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One-Dimensional Coordination Polymers: $[\{(\text{pyridine})_2\text{Eu}(\mu\text{-SeC}_6\text{H}_5)_2\}_4]_\infty$ and $[(\text{THF})_3\text{Eu}(\mu\text{-SeC}_6\text{H}_5)_2]_\infty$

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Molecular precursors[1] can be used to prepare a variety of new materials, from metastable solid-state compounds[1a] to quantum-confined nanometer-sized clusters.[1e] There has recently been a surge of interest in the preparation of rare earth chalogenates for use in materials synthesis.[1f,g] This interest stems primarily from the extraordinary optical and magnetic properties of rare earth compounds, the use of rare earths in semiconductor technology, and the desire to illuminate the relationships between molecular and solid-state properties. Simple organochalcogenolate ligands tend to span metal centers,[2] and this tendency can be used to prepare polymeric materials that resemble solid-state compounds in limited dimensionality. In this communication, we describe the synthesis and structural characterization of two one-dimensional coordination polymers of bis(phenylselenolato)europium(II): $[(\text{THF})_3\text{Eu}(\mu\text{-SeC}_6\text{H}_5)_2]_\infty$ and $[\{(\text{pyridine})_2\text{Eu}(\mu\text{-SeC}_6\text{H}_5)_2\}_4]_\infty$.

The divalent complexes are prepared from a Eu(III) starting material. Addition of 3 equiv of NaSeC_6H_5 to a solution of EuCl_3 in THF[3] results in the immediate formation of a light yellow-orange solution. Filtration and saturation of this solution gives light yellow needles, which can be redissolved in THF or pyridine. Single crystal X-ray characterization[4] of the complex showed it to be $[(\text{THF})_3\text{Eu}(\mu\text{-SeC}_6\text{H}_5)_2]_\infty$ (**1**), a coordination polymer with seven-coordinate metal centers bridged to adjacent ions through pairs of phenylselenolato ligands. Figure 1 shows the extended one-dimensional network of the EuSe_4O_3 coordination spheres of **1**. The average Eu–Se distance of 3.14(1) Å (−100 °C) is close to the value predicted from ionic radius summation rules[5] (3.17 Å at room temperature). Once isolated, the crystals rapidly become opaque, and the metal loses two THF ligands to form a complex which gave an elemental analysis consistent with the stoichiometry $(\text{THF})\text{Eu(II)}(\mu\text{-SeC}_6\text{H}_5)_2$. The compound decomposes without melting and is optically transparent between 320 and 800 nm in THF.

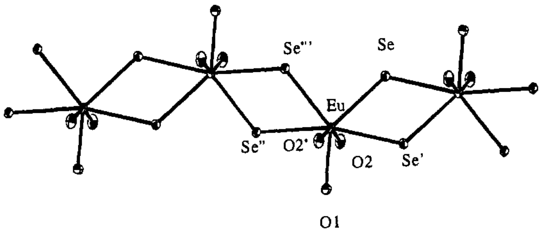

Figure 1. Extended coordination spheres in $[(\text{THF})_3\text{Eu(II)}(\mu\text{-SeC}_6\text{H}_5)_2]_\infty$ (carbon atoms removed for clarity). The seven-coordinate metal ion is bridged to two adjacent metal ions through pairs of phenylselenolato ligands. Each europium ion is on a two-fold rotation axis which runs through the central THF ligand and relates the remaining two THF ligands and the two pairs of bridging phenylselenolato ligands. Thermal ellipsoids (ORTEP) are drawn at the 50% probability level. Average distances (Å): Eu–Se, 3.14(1); Eu–O, 2.58(1). Significant angles (deg): Se–Eu–Se', 62.3(1); Se–Eu–Se''', 87.7(1); Eu–Se–Eu, 118.7(1), Eu–Se–C, 120.0(2).

If the $\text{NaSeC}_6\text{H}_5/\text{EuCl}_3$ reaction mixture is taken to dryness and redissolved in a mixture of THF and pyridine, an orange solution color develops. Filtration of this solution, followed by layering with diethyl ether, leads to the formation of orange needles over a period of days.[6] The molecular structure of the orange product was determined by single crystal x-ray diffraction[7] to be that of the one-dimensional coordination polymer $[\{(\text{pyridine})_2\text{Eu}(\mu\text{-SeC}_6\text{H}_5)_2\}_4]_\infty$ (**2**). Figure 2 shows the extended one-dimensional network of the EuSe_4N_2 coordination spheres of **2**. Each octahedral metal is bound to *trans* pyridine ligands and a pair of two *cis* phenylselenolato ligands which span two metal centers. The average Eu–Se distance (3.10(3) Å) in six-coordinate **2** is slightly shorter than the average Eu–Se distance (3.14(1) Å) found in seven-coordinate **1**. The phenyl groups (Eu–Se–C av. 113°) are staggered (both down, Se1, Se8; one up, one down, Se2, Se3; both up, Se4, Se5; one up, one down, Se6, Se7) along the chain. The complex is structurally related to the magnetically

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[1] (a) MacInnes, A. N.; Power, M. B.; Barron, A. R. *Chem. Mater.* **1992**, *4*, 11–12. (b) Farneth, W. E.; Herron, N.; Wang, Y. *Chem. Mater.* **1992**, *4*, 916–922. (c) Osakada, K.; Yamamoto, A. *Inorg. Chem.* **1990**, *30*, 2328–2332. (d) Osakada, K.; Yamamoto, T. *J. Chem. Soc., Chem. Commun.* **1987**, 1117–1118. Nomura, R.; Fujii, S.; Kanaya, K.; Matsuda, H. *Polyhedron* **1990**, *9*, 361. (e) Brennan, J.; Siegrist, T.; Stuczynski, S.; Carroll, C.; Rynders, P.; Brus, L.; Steigerwald, M. *Chem. Mater.* **1990**, *2*, 403–408. (f) Cary, D. R.; Arnold, J. *J. Am. Chem. Soc.* **1993**, *115*, 2520–2521. (g) Strzelecki, A. R.; Timinski, P. A.; Hesel, B. A.; Bianconi, P. A. *J. Am. Chem. Soc.* **1992**, *114*, 3159–3160.

[2] (a) Dance, I.; Garbutt, R.; Craig, D.; Scudder, M. *Inorg. Chem.* **1987**, *26*, 4057–4064. (b) Arnold, A.; Canty, A.; Skelton, B.; White, A. *J. Chem. Soc., Dalton Trans.* **1982**, 607–613. (c) Canty, A.; Raston, C.; White, A. *Aust. J. Chem.* **1981**, *34*, 57–64. (d) Dance, I. G. *J. Am. Chem. Soc.* **1980**, *102*, 3445–3451. (e) Arnold, A.; Canty, A. *Inorg. Chim. Acta* **1981**, *55*, 171–176. (f) Burgi, H. *Helv. Chim. Acta* **1974**, *57*, 513–519. (g) Gharia, K. S.; Singh, M.; Mathur, S.; Roy, R.; Sankhla, B. S. *Synth. React. Inorg. Met-Org. Chem.* **1982**, *12*, 337–345.

[3] Diphenyl diselenide (1.4 g, 4.5 mmol) was dissolved in diethyl ether (60 mL), and sodium triethylborohydride (9 mL of a 1.0 M solution in THF, 9 mmol) was added by syringe. The solution was stirred for 30 min and then concentrated to dryness to give a white solid. Europium trichloride (0.77 g, 3.0 mmol) was dissolved in THF (100 mL) and added to the Schlenk tube containing the NaSePh. After 5 h, the solution was filtered. Upon concentration of the solution to 15 mL, the color changed to deep orange, and the solution was cooled to −70 °C. After 16 h, a yellow precipitate had formed. This was redissolved by heating to 40 °C, and the solution was then cooled to room temperature. After 48 h, light yellow crystals (0.65 g, 32%), which do not melt but turn orange at 300–350 °C and red at 400 °C, were isolated. The crystals rapidly desolvate at room temperature when isolated from the supernate, and elemental analysis indicates that the complex approaches a final stoichiometry of $(\text{THF})\text{Eu(SePh)}_2$. Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{EuOSe}_2$: C, 35.8; H, 3.39. Found: C, 33.9; H 3.41. IR (Nujol, NaCl): 1574(w), 1462(s), 1435(m), 1377(m), 1326(w), 1298(w), 1261(w), 1181(w), 1165(w), 1067(w), 1020(w), 999(w), 899(w), 801(w), 729(m), 691(m), 669(w) cm^{-1}. UV–visible (in THF): no $\lambda_{\max}$ from 320 to 800 nm.

[4] **1** crystallizes in the monoclinic space group $P2/a$, with a = 10.102(4) Å, b = 11.720(3) Å, c = 11.062(4) Å, β = 107.11°, V = 1251.7(8) Å^3, Z = 2, ρ_{calc} = 1.805 Mg/m^{-3}, (Mo Kα radiation at −100 °C). Full-matrix least-squares refinement with 2028 unique reflections [$F > 4\,\sigma(F)$] gave $R(F)$ = 0.030, $R_w(F)$ = 0.039. Complete crystallographic details are given in the supplementary material.

[5] Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751–767.

[6] Diphenyl diselenide (1.4 g, 4.5 mmol) was dissolved in diethyl ether (60 mL), and sodium triethylborohydride (9 mL of a 1.0 M solution in THF, 9 mmol) was added by syringe. The solution was stirred for 30 min and then concentrated to dryness to give a white solid. Europium trichloride (0.77 g, 3.0 mmol) was dissolved in THF (100 mL) and added to the NaSePh solution. Upon mixing, an orange solution formed; this was stirred for 1 h, and then the solvent was removed under vacuum. The solid was dissolved in pyridine (5 mL) and THF (50 mL), and the solution was stirred for 18 h, filtered, and concentrated to 25 mL. This orange solution was layered with diethyl ether (50 mL) and allowed to sit at room temperature. After 2 days, orange crystals (1.25 g, 66%), which desolvate at room temperature and turn red at 400 °C, were collected. Crystals suitable for structure determination were grown by layering the pyridine/THF with toluene. Elemental analysis indicates that the sample decomposes when isolated to form a complex of stoichiometry $(\text{pyridine})\text{Eu(SePh)}_2$. Anal. Calcd for $\text{C}_{17}\text{H}_{15}\text{NEuSe}_2$: C, 37.6; H, 2.79; N, 2.58. Found: C, 37.5; H, 2.80; N, 2.72. IR (Nujol, NaCl): 1260(w), 1594(m), 1571(m), 1465(s), 1439(s), 1378(s), 1296(w), 1261(m), 1216(w), 1178(w), 1148(m), 1097(m), 1067(m), 1033(m), 1020(m), 1000(m), 895(w), 754(m), 730(s), 691(s), 665(m), 616(m) cm^{-1}. UV–visible (in pyridine): $\lambda_{\max}$ = 392 nm.

[7] **2** crystallizes in the triclinic space group $P\bar{1}$, with a = 9.856(6) Å, b = 19.020(15) Å, c = 24.712(16) Å, α = 105.21(7)°, β = 97.96(5)°, γ = 100.59(8)°, V = 4308(3) Å^3, Z = 2, ρ_{calc} = 1.919 Mg/m^3 (Mo Kα radiation at −100 °C). Full-matrix least-squares refinement with 5640 unique reflections [$F > 6\,\sigma(F)$] gave $R(F)$ = 0.051, $R_w(F)$ = 0.055. Complete crystallographic details are given in the supplementary material.

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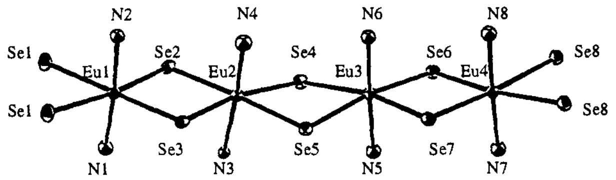

Figure 2. Extended coordination spheres in $[\{(\text{pyridine})_2\text{Eu}(\mu\text{-SeC}_6\text{H}_5)_2\}_4]_\infty$ (carbon atoms removed for clarity). The distorted octahedral Eu(II) ions are bound to *trans* pyridine ligands and two pairs of bridging phenylselenolato ligands which bind to the adjacent metal ions in a one-dimensional array. Thermal ellipsoids (ORTEP) are drawn at the 50% probability level. Average distances (Å): Eu–Se, 3.10(3); Eu–N, 2.69(2). Average angles (deg): Se–Eu–Se (*cis* Se bound to the same adjacent Eu), 77(7); Se–Eu–Se (*cis* Se bound to different neighboring Eu), 103(5); Eu–Se–C, 113(1); Eu–Se–Eu, 102(7); N–Eu–N, 175(3).

coupled $\text{MCl}_2(\text{py})_2$ transition-metal polymers,[8] and the octahedral europium ion represents a one-dimensional fragment of the solid-state EuSe lattice, which adopts the NaCl structure. Compound **2** is extremely sensitive with respect to pyridine dissociation. After minutes at room temperature, the crystals become opaque, and elemental analysis indicates that a 1:1 pyridine:europium complex is formed. Upon heating, the compound does not melt but gradually turns red and decomposes at 400 °C. The UV–visible spectrum of **2** dissolved in pyridine contains a diagnostic broad absorption at 392 nm. The complete absence of a UV–visible absorption for **1** suggests that the absorption in **2** involves transfer of an electron from the divalent metal ion to a pyridine ligand.

Both of these air and moisture sensitive compound reflect the tendency of chalcogenolate ligands to bridge metal centers and the tendency of the rare earth elements to optimize electrostatic interactions. We are currently examining the effects of dimensionality and structure on the magnetic and solid-state optical properties of these compounds.

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Supplementary Material Available: Tables of crystallographic details, additional bond geometries, and complete ORTEP diagrams for **1** and **2** (34 pages); listings of observed and calculated structure fators for **1** and **2** (46 pages). Ordering information is given on any current masthead page.

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[8] Richards, P. R.; Quinn, R. K.; Morosin, B. *J. Chem. Phys.* **1973**, *59*, 4474–4478.