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Chalcogen-Rich Lanthanide Clusters: Compounds with Te^{2-}, $(TeTe)^{2-}$, TePh, TeTePh, $(TeTeTe(Ph)TeTe)^{5-}$, and $[(TeTe)_4TePh]^{9-}$ Ligands; Single Source Precursors to Solid-State Lanthanide Tellurides

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Lanthanide metals react with PhTeTePh and elemental Te in pyridine to give $(py)_yLn_4(Te)(TeTe)_2(TeTeTe(Ph)TeTe)(Te_xTePh)$ (Ln = Sm ($y = 9$; $x = 0$); Tb, Ho ($y = 8$, $x = 0.1$)), and $(py)_7Tm_4(Te)[(TeTe)_4TePh](Te_{0.6}TePh)$ clusters. The Sm, Tb, and Ho compounds contain a square array of Ln(III) ions all connected to a central Te^{2-} ligand. Two adjacent edges of the square are bridged by ditelluride ligands, with the Ln ion that is η^2 bound to both of these TeTe ligands also coordinating to a terminal TePh ligand. The other two edges of the square are spanned by ditellurides that both coordinate a TePh ligand that has been displaced from the Ln ion by pyridine, to give the pentaanion $(\mu\text{-}\eta^2\text{-}\eta^2\text{-}Te_2Te(Ph)Te_2)^{5-}$. In the Tm compound, the displaced TePh interacts with all four TeTe units. The compounds are air-, light-, and temperature-sensitive. Upon thermolysis, they decompose to give solid-state $TbTe_{2-x}$, HoTe, or TmTe, with elimination of Te and $TePh_2$.

Introduction

Inorganic compounds of tellurium are challenging synthetic targets, because bonds to this element are considerably weaker than bonds to the lighter chalcogens sulfur or selenium, and thus, compounds are relatively unstable. Because this relative instability often leads to the formation of materials with highly unusual or useful physical properties (i.e., CdHgTe semiconductors,[1] Bi_2Te_3 thermoelectric materials[2]), the chemistry of metal tellurium compounds continues to attract attention. From a fundamental perspective, compounds with Te are interesting because they often adopt unconventional molecular or solid-state structures with a wide range of Te−Te bonds, a chemistry that parallels that of the complex polyiodide compounds. Stabilities are defined by shallow potential energy surfaces, and structures are often unpredictable.

Lanthanide (Ln) ions, with their valence 4f obitals effectively shielded by filled $5s^2$ and $5p^6$ orbitals, also tend to adopt molecular structures defined by shallow potential energy surfaces, and the combination of ionic Ln metal and covalent Te ligands yields compounds that are particularly difficult to isolate and characterize. This is reflected in the literature, where over a hundred examples of structurally characterized compounds containing Ln−S bonds, more than 35 examples of compounds with Ln−Se bonds, and only 12 analogous Ln−Te compounds have been described.[3] A majority of the 12 Ln−Te compounds contain relatively electronegative, sterically demanding ancillary ligands[4−7] (i.e., C_5Me_5 or Cp*) that kinetically passivate the Ln−Te bond. Most of the remaining examples are divalent $Ln(ER)_2$ coordination complexes of the redox active Sm, Eu, or Yb.[8−10] The tendency of the trivalent redox active metals to reductively eliminate RTeTeR clearly reflects the inability of Te ligands to stabilize Ln(III) oxidation states. In the absence of stabilizing ancillary anions, the only reported example of an isolable Ln(III)−Te compound is $(Me_2PCH_2$-

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(1) Andresen, B. F.; Scholl, M. S., Eds. *Infrared Technology and Applications XXIV;* SPIE Proceedings Vol. 3436, San Diego, CA, 1998.

(2) Mathiprakasam, B.; Heenan, P., Eds., *Proceedings of the Thirteenth International Conference on Thermoelectrics*; AIP Conference Proceedings 316, Midwest Research Institute, 1995.

(3) Nief, F. *Coord. Chem. Rev.* **1998**, *178*, 13.

(4) Berg, D.; Andersen, R. A.; Zalkin, A. *Organometallics*, **1988**, *7*, 1858.

(5) Evans, W. J.; Rabe, G. W.; Ziller, J. W.; Doedens, R. J. *Inorg. Chem.* **1994**, *33*, 2719.

(6) Zalkin, A.; Berg, D. *Acta Crystallogr.* **1988**, *C44*, 1488.

(7) Recknagel, A.; Noltemeyer, M.; Stalke, D.; Pieper, U.; Schmidt, H. G.; Edelmann, F. T. *J. Organomet. Chem.* **1991**, *411*, 347.

(8) Khasnis, D. V.; Lee, J.; Brewer, M.; Emge, T. J.; Brennan, J. G. *J. Am. Chem. Soc.* **1994**, *116*, 7129.

(9) Brewer, M.; Khasnis, D.; Buretea, M.; Berardini, M.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1994**, *33*, 2743.

(10) Cary, D. R.; Arnold, J. *Inorg. Chem.* **1994**, *33*, 1791.

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$CH_2PMe_2)_2La(TeSi(SiMe_3)_3)_3$.[11,12] Without this chelating phosphine ligand, the analogous Ce derivative, “$Ce(TeSi(SiMe_3)_3$”, decomposes below room temperature to give the equally unstable tellurido cluster $Ce_5Te_3(TeSi(SiMe_3)_3)_9$.[11,12]

While the past three years has experienced a burst of activity describing the synthesis and characterization of stable lanthanide clusters coordinated to chalcogenido (E^{2-}, E = S, Se)[13-18] ligands, extension of this work to compounds of Te has not yet appeared. The recent high-yield synthesis of chalcogen-rich Ln compounds with $(EE)^{2-}$ ligands,[19,20] rather than E^{2-} ligands, from the reactions of lanthanide chalcogenolates with elemental E, leads to the suggestion that $(EE)^{2-}$ may stabilize Ln ions more effectively than E^{2-}, possibly to the extent that compounds with Te can be isolated routinely. This paper outlines initial investigations into the synthesis, characterization, stability, and thermolysis of Te-rich Ln clusters.

Experimental Section

General Methods. 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 K/benzophenone and collected immediately prior to use. Anhydrous pyridine (Aldrich) was purchased and refluxed over KOH. PhTeTePh was prepared according to literature procedures.[21] Ln and Hg were purchased from Strem. Melting points were taken in sealed capillaries and are uncorrected. IR spectra were recorded on a Mattus Cygnus 100 FTIR spectrometer from 4000 to 600 cm^{-1} as Nujol mulls on NaCl plates. 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 performed by Quantitative Technologies, Inc. (Whitehouse NJ). These compounds are sensitive to the thermal dissociation of neutral donor ligands at room temperature, so the experimentally determined elemental analyses are often found to be lower than the computed analyses. The reported values were closest to the calculated values, but analytical determinations gave a range of values that were usually consistent with the one of the three unit cell formulations described below. Magnetic susceptibility was measured on a SQUID magnetometer in a 1 T field. NMR spectra were obtained on either Varian 300 or 400 MHz NMR spectrometers, and chemical shifts are reported in δ (ppm). XR powder diffraction profiles were obtained on a SCINTAG PAD V diffractometer with Cu Kα radiation. GCMS data were collected on a 5890 Series II gas chromatograph with an HP 5971 mass selective detector.

Synthesis of $(py)_9Sm_4(\mu_4\text{-}Te)(\mu_2\text{-}TeTe)_2(\mu_2\text{-}TeTeTe(Ph)TeTe)(TePh)\cdot 5py$ (1). Samarium metal (0.30 g, 2.0 mmol) and Hg (0.05 g, 0.25 mmol) were added to a solution of diphenyl ditelluride (0.82 g, 2.0 mmol) in pyridine (50 mL). The reaction flask was wrapped in aluminum foil up to the stopper. The next day elemental tellurium was added (0.38 g, 3.0 mmol) to the yellow solution and unreacted Sm. The following day the solution was dark red, and a brick red solid had precipitated. The solution was filtered and layered with 20 mL of hexanes to give dark red needles (100 mgs, 10%) that could be separated by hand from the dark solid major product.

Synthesis of $(py)_8Tb_4(\mu_4\text{-}Te)(\mu_2\text{-}TeTe)_2(\mu_2\text{-}TeTeTe(Ph)TeTe)(Te_{0.1}TePh)\cdot 4.5py$ (2). Terbium metal (0.32 g, 2.0 mmol) and Hg (0.05 g, 0.25 mmol) were added to a solution of diphenyl ditelluride (0.82 g, 2.0 mmol) in pyridine (50 mL). The flask was wrapped in aluminum foil. After stirring for 1 day, elemental tellurium (0.38 g, 3.0 mmol) was added to the dark golden brown mixture that still contained unreacted Tb. Two days later the metal had been consumed and there was a significant amount of dark red precipitate. The flask was heated to between 60 and 75 °C for ca. 1 h to dissolve the red solid. The red solution was filtered into a flask with either a flat bottom (modified Erlenmeyer) or a large round-bottom and concentrated by ca. 3 mL. Hexanes (ca. 8 mL) were added rapidly into the solution that was then re-covered with aluminum foil and allowed to stand at rt for 2 days to give deep red crystals (0.34 g, 35%) that were washed with hexane (5 mL) and did not decompose or melt below 300 °C. Anal. Calcd for $C_{64.5}H_{62.5}N_{10.5}Tb_4Te_{11.1}$: C, 25.5; H, 2.07; N, 4.84. Found: C, 25.3; H, 2.19; N, 4.33. IR: 3077 (m), 2933 (s), 2856 (s), 1630 (w), 1597 (s), 1580 (s), 1481 (m), 1465 (s), 1437 (s), 1384 (s), 1218 (m), 1145 (w), 1068 (m), 1038 (m), 1030 (m), 1004 (m), 991 (m), 825 (w), 745 (s), 732 (w), 702 (s), 623 (w), 602 (m), 451 (w), 405 (w) cm^{-1}. Magnetic susceptibility: μ_{eff} (5−250 K) = 7.87 (500 G); 7.91 (10 kG). The compound does not show an absorption maximum from 350 to 800 nm in THF. No ^1H NMR resonances were detected in either THF or pyridine. Thermolysis: 100 mg of **1** was placed in a quartz tube under vacuum for 5 min. The tube was then sealed and the sample temperature was increased at the rate of 20 °C/min with one end of the tube submerged in liquid nitrogen. The temperature was held at 550 °C for 5 h and then the tube was removed and allowed to cool rapidly to give ca. 25 mg of nonvolatile solid. Powder diffraction X-ray analysis revealed only $TbTe_{2-x}$ ($0 < x < 0.3$).[22]

Synthesis of $(py)_8Ho_4(\mu_4\text{-}Te)(\mu_2\text{-}TeTe)_2(\mu_2\text{-}TeTeTe(Ph)TeTe)(Te_{0.1}TePh)\cdot 4.5py$ (3): Method 1. Holmium metal (0.33 g, 2.0 mmol), Hg (0.05 g, 0.25 mmol), and diphenyl ditelluride (0.79 g, 1.93 mmol) were added to pyridine (50 mL), the reaction flask was wrapped in aluminum foil, and the mixture stirred. The next day elemental tellurium (0.38 g, 3.0 mmol) was added to the yellow solution and unreacted Ho. The following day the solution was dark red, and a brick red solid had precipitated. The solution was filtered into a Schlenk flask with an outer diameter of 41 mm, concentrated to 45 mL, layered with hexanes (20 mL), and then placed in the dark to give dark red needles (100 mgs, 10%) that did not melt up to 310 °C but slowly turned black and began eliminating a gas at ca. 230 °C. Anal. Calcd for $C_{64.5}H_{62.5}N_{10.5}Ho_4Te_{11}$: C, 25.4; H, 2.07; N, 4.83. Found: C, 24.8; H, 2.06; N, 4.73. IR: 2865 (s), 2361 (w), 1596 (m), 1579 (s), 1463 (s), 1377 (s), 1216 (m), 1144 (m), 1067 (m), 1030 (m), 990 (m), 744 (m), 727 (m), 701 (s), 622

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(11) Cary, D. R.; Ball, G. E.; Arnold, J. *J. Am. Chem. Soc.* **1995**, *117*, 3492.

(12) Cary, D. R.; Arnold, J. *J. Am. Chem. Soc.* **1993**, *115*, 2520.

(13) Freedman, D.; Emge, T. J.; Brennan, J. G. *J. Am. Chem. Soc.* **1997**, *119*, 11112.

(14) Melman, J. H.; Emge, T. J.; Brennan, J. G. *Chem. Commun.* **1997**, 2269.

(15) Freedman, D.; Melman, J. H.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1998**, *37*, 4162.

(16) Melman, J. H.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1999**, *38*, 2117.

(17) Freedman, D.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1999**, *38*, 4400.

(18) Freedman, D.; Sayan, S.; Emge, T. J.; Croft, M.; Brennan, J. G. *J. Am. Chem. Soc.* **1999**, *121*, 11713.

(19) Melman, J. H.; Fitzgerald, M.; Freedman, D.; Emge, T. J.; Brennan, J. G. *J. Am. Chem. Soc.* **1999**, *121*, 10247.

(20) (a) Kornienko, A.; Emge, T.; Brennan, J. G. *J. Am. Chem. Soc.* **2001**, *123*, 11933. (b) Kornienko, A.; Melman, J. H.; Hall, G.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **2002**, *41*, 121.

(21) (a) Petragnani, N.; DeMoura, M. *Chem. Ber.* **1963**, *96*, 249. (b) Haller, W. S.; Irgolic, K. J. *J. Organomet. Chem.* **1973**, *38*, 97.

(22) Pardo, M. P.; Flahaut, J.; Domange, L. *Bull. Chem. Soc. Fr.* **1963**, *256*, 953.

Table 1. Summary of Crystallographic Details for **1**, **2**, and **4**[a]

compound	**1**	**2**	**4**
empirical formula	$C_{82}H_{80}N_{14}Sm_4Te_{11}$	$C_{64.50}H_{62.50}N_{10.50}Tb_4Te_{11.12}$	$C_{57}H_{55}N_9Te_{11.62}Tm_4$
fw	3266.60	3039.98	3025.17
space group (No.)	$P2_1/n$ (14)	$P2_1/c$ (14)	C2 (5)
a (Å)	12.191(5)	12.85(1)	23.407(7)
b (Å)	27.484(5)	31.13(1)	23.20(2)
c (Å)	28.484(5)	20.37(1)	17.507(9)
α (deg)	90.00	90.00(5)	90.00
β (deg)	91.56(2)	91.50(5)	113.38(4)
γ (deg)	90.00	90.00(5)	90.00
V (Å$^{3)}$	9540(5)	8146(8)	8728(9)
Z	4	4	4
D(calcd) (g/cm^{-3})	2.274	2.479	2.302
temperature (°C)	−120	−120	−120
λ (Å)	0.71073	0.71073	0.71073
abs coeff (mm^{-1})	5.770	7.378	7.869
$R(F)^b$ $[I > 2\sigma(I)]$	0.066	0.067	0.091
$R_w(F^2)^b$ $[I > 2\sigma(I)]$	0.152	0.155	0.221

[a] Additional crystallographic details are given in the Supporting Information. [b] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

(w) cm^{-1}. Magnetic susceptibility: μ_{eff} (5−250 K) = 10.6 (500 G); 10.4 (10 kG). Unit cell (Mo Kα, −120 °C): monoclinic space group $P2_1/c$, $a = 12.775(3)$ Å, $b = 31.326(12)$ Å, $c = 20.113(3)$ Å, $\beta = 91.55$ (2)°, $V = 8046(4)$ Å^3 determined from 25 reflections with $13.1° < \theta < 16.4°$. The ^{1}H NMR spectrum contained only pyridine resonances at 8.54, 7.66, and 7.23 ppm. The compound does not show an absorption maximum from 350 to 800 nm in either THF or pyridine. Thermolysis: 100 mg of the sample was placed in a quartz tube under vacuum for 5 min. The tube was then sealed and the sample temperature was increased at the rate of 20 °C/min with one end of the tube submerged in liquid nitrogen. The temperature was kept between 475 and 490 °C for 5 h. The quartz tube was removed and allowed to cool at room temperature. Powder diffraction X-ray analysis of the nonvolatile black powder revealed only HoTe.[23] Analysis of the residue by GCMS identified Ph_2Te as the only organic product of the reaction.

Method 2. Holmium metal (0.33 g, 2 mmol) and Hg (0.05 g, 0.25 mmol) were added to a solution of diphenyl ditelluride (0.82 g, 2.0 mmol) in pyridine (50 mL). The flask was wrapped in aluminum foil up to the neck, and after 1 day elemental tellurium (0.38 g, 3.0 mmol) was added to the yellow solution that still contained unreacted metal. Two days later all the metal had reacted and there was a significant amount of dark red precipitate. After heating (60−75 °C, 1 h) to dissolve the precipitate, the solution was filtered to a flask with either a flat bottom (modified Erlenmeyer) or a large round-bottom that was shielded from light. The volume was reduced by ca. 3 mL and then saturated by rapid addition of ca. 8 mL of hexanes. After 2 days, dark red crystals (0.45 g, 46%) were collected.

Synthesis of $(py)_7Tm_4(\mu_4\text{-}Te)[(TeTe)_4TePh](Te_{0.6}TePh)\cdot 2py$ (4). Thulium metal (0.34 g, 2.0 mmol), Hg (0.05 mg, 0.25 mmol), and PhTeTePh (0.82 g, 2.0 mmol) were added to pyridine (50 mL), the flask was wrapped in aluminum foil, and the mixture was stirred. After 1 day, elemental tellurium (380 mg, 3.0 mmol) was added to the dark red solution that still contained unreacted Tm. Two days later the metal had reacted and there was a significant amount of dark red precipitate. The flask was heated (60−75 °C) for ca. 1 h until all the red precipitate redissolved. The red solution was filtered and saturated as above to give deep red crystals (0.45 g, 46%) that did not melt up to 300 °C but slowly desolvated and darkened above 200 °C. If the crystals are not dried thoroughly before the melting point determination, they do not melt but begin turning gray at ca. 180 °C and become more silver/gray and flaky by 250 °C. Anal. Calcd for $C_{57}H_{55}N_9Tm_4Te_{11.6}$: C, 22.6; H, 1.83; N, 4.17. Found: C, 23.2; H, 2.13; N, 3.90. IR: 2923 (s), 1978 (w), 1941 (w), 1864 (w), 1632 (w), 1596 (m), 1579 (m), 1437 (s), 1366 (s), 1216 (m), 1145 (m), 1068 (m), 1030 (m), 990 (m), 745 (m), 702 (s), 606 (m) cm^{-1}. Magnetic susceptibility: μ_{eff} (5−250 K) = 7.65 μB (500 G, C = 5.87); 7.24 μB (10 kG, C = 6.56). The compound does not show an absorption maximum from 350 to 800 nm in pyridine. ^{1}H NMR (THF) revealed only displaced pyridine resonances at 8.61, 7.65, 7.28 ppm. Thermolysis: The compound was treated as in **1**. X-ray powder diffraction analysis identified TmTe[24] as the only crystalline Ln-containing product of the reaction, and GCMS identified Ph_2Te as the only organic product.

X-ray Structure Determination of 1, 2, and 4. Data for **1**, **2**, and **4** were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at −120 °C. Samples must be completely cooled before exposure to any X-ray source. The check reflections measured every hour showed less than 3% intensity variation. The data were corrected for Lorenz effects, polarization, and absorption, the latter by a numerical (SHELX76)[25] method. The structures were solved by Patterson methods (SHELXS86).[26] All non-hydrogen atoms were refined (SHELXL97) based upon F_{obs}^2. All hydrogen atom coordinates were calculated with idealized geometries (SHELXL97).[27] Scattering factors (f_o, f', f'') are as described in SHELXL97. Crystallographic data and final R indices for **1**, **2**, and **4** are given in Table 1. Significant bond distances and angles for **1**, **2**, and **4** are given in Tables 2, 3, and 4, respectively. Complete crystallographic details are given in the Supporting Information. ORTEP diagrams[28] for **1**, **2**, and **4** are shown in Figures 1−3, respectively.

Results

Lanthanide tellurido clusters $(py)_8Ln_4(\mu_4\text{-}Te)(\mu_2\text{-}TeTe)_2$-$(\mu_2\text{-}\eta^2,\eta^2\text{-}Te_5Ph)(Te_{0.1}TePh)$ [Ln = Tb(**2**), Ho(**3**)] can be

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(23) The XRPD profile of the Ho thermolysis product matched that for TbTe: Cannon, J.; Hall, H. *Inorg. Chem.* **1970**, *9*, 1639

(24) (a) Dismuskes, J. P.; White, J. G. *Inorg. Chem.* **1965**, *4*, 970. (b) Brixner, L. H. *J. Inorg. Nucl. Chem.* **1960**, *15*, 199. (c) Devi, S. U.; Singh, S. *Solid State Commun.* **1984**, *52*, 303.

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

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

(27) Sheldrick, G. M. SHELXL97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.

(28) (a) Johnson, C. K.; ORTEP II, Report ORNL-5138. Oak Ridge National Laboratory, Oak Ridge, TN, 1976. (b) Zsolnai, L. XPMA and ZORTEP, Programs for Interactive ORTEP Drawings, University of Heidelberg, Germany, 1997.

Table 2. Significant Distances (Å) and Angles (deg) for **1**

Sm(1)−N(1)	2.591(17)	Sm(1)−Te(11)	3.067(2)	Sm(1)−Te(5)	3.1079(19)
Sm(1)−Te(1)	3.1208(18)	Sm(1)−Te(2)	3.1261(18)	Sm(1)−Te(3	3.1274(18)
Sm(1)−Te(4)	3.1599(18)	Sm(2)−N(2B)	2.63(2)	Sm(2)−N(4)	2.647(17)
Sm(2)−N(3)	2.663(17)	Sm(2)−N(2A)	2.67(2)	Sm(2)−Te(7)	3.1150(18)
Sm(2)−Te(6)	3.1498(18)	Sm(2)−Te(5)	3.1517(18)	Sm(2)−Te(4)	3.2248(18)
Sm(2)−Te(1)	3.2316(18)	Sm(3)−N(5)	2.620(17)	Sm(3)−N(7)	2.662(18)
Sm(3)−N(6)	2.673(16)	Sm(3)−Te(7)	3.130(2)	Sm(3)−Te(9)	3.1436(18)
Sm(3)−Te(6)	3.1702(18)	Sm(3)−Te(8)	3.1792(19)	Sm(3)−Te(1)	3.2740(18)
Sm(4)−N(8)	2.571(17)	Sm(4)−N(9)	2.583(17)	Sm(4)−Te(9)	3.0583(18)
Sm(4)−Te(1)	3.0753(18)	Sm(4)−Te(3)	3.100(2)	Sm(4)−Te(8)	3.0998(18)
Sm(4)−Te(2)	3.1678(18)	Te(2)−Te(3)	2.771(2)	Te(3)−Te(10)	3.849(2)
Te(4)−Te(5)	2.764(2)	Te(5)−Te(10)	3.617(2)	Te(6)−Te(7)	2.909(2)
Te(7)−Te(10)	3.156(2)	Te(8)−Te(9)	2.940(2)	Te(9)−Te(10)	3.085(2)

N(1)−Sm(1)−Te(11)	84.9(4)	N(1)−Sm(1)−Te(5)	86.0(4)	N(5)−Sm(3)−N(7)	132.8(5)	N(5)−Sm(3)−N(6)	65.9(5)
Te(11)−Sm(1)−Te(5)	128.40(6)	N(1)−Sm(1)−Te(1)	169.5(4)	N(7)−Sm(3)−N(6)	67.9(5)	N(5)−Sm(3)−Te(7)	132.1(4)
Te(11)−Sm(1)−Te(1)	105.60(6)	Te(5)−Sm(1)−Te(1)	86.91(5)	N(7)−Sm(3)−Te(7)	75.7(4)	N(6)−Sm(3)−Te(7)	131.7(4)
N(1)−Sm(1)−Te(2)	91.4(4)	Te(11)−Sm(1)−Te(2)	86.28(5)	N(5)−Sm(3)−Te(9)	137.6(4)	N(7)−Sm(3)−Te(9)	78.6(4)
Te(5)−Sm(1)−Te(2	144.66(5)	Te(1)−Sm(1)−Te(2)	89.87(5)	N(6)−Sm(3)−Te(9)	124.2(4)	Te(7)−Sm(3)−Te(9)	75.73(5)
N(1)−Sm(1)−Te(3)	82.5(4)	Te(11)−Sm(1)−Te(3)	136.34(5)	N(5)−Sm(3)−Te(6)	84.2(4)	N(7)−Sm(3)−Te(6)	88.8(4)
Te(5)−Sm(1)−Te(3)	92.19(5)	Te(1)−Sm(1)−Te(3)	90.04(5)	N(6)−Sm(3)−Te(6)	92.8(4)	Te(7)−Sm(3)−Te(6)	54.98(4)
Te(2)−Sm(1)−Te(3)	52.60(4)	N(1)−Sm(1)−Te(4)	89.8(4)	Te(9)−Sm(3)−Te(6)	130.71(5)	N(5)−Sm(3)−Te(8)	89.8(4)
Te(11)−Sm(1)−Te(4)	76.95(5)	Te(5)−Sm(1)−Te(4)	52.32(4)	N(7)−Sm(3)−Te(8)	94.1(4)	N(6)−Sm(3)−Te(8)	83.3(4)
Te(1)−Sm(1)−Te(4)	92.05(5)	Te(11)−Sm(1)−Te(4)	76.95(5)	Te(7)−Sm(3)−Te(8)	131.14(5)	Te(9)−Sm(3)−Te(8)	55.42(4)
Te(5)−Sm(1)−Te(4)	52.32(4)	Te(1)−Sm(1)−Te(4)	92.05(5)	Te(6)−Sm(3)−Te(8)	173.75(5)	N(5)−Sm(3)−Te(1)	74.7(4)
Te(2)−Sm(1)−Te(4)	163.02(5)	Te(3)−Sm(1)−Te(4)	144.23(5)	N(7)−Sm(3)−Te(1)	151.9(4)	N(6)−Sm(3)−Te(1)	140.2(4)
N(2B)−Sm(2)−N(4)	66.0(8)	N(2B)−Sm(2)−N(3)	131.1(8)	Te(7)−Sm(3)−Te(1)	80.14(4)	Te(9)−Sm(3)−Te(1)	81.75(4)
N(4)−Sm(2)−N(3)	65.2(5)	N(2B)−Sm(2)−N(2A)	2.3(12)	Te(6)−Sm(3)−Te(1)	89.00(4)	Te(8)−Sm(3)−Te(1)	90.97(4)
N(4)−Sm(2)−N(2A)	68.1(7)	N(3)−Sm(2)−N(2A)	133.3(7)	N(8)−Sm(4)−N(9)	89.8(5)	N(8)−Sm(4)−Te(9)	95.9(4)
N(2B)−Sm(2)−Te(7)	134.1(7)	N(4)−Sm(2)−Te(7)	130.4(4)	N(9)−Sm(4)−Te(9)	140.4(4)	N(8)−Sm(4)−Te(1)	174.5(4)
N(3)−Sm(2)−Te(7)	79.7(4)	N(2A)−Sm(2)−Te(7)	133.7(7)	N(9)−Sm(4)−Te(1)	91.5(4)	Te(9)−Sm(4)−Te(1)	86.46(5)
N(2B)−Sm(2)−Te(6)	87.3(7)	N(4)−Sm(2)−Te(6)	89.5(4)	N(8)−Sm(4)−Te(3)	84.0(4)	N(9)−Sm(4)−Te(3)	137.2(4)
N(3)−Sm(2)−Te(6)	90.1(4)	N(2A)−Sm(2)−Te(6)	88.3(7)	Te(9)−Sm(4)−Te(3)	82.33(5)	Te(1)−Sm(4)−Te(3)	91.41(5)
Te(7)−Sm(2)−Te(6)	55.32(4)	N(2B)−Sm(2)−Te(5)	134.5(7)	N(8)−Sm(4)−Te(8)	89.1(4)	N(9)−Sm(4)−Te(8)	84.1(4)
N(4)−Sm(2)−Te(5)	124.4(4)	N(3)−Sm(2)−Te(5)	78.1(4)	Te(9)−Sm(4)−Te(8)	57.03(5)	Te(1)−Sm(4)−Te(8)	96.36(5)
N(2A)−Sm(2)−Te(5)	132.7(7)	Te(7)−Sm(2)−Te(5)	77.04(5)	Te(3)−Sm(4)−Te(8)	137.83(5)	N(8)−Sm(4)−Te(2)	84.9(4)
Te(6)−Sm(2)−Te(5)	132.30(5)	N(2B)−Sm(2)−Te(4)	88.7(7)	N(9)−Sm(4)−Te(2)	84.9(4)	Te(9)−Sm(4)−Te(2)	134.55(5)
N(4)−Sm(2)−Te(4)	88.7(4)	N(3)−Sm(2)−Te(4)	92.4(4)	Te(1)−Sm(4)−Te(2)	89.93(5)	Te(3)−Sm(4)−Te(2)	52.46(4)
N(2A)−Sm(2)−Te(4)	87.8(7)	Te(7)−Sm(2)−Te(4)	128.20(5)	Te(8)−Sm(4)−Te(2)	167.42(5)	C(1)−Te(10)−Te(9)	94.4(6)
Te(6)−Sm(2)−Te(4)	176.06(5)	Te(5)−Sm(2)−Te(4)	51.35(4)	C(1)−Te(10)−Te(7)	102.5(6)	Te(9)−Te(10)−Te(7)	76.20(5)
N(2B)−Sm(2)−Te(1)	72.6(7)	N(4)−Sm(2)−Te(1)	138.5(4)	C(1)−Te(10)−Te(5)	146.7(6)	Te(9)−Te(10)−Te(5)	113.99(5)
N(3)−Sm(2)−Te(1)	156.3(4)	N(2A)−Sm(2)−Te(1)	70.4(6)	Te(7)−Te(10)−Te(5)	69.99(4)	C(1)−Te(10)−Te(3)	135.0(6)
Te(7)−Sm(2)−Te(1)	81.03(5)	Te(6)−Sm(2)−Te(1)	90.12(5)	Te(9)−Te(10)−Te(3)	70.58(5)	Te(7)−Te(10)−Te(3)	113.75(5)
Te(5)−Sm(2)−Te(1)	84.29(5)	Te(4)−Sm(2)−Te(1)	88.87(5)	Te(5)−Te(10)−Te(3)	73.92(4)		

isolated as pure materials in 35−45% yields from the reactions of elemental Ln with PhTeTePh and Te in pyridine (reaction 1).

$$4\mathrm{Ln} + 2\mathrm{PhTeTePh} + 9\mathrm{Te} \rightarrow (\mathrm{py})_8\mathrm{Ln}_4(\mathrm{Te})(\mathrm{TeTe})_2(\mathrm{Te}_5\mathrm{Ph})(\mathrm{Te}_{0.1}\mathrm{TePh}) \tag{1}$$

These compounds cocrystallize with ca. 10% of the tetrametallic cluster containing an additional Te atom inserted into the Ln−TePh bond. The isomorphous Sm cluster $(\mathrm{py})_9\mathrm{Sm}_4(\mathrm{Te})(\mathrm{TeTe})_2(\mathrm{Te}_5\mathrm{Ph})(\mathrm{TePh})$ (**1**) can also be prepared, but has not yet been isolated (other than by hand) in pure form. Structural characterization of **1** reveals it to be isomorphous with **2** and **3**, but without the compositional disorder in the terminal TePh site. A related Tm cluster $(\mathrm{py})_7\mathrm{Tm}_4(\mu_4\text{-}\mathrm{Te})[(\mathrm{TeTe})_4\mathrm{TePh}](\mathrm{Te}_{0.6}\mathrm{TePh})$ (**4**) can also be prepared, and again, the product is similarly disordered, with a TeTePh/TePh occupancy of 62:38. In all compositionally disordered structures, lattice pyridine is also disordered between two positions, with site occupancies that are directly related to the percentage of inserted Te.

These compounds are sensitive to oxygen and water, they desolvate when isolated at room temperature, and are sensitive to light throughout the synthetic process. While this structure appears general for the middle of the lanthanide series, limits are imposed at Sm, which requires manual isolation, and at Yb, which does not form stable Ln(III) compounds with only Te-based anions.[29]

The general structures of 1 and **2** contain a square array of Ln(III) ions all connected to a central Te^{2-}. Two edges of the square are bridged by $(\mathrm{TeTe})^{2-}$, and the Ln coordinating both of these $(\mathrm{TeTe})^{2-}$ ligands is also coordinated to a terminal TePh. The remaining two edges of the square are also bridged by $(\mathrm{TeTe})^{2-}$, but the second TePh moiety has been displaced from a Ln coordination site and instead bonds to two TeTe ligands in a variable fashion, to give what is formally $(\mathrm{TeTeTe(Ph)TeTe}).^{5-}$ There is a broad range of interactions between TePh and the TeTe units, as illustrated in Figure 4: in **1**, there are two clearly asymmetric bonds to TeTe (differing by 0.07 Å), and the third nearest TeTe unit is a further 0.46 Å away. In **2**, which has a detectable amount of TeTePh substituting for the terminal TePh, the displaced TePh ligand coordinates the two TeTe units with greater asymmetry (0.28 Å), and the next nearest TeTe is only 0.34 Å further away from the "$\mathrm{Te}_5\mathrm{Ph}$" moiety.

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(29) Flahaut, J.; Laruelle, P.; Pardo, M.; Guittard, M. *Bull Chem. Soc. Fr.* **1965**, 1399.

Table 3. Significant Distances (Å) and Angles (deg) for **2**

Tb(1)−N(2)	2.51(2)	Tb(1)−N(1)	2.561(19)	Tb(1)−Te(9)	3.021(3)
Tb(1)−Te(3)	3.046(3)	Tb(1)−Te(1)	3.050(3)	Tb(1)−Te(8)	3.077(3)
Tb(1)−Te(2)	3.141(3)	Tb(2)−N(3)	2.55(2)	Tb(2)−Te(11)	2.994(3)
Tb(2)−Te(4)	3.073(3)	Tb(2)−Te(2)	3.078(3)	Tb(2)−Te(3)	3.086(3)
Tb(2)−Te(5)	3.127(3)	Tb(2)−Te(1)	3.136(3)	Tb(3)−N(5)	2.456(19)
Tb(3)−N(4)	2.52(2)	Tb(3)−Te(7)	3.006(3)	Tb(3)−Te(5)	3.020(3)
Tb(3)−Te(1)	3.042(3)	Tb(3)−Te(6)	3.127(3)	Tb(3)−Te(4)	3.151(3)
Tb(4)−N(6)	2.560(18)	Tb(4)−N(7)	2.57(2)	Tb(4)−N(8)	2.63(2)
Tb(4)−Te(8)	3.113(3)	Tb(4)−Te(7)	3.132(3)	Tb(4)−Te(9)	3.137(3)
Tb(4)−Te(6)	3.144(3)	Tb(4)−Te(1)	3.317(3)	Te(2)−Te(3)	2.762(3)
Te(3)−Te(10)	3.836(4)	Te(4)−Te(5)	2.772(3)	Te(5)−Te(10)	3.665(3)
Te(6)−Te(7)	2.843(3)	Te(7)−Te(10)	3.327(3)	Te(8)−Te(9)	2.960(3)
Te(9)−Te(10)	3.051(3)				

N(2)−Tb(1)−N(1)	87.3(7)	N(2)−Tb(1)−Te(9)	142.5(5)	N(4)−Tb(3)−Te(5)	90.7(5)	Te(7)−Tb(3)−Te(5)	81.49(7)
N(1)−Tb(1)−Te(9)	98.5(4)	N(2)−Tb(1)−Te(3)	135.9(5)	N(5)−Tb(3)−Te(1)	90.3(5)	N(4)−Tb(3)−Te(1)	169.8(5)
N(1)−Tb(1)−Te(3)	86.9(5)	Te(9)−Tb(1)−Te(3)	81.47(7)	Te(7)−Tb(3)−Te(1)	89.26(7)	Te(5)−Tb(3)−Te(1)	91.50(7)
N(2)−Tb(1)−Te(1)	88.4(5)	N(1)−Tb(1)−Te(1)	174.1(4)	N(5)−Tb(3)−Te(6)	86.0(5)	N(4)−Tb(3)−Te(6)	91.5(5)
Te(9)−Tb(1)−Te(1)	87.35(7)	Te(3)−Tb(1)−Te(1)	93.39(7)	Te(7)−Tb(3)−Te(6)	55.21(6)	Te(5)−Tb(3)−Te(6)	136.22(7)
N(2)−Tb(1)−Te(8)	85.4(5)	N(1)−Tb(1)−Te(8)	88.4(4)	Te(1)−Tb(3)−Te(6)	93.84(8)	N(5)−Tb(3)−Te(4)	84.1(5)
Te(9)−Tb(1)−Te(8)	58.07(7)	Te(3)−Tb(1)−Te(8)	138.02(7)	N(4)−Tb(3)−Te(4)	82.7(5)	Te(7)−Tb(3)−Te(4)	134.81(7)
Te(1)−Tb(1)−Te(8)	95.25(7)	N(2)−Tb(1)−Te(2)	83.0(5)	Te(5)−Tb(3)−Te(4)	53.33(7)	Te(1)−Tb(3)−Te(4)	90.66(7)
N(1)−Tb(1)−Te(2)	85.2(4)	Te(9)−Tb(1)−Te(2)	134.20(7)	Te(6)−Tb(3)−Te(4)	169.17(6)	N(6)−Tb(4)−N(7)	67.0(6)
Te(3)−Tb(1)−Te(2)	53.01(6)	Te(1)−Tb(1)−Te(2)	90.33(7)	N(6)−Tb(4)−N(8)	137.0(6)	N(7)−Tb(4)−N(8)	70.0(6)
Te(8)−Tb(1)−Te(2)	166.93(6)	N(3)−Tb(2)−Te(11)	91.3(5)	N(6)−Tb(4)−Te(8)	91.2(4)	N(7)−Tb(4)−Te(8)	89.3(5)
N(3)−Tb(2)−Te(4)	92.3(4)	Te(11)−Tb(2)−Te(4)	73.71(8)	N(8)−Tb(4)−Te(8)	88.0(5)	N(6)−Tb(4)−Te(7)	77.9(4)
N(3)−Tb(2)−Te(2)	90.3(4)	Te(11)−Tb(2)−Te(2)	89.00(8)	N(7)−Tb(4)−Te(7)	126.7(4)	N(8)−Tb(4)−Te(7)	131.3(5)
Te(4)−Tb(2)−Te(2)	162.55(7)	N(3)−Tb(2)−Te(3)	81.3(5)	Te(8)−Tb(4)−Te(7)	131.45(7)	N(6)−Tb(4)−Te(9)	77.9(4)
Te(11)−Tb(2)−Te(3)	141.18(7)	Te(4)−Tb(2)−Te(3)	144.18(7)	N(7)−Tb(4)−Te(9)	130.3(6)	N(8)−Tb(4)−Te(9)	133.7(5)
Te(2)−Tb(2)−Te(3)	53.25(6)	N(3)−Tb(2)−Te(5)	86.2(5)	Te(7)−Tb(4)−Te(9)	74.92(6)	N(6)−Tb(4)−Te(6)	93.3(4)
Te(11)−Tb(2)−Te(5)	126.54(8)	Te(4)−Tb(2)−Te(5	53.10(6)	N(7)−Tb(4)−Te(6)	88.6(5)	N(8)−Tb(4)−Te(6)	85.9(5)
Te(2)−Tb(2)−Te(5)	144.33(7)	Te(3)−Tb(2)−Te(5)	91.19(7)	Te(8)−Tb(4)−Te(6)	173.82(6)	Te(7)−Tb(4)−Te(6)	53.87(6)
N(3)−Tb(2)−Te(1)	170.1(5)	Te(11)−Tb(2)−Te(1)	98.51(8)	Te(9)−Tb(4)−Te(6)	128.67(7)	N(6)−Tb(4)−Te(1)	154.2(4)
Te(4)−Tb(2)−Te(1)	90.36(7)	Te(2)−Tb(2)−Te(1	89.93(7)	N(7)−Tb(4)−Te(1)	138.8(5)	N(8)−Tb(4)−Te(1)	68.9(4)
Te(3)−Tb(2)−Te(1)	90.96(7)	Te(5)−Tb(2)−Te(1)	87.80(7)	Te(8)−Tb(4)−Te(1)	89.42(7)	Te(7)−Tb(4)−Te(1)	82.35(7)
N(5)−Tb(3)−N(4)	81.4(7)	N(5)−Tb(3)−Te(7)	141.1(5)	Te(9)−Tb(4)−Te(1)	80.96(7)	Te(6)−Tb(4)−Te(1)	88.37(7)
N(4)−Tb(3)−Te(7)	100.9(5)	N(5)−Tb(3)−Te(5)	137.4(5)				

Coordination of TePh to $(TeTe)^{2-}$ effectively decreases the $(TeTe)^{2-}$ bond length, and the magnitude of the lengthening is inversely proportional to the intensity of the PhTe−(TeTe) interaction, as judged by the length of the PhTe−TeTe bond (Figure 4). For **1**, TePh has a bond to Te(9) that is 0.71 Å shorter than the bond to Te(7), and the Te(9)−Te(8) bond is longer, by 0.031(1) Å, than the Te(7)−Te(6) bond. More dramatically, in **2** the bond from PhTe to Te(9) is 0.276 Å shorter than the bond to Te(7), and the Te(9)−Te(8) bond is significantly longer, by 0.117(3) Å, than the Te(7)−Te(6) bond. In both **1** and **2**, the TeTe ligands that do not interact with TePh have TeTe bond lengths within a well-defined range [2.762(2)−2.772(3) Å] of values.

Cluster **4** is more complex, with significantly weaker interactions between the displaced TePh and the two remaining TeTe units, leading to an alternative description of the anionic tellurium fragment as a $(Te_9Ph)^{9-}$ ligand. In **4**, the TePh coordinates more strongly to Te(7) and Te(9), and again these ditelluride units have TeTe bonds ca. 0.1 Å longer than the “uninvolved” TeTe ligands in **1** and **2**. In addition, there are additional “bonds” from TePh to Te(5) and Te(3) that are only ca. 0.2 Å longer than those to Te(7) and Te(9). In one of these ligands, there is a clear lengthening of the Te(5)−Te(4) bond, to 2.834(11) Å, while in the second ligand the bond [Te(3)−Te(2), 2.795(11) Å] is less influenced by coordination to the central TePh. Again, in both of these weaker interactions, the lengthening of the TeTe bond is inversely proportional to the length of the PhTe−TeTe bond.

The multitude of allowed electronic transitions that are entirely ligand based, as well as Te to Ln charge-transfer excitations, produce a featureless visible spectrum when the compounds are redissolved in pyridine. Magnetic susceptibility measurements indicate that there are no interactions between neighboring Ln(III) ions. Measurements of χ vs T were obtained for **3** and **4** and are plotted in Figures 5 and 6, respectively. The χ^{-1} results reveal distinct Curie Weiss (CW) behavior [$\chi = C/(\theta + T)$] for both compounds at all temperatures.

Numerous $LnTe_x$ phases were observed in the thermal decomposition of **2**−**4**. Both **3** and **4** decompose to give LnTe (reaction 2)

$$(py)_xLn_4(Te)(TeTe)_2(Te_5Ph)(TePh) \rightarrow LnTe_x + Te + Ph_2Te + py \quad (2)$$

with elimination of $TePh_2$ and Te. Under identical conditions the Tb compound **2** gives $TbTe_{2-x}$. Phase purity of the final solid-state product depends significantly on the thermolysis conditions. If **4** is heated at 550 °C and then cooled slowly, three products (TmTe, $TmTe_3$, and Tm_2Te_3) are detected by XRPD. In contrast, if the sample is first heated and then cooled immediately, TmTe is the only crystalline product observed in the XRPD profile. Again, $TePh_2$ was identified as the only volatile product by GCMS.

Discussion

The comparative ease with which polytellurido compounds of the lanthanides can be isolated, relative to the synthesis

Table 4. Significant Distances (Å) and Angles (deg) for **4**

Tm(1)−N(1)	2.50(2)	Tm(1)−Te(2)	2.993(10)	Tm(1)−Te(3)	3.000(8)
Tm(1)−Te(1A)	3.033(4)	Tm(1)−Te(4)	3.060(10)	Tm(1)−Te(5)	3.092(9)
Tm(1)−Te(1)	3.130(3)	Tm(2)−N(3)	2.52(3)	Tm(2)−N(2)	2.51(4)
Tm(2)−Te(5)	2.993(8)	Tm(2)−Te(1)	3.018(8)	Tm(2)−Te(7)	3.030(8)
Tm(2)−Te(6)	3.056(7)	Tm(2)−Te(4)	3.066(7)	Tm(3)−N(5)	2.415(18)
Tm(3)−N(4)	2.481(17)	Tm(3)−Te(9)	2.984(7)	Tm(3)−Te(7)	3.005(7)
Tm(3)−Te(8)	3.024(8)	Tm(3)−Te(1)	3.101(3)	Tm(3)−Te(6)	3.101(8)
Tm(4)−N(7)	2.37(3)	Tm(4)−N(6)	2.43(3)	Tm(4)−Te(3)	3.008(8)
Tm(4)−Te(9)	3.036(7)	Tm(4)−Te(8)	3.044(7)	Tm(4)−Te(1)	3.081(8)
Tm(4)−Te(2)	3.097(7)	Te(2)−Te(3)	2.795(10)	Te(3)−Te(10)	3.543(9)
Te(4)−Te(5)	2.834(11)	Te(5)−Te(10)	3.521(9)	Te(6)−Te(7)	2.872(10)
Te(7)−Te(10)	3.292(9)	Te(8)−Te(9)	2.836(9)	Te(9)−Te(10)	3.336(9)

N(1)−Tm(1)−Te(2)	93.6(10)	N(1)−Tm(1)−Te(3)	90.4(9)	N(5)−Tm(3)−N(4)	83.1(8)	N(5)−Tm(3)−Te(9)	136.2(9)
Te(2)−Tm(1)−Te(3)	55.6(2)	N(1)−Tm(1)−Te(1A)	90.8(7)	N(4)−Tm(3)−Te(9)	90.0(8)	N(5)−Tm(3)−Te(7)	139.2(9)
Te(2)−Tm(1)−Te(1A)	85.4(3)	Te(3)−Tm(1)−Te(1A)	141.0(3)	N(4)−Tm(3)−Te(7)	89.3(7)	Te(9)−Tm(3)−Te(7)	83.53(10)
N(1)−Tm(1)−Te(4)	86.7(10)	Te(2)−Tm(1)−Te(4)	163.98(12)	N(5)−Tm(3)−Te(8)	80.5(9)	N(4)−Tm(3)−Te(8)	90.8(9)
Te(3)−Tm(1)−Te(4)	140.4(2)	Te(1A)−Tm(1)−Te(4)	78.5(3)	Te(9)−Tm(3)−Te(8)	56.3(2)	Te(7)−Tm(3)−Te(8)	139.9(2)
N(1)−Tm(1)−Te(5)	85.2(9)	Te(2)−Tm(1)−Te(5)	141.2(2)	N(5)−Tm(3)−Te(1)	97.6(6)	N(4)−Tm(3)−Te(1)	178.8(8)
Te(3)−Tm(1)−Te(5)	85.57(12)	Te(1A)−Tm(1)−Te(5)	133.3(3)	Te(9)−Tm(3)−Te(1)	90.18(16)	Te(7)−Tm(3)−Te(1)	89.48(16)
Te(4)−Tm(1)−Te(5)	54.9(2)	N(1)−Tm(1)−Te(1)	174.3(9)	Te(8)−Tm(3)−Te(1)	90.37(19)	N(5)−Tm(3)−Te(6)	83.8(9)
Te(2)−Tm(1)−Te(1)	90.9(2)	Te(3)−Tm(1)−Te(1)	89.31(19)	N(4)−Tm(3)−Te(6)	89.7(9)	Te(9)−Tm(3)−Te(6)	139.6(2)
Te(1A)−Tm(1)−Te(1)	92.99(9)	Te(4)−Tm(1)−Te(1)	89.9(2)	Te(7)−Tm(3)−Te(6)	56.1(2)	Te(8)−Tm(3)−Te(6)	164.06(9)
Te(5)−Tm(1)−Te(1)	89.08(18)	N(3)−Tm(2)−N(2)	85.5(16)	Te(1)−Tm(3)−Te(6)	89.4(2)	N(7)−Tm(4)−N(6)	85.9(15)
N(3)−Tm(2)−Te(5)	89.7(9)	N(2)−Tm(2)−Te(5)	139.5(12)	N(7)−Tm(4)−Te(3)	135.8(11)	N(6)−Tm(4)−Te(3)	93.2(10)
N(3)−Tm(2)−Te(1)	176.4(10)	N(2)−Tm(2)−Te(1)	90.8(12)	N(7)−Tm(4)−Te(9)	141.7(11)	N(6)−Tm(4)−Te(9)	90.7(10)
Te(5)−Tm(2)−Te(1)	93.11(19)	N(3)−Tm(2)−Te(7)	92.0(10)	Te(3)−Tm(4)−Te(9)	82.5(2)	N(7)−Tm(4)−Te(8)	86.1(11)
N(2)−Tm(2)−Te(7)	138.1(12)	Te(5)−Tm(2)−Te(7)	82.1(2)	N(6)−Tm(4)−Te(8)	87.1(10)	Te(3)−Tm(4)−Te(8)	138.1(2)
Te(1)−Tm(2)−Te(7)	90.60(16)	N(3)−Tm(2)−Te(6)	87.5(10)	Te(9)−Tm(4)−Te(8)	55.60(18)	N(7)−Tm(4)−Te(1)	91.8(11)
N(2)−Tm(2)−Te(6)	81.8(12)	Te(5)−Tm(2)−Te(6)	138.2(3)	N(6)−Tm(4)−Te(1)	176.7(10)	Te(3)−Tm(4)−Te(1)	90.11(19)
Te(1)−Tm(2)−Te(6)	91.81(16)	Te(7)−Tm(2)−Te(6)	56.3(2)	Te(9)−Tm(4)−Te(1)	89.61(18)	Te(8)−Tm(4)−Te(1)	90.40(16)
N(3)−Tm(2)−Te(4)	87.8(10)	N(2)−Tm(2)−Te(4)	83.9(12)	N(7)−Tm(4)−Te(2)	81.3(11)	N(6)−Tm(4)−Te(2)	92.1(10)
Te(5)−Tm(2)−Te(4)	55.8(2)	Te(1)−Tm(2)−Te(4)	91.94(19)	Te(3)−Tm(4)−Te(2)	54.5(2)	Te(9)−Tm(4)−Te(2)	137.0(3)
Te(7)−Tm(2)−Te(4)	137.9(3)	Te(6)−Tm(2)−Te(4)	165.2(3)	Te(8)−Tm(4)−Te(2)	167.4(3)	Te(1)−Tm(4)−Te(2)	89.90(17)

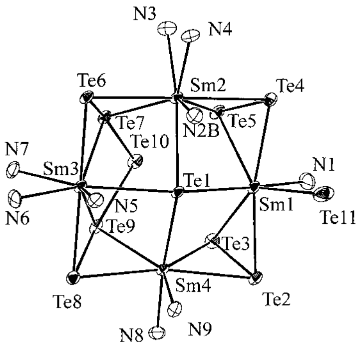

Figure 1. ORTEP diagram of (py)$_9$SmTe(TeTe)$_2$(TeTeTe(Ph)TeTe)(TePh) with the C and H atoms removed for clarity and with the thermal ellipsoids drawn at the 50% probability level.

of Ln clusters with Te^{2-}, suggests that the ditellurido ligand stabilizes Ln(III) ions more effectively than Te^{2-}. These compounds can be prepared either by first adding PhTeTePh to Ln, followed by addition of Te, or in a one-step reaction. Absence of light throughout the synthetic procedure is crucial to the successful isolation of these cluster compounds, as found in the synthesis of tellurolate-capped tellurido clusters of the transition metals.[30] When solutions of the initial insertion of Ln into the PhTe−TePh bond were exposed to light and the reaction was then insulated, no product was recovered. Similarly, when the first insertion step was insulated but the reaction was then exposed to light, no product formed. The compounds are also light-sensitive after isolation and will turn from red to black within hours under ambient conditions.

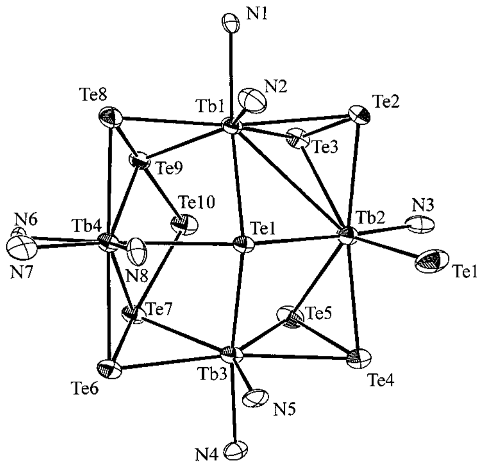

Figure 2. ORTEP diagram of (py)$_8$TbTe(TeTe)$_2$(TeTeTe(Ph)TeTe)(Te$_{0.1}$TePh) with the C and H atoms removed for clarity and with the thermal ellipsoids drawn at the 50% probability level.

Clusters **1**−**4** share the same fundamental structural features recently reported for the sulfur-rich iodo cluster (THF)$_6$Yb$_4$(SS)$_4$(S)I$_2$,[19] with a square array of Ln(III) ions, the central chalcogenido ligand, and two edges spanned by TeTe units. The central Te^{2-} resides 1.00 Å (**1**), 1.11 Å (**2**), or 1.17 Å (**4**) above the plane defined by the Ln$_4$ core. When corrected for differences in Ln ionic radii,[31] the terminal tellurolate Ln−Te bond lengths [**1**, 3.067(2) Å; **2**, 2.994(3) Å; **4**, 3.033(4) Å] are as expected, given the scant literature precedent, i.e., the terminal Ln−TeR bonds in [(py)$_2$Ho(PhNNPh)(TePh)]$_2$ [3.063(1) Å],[32] Cp*$_2$YbTePh(NH$_3$) (3.039-

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(30) Corrigan, J.; Fenske, D. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1981.

(31) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751.

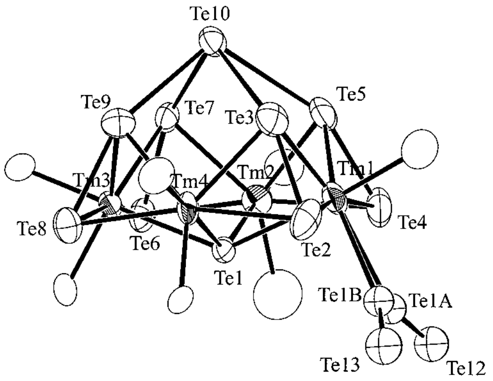

Figure 3. ORTEP diagram of $(py)_7TmTe[(TeTe)_4TePh](Te_{0.6}TePh)$ with the C and H atoms removed for clarity and with the thermal ellipsoids drawn at the 50% probability level.

(1) Å),[6] $Cp^*_2Sm(thf)(TeMes)$ [3.088(2) Å],[7] and $La(TeSiR_3)_3(DMPE)_2$ [av 3.155(5) Å].[11,12] The Ln−N distances agree with previously reported values for pyridine derivatives of $Ln(EPh)_3$.

The tellurium clusters reported here are also structurally similar to the recently described selenium-rich clusters $(py)_8Yb_4Se(SeSe)_3(SeSeSePh)(SePh)$ and $(py)_8Yb_4Se(SeSe)_3(SeSeTePh)(SeTePh)$ that also have an EPh ligand displaced from a Yb(III) ion and coordinating to an EE moiety.[20] The major difference between the products described here and the selenium-rich clusters is the extent that the displaced EPh interacts with the EE units. Chemically, the tellurium-rich clusters are also considerably more unstable.

Similarities with polyiodide chemistry are clearly evident in the structures. From Figure 4, which shows a schematic diagram of the Te_5Ph^{5-} ligands in **1**, **2**, and **4**, it is clear that the interaction of TePh with the TeTe diads depends significantly on environment. In cluster **1**, there is a modest asymmetry to the interaction between PhTe and the two TeTe units. A greater difference is noted in the Tb cluster **2**, while in **4**, the bonding description becomes increasingly less clear. Such a continuum[33] of bonding interactions are often found for the heavier halides, chalcogenides, pnictides, and latter transition metals, with chalcogenido interactions being described as complicated van der Waals interactions.[33,34]

In all three structures, coordination of PhTe to Te(9)−Te(8) and Te(7)−Te(6) is clearly more significant, as judged by the shorter $PhTe-Te_2$ bonds and the considerable lengthening of these Te−Te bonds, relative to the remaining two ditelluride ligands. Essentially the same features are found in the numerous structures of I_5^- compounds,[35−38] where I_2 units that bond more strongly to the I^- also consistently have the longer I−I bond. Both tellurido and iodide structural features can be explained by noting that X^- is donating electron density into the σ^* orbital of the XX, thus lengthening the XX bond. While bond lengths in the TeTe units would lead to the conclusion that these polytelluride ligands are best described as Te_5Ph^{5-} for **1** and **2** and Te_9Ph^{9-} for **4**, there are alternative methods for assessing or qualifying these nebulous interactions. In the literature, there is a general consensus that distances less than 3.75 Å constitute a significant TeTe interaction.[39−47] Given this breakpoint, the multitellurium ligands in this work would be described as Te_5Ph^{5-} (**1**), Te_7Ph^{7-} (**2**), and Te_9Ph^{9-} (**4**).

A comparison of the poly-Te ligands in **1**−**4** with the recently described Te(Ph)Te(Ph)Te(Ph) would also be appropriate.[48] Oddly enough, this tritellurolate analogue of I_3^- was also obtained in synthetic studies of lanthanide compounds, but in this case, introduction of the sterically demanding, highly electronegative ancillary pyrazolylborate ligand completely excludes coordination of Te to the Ln to produce an outer sphere $(TePh)_3^-$ ion. In this unusual anion, there are a pair of inequivalent Te−Te bonds [3.112(1) Å, 2.939(1) Å] that are considerably longer than the TeTe bond in PhTeTePh [2.712(2) Å][49] and are distinctly similar to the TeTe interactions noted in the present work.

Discrete molecular compounds with ditelluride ligands are uncommon.[50−53] Of the reported ditellurides, most are found in combination with chalcophilic metals, and they exhibit a wide range [i.e., 2.665(2) Å in $(R_3P)_3Ni(TeTe)$,[50] 2.841(2) Å in $Mo_4Te_{16}{}^{2-}$ [51]] of Te−Te bond lengths. There also exists a limited, but rich, structural chemistry of solid-state materials with extensive networks of weak TeTe interactions.[52−60] Lanthanide complexes are scarce, but again, with highly electronegative, sterically demanding ancillary ligands, compounds with ditelluride linkages spanning a pair of Ln(III) ions can be isolated, i.e., $[(Cp^*)_2Ln]_2(TeTe)$ (Ln = Sm,[5]

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(32) Kornienko, A.; Freedman, D.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **2001**, *40*, 140.

(33) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597.

(34) Klinkhammer, K. W.; Pyykko, P. *Inorg. Chem.* **1995**, *34*, 4134.

(35) Blake, A.; Lippolis, V.; Schroder, M. *Chem. Commun.* **1996**, 2207.

(36) Ercolani, C.; Pennesi, G.; Trigiante, G. *Inorg. Chem.* **1995**, *34*, 2535.

(37) Hills, A.; Hughes, D. L.; Leigh, G. J.; Sanders, J. R. *J. Chem. Soc., Dalton Trans.* **1991**, 61.

(38) Beno, M.; Geiser, U.; Kostka, K.; Wang, H.; Webb, K.; Firestone, M.; Carlson, K.; Nunez, L.; Whangbo, M.; Williams, J. *Inorg. Chem.* **1987**, *26*, 1912.

(39) Jobic, S.; Deniard, P.; Brec, R.; Rouxel, J.; Jouanneaux, A.; Fitsch, A. *Z. Anorg. Allg. Chem.* **1991**, *598/599*, 199.

(40) Monconduit, L.; Evain, M.; Boucher, F.; Brec, R.; Rouxel, J. *Z. Anorg. Allg. Chem.* **1992**, *616*, 177.

(41) Canadell, E.; Monconduit, L.; Evain, M.; Brec, R.; Rouxel, J.; Whangbo, M.-H. *Inorg. Chem.* **1993**, *32*, 10.

(42) Evain, M.; Monconduit, L.; van der Lee, A.; Brec, R.; Rouxel, J.; Canadell, E. *New J. Chem.* **1994**, *18*, 215.

(43) van der Lee, A.; Evain, M.; Monconduit, L.; Brec, R.; Petricek, V. *Inorg. Chem.* **1994**, *33*, 3032.

(44) Evain, M.; Monconduit, L.; Brec, R. *J. Solid State Chem.* **1995**, *119*, 394.

(45) Canadell, E.; Jobic, S.; Brec, R.; Rouxel, J.; Whangbo, M.-H. *J. Solid State Chem.* **1992**, *99*, 189.

(46) Whangbo, M.-H.; Canadell, E. *J. Am. Chem. Soc.* **1992**, *114*, 9587.

(47) Canadell, E.; Mathey, Y.; Whangbo, M.-H. *J. Am. Chem. Soc.* **1988**, *110*, 104.

(48) Hillier, A. C.; Liu, S.; Sella, A.; Elsegood, M. R. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2745.

(49) Llabres, P. G.; Dideberg, O.; DuPont, L. *Acta Crystallogr.* **1972**, *B28*, 2438.

(50) DiVaira, M.; Peruzzini, M.; Stoppioni, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 916.

(51) Eichhorn, B. W.; Haltshauer, R. C.; Cotton, F. A.; Wilson, B. *Inorg. Chem.* **1988**, *27*, 4084.

(52) Sroof, L.; Pennington, W.; Krolis, J. *Inorg. Chem.* **1992**, *31*, 2056.

(53) Fenske, D.; Steck, J.-C.; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 238.

(54) Stauf, S.; Reisner, C.; Tremel, W. *Chem. Commun.* **1996**, 1749.

(55) Ibers, J. A.; Bollinger, J. C.; Roof, L. C. *Inorg. Chem.* **1995**, *34*, 1430.

(56) Smith, D. M.; Roof, L. C.; Ibers, J. A. *Inorg. Chem.* **1996**, *35*, 4999.

(57) Dhingra, S. S.; Haushalter, R. C. *Inorg. Chem.* **1994**, *33*, 2735.

(58) Alemany, P.; Jobic, S.; Brec, R.; Canadell, E. *Inorg. Chem.* **1997**, *36*, 5050.

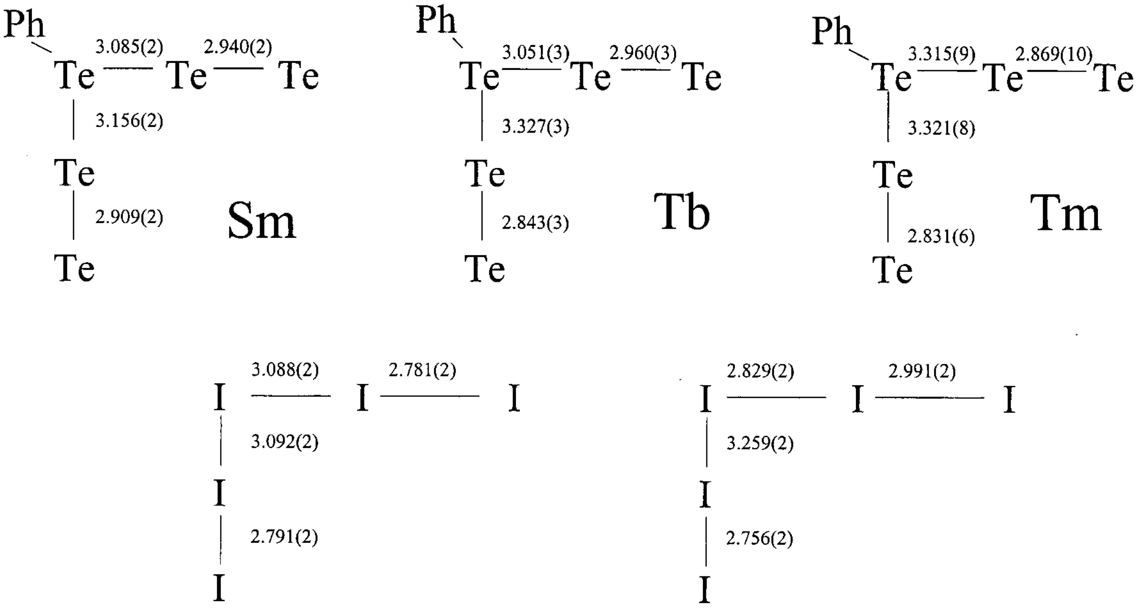

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Figure 4. Bond length variations in the "TeTeTe(Ph)TeTe" ligands in **1** (Sm) and **2** (Tb), the two most significant PhTe−(TeTe) interactions in **4** (Tm), and variations in typical symmetric and asymmetric I_5^- ligands.

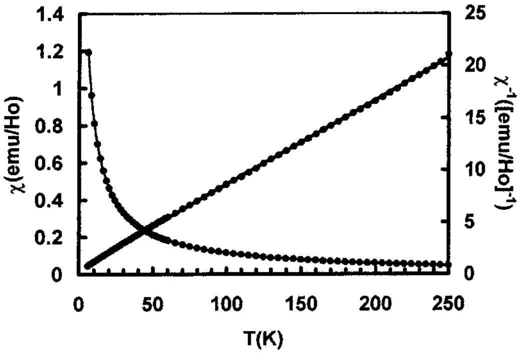

Figure 5. The temperature-dependent magnetic susceptibility (χ) and its inverse (χ^{-1}) for $(py)_8HoTe(TeTe)_2(TeTeTe(Ph)TeTe)(Te_{0.1}TePh)$.

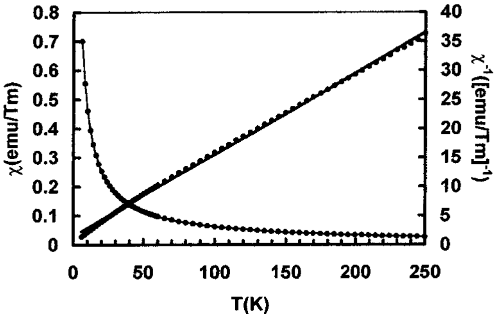

Figure 6. The temperature-dependent magnetic susceptibility (χ) and its inverse (χ^{-1}) for $(py)_7TmTe[(TeTe)_4TePh](Te_{0.6}TePh)$.

Yb^4). In these organometallic compounds, the TeTe bond lengths are 2.773(1) Å (Sm) and 2.769(1) Å (Yb). There is no precedence for either $(Te_5Ph)^{5-}$ (Te_7Ph),$^{7-}$ or (Te_9Ph).$^{9-}$

Measuring the magnetic and electronic properties of **3** and **4** was complicated by the extreme sensitivity of the samples. Still, magnetic susceptibility measurements of both compounds clearly revealed a complete absence of significant interactions between neighboring Ln(III) spin systems. Plots of $1/\chi$ vs T showed ideal Curie Weiss behavior at all temperatures. Magnetic moments for both **3** (10.6 μ_B) and **4** (7.60 μ_B) were found to be surprisingly close to the values for the respective Ln_2O_3 (Ln = Ho, μ = 10.6 μ_B;[61] Ln = Tm, μ = 7.56 μ_B[62]), given the extreme sensitivity of the compounds, particularly to light and heat. Of the solid-state telluride compounds available for comparison, only the magnetic properties of Tm_2Te_3 (μ = 7.56 μ_B; $T_p = -6$ K, ideal Curie−Weiss behavior > 10 K)[63] have been reported, and again, the properties are essentially indistinguishable from those of **4**.

In the electronic spectra, there are no well-defined absorption maxima for **2**−**4**. Given the multitude of allowed transitions associated with the different Te−Te bonds, the vibrational broadening associated with the PhTe ligand, and the four different Te to Ln CT excitations that tail into the visible spectrum, a featureless spectrum was unfortunately both anticipated and observed. This contrasts with the well-resolved electronic spectrum of $(THF)_6Yb_4(SS)_4(S)I_2$, which has a less complicated chalcogen array, a $\sigma \rightarrow \sigma^*$ manifold in the UV spectrum, and only LMCT absorptions shifted clearly into the visible spectrum because of the relative stability of the Yb(II) excited state.[19]

Thermolysis. Thermolyses of **2**, **3**, and **4**, give the single-phase products $TbTe_{2-x}$, HoTe, and TmTe, respectively, with elimination of Ph_2Te and Te, thus adding to the already

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(59) Pell, M. A.; Ibers, J. A. *Chem. Mater.* **1996**, *8*, 1386.

(60) Li, J.; Chen. Z.; Emge, T.; Proserpio, D. M. *Inorg. Chem.* **1997**, 36, 1437.

(61) Pinaeva, M. M.; Krylov, E. I.; Ryakov, V. M. *Inorg. Mater. USSR* **1965**, *1*, 1428.

(62) Perakis, N.; Kern, F. *Physik Kond. Mater.* **1965**, *247*, 249.

(63) Pokrzywnicki, S. *Sci Papers Inst. Inorg. Chem. Rare Elements Wroclaw Polytech Inst. No. 45* **1979**, 1/69, 45; *Chem. Abstr.* **1980**, *92*, 87141.

diverse reactivity patterns noted in $Ln(ER)_x$ thermolyses.[64−68] Unusual Te-rich solid-state products might have been anticipated, given the presence of excess Te in the starting materials, but the tendency of Te-rich Ln phases to lose Te by evaporation is clearly a significant factor in product determination. The elimination of Ph_2Te has considerable literature precedent.[69] Of the comparable lanthanide chalcogenolate thermolyses in the literature, there are certain similarities with the present work. While most $Ln(ER)_3$ give Ln_2E_3 (Ln = La, Ce; E = Te; Ln = Yb, E = Se; Ln = Ho, Tm, Yb, E = S) (reaction 3), LnE (reaction 4) solid-state phases have been noted with a readily reduced Eu(III) precursor, and phase-separated ($LnSe/LnSe_2$) products have also been observed (reaction 5).

$$2Ln(EPh)_3 \rightarrow Ln_2E_3 + 3ER_2 \qquad (3)$$

$$2Ln(EPh)_3 \rightarrow 2LnE + REER + 2ER_2 \qquad (4)$$

$$2Ln(EPh)_3 \rightarrow LnE_2 + LnE + 3ER_2 \qquad (5)$$

Thermolysis of clusters 2−4 clearly resembles reaction 5 with the presence of excess Te accounting for the observation of the Te-rich phase in **2** and subsequent Te evaporation producing the metallic LnTe (NaCl phase) solids. There are, unfortunately, no well-defined $LnTe_x$ phase diagrams available in the literature that might help to explain why the individual phases are observed.

Conclusion

Tellurido clusters of redox-inactive lanthanides are isolable compounds that are oxygen-, water-, heat-, and light-sensitive. The compounds are clearly trivalent, as judged by magnetic susceptibility and X-ray diffraction experiments. These materials are useful single source precursors to solid-state $LnTe_x$. Significantly, because tellurolate ligands are so readily displaced from Ln coordination spheres, lanthanide compounds with tellurolate ligands can be useful for doping Ln ions into Te rich matrixes.[70]

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Supporting Information Available: X-ray crystallographic files in CIF format for the crystal structures of **1**, **2**, and **4** are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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(64) Brewer, M.; Lee, J.; Brennan, J. G. *Inorg. Chem.* **1995**, *34*, 5919.

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

(66) Berardini, M.; Brennan, J. *Inorg. Chem*. **1995**, *34*, 6179.

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

(68) Lee, J.; Brewer, M.; Berardini, M.; Brennan, J. *Inorg. Chem.* **1995**, *34*, 3215

(69) Brennan, J.; Siegrist, T.; Stuczynski, S.;.Carroll, C.; Rynders, P.; Brus, L.; Steigerwald, M. *Chem. Mater*. **1990**, *2*, 403.

(70) Harbison; B. B.; Sanghera; J. S.; Shaw; L. B.; Aggarwal, I. D. US Patent 6,015,765, **2000**.