(14)	4560.9(12)	4561.7(10)
Z	4	4	4
D _c /g cm ⁻³	1.616	1.374	1.376
μ/mm ⁻¹	2.386	1.683	1.682
crystal size/mm ³	0.50 × 0.30 × 0.15	0.42 × 0.38 × 0.20	0.31 × 0.20 × 0.13
θ range/deg	2.11–28.00	1.89–28.00	1.75–28.00
reflins collected	28 349	40 071	39 853
ind reflins (R _{int})	7527 (0.0392)	10 773 (0.0352)	10 829 (0.0674)
reflins w/ I > 2σ(I)	6186	7949	7512
data/restraints/parameters	7527/0/397	10 773/0/509	10 829/0/472
GOF on F ²	1.051	1.058	1.004
R ₁ [I > 2σ(I)]	0.0282	0.0356	0.0386
wR ₂ [I > 2σ(I)]	0.0615	0.0841	0.0755

Table 2. Summary of Crystallographic Data for [Ln(S₂CNEt₂)₃phen]

	(4) Ln = Nd	(5) Ln = Sm	(6) Ln = Gd	(7) Ln = Ho	(8) Ln = Er
molecular formula	NdS ₆ N ₅ C ₂₇ H ₃₈	SmS ₆ N ₅ C ₂₇ H ₃₈	GdS ₆ N ₅ C ₂₇ H ₃₈	HoS ₆ N ₅ C ₂₇ H ₃₈	ErS ₆ N ₅ C ₂₇ H ₃₈
formula weight	769.22	775.33	782.23	789.91	792.24
T/K	189(2)	190(2)	190(2)	189(2)	173(2)
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c
a/Å	16.917(4)	16.951(2)	16.963(3)	16.969(4)	16.940(3)
b/Å	10.596(3)	10.6027(15)	10.5913(16)	10.577(2)	10.5464(17)
c/Å	18.649(5)	18.622(3)	18.591(3)	18.542(4)	18.498(3)
β/deg	96.759(4)	96.852(2)	96.834(3)	96.869(4)	96.879(2)
V/Å ³	3319.8(14)	3322.9(8)	3316.3(9)	3304.1(12)	3281.0(9)
Z	4	4	4	4	4
D _c /g cm ⁻³	1.539	1.550	1.567	1.588	1.604
μ/mm ⁻¹	1.967	2.170	2.403	2.799	2.965
crystal size/mm ³	0.60 × 0.28 × 0.18	0.35 × 0.18 × 0.16	0.38 × 0.32 × 0.18	0.50 × 0.36 × 0.28	0.28 × 0.22 × 0.16
θ range/deg	2.20–28.00	2.20–28.00	2.21–28.00	2.21–28.00	2.22–28.00
reflins collected	28 600	29 001	29 282	27 935	27 219
ind reflins (R _{int})	7828 (0.0503)	7814 (0.0355)	7844 (0.0386)	7674 (0.0226)	7620 (0.0290)
reflins w/ I > 2σ(I)	5907	6596	6485	6899	6761
data/restraints/parameters	7828/0/358	7814/0/358	7844/0/358	7674/0/358	7620/0/358
GOF on F ²	1.078	1.095	1.108	1.049	1.092
R ₁ [I > 2σ(I)]	0.0322	0.0256	0.0289	0.0221	0.0201
wR ₂ [I > 2σ(I)]	0.0644	0.0597	0.0575	0.0495	0.0445

6-(trimethyl)phenyl).⁴⁸ Unfortunately, most of these compounds are quite air- and water-sensitive.

The lanthanide dithiocarbamates by contrast are conveniently prepared in air via metathetical reaction of the lanthanide nitrate and sodium dithiocarbamate in either water–methanol or acetonitrile solutions. The synthesis and structures for the neutral complexes Ln(S₂CNR₂)₃ (Ln = La, Sm, Eu; R = ethyl) were first reported by Brown.⁴⁹ More recently, the neutral Ce(IV) complex Ce(S₂CNEt₂)₄ and several anionic species of the general formula MLn(S₂CNR₂)₄ (M = Na⁺ or Me₄N⁺) have also been reported.^{50,51} The

reaction of Ln(III) nitrate with an alkali metal dithiocarbamate salt in the presence of the appropriate bidentate ligand generally resulted in the formation of crystals after isolation and recrystallization (vide infra). The molecular structures of **1–8** were determined by using single-crystal X-ray diffraction. Tables 1 and 2 give a listing of crystallographic details, and Tables 3 and 4 list the significant bond lengths and angles. The complexes were all monomeric with bidentate dithiocarboxylic ligands. The lanthanide compounds were all isostructural, with the exception of Yb and Lu, which are not reported here.

Crystal Structures of [Eu(S₂CNMeEt)₃Phen] 1, [Eu(S₂CNⁿPr₂)₃Phen] 2, and [Eu(S₂CN^tBu)₂Phen] 3. The structure of the prototypical europium complex is illustrated in Figure 1. The Eu(III) ion has a coordination number of 8, with a distorted square antiprismatic geometry. The dithiocarbamates are bidentate, with the neutral phenanthroline ligand filling the coordination sphere. Selected bond lengths

(47) Strzelecki, A. R.; Timinski, P. A.; Helsel, B. A.; Bianconi, P. A. *J. Am. Chem. Soc.* **1992**, *114*, 3159–3160.

(48) Brown, D.; Holah, D. G.; Rickard, C. E. *J. Chem. Soc. A* **1970**, 786.

(49) Kobayashi, T.; Naruke, H.; Yamase, T. *Chem. Lett.* **1997**, 907.

(50) Ciampolini, M.; Nardi, N.; Colamarino, P.; Orioli, P. *J. Chem. Soc., Dalton Trans.* **1977**, 379.

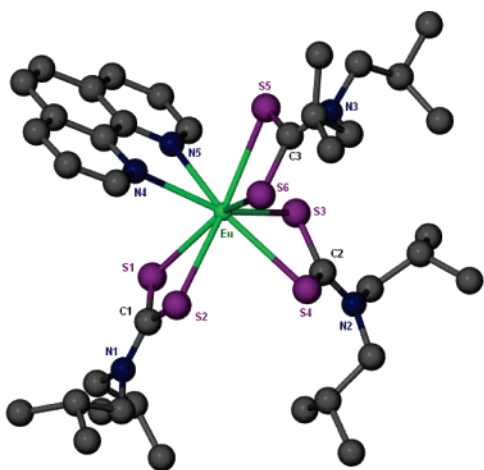
(51) Berardini, M.; Brennan, J. *Inorg. Chem.* **1995**, *34*, 6179–6185.

Table 3. Selected Bond Lengths and Angles for [Eu(S₂CNRR')₃phen], R = Methyl, R' = Ethyl (1), R = R' = ⁿPropyl (2), R = R' = ⁱButyl (3)

(1) R = Me; R' = Et		(2) R = R' = ⁿ Propyl		(3) R = R' = ⁱ Butyl	
Eu(1)–N(4)	2.549(2)	Eu(1)–N(4)	2.600(3)	Eu(1)–N(4)	2.612(3)
Eu(1)–N(5)	2.596(2)	Eu(1)–N(5)	2.584(3)	Eu(1)–N(5)	2.568(3)
Eu(1)–S(1)	2.9011(9)	Eu(1)–S(1)	2.8240(9)	Eu(1)–S(1)	2.8513(9)
Eu(1)–S(2)	2.8237(10)	Eu(1)–S(2)	2.8618(9)	Eu(1)–S(2)	2.8408(9)
Eu(1)–S(3)	2.8611(9)	Eu(1)–S(3)	2.8504(9)	Eu(1)–S(3)	2.8369(10)
Eu(1)–S(4)	2.8692(10)	Eu(1)–S(4)	2.8911(9)	Eu(1)–S(4)	2.8827(10)
Eu(1)–S(5)	2.8605(9)	Eu(1)–S(5)	2.8256(10)	Eu(1)–S(5)	2.8873(9)
Eu(1)–S(6)	2.8444(9)	Eu(1)–S(6)	2.8977(13)	Eu(1)–S(6)	2.8119(9)
S(1)–Eu(1)–S(2)	62.23(2)	S(1)–Eu(1)–S(2)	62.75(2)	S(1)–Eu(1)–S(2)	62.86(2)
S(3)–Eu(1)–S(4)	61.91(2)	S(3)–Eu(1)–S(4)	61.95(2)	S(3)–Eu(1)–S(4)	61.92(3)
S(5)–Eu(1)–S(6)	62.50(3)	S(5)–Eu(1)–S(6)	60.99(3)	S(5)–Eu(1)–S(6)	62.63(3)

Table 4. Summary of Crystallographic Data for [Ln(S₂CNEt₂)₃phen], Ln = Nd (4), Sm (5), Gd (6), Ho (7), Er (8)

(4) Ln = Nd		(5) Ln = Sm		(6) Ln = Gd		(7) Ln = Ho		(8) Ln = Er	
Nd(1)–N(4)	2.612(3)	Sm(1)–N(4)	2.583(2)	Gd(1)–N(4)	2.555(2)	Ho(1)–N(4)	2.544(2)	Er(1)–N(4)	2.4997(18)
Nd(1)–N(5)	2.622(3)	Sm(1)–N(5)	2.602(2)	Gd(1)–N(5)	2.579(2)	Ho(1)–N(5)	2.518(2)	Er(1)–N(5)	2.5336(17)
Nd(1)–S(1)	2.9396(10)	Sm(1)–S(1)	2.9257(7)	Gd(1)–S(1)	2.9125(8)	Ho(1)–S(1)	2.8894(8)	Er(1)–S(1)	2.8828(6)
Nd(1)–S(2)	2.8158(10)	Sm(1)–S(2)	2.7920(7)	Gd(1)–S(2)	2.7733(8)	Ho(1)–S(2)	2.7374(8)	Er(1)–S(2)	2.7223(6)
Nd(1)–S(3)	2.8751(10)	Sm(1)–S(3)	2.8523(7)	Gd(1)–S(3)	2.8352(9)	Ho(1)–S(3)	2.8078(8)	Er(1)–S(3)	2.7902(7)
Nd(1)–S(4)	2.9258(10)	Sm(1)–S(4)	2.9089(7)	Gd(1)–S(4)	2.8878(8)	Ho(1)–S(4)	2.8665(8)	Er(1)–S(4)	2.8505(7)
Nd(1)–S(5)	2.8662(9)	Sm(1)–S(5)	2.8439(7)	Gd(1)–S(5)	2.8265(8)	Ho(1)–S(5)	2.7952(7)	Er(1)–S(5)	2.7820(6)
Nd(1)–S(6)	2.8901(11)	Sm(1)–S(6)	2.8661(7)	Gd(1)–S(6)	2.8447(8)	Ho(1)–S(6)	2.8087(8)	Er(1)–S(6)	2.7958(7)
S(1)–Nd(1)–S(2)	61.72(3)	S(1)–Sm(1)–S(2)	62.15(2)	S(1)–Gd(1)–S(2)	62.54(2)	S(1)–Ho(1)–S(2)	63.518(17)	S(1)–Er(1)–S(2)	63.301(18)
S(3)–Nd(1)–S(4)	61.00(2)	S(3)–Sm(1)–S(4)	61.479(19)	S(3)–Gd(1)–S(4)	61.86(2)	S(3)–Ho(1)–S(4)	61.99(2)	S(3)–Er(1)–S(4)	62.528(17)
S(5)–Nd(1)–S(6)	61.91(2)	S(5)–Sm(1)–S(6)	62.463(17)	S(5)–Gd(1)–S(6)	62.91(2)	S(5)–Ho(1)–S(6)	63.10(2)	S(5)–Er(1)–S(6)	63.811(15)

**Figure 1.** Molecular structure of [Eu(S₂CN(ⁱBu)₂)₃phen].

and angles are given in Table 3. Generally, the cell volumes increase with increasing chain length of the dialkyldithiocarbamate ligand.

The Eu–S bond distances which ranged from 2.85(4) to 2.86(4) are close to that reported for trivalent europium Eu–S,⁵² and to similar dithiocarbamate complexes (2.783(1)–2.914(2)).⁵³ These are consistent with values predicted by the summation of ionic radii for eight coordinate Eu³⁺ and S²⁻ (2.90 Å).⁵⁴ The C–S bonds in the dithiocarbamate complexes were approximately 1.72(2), significantly shorter than the idealized C–S single bond (1.81 Å).⁵⁵ The C–N bond lengths, which range from 1.33(1)–1.35(1), are be-

tween a single bond (C–N ~1.47 Å) and a double bond (C=N ~1.30 Å).⁵⁶ The Eu–N bond lengths ranged between 2.57(2)–2.59(2), close to previously reported trivalent, eight coordinate europium complexes (2.52(1) Å⁵⁷ and 2.54–2.67 Å⁵⁸). The R group has little impact on the metal coordination chemistry, although it does appear to influence the extent of electron delocalization on sulfur. The η² coordination of the dithiocarbamate restricts the S–Eu–S bond angle, but there is nothing unusual in the bond angles.

Crystal Structures of [Ln(S₂CNEt₂)₃Phen], Ln = Nd, Sm, Gd, Ho, and Er (4, 5, 6, 7, 8). The Ln(S₂CNEt₂)₃phen complexes are isostructural for Ln = Nd, Sm, Gd, Ho, Er with all lanthanides exhibiting eight-fold coordination. This is in contrast to the lanthanide benzenethiolates Ln(SPh)₃(pyridine)₃, which exhibit an increasing tendency to oligomerize with larger Ln(III) ions (and even more strikingly with the analogous selenolate ligands).⁵⁹ The bond geometries are quite similar in these dithiocarbamate complexes. With similar oxidation state and coordination number, this series of compounds have systematic variations in Ln–S and Ln–N bond lengths, supporting an ionic bonding model. The Ln–S bond lengths range from Nd–S 2.89(7) > Sm–S 2.87(7) > Gd–S 2.85(4) > Ho–S 2.82(8) and Er–S 2.80(8), as expected for the decrease in ionic radii across the lanthanide series. There is a similar decrease in the Ln–N bond distances (2.62(1) for Nd, 2.59(1) for Sm, 2.57(1) for Gd,

(55) Su, C.; Tan, M.; Tang, N.; Gan, X.; Zhang, Z.; Xue, Q.; Yu, K. *Polyhedron* **1997**, *16*, 1643–1650.

(56) Berardini, M.; Brennan, J. *Inorg. Chem.* **1995**, *34*, 6179–6185.

(57) Varand, V. L.; Klevtsova, R. F.; Glinkaya, L. A.; Larionov, S. V. *Russ. J. Coord. Chem.* **2000**, *26*, 869–877.

(58) Lee, J.; Freedman, M. J. H.; Brewer, M.; Sun, L.; Emge, T. J.; Long, F. H.; Brennan, J. G. *Inorg. Chem.* **1998**, *37*, 2512–2519.

(59) Su, C.; Tan, M.; Tang, N.; Gan, X.; Zhang, Z.; Xue, Q.; Yu, K. *Polyhedron* **1997**, *16*, 1643–1650.

(52) Su, C.; Tan, M.; Tang, N.; Gan, X.; Liu, W.; Wang, X. *J. Coord. Chem.* **1996**, *38*, 207–218.

(53) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751–767.

(54) Curry, J. D.; Jandacek, R. J. *J. Chem. Soc., Dalton Trans.* **1972**, 1120.

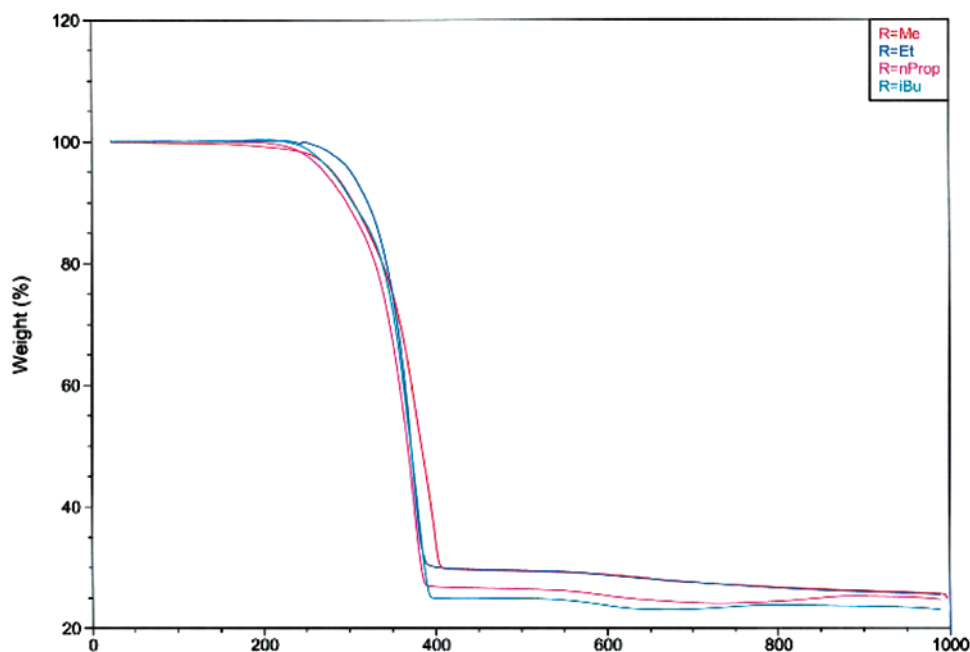


Figure 2. Thermogravimetric analysis of $\text{Eu}(\text{S}_2\text{CNR}_2)_3\text{phen}$. The R groups are identified by red = methyl, blue = ethyl, purple = *n*-propyl, green = isobutyl.

2.53(2) for Ho, and 2.52(2) for Er). However, the C–S bond (1.720 ± 0.003) and C–N bond lengths (1.329 ± 0.001) appear to be independent of the lanthanide metal identity. On the basis of the infrared spectra, we believe the Yb and Lu complexes have a different structure type. Unfortunately, single crystals of these two members of the series have yet to be isolated.

The IR spectra of all complexes exhibit a single $\nu_{\text{C-S}}$ band in the range $997\text{--}1005\text{ cm}^{-1}$, indicative of bidentate coordination.⁶⁰ The infrared spectra of the $\text{Eu}(\text{S}_2\text{CNR}_2)_3\text{phen}$ complexes show a systematic decrease in the C–N stretch from 1490 to 1466 cm^{-1} as the length of the R group increases. By contrast, for $\text{Ln}(\text{S}_2\text{CNET}_2)_3\text{phen}$ the C–N stretch was consistently $1481\text{--}1482\text{ cm}^{-1}$ for Ln = Nd, Sm, Eu, Gd, Ho, and Er. The independence of the C–N stretch on metal or S bonding mode has been seen previously in dithiocarbamates.⁶¹

The UV–visible absorption spectra of the complexes exhibit strong absorptions at approximately 230 and 263–265 nm, which are characteristic π to π^* bands for phenanthroline. Weak f–f transitions are observed for all complexes except the colorless gadolinium complex. The europium complexes, $\text{Eu}(\text{S}_2\text{CNR}_2)_3\text{phen}$, exhibit a ligand to metal charge transfer (LMCT) absorption at approximately 434 nm. The charge-transfer nature of this band is evident in a small but distinct change in λ_{max} when the solvent is changed. The deep garnet color of the redox active Eu(III) (indicative of charge transfer) is in contrast to the characteristic pale colors of lanthanide ions found in the Nd, Sm, Gd, Ho, and Er complexes. By comparison with $\text{Ln}(\text{SPh})_3$,⁶² it might be expected that the redox active Sm complexes should also exhibit a strong LMCT absorption. However,

we see only weak absorptions at 417, 429, and 467 nm. The UV–visible absorption data are also consistent with the NMR spectroscopy. The proton NMR spectroscopy of the europium complexes suggests that there is significant electron delocalization from the metal to the phenanthroline, with the ortho protons shifted to 12 ppm (whereas for the Nd and Sm, these protons are closer to 8 ppm).

The thermal properties of these complexes were investigated using thermogravimetric analysis (TGA) and differential thermal analysis (DTA). We observed that thermal decomposition occurs in one step between 280 and 350 °C independent of the R group (see Figure 2). In the case of europium, the final weight corresponded to a mass of 1 Eu and 1 S from the starting material with the loss of the remaining C, H, S, and N atoms. This was in contrast to previous studies of europium and erbium dithiocarbamate complexes, which appear to vary with mixed alkyl groups.⁶³ The decomposition pathway was further investigated by thermolysis experiments carried out under vacuum at 900 °C. The crystalline portion of the resulting black powder was identified as EuS based on the X-ray powder diffraction pattern (see Figure 3). Given that the decomposition of the Eu(III) precursor, $\text{Eu}(\text{S}_2\text{CNR}_2)_3\text{L}$ complexes, results in the formation of EuS, clearly oxidation–reduction chemistry occurs. For the $\text{Eu}(\text{S}_2\text{CNET}_2)_3\text{phen}$ analogue, we have isolated the organic oil formed as the precursor decomposed. Using GC–MS, we observe peaks in the mass spectrum corresponding to phenanthroline, and oxidation products including $(\text{Et}_2\text{NCS}_2)_2$ and $(\text{Et}_2\text{NCS})_2\text{S}$, and $(\text{Et}_2\text{NCS})^+$ and the tetraethyl thiourea $(\text{Et}_2\text{NCSNET}_2)$. On the basis of this, we propose

(60) Chatt, J.; Duncanson, L. A.; Venanzi, L. M. *Suom. Kemistil. B* **1956**, 75–82.

(61) Lee, J.; Freedman, D.; Melman, J. H.; Brewer, M.; Sun, L.; Emge, T. J.; Long, F. H.; Brennan, J. G. *Inorg. Chem.* **1998**, 37, 2512–2519.

(62) Ivanov, R. A.; Korsakov, I. E.; Formanovskii, A. A.; Paramonov, S. E.; Kuz'mina, N. P.; Kaul, A. R. *Russ. J. Coord. Chem.* **2002**, 28, 670–672.

(63) Lee, J.; Brewer, M.; Berardini, M.; Brennan, J. G. *Inorg. Chem.* **1995**, 34, 3215–3219.

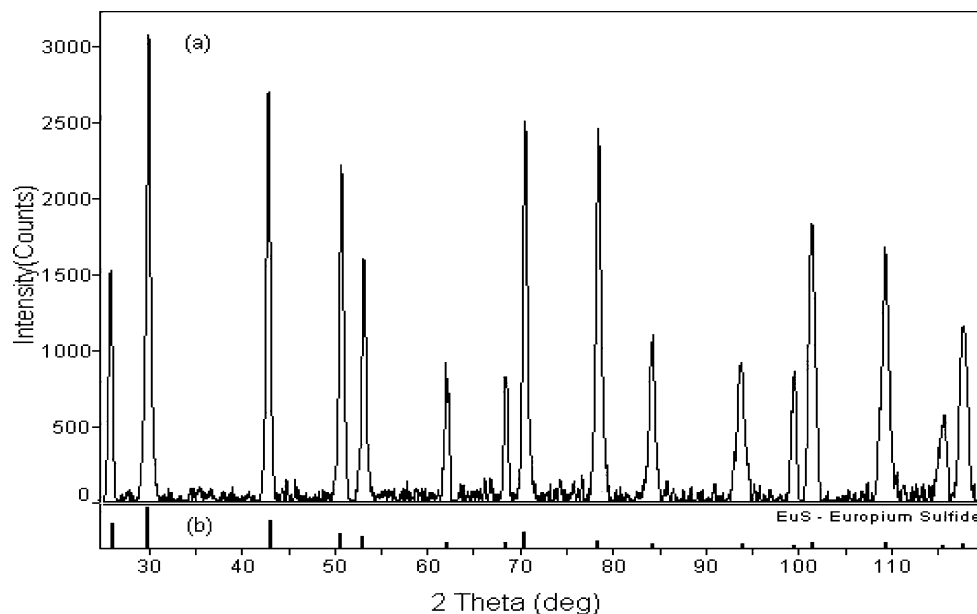


Figure 3. X-ray powder diffraction pattern of (a) black solid from decomposed $[\text{Eu}(\text{S}_2\text{CN}(\text{Et})_2)_3\text{phen}]$ and (b) EuS from database.

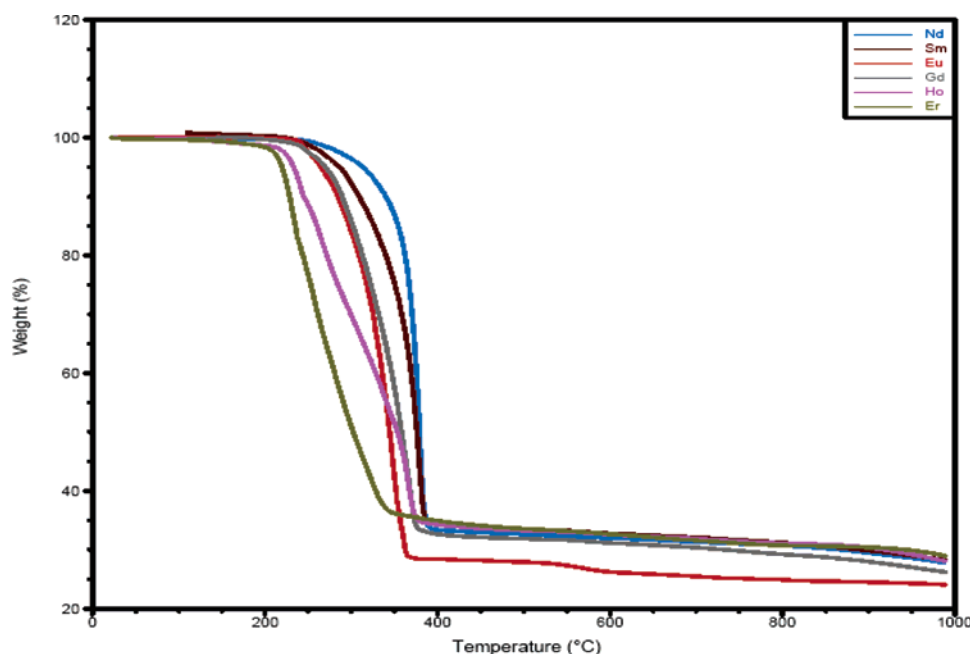
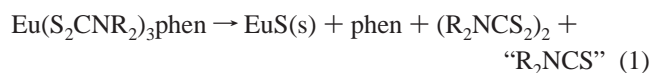


Figure 4. Thermogravimetric analysis of $\text{Ln}(\text{S}_2\text{CNR}_2)\text{Phen}$, Ln = Nd (blue), Sm (brown), Eu (red), Gd (grey), Ho (pink), Er (olive).

the following general pathway for the thermolysis of $\text{Eu}(\text{S}_2\text{CNR}_2)_3\text{phen}$:



The fact that additional products were formed, however, suggests a more complex multistep mechanism than suggested by eq 1.

We also evaluated the thermal decomposition of the structurally characterized precursors **4–8**, using TGA-DTA. Generally, lanthanide thiolate complexes thermally decompose to produce LnS for divalent precursors and Ln_2S_3 from the trivalent precursors.⁶⁴ The exceptions to this are the europium thiolates, which tend to form EuS independent of

the starting oxidation state.⁶⁵ While the decomposition temperature appears invariant with the organic ligand, it does depend on the lanthanide ionic radii (see Figure 4). The onset of decomposition generally decreases in temperature as the ionic radii decreases across the series proceeding from Nd to Ho. This is not surprising given the difference in lattice energy for the lanthanide sulfide materials formed, and the relative insensitivity of the lattice energy to the structure or degree of crystallinity of the final product. The TGA data do not provide definitive evidence as to whether the products formed are LnS or Ln_2S_3 because the mass difference is relatively small, and unfortunately the materials appear to be amorphous by X-ray powder diffraction. Interestingly, the GC–MS of the oil formed from thermolysis experiments of the series of $\text{Ln}(\text{S}_2\text{CNET}_2)_3\text{phen}$ gave the same oxidation products as the $\text{Eu}(\text{S}_2\text{CNET}_2)_3\text{phen}$ in similar ratios.

(64) Berardini, M.; Brennan, J. *Inorg. Chem.* **1995**, *34*, 6179–6185.

Conclusions

The series of [Eu(S₂CNR₂)₃phen] (R = Me/Et, ⁱPropyl, ⁱButyl) and [Ln(S₂CNEt₂)₃phen], Ln = Nd, Sm, Gd, Ho, and Er, have been synthesized, and their structures were determined using single-crystal X-ray diffraction. The Ln–S and Ln–N bond lengths reflect an ionic bonding model with a general decrease with decreasing lanthanide ionic radii. The infrared spectra provide a sensitive measure of the resonance forms of the dithiocarbamate ligand. Because these complexes are monomeric, air- and water-stable, and decompose via an internal redox reaction, they appear to be interesting single-source precursors to lanthanide chalcogenide materials. The structure and morphology of the LnE or Ln₂E₃ final products are likely to depend on the conditions of the decomposition reaction (i.e., solvent-free or solvent-based reaction, capping ligands, temperature and duration of

nucleation and growth phases), as they do for other kinds of metal chalcogenide particles. These questions and the effect of particle size and shape on magnetic properties will be addressed systematically in future work.

Acknowledgment. We thank the National Science Foundation for funding this work (NER: 0304273) and K. Travis Holman for helpful discussions on crystallography.

Supporting Information Available: Crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, and structures of compounds **1–8** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

CM0478071