Rare Earth Phenyltellurolates: 1D Coordination Polymers

Dilip V. Khasnis, Meggan Brewer, Jongseong Lee, Thomas J. Emge, and John G. Brennan[*]

Contribution from the Department of Chemistry, Rutgers,
The State University of New Jersey, Piscataway, New Jersey 08855-0939

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Abstract: THF coordination complexes of $Eu(TePh)_2$ and $Yb(TePh)_2$ crystallize as one-dimensional polymers. Transmetalation, rather than salt elimination, is the superior synthetic approach to these materials. Addition of 3 equiv of $NaTeC_6H_5$ to a solution of $EuCl_3$ in THF gives crystals of the bimetallic one-dimensional coordination polymer $[(THF)_3Eu(TeC_6H_5)_2NaTePh]_\infty$ (**1**). If the reaction product is dissolved in pyridine, crystalline $(pyridine)_5Eu(TeC_6H_5)_2$ is isolated. Recrystallization of $(pyridine)_5Eu(TeC_6H_5)_2$ from THF gives the one-dimensional polymer $[(THF)_2Eu(TeC_6H_5)_2]_\infty$ (**2**), which can also be prepared by the transmetalation reaction between $Hg(TePh)_2$ and Eu in THF. The analogous Yb salt elimination reactions do not give crystalline material, but the THF complex of $Yb(TePh)_2$ can be prepared by transmetalation using $Hg(TePh)_2$, and crystallizes as $[(THF)_2Yb(TeC_6H_5)_2 \cdot {}^1/_2THF]_\infty$ (**3**). All three coordination polymers (**1–3**) were characterized by low-temperature single-crystal X-ray diffraction. The structure of **1** contains pairs of divalent europium ions bridged by a pair of μ_3-PhTe ligands that are also coordinated to one Na. The Europium coordination sphere also includes three THF ligands, one μ_3-PhTe ligand that bridges one of the Eu and two Na ions that separate the pair of europium atoms from the next pair of Eu(II) ions, and one μ_2-PhTe ligand that bridges one Eu and Na. The structure of **2** contains a one-dimensional array of octahedral metal ions bound to *cis*-THF ligands and a pair of two bridging μ_2-phenyltellurolato ligands. Polymer **3** also contains octahedral metal ions with *cis*-THF, but in this structure the metal ions are connected to adjacent metals by an alternating number (1-3-1-3) of μ_2-phenyltellurolates. Crystal data (Mo Kα, −100 °C): **1**, space group $P\bar{1}$, $a = 9.800(3)$ Å, $b = 13.453(8)$ Å, $c = 14.019(4)$ Å, $\alpha = 104.81(4)°$, $\beta = 103.50(2)°$, $\gamma = 100.50(2)°$; **2**, space group $P\bar{1}$, $a = 8.533(4)$ Å, $b = 10.285(2)$ Å, $c = 13.490(4)$ Å, $\alpha = 71.57(2)°$, $\beta = 88.69(3)°$, $\gamma = 85.32(3)°$; **3**, space group $P2_1/c$, $a = 13.805(5)$ Å, $b = 19.149(5)$ Å, $c = 18.115(8)$ Å, $\beta = 100.30(3)°$.

Introduction

Complexes of the electropositive rare earths with the more electropositive chalcogen (S, Se, or Te) based ligands are important for both fundamental and applied reasons. Fundamentally, the nature of bonding between these electropositive metal ions and the heavier, less electronegative chalcogenolates is unexplored. While bonding in the solid state compounds has long been discussed in terms of covalent vs ionic bonding character,[1] little is known about the bonding of molecular chalcogen based compounds. Chalcogenolates of europium are particularly interesting from a fundamental perspective because the related solid-state chalcogenides are considered classic magnetic systems:[2] EuS is a ferromagnet,[2a,b] EuSe is a metamagnet,[2c] and EuTe is an antiferromagnet[2d,e] (EuTe is also a semiconductor).[3] While such magnetic interactions are common in rare earth solid state chemistry, they are rare in molecular rare earth chemistry. If the relationships between molecular and solid state properties are to be defined in terms of how long range order influences physical properties, we need to develop systems that contain the rare earth elements in limited dimension (i.e. nanometer sized clusters) or limited dimensionality (i.e. coordination polymer) forms.

In the past, rare earth chalcogenolate chemistry was dominated by compounds containing the pentamethylcyclopentadienyl (Cp*) ligand. Use of this ligand virtually ensures the molecularity of rare earth chemistry and has led to structural characterization of the first molecular rare earth compounds with direct bonds to the heavier chalcogenides.[4] Unfortunately, the steric requirements of Cp* are such that interpretation of metal–chalcogen bonding from bond geometries is not straightforward. More recently, there has been a surge of interest in preparing rare earth chalcogenolate complexes, where the only anionic ligands are chalcogenolates.[5] This synthetic effort is motivated by the expanding use of the rare earths to dope the covalent II–VI or III–V semiconductors,[6] by the desire to explore low-temperature synthetic approaches to rare earth chalcogenide based materials,

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(1) (a) Gerth, G.; Kienle, P.; Luchner, K. *Phys. Lett. A* **1968**, *27*, 557–8. (b) Eatough, N. L.; Hall, H. T. *Inorg. Chem.* **1970**, *9*, 417–8. (c) Dagys, R. S.; Anisimov, F.G. *Sov. Phys. Solid State* **1984**, *26*, 547–8 . (d) Wachter, P. *Crit. Rev. Solid State* **1972**, *3*, 189–241. (e) Byrom, E.; Ellis, D. E.; Freeman, A. J. *Phys. Rev. B* **1976**, *14*, 3558–68. (f) Zhukov, V. P.; Gubanov, V. A.; Weber, J. *J. Chem. Phys. Solids* **1981**, *42*, 631–9.

(2) (a) Kojima, K.; Komaru, T.; Hirara, T. *J. Phys. Soc. Jpn.* **1976**, *40*, 1570–4. (b) Sauer, C.; Kobler, U.; Zinn, W.; Kalrius, G. M. *J. Phys. Colloq. (Paris)* **1974**, *35*, C6 269–74. (c) Griessen, R.; Landolt, M.; Ott, H. R. *Solid State Commun.* **1971**, *9*, 2219–23. (d) Will, G.; Pickart, S. J.; Alperin, H. A.; Nathans, R. *J. Phys. Chem. Solids* **1963**, *24*, 1679–81. (e) Will, G. *Angew. Chem.* **1969**, *81*, 984–5.

(3) (a) Johanson, W. R.; McCollum, D. C. *Phys. Rev. B* **1980**, *22*, 2435–8. (b) Oliveira, N. F.; Foner, S.; Shapira, Y.; Reed, T. B. *Phys. Rev. B* **1972**, *5*, 2634–46.

(4) (a) Schumann, H.; Albrecht, I.; Hahn, E. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 985–6.5–6. (b) Berg, D.; Burns, C.; Andersen, R. A.; Zalkin, A. *Organometallics* **1988**, *8*, 1858–63. (c) Berg, D. J.; Burns, C.; Andersen, R. A.; Zalkin, A. *Organometallics* **1989**, *8*, 1865–70. (d) Zalkin, A.; Berg, D. J. *Acta Crystallogr.* **1988**, *44C*, 1488–1489. (e) Evans, W.; Grate, J. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 405–9. (f) Evans, W, Rabe, G.; Ziller, J.; Doedens, R. Submitted for publication.

(5) (a) Strzelecki, A. R.; Timinski, P. A.; Hesel, B. A.; Bianconi, P. A. *J. Am. Chem. Soc.* **1992**, *114*, 3159–3160. (b) Cary, D. R.; Arnold, J. *J. Am. Chem. Soc.* **1993**, *115*, 2520–2521. (c) Berardini, M.; Emge, T.; Brennan, J. G. *J. Chem. Soc., Chem. Commun.* **1993**, 1537–8. (d) Berardini, M.; Emge, T.; Brennan, J. G. *J. Am. Chem. Soc.* **1993**, *115*, 8501–2. (e) Brewer, M.; Khasnis, D.; Buretea, M.; Berardini, M.; Emge, T.; Brennan, J. *Inorg. Chem.* **1994**, *33*, 2743–7. (f) Mashima, K.; Nakayama, Y.; Kanehisa, N.; Kai, Y.; Nakamura, A. *J. Chem. Soc., Chem. Commun.* **1993**, 1847–8. (g) Berardini, M.; Emge, T.; Brennan, J. *J. Am. Chem. Soc.* **1994**, *116*, in press.

(6) (a) Singer, K. E.; Rutter, P.; Praker, A. R.; Wright, A. C. *Appl. Phys. Lett.* **1994**, *64*, 707–9. (b) Swiatek, K.; Godlewski, M.; Niinisto, L.; Leskela, M. *J. Appl. Phys.* **1993**, *74*, 3442–6. (c) Taniguchi, M.;Takahei, K. *J. Appl. Phys* **1993**, *73*, 943–7. (d) Jourdan, N.; Yamaguchi, H.; Harikoshi, Y. *Jpn. J. Appl. Phys.* **1993**, *32* (*2*), 1784–7. (e) Hsu, C. T.; Lin, Y. J.; Su, Y. K.; Yokoyama, H. *J. Appl. Phys.* **1992**, *72*, 4655–9. (f) Sohn, S. H.; Hyun, D. G.; Noma, M.; Hosomi, S.; Hamakawa, Y. *J. Appl. Phys.* **1992**, *72*, 4877–83. (g) Taniguchi, M.; Nakagone, H. *Appl. Phys. Lett.* **1991**, *58*, 2930–2. (h) Uwai, K.; Nakagone, H.; Takahei, K. *Appl. Phys. Lett.* **1987**, *50*, 977–9. (i) Palmstrom, C. J.; Mounier, S.; Finstad, T. G.; Miceli, P. F. *Appl. Phys. Lett.* **1990**, *56*, 382–4. (j) Kozanecki, A.; Karpinska, K.; Zalinski, Z. *Appl. Phys. Lett.* **1992**, *62*, 84–6.

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and because these systems are more suitable for studying the nature of the bond between the rare earths and the more electropositive elements. Rare earth complexes of unsubstituted arylchalcogenolate ligands can be isolated as one dimensional polymers[5d] from organic donor solvents, and the limited dimensionality of these systems can be studied to provide insight on how molecular properties evolve into solid state properties.

In this paper, we describe the synthesis, structural characterization, and optical properties of $[(THF)_3Eu(TeC_6H_5)_2NaTePh]_\infty$ (**1**), $[(THF)_2Eu(TeC_6H_5)_2]_\infty$ (**2**), and $[(THF)_2Yb(TeC_6H_5)_2 \cdot {}^1/_2THF]_\infty$ (**3**). All three polymers show different connectivity along the polymer backbone. The three structures are also different from the polymeric phenylselenolates of europium,[5d] illustrating the diversity of rare earth chalcogenolate structural chemistry.

Experimental Section

General Procedures. All syntheses were carried out under ultrapure nitrogen (JWS), using conventional drybox or Schlenk techniques. Solvents (Fisher) were refluxed continuously over molten alkali metals or sodium/benzophenone and collected immediately prior to use. Anhydrous pyridine and $NaHBEt_3$ (Aldrich) were purchased and used as received. PhTePh[7] and $Hg(TePh)_2$[8] were prepared according to literature procedure. Melting points were taken in sealed capillaries and are uncorrected. IR spectra were taken on a Mattus Cygnus 100 FTIR spectrometer and recorded from 4000 to 450 cm^{-1}. Electronic spectra were recorded on a Varian DMS 100S spectrometer with the samples in a 0.10 mm quartz cell attached to a Teflon stopcock. Elemental analyses were preformed by Quantitative Technologies, Inc. (Salem, NJ).

Synthesis of $[(THF)_3Eu(TeC_6H_5)_2NaTePh]_\infty$ (1). Method A: A solution of diphenylditelluride (1.23 g, 3.00 mmol) in diethyl ether (10 mL) was treated dropwise with sodium triethylborohydride (6 mL of a 1 M solution, 6.00 mmol) in THF. The reaction mixture was stirred for 4 h and evaporated to dryness. The colorless solid was washed with hexane (2 × 10 mL), pumped to dryness, and then treated with a solution of $EuCl_3$ (520 mg, 2.00 mmol) in THF (20 mL). The solution was stirred for 6 h, filtered to remove a white precipitate (that, when exposed to air, turns deep red), evaporated to dryness, and washed with hexane (5 × 10 mL). Diphenylditelluride (0.38 g, 0.95 mmol) was recovered from the hexane. The product was redissolved in THF (15 mL), filtered, and layered with hexane to yield pale yellow crystals (0.28 g, 17%) of **1**, mp 270–272 °C dec, that desolvate within an hour to give a complex of stoichiometry $(THF)Eu(TeC_6H_5)_2NaTePh$. Anal. Calcd for $NaC_{22}H_{23}EuOTe_3$: C, 30.7; H, 2.67. Found: C, 29.6; H, 2.76. IR (Nujol, KBr): 1569 (m), 1322 (w), 1261 (w),1293 (m), 1258 (w),1231 (w), 1177 (w), 1014 (m), 953 (m), 919 (m), 730 (s), 693 (s), 649 (s) cm^{-1}.

Method B: A solution of sodium phenyltellurolate (0.11 g 0.50 mmol) in THF (10 mL) was added to **2** (0.32 g, 0.50 mmol). The solution was stirred for 3 h, filtered, and layered with hexane to yield pale yellow crystals (0.38 g, 88%) of **1**.

Synthesis of $(pyridine)_5Eu(TeC_6H_5)_2$ (4). A solution of diphenylditelluride (1.23 g, 3.00 mmol) in diethyl ether (10 mL) was treated dropwise with sodium triethylborohydride (6 mL of a 1 M solution, 6.00 mmol) in THF. The reaction mixture was stirred for 4 h and evaporated to dryness. The colorless solid was washed with hexane (2 × 10 mL), pumped to dryness, and then treated with a solution of $EuCl_3$ (520 mg, 2.00 mmol) in THF (20 mL). The solution was stirred for 6 h, filtered, evaporated to dryness, and washed with diethyl ether (2 × 10 mL). The product was redissolved in pyridine (15 mL), filtered, and layered with diethyl ether to yield dark red crystals of **2** (0.60 g, 32%), mp 215–217 °C dec. Anal. Calcd for $C_{37}H_{35}N_5EuTe_2$: C, 46.4; H, 3.66; N, 7.32. Found: C, 45.9; H, 3.58; N, 7.18. IR (Nujol, KBr): 1592 (m), 1568 (m), 1322 (w), 1218 (w), 1152 (w), 1068 (w), 1056 (w), 1032 (m), 1014 (m), 753 (s), 733 (s), 702 (s), 649 (s), 616 (s) cm^{-1}. λ_{max} (pyridine) 382 nm. The complex is isostructural with $(pyridine)_5Yb(TePh)_2$.[5e]

Synthesis of $[(THF)_2Eu(TeC_6H_5)_2]_\infty$ (2). Method A: **4** (400 mg, 0.42 mmol) was dissolved in THF (15 mL). The solution was filtered and layered with hexane to yield light yellow crystals (358 mg, 97%; mp 207–209 °C dec) of **2** that desolvate within an hour to give a compound of stoichiometry $(THF)Eu(TeC_6H_5)_2$. Anal. Calcd for $C_{16}H_{18}EuOTe_2$: C, 30.3; H, 2.84. Found: C, 30.1; H, 2.87. IR (Nujol, KBr): 1569 (m), 1261 (w), 1231 (w), 1058 (w), 1028 (m), 871 (m), 806 (m), 727 (s), 693 (s), 649 (m) cm^{-1}. When dissolved in either THF or acetonitrile the compound is optically transparent from 300 to 800 nm. ^1H NMR (CD_3CN, 30 °C), δ ppm: 7.4, 7.0, 6.36 (5H), 3.53 (4H), 1.43 (4H). Line widths range between $\nu_{1/2}$ = 100 and 200 Hz, and so these integrations are approximate.

Table 1. Summary of Crystallographic Details[a]

compd no.	**1**	**2**	**3**
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a (Å)	9.800(3)	8.533(4)	13.805(5)
b (Å)	13.453(8)	10.285(2)	19.149(5)
c (Å)	14.019(4)	13.490(4)	18.115(8)
α (deg)	104.81(4)	71.57(2)	90.00
β (deg)	103.50(2)	88.69(3)	100.30(3)
γ (deg)	100.50(2)	85.32(3)	90.00
V (Å^3)	1679(1)	1119(1)	4712(3)
Z	2	2	4
r_{calc} (Mg/m^{-3})	1.989	2.093	2.100
no. of unique reflcns [$I > 2\,\sigma(I)$]	4043	4447	4786
$R(F)$	0.056	0.029	0.035
$wR(F^2)$	0.180	0.077	0.085

[a] Additional crystallographic details are given in the supplemental material.

Method B: A suspension of mercury(II) phenyltellurolate (2.00 g, 3.25 mmol) and europium metal (0.49 g, 3.25 mmol) in THF (50 mL) was stirred for 72 h. The yellow solution was separated from the black precipitate by filtration and pumped to dryness to yield pale yellow microcrystalline material which was recrystallized from a THF/hexane mixture to give **2** (1.83 g, 90%).

Synthesis of $[(THF)_2Yb(TeC_6H_5)_2 \cdot {}^1/_2 THF)]_\infty$ (3). A suspension of mercury(II) phenyltellurolate (2.00 g, 3.25 mmol) and ytterbium metal (0.563 g, 3.25 mmol) in THF (50 mL) was stirred for 72 h. The dark red solution was filtered, concentrated to 30 mL, and layered with hexane to yield red crystals of **3** (1.95 g, 92%; mp 148–150 °C dec) that desolvate within an hour to give a stoichiometry $(THF)Yb(TeC_6H_5)_2$. Anal. Calcd for $YbC_{16}H_{18}OTe_2$: C, 29.4; H, 2.76. Found: C, 29.3; H, 3.10. IR (Nujol, KBr): 1592 (m), 1568(m), 1322 (w), 1218 (w), 1152 (w), 1068 (w), 1056 (w), 1032 (m), 1014 (m), 753 (s), 733 (s), 702 (s), 649 (s), 616 (s) cm^{-1}. λ_{max} (THF) 450 nm; λ_{max} (CH_3CN) 413 nm, λ_{max} (pyridine) 391, 525 nm. ^1H NMR (CD_3CN, 30 °C), δ ppm: 7.74 (2H), 6.94 (1H), 6.77 (2H), 3.63 (5H), 1.77 (5H).

X-ray Structure Determination of 1, 2, and 3. Data for **1**, **2**, and **3** were collected on a CAD4 diffractometer with graphite monochromatized Mo Kα radiation (λ = 0.71073) at −100 °C. In all three structures, three check reflections were measured every 3 h and showed no significant intensity loss. The data were corrected for Lorenz effects and polarization. The absorption corrections were based on a Gaussian grid method (SHELX76).[9] The three structures were solved by Patterson methods (SHELXS86).[10] All non-hydrogen atoms in **2** and **3** and the Eu, Te, and Na atoms in **1** were refined (SHELXL93)[11] with anisotropic thermal parameters. All hydrogen atom coordinates were calculated with bond distances of 0.95 Å. Polymer **3** contained half of a THF solvent molecule that was disordered about a center of inversion. Crystallographic data and final R indices are given in Table 1. Complete crystallographic results are given in the supplemental material.

Results and Discussion

Synthesis and Characterization. Divalent phenyltellurolate complexes of the rare earths Eu and Yb can be prepared by reacting MCl_3 with 3 equiv of NaTePh or by transmetalation with mercury bis(phenyltellurolate), with transmetalation being the superior synthetic approach. The isolation of only divalent products from both elemental and trivalent rare earth starting materials indicates that the tris(phenyltellurolates) of Eu and Yb are both unstable with respect to reductive elimination of diphenylditelluride. This is expected for europium, which does not form a trivalent tris(chalcogenolate) complex with the more

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(7) Engman, L.; Persson, J. *J. Organomet. Chem.* **1990**, *388*, 71–74.

(8) Okamoto, Y.; Yano, T. *J. Organomet. Chem.* **1971**, *29*, 99–103.

(9) Sheldrick, G. M. SHELX76, Program for Crystal Structure Determination, University of Cambridge, England, 1976.

(10) Sheldrick, G. M. SHELXS86, Program for the Solution of Crystal Structures, University of Gottingen, Germany, 1986.

(11) Sheldrick, G. M. SHELXL-93, Program for Crystal Structure Refinement, University of Gottingen, Germany, 1993.

electronegative phenylselenolate ligand,[5d] but was not obvious for Yb. The stability of $Yb(TePh)_3(THF)_x$ was less predictable for a number of reasons. First, Yb is a significantly stronger reducing agent than is Eu, and has a more stable trivalent oxidation state. Second, a trivalent phenyltellurolate complex of Yb, $Cp^*{}_2$-Yb^{III}(phenyltellurolate), has been reported.[4b] Third, a tris(phenylselenolate) of Yb(III) has been described previously.[5c] Finally, in the salt elimination reaction of $YbCl_3$ with NaTePh in THF, reduction of the metal and elimination of PhTeTePh was not observed until the THF was removed and pyridine was added to the reaction mixture.[5e] The isolation of only divalent $Yb(TePh)_2$ coordination complexes from the transmetalation reactions reported here, coupled with the absence of any reaction between $Yb(TePh)_2(THF)_x$ and PhTeTePh in THF, indicates that any tris(phenyltellurolate) complex of Yb will have a limited stability.

Phenyltellurolates of Eu can be prepared by salt elimination or transmetalation. Addition of 3 equiv of $NaTeC_6H_5$ to a solution of $EuCl_3$ in THF resulted in the immediate formation of diphenylditelluride and the precipitation of a colorless solid. The precipitate, which we initially assumed to be NaCl, tested positive for Cl^-, but was also air sensitive and decomposed to liberate diphenylditelluride. After days at room temperature, the reaction was filtered, and saturation of the solution by layering with hexane gave light yellow crystals of the bimetallic 1D coordination polymer $[(THF)_3Eu(TeC_6H_5)_2NaTePh]_\infty$ (**1**). This compound is insoluble in apolar solvents, but readily dissolves in donor solvents such as pyridine, THF, or acetonitrile. In THF or acetonitrile the compound is optically transparent between 300 and 800 nm.

Because these compounds were prepared for use as precursors to rare earth chalcogenide clusters and solid state compounds, the presence of Na was viewed as an impurity. The NaTePh was eliminated by dissolving the initially insoluble products with a stronger donor solvent, and allowing the reaction to proceed to completion. When the resultant yellow-orange solid of the NaTePh/$EuCl_3$ reaction was extracted with pyridine, crystalline $Eu(TePh)_2(pyridine)_5$ (**4**) was isolated. The yield of this reaction product, based on Eu, is twice that of **1**. In pyridine, molecular **4** displays a broad characteristic charge transfer absorption at 382 nm. By comparison with the optically transparent divalent phenyltellurolate THF complexes **1** and **2**, and by analogy with europium bis(phenylselenolate) in THF and pyridine,[5d] this optical absorption has been tentatively assigned to a metal-to-pyridine charge transfer excitation. This charge transfer excitation energy is 0.89 eV larger than the optical absorption energy of the isostructural Yb complex, and the similarity between this energy difference and the previously reported 0.72 eV difference between Eu and Yb reduction potentials supports the assignment. Further, the higher charge transfer excitation energy of the phenyltellurolate complex, relative to the analogous phenylselenolate, is consistent with the diminished ability of the more electropositive chalcogenolates to stabilize a trivalent metal ion in the excited state. This trend was also observed in the series of ytterbium chalcogenolates $Yb(EPh)_2(pyridine)_x$ (E = S, Se (x = 4); E = Te (x = 5).[5e] Compound **4** is particularly stable with respect to pyridine dissociation and, when isolated, can be handled in an inert atmosphere for over an hour with no measurable loss of crystallinity (in contrast to the more sterically congested Yb complex, which becomes completely amorphous over the same time period).

The pyridine donor ligands can be replaced in the presence of a large excess of a less basic solvent. If **4** is redissolved in THF and the solution is layered with hexane, compound **2** crystallizes as long (ca. 1 mm) yellow needles. Like **1**, compound **2** is optically transparent in THF from 300 to 800 nm. The melting point of **2** is 80° lower than the melting point of **1**, and this lower lattice energy suggests that it will be impossible to isolate pure **2** in the presence of NaTePh. In fact, the most efficient synthesis of **1** is to first prepare **2** by the transmetalation reaction described below, redissolve the compound in THF, add of 1 equiv of NaTePh, and layer the solution with hexane.

Table 2. Selected Bond Lengths (Å) and angles (deg) for **1**[a]

Eu–O(2)	2.56(1)	Eu–O(3)	2.57(1)
Eu–O(1)	2.57(1)	Eu–Te(1)	3.324(2)
Eu–Te(2)′	3.359(2)	Eu–Te(2)	3.404(2)
Eu–Te(3)	3.427(2)	Na–Te(1)	3.095(6)
Na–Te(2)	3.107(6)	Na–Te(3)″	3.156(7)
Na–Te(3)′	3.220(6)	Na–Na‴	4.06(1)
Te(1)–C(1)	2.10(1)	Te(2)–C(7)	2.11(2)
Te(2)–Eu	3.359(2)	Te(3)–C(13)	2.11(1)
Te(3)–Na⁗	3.155(7)	Te(3)–Na′	3.220(6)
O(2)–Eu–O(3)	72.5(3)	O(2)–Eu–O(1)	146.5(3)
O(3)–Eu–O(1)	74.7(3)	O(2)–Eu–Te(1)	95.7(2)
O(3)–Eu–Te(1)	94.5(2)	O(1)–Eu–Te(1)	93.5(2)
O(2)–Eu–Te(2)′	134.9(2)	O(3)–Eu–Te(2)′	151.4(3)
O(1)–Eu–Te(2)′	78.6(2)	Te(1)–Eu–Te(2)′	76.94(4)
O(2)–Eu–Te(2)	74.3(2)	O(3)–Eu–Te(2)	146.8(3)
O(1)–Eu–Te(2)	138.0(2)	Te(1)–Eu–Te(2)	89.58(5)
Te(2)′–Eu–Te(2)	61.41(5)	O(2)–Eu–Te(3)	98.2(2)
O(3)–Eu–Te(3)	92.5(2)	O(1)–Eu–Te(3)	76.4(2)
Te(1)–Eu–Te(3)	165.74(4)	Te(2)′–Eu–Te(3)	91.02(4)
Te(2)–Eu–Te(3)	91.31(5)	Te(1)–Na–Te(2)	99.7(2)
Te(1)–Na–Te(3)″	111.6(2)	Te(2)–Na–Te(3)″	124.7(2)
Te(1)–Na–Te(3)′	121.1(2)	Te(2)–Na–Te(3)′	99.8(2)
Te(3)″–Na–Te(3)′	101.0(2)	Te(1)–Na–Na‴	134.2(3)
Te(2)–Na–Na‴	125.4(3)	Te(3)″–Na–Na‴	51.2(2)
Te(3)′–Na–Na‴	49.8(1)	C(1)–Te(1)–Na	113.7(4)
C(1)–Te(1)–Eu	103.6(4)	Na–Te(1)–Eu	85.8(1)
C(7)–Te(2)–Na	117.5(4)	C(7)–Te(2)–Eu′	124.5(4)
Na–Te(2)–Eu′	85.0(1)	C(7)–Te(2)–Eu	113.9(4)
Na–Te(2)–Eu	84.3(1)	Eu′–Te(2)–Eu	118.59(5)
C(13)–Te(3)–Na⁗	104.7(4)	C(13)–Te(3)–Na′	101.6(4)
Na⁗–Te(3)–Na′	79.0(2)	C(13)–Te(3)–Eu	118.5(4)
Na⁗–Te(3)–Eu	135.5(1)	Na′–Te(3)–Eu	82.2(1)

[a] Symmetry transformations used to generate equivalent atoms: (′) $-x,-y+1,-z+2$; (″) $x-1,y,z$; (‴) $-x-1,-y+1,-z+2$; (⁗) $x+1,y,z$.

The yields in these salt elimination reactions do not improve with higher reaction temperatures because the tellurolates decompose in refluxing THF or pyridine,[12] and so an alternative synthetic approach was also explored. The transmetalation reaction between $Hg(TePh)_2$ and Eu in THF proceeds cleanly to give elemental Hg and europium phenyltellurolates—in comparison to the 10% yield of the salt elimination approach, transmetalation gives compound **2** in 90% yield.

Transmetalation is also the most reliable synthetic approach to polymer **3**, which can be isolated in better than 90% yield from the reaction of Yb with $Hg(TePh)_2$ in THF. The optical properties of polymer **3** are solvent dependent, with λ_{max} values of 450 in THF and 413 in CH_3CN, and these absorptions are tentatively assigned to an f → d excitation. In pyridine, **3** displays two optical absorption maxima: a relatively sharp f → d absorption at 391 nm, and a broad absorption at 525 nm, which has been assigned as a metal-to-pyridine charge transfer excitation. If the optical excitations are in fact f → d transitions, we will eventually be able to monitor the energy of the excitation as a function of neutral ligand donor/acceptor properties to establish the magnitude of crystal field effects, once solution coordination numbers have been established.

Structure. All three coordination polymers were characterized by low-temperature single-crystal X-ray diffraction. Table 1 gives a listing of crystallographic details for **1–3**, and Tables 2–4 give lists of selected bond geometries for **1–3**, respectively.

Figure 1 shows an ORTEP diagram of **1**. The structure consists of alternating pairs of seven coordinate Eu(II) ions and tetrahedrally coordinated Na atoms. The Eu pair are bridged through a unique pair of μ_3-phenyltellurolate ligands (Eu–Te(2) = 3.38(1) Å) that also bind to one of the two adjacent Na ions. A second μ_3-phenyltellurolate ligand (Eu–Te(3) = 3.324(2) Å)

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(12) Unpublished results from this laboratory.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **2**[a]

Eu–O(2)	2.491(3)	Eu–O(1)	2.512(3)
Eu–Te(2)′	3.335(2)	Eu–Te(1)	3.346(1)
Eu–Te(1)″	3.349(2)	Eu–Te(2)	3.359(1)
Te(1)–C(1)	2.122(5)	Te(1)–Eu″	3.349(2)
Te(2)–C(7)	2.122(4)	Te(2)–Eu′	3.335(2)
O(2)–Eu–O(1)	98.2(1)	O(2)–Eu–Te(2)′	83.73(8)
O(1)–Eu–Te(2)′	86.64(9)	O(2)–Eu–Te(1)	93.68(8)
O(1)–Eu–Te(1)	164.36(9)	Te(2)′–Eu–Te(1)	104.84(3)
O(2)–Eu–Te(1)″	88.73(9)	O(1)–Eu–Te(1)″	84.31(8)
Te(2)′–Eu–Te(1)″	167.29(1)	Te(1)–Eu–Te(1)″	85.79(3)
O(2)–Eu–Te(2)	154.78(9)	O(1)–Eu–Te(2)	103.98(8)
Te(2)′–Eu–Te(2)	85.66(3)	Te(1)–Eu–Te(2)	67.10(2)
Te(1)″–Eu–Te(2)	105.18(3)	C(1)–Te(1)–Eu	119.6(1)
C(1)–Te(1)–Eu″	95.6(1)	Eu–Te(1)–Eu″	94.21(3)
C(7)–Te(2)–Eu′	99.1(1)	C(7)–Te(2)–Eu	118.5(1)
Eu′–Te(2)–Eu	94.34(3)		

[a] Symmetry transformations used to generate equivalent atoms: (′) $-x+1,-y+1,-z+1$; (″) $-x,-y+1,-z+1$.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **3**[a]

Yb(1)–O(2)	2.394(6)	Yb(1)–O(1)	2.397(6)
Yb(1)–Te(1)	3.1358(14)	Yb(1)–Te(2)	3.1701(13)
Yb(1)–Te(3)	3.1964(14)	Yb(1)–Te(4)	3.2106(14)
Yb(1)–Yb(2)	4.109(2)	Yb(2)–O(4)	2.384(7)
Yb(2)–O(3)	2.400(6)	Yb(2)–Te(1)′	3.155(1)
Yb(2)–Te(4)	3.2001(14)	Yb(2)–Te(2)	3.218(2)
Yb(2)–Te(3)	3.2240(13)	Te(1)–C(1)	2.120(9)
Te(1)–Yb(2)″	3.1553(14)	Te(2)–C(7)	2.133(10)
Te(3)–C(13)	2.141(10)	Te(4)–C(19)	2.130(9)
O(2)–Yb(1)–O(1)	96.7(2)	O(2)–Yb(1)–Te(1)	88.5(2)
O(1)–Yb(1)–Te(1)	83.5(2)	O(2)–Yb(1)–Te(2)	90.3(2)
O(1)–Yb(1)–Te(2)	87.8(2)	Te(1)–Yb(1)–Te(2)	171.04(2)
O(2)–Yb(1)–Te(3)	89.3(2)	O(1)–Yb(1)–Te(3)	169.5(2)
Te(1)–Yb(1)–Te(3)	105.29(3)	Te(2)–Yb(1)–Te(3)	83.58(3)
O(2)–Yb(1)–Te(4)	171.1(2)	O(1)–Yb(1)–Te(4)	87.9(2)
Te(1)–Yb(1)–Te(4)	99.59(4)	Te(2)–Yb(1)–Te(4)	82.21(3)
Te(3)–Yb(1)–Te(4)	85.03(4)	O(4)–Yb(2)–O(3)	85.0(2)
O(4)–Yb(2)–Te(1)′	86.8(2)	O(3)–Yb(2)–Te(1)′	89.37(14)
O(4)–Yb(2)–Te(4)	92.5(2)	O(3)–Yb(2)–Te(4)	95.32(14)
Te(1)′–Yb(2)–Te(4)	175.18(2)	O(4)–Yb(2)–Te(2)	102.0(2)
O(3)–Yb(2)–Te(2)	172.4(2)	Te(1)′–Yb(2)–Te(2)	93.83(4)
Te(4)–Yb(2)–Te(2)	81.64(4)	O(4)–Yb(2)–Te(3)	174.5(2)
O(3)–Yb(2)–Te(3)	90.5(2)	Te(1)′–Yb(2)–Te(3)	96.33(3)
Te(4)–Yb(2)–Te(3)	84.75(3)	Te(2)–Yb(2)–Te(3)	82.39(3)
C(1)–Te(1)–Yb(1)	107.5(2)	C(1)–Te(1)–Yb(2)″	102.5(2)
Yb(1)–Te(1)–Yb(2)″	149.34(3)	C(7)–Te(2)–Yb(1)	112.1(2)
C(7)–Te(2)–Yb(2)	108.7(2)	Yb(1)–Te(2)–Yb(2)	80.06(4)
C(13)–Te(3)–Yb(1)	100.9(2)	C(13)–Te(3)–Yb(2)	112.1(3)
Yb(1)–Te(3)–Yb(2)	79.58(3)	C(19)–Te(4)–Yb(2)	108.5(3)
C(19)–Te(4)–Yb(1)	112.3(3)	Yb(2)–Te(4)–Yb(1)	79.72(3)

[a] Symmetry transformations used to generate equivalent atoms: (′) $x,-y+{}^{1}/_{2},z+{}^{1}/_{2}$; (″) $x,-y+{}^{1}/_{2},z-{}^{1}/_{2}$.

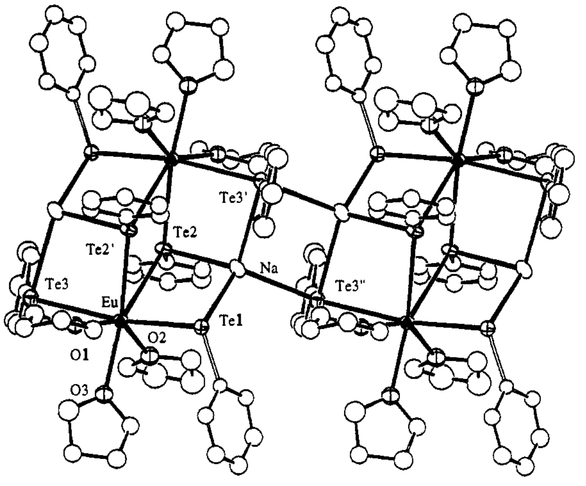

Figure 1. ORTEP diagram of the light yellow 1D bimetallic coordination polymer $[(THF)_3Eu^{II}(\mu\text{-}TeC_6H_5)_2Na\text{-}\mu\text{-}TePh]_\infty$. The seven coordinate Eu(II) ions are bound to three THF ligands, a pair of μ_3-phenyltellurolate ligands which bridge the two europium ions and a Na ion, a μ_3-tellurolate which bridges a single Eu ion and two adjacent Na atoms, and a μ_2-tellurolate that bridges a Eu ion and one Na. Average distances (Å): Eu–Te, 3.38(2); Eu–O, 2.57(1); Na–Te, 3.14(2). Significant angles (deg): Te2–Eu–Te2a, 61.45(5); Te2–Eu–Te1, 89.58(5); Te2–Eu–Te3, 91.31(5); Eu–Te–Eua, 118.6(1); Eu–Te–C, 115.1 (range 103.6(C1)–124.5(C7); Na–Te–C, 109.4 (range 101.6(C13)–117.6(C7); Te–Na–Te, 109.65 (range 91.0–124.7).

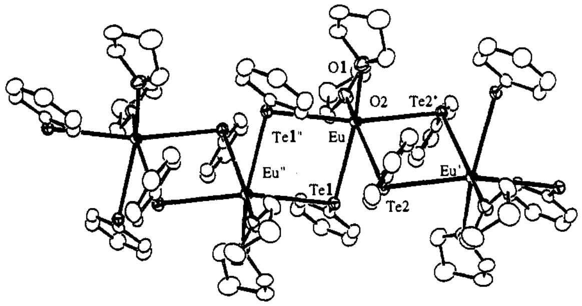

Figure 2. ORTEP diagram of the light yellow 1D coordination polymer $[(THF)_2Eu^{II}(\mu\text{-}TeC_6H_5)_2]_\infty$. The octahedral Eu(II) ion is bridged to two adjacent metal ions through pairs of phenyltellurolato ligands and *cis*-THF ligands. Average distances (Å): Eu–Te, 3.35(1), Eu–O, 2.50(1) Å. Significant angles (deg): O1–Eu–O2, 98.2(1); Te1–Eu–Te2, 67.1(2); O–Eu–Te(cis), 90.2 (av); Eu–Te–C, 107.9 (range 95.6–119.6); Eu–Te–Eu (av), 94.3(1).

bridges between one Eu and two Na ions, while the third type of phenyltellurolate bridges one Na and one Eu (Eu–Te(1) = 3.324(2) Å). The compound can be viewed as alternating pairs of paramagnetic ions separated by diamagnetic spacers. Seven-coordinate Eu(II), with three neutral donors and four bridging phenylchalcogenolate ligands, was also observed in the monometallic polymer $[(THF)_3Eu(SeC_6H_5)_2]_\infty$, but the phenylselenolate ligands spanned only two metal centers. In **1**, the tellurolates must bridge additional metal centers to satisfy the additional coordination requirements of the Na ions, which generally coordinate at least four monodentate ligands. One previously reported alkali/rare earth chalcogenolate compound, $LiYb(SePh)_4(pyridine)_4$,[5c] also contained a pair of chalcogenolate ligands bridging alkali and rare earth metal centers, but in that case the stronger pyridine donor was competitive with bridging phenylselenolate, and a molecular structure with both bridging and terminal phenylselenolates was observed. In tellurolate chemistry, pyridine displaces the less basic Te ligands, and molecular pyridine complexes result.

X-ray structural characterization of **2** revealed a new type of rare earth chalcogenolate coordination polymer, with octahedral metal centers bridged to adjacent metal ions through pairs of phenyltellurolates, and *cis* THF (Figure 2). While this structure represents a 1D array of paramagnets, a magnetic susceptibility study on the related selenolate polymer[5d] $[(pyridine)_2Eu(SeC_6H_5)_2]_\infty$ showed no magnetic ordering as low as 2 K,[13] and so we anticipate no measurable magnetic interactions between the Eu(II) ions in **1** or **2**, where the Eu-Eu distances are greater (in $(pyridine)_2Eu(SeC_6H_5)_2$, the Eu-Eu distances range from 4.64 to 5.05 Å, in **1**, Eu-Eu = 5.82 Å, and in **2**, Eu-Eu = 4.90 Å). The coordination of two neutral donors in **2**, and three THF ligands in **1**, can be rationalized in terms of steric interactions within the secondary coordination spheres of **1** and **2**. The Na ions present in **1** force the phenyltellurolate ligands to span more than two metal ions, and this produces a larger effective ionic radius for the tellurolate ligands. This larger ligand ionic radius, in turn, increases the distance of the phenyl groups from the europium center, alleviates steric strain within the molecule, and permits coordination of an additional neutral donor to the Eu ion in **1**.

Structural characterization of **3** showed yet another type of chalcogenolate connectivity between rare earths. Figure 3 shows

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(13) N. Edelstein, private communication.

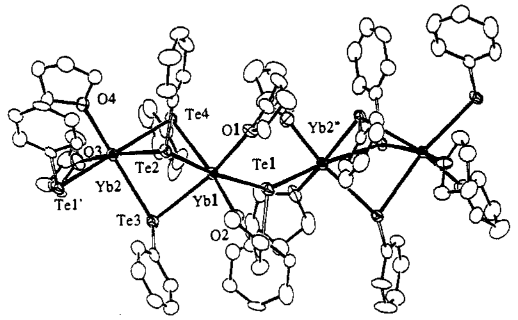

Figure 3. ORTEP diagram of the red 1D coordination polymer $[(THF)_2Yb^{II}(\mu\text{-}TeC_6H_5)_2\cdot{}^1/_2THF]_\infty$. The octahedral Yb(II) ions are bound to *cis*-THF ligands, and the metals are bridged asymmetrically to the two adjacent metal ions, with one μ^2-TePh connecting to one metal and three μ-TePh ligands bound to the other, in a nonlinear array. Significant distances (Å): Yb(1)–Te(1), 3.136(1); Yb(1)–Te(2), 3.170(1); Yb(1)–Te(3), 3.196(1); Yb(1)–Te(4), 3.211(1); Yb(1)–Yb(2), 4.109(2); Yb(2)–Te(1)′, 3.155(1); Yb(2)–Te(4), 3.200(1); Yb(2)–Te(2), 3.218(2); Yb(2)–Te(3), 3.224(1); Te(1)–Yb(2)″, 3.155(1). Average distance (Å): Yb–O, 2.39(1).

an ORTEP diagram of 3, where the diamagnetic octahedral metal ions are connected to adjacent metal ions through an alternating (1,3,1,3) number of μ_2-phenyltellurolate ligands, and *cis*-THFs. The Yb–Te distances show an unexpected pattern, with the Yb–Te distances in the tellurolate ligands *trans* to a THF (Te3 and Te4) being slightly longer than the distance to tellurolates (Te1, Te2) that are *trans* to another tellurolate, but this is probably not chemically significant; $Yb(TePh)_2(pyridine)_5$ contained statistically inequivalent (3.25(1) and 3.33(1) Å) Yb–Te distances with the tellurolate ligands occupying the two axial positions in a trigonal bipyramid.[5e] In **2**, the Eu–Te distances in tellurolates *cis* and *trans* to THF ligands are statistically equivalent.

This alternating distribution of bridging chalcogenolate ligands between metal centers is unprecedented in rare earth chalcogenolate chemistry, which thus far has been limited to molecules[5e] or one dimensional polymers[5d] with symmetric bridges between metal centers. Since the chalcogenolates are often considered pseudo-halides, a comparison with halide structures is also appropriate. The connectivity in polymer **3** is unlike the THF complexes of the rare earth chlorides, which crystallize as molecules[14] or, in one recently reported instance, as a symmetric dimer.[15]

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Supplementary Material Available: Tables of crystallographic details and additional structural information for **1**, **2**, and **3** (17 pages); listings of observed and calculated structure factors for **1**, **2**, and **3** (49 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(14) (a) Chen, W.; Jin, Z.; Xing, Y.; Fan, Y.; Yang, Q. *Inorg. Chim. Acta* **1987**, *130*, 125–9. (b) Lin, S. H.; Dong, Z. C.; Huang, J. S.; Zhang, Q. E.; Lu, J. X. *Acta Crystallogr. C* **1991**, *47*, 426–7.

(15) Deacon, G. B.; Feng, T.; Nickel, S.; Skelton, B. W.; White, A. *J. Chem. Soc., Chem. Commun.* **1993**, 1328–9.