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Heterometallic Ln/Hg Tellurido Clusters

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"Ln(TePh)$_3$" (Ln = Er, Tm, Lu), prepared in situ by the reduction of PhTeTePh with elemental Ln in the presence of Hg catalyst, reacts with elemental Te to give heterometallic clusters with the formula (py)$_7$Ln$_3$HgTe$_4$(TePh)$_3$. Structural characterization of all three isostructural derivatives reveals a cubane arrangement of metal ions, with a distorted tetrahedral Hg(II) ion coordinated to three μ_3 coordinate Te^{2-} and a terminal TePh ligand. There are two chemically inequivalent types of octahedral Ln(III) ions, one bound to three Te^{2-} and three pyridine donors, and two that coordinate two pyridine, three Te^{2-}, and a terminal TePh ligand. The Lu compound decomposes at elevated temperatures to give LuTe.

Introduction

The synthetic chemistry of chalcogenido (E^{2-}; E = S, Se, Te) clusters containing both Ln and the group 12 metals (M; M = Zn, Cd, and Hg) has been motivated by a range of applications, from chalcogenido based optical fibers,[1] doped semiconductors[2] and LEDs,[3] to fluorescent nanocluster labels.[4] This chemistry is complicated by the extremely disparate nature of Ln and M, with Ln exhibiting classically ionic, oxophilic character and the group 12 metals considered to be among the most covalent, chalcophilic metals in the periodic chart. Early attempts to prepare compounds with Ln−E−M linkages demonstrated that while Ln, E, and M may be present in a product, there is not necessarily an E bound to both Ln and M. In simple chalcogenolate chemistry, reactions of Ln(EPh)$_3$ with M(EPh)$_2$ gave well-defined heterometallic compounds,[5] but the presence of excess M(EPh)$_2$ often led to the formation of complex salts, with covalent metals abstracting EPh from the lanthanide to form ionic compounds with lanthanide cations and main group anions.[6] This reactivity was noted again in cluster preparations, where, for example, the facile synthesis of ionic species such as [Yb(THF)$_6$]$^{2+}$[Fe$_4$Se$_4$(SePh)$_4$]$^{2-}$ or [(THF)$_8$Sm$_4$Se(SePh)$_8$]$^{2+}$-[Zn$_8$Se(SePh)$_{16}$]$^{2-}$ underscored the ease with which Ln-EPh bonds can be cleaved.[7] The ionic Zn/Ln heterocluster material[7] was particularly insightful, because although spectroscopic methods might correctly indicate the presence of Sm−Se^{2-} and Zn−Se^{2-} bonds, the compound contains no Sm−Se−Zn connectivity. Subsequent thermal decomposition of this cluster salt resulted in a continuation of metal separation, leading to the formation of a crystalline mixture containing solid-state Ln$_2$Se$_3$ and ZnSe.[5]

Once it became clear that the presence of excess M(EPh)$_x$ in solution was detrimental to the preparation of heterometallic clusters, synthetic conditions were adjusted and the first[8] structurally characterized examples of compounds with Ln−E^{2-}−M linkages[9] were subsequently prepared. Double cubane structures with the formula (py)$_8$Ln$_4$M$_2$Se$_6$(SePh)$_4$ (Ln = Er, Yb, Lu; M = Cd, Hg)[8] were shown to adopt a boxkite arrangement of tetrahedral M and octahedral Ln connected by μ_3 or μ_4 Se^{2-}. In contrast to the phase separation

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noted in the thermal decomposition studies of the ionic SmZn selenolate, the Cd compounds decomposed at elevated temperatures to give ternary solid-state compounds $CdLn_2Se_4$.

Ln chemistry with tellurium based anions is considerably less developed than is the analogous chemistry of the lighter chalcogenides (see for example the abundance of $Ln(SR)_{2,3}$[10] and the paucity of $Ln(TeR)_{2,3}$ compounds),[11−13] and there are no known examples of compounds with Ln−Te−M linkages. These Ln−Te compounds are scarce because in addition to the air, moisture, and thermal sensitivity displayed by the lighter chalcogenido derivatives, compounds with Ln−Te bonds are also light sensitive,[13d] both in solution and when isolated in crystalline form. This sensitivity may eventually be useful, i.e., for controlling the deposition of Ln doped semiconductor thin films, but a rational approach to any applied process requires a firm understanding of the chemistry leading up to, and the reactivity of, compounds with Ln−Te or Ln−Te−M bonds. In this manuscript we outline our first investigations into the synthesis and reactivity of these elusive products.

Experimental Section

General Methods. All syntheses were carried out under ultrapure nitrogen (JWS), using conventional drybox or Schlenk techniques. Solvents (Aldrich) were purified with a dual column Solv-Tek solvent purification system and collected immediately prior to use. Ln metals were purchased from Strem. Ph_2Te_2 was prepared according to literature procedure.[14] 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 600 cm^{-1} as a Nujol mull on NaCl plates. Electronic spectra were recorded on a Perkin-Elmer (Lambda 9) 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). X-ray powder diffraction data were obtained with a Bruker HiStar area detector and the Bruker *GADDS* [General Area Detector Diffraction System, Vers. 4.1, Bruker-AXS, Madison, WI (2001)] and Materials Data Jade-7 software packages [Material Data Inc., Livermore, CA (2007)]. ESI-MS data were recorded on a Thermo Finnigan LCQ DUO system with the sample dissolved in CH_2Cl_2. Mass spectra were acquired in the negative ion detection mode scanning a mass range from $m/z = 150$ to $m/z = 1000$. In the case of isotopic patterns, the value given is for the most intense peak. ^1H NMR spectra were obtained on a Bruker 500 MHz spectrometer.

Synthesis of $(py)_7Er_3Hg(Te)_4(TePh)_3\cdot 2py$ (1). Elemental Er (0.167 g, 1.00 mmol), PhTeTePh (0.616 g, 1.50 mmol), and Hg (0.045 g, 0.225 mmol) were combined in pyridine (50 mL) and stirred until all the metals were completely dissolved producing a dark red brown solution. Elemental Te (0.255 g, 2.00 mmol) was added to the resulting solution and stirred for 2 days. A dark brown solution with a gray black powdery precipitate was produced. The solution was filtered, reduced in volume to 30 mL, and layered with hexane. After 2−3 days dark red blocks (0.460 g, 79%) appeared. The crystals do not melt but turn to a charcoal black powder with evolution of a brown gas between 130 and 145 °C and remain unchanged up to 300 °C. IR: 2923 (m), 2725 (s), 1463 (m), 1467 (w), 1377 (s), 1373 (m), 1221 (s), 1148 (s), 1029 (s), 1000 (s), 743 (m), 727 (m), 690 (w), 645 (w), 641 (w) cm^{-1}. UV−vis.: The compound does not show any absorption maximum from 350 to 750 nm when dissolved in pyridine, with the red color coming from allowed Te-to-Hg charge transfer absorptions that obscure transitions localized on the Er ion. Anal. Calcd. for $C_{63}H_{60}HgTe_7N_9Er_3$: C, 29.8; H, 2.36; N, 4.96. Found: C, 29.5; H, 2.24; N, 4.49. Emission experiments on Er compound could not be obtained because of the compound is light sensitive.

Synthesis of $(py)_7Tm_3Hg(Te)_4(TePh)_3\cdot 2py$ (2). As for **1**, Tm (0.169 g, 1.00 mmol), PhTeTePh (0.616 g, 1.50 mmol), and Hg (0.045 g, 0.225 mmol) in pyridine (50 mL) followed by elemental Te (0.255 g, 2.00 mmol) gave dark red blocks (0.390 g, 68%) that do not melt but turn to a charcoal black powder with evolution of brown gas between 133 and 145 °C and remain unchanged up to 300 °C. IR: 2922 (m), 2726 (s), 1463 (m), 1469 (w), 1378 (s), 1370 (m), 1219 (s), 1147 (s), 1030 (s), 1001 (s), 745 (m), 729 (m), 690 (w), 645 (w), 640 (w) cm^{-1}. UV−vis.: The compound does not show any absorption maximum from 350 to 750 nm when dissolved in pyridine. Anal. Calcd. for $C_{63}H_{60}HgTe_7N_9Tm_3$: C, 29.7; H, 2.36; N, 4.95. Found: C, 29.4; H, 2.14; N, 4.57.

Synthesis of $(py)_7Lu_3Hg(Te)_4(TePh)_3\cdot 2py$ (3). As for **1**, Lu (0.175 g, 1.00 mmol), PhTeTePh (0.616 g, 1.50 mmol) and Hg (0.045 g, 0.225 mmol) in pyridine (50 mL) followed by elemental Te (0.255 g, 2.00 mmol) gave dark red blocks (0.25 g, 43%) that did not melt but turned to a charcoal black powder with evolution of brown gas between 131 and 145 °C and remain unchanged up to 300 °C. IR: 2922 (m), 2724 (s), 1465 (m), 1470 (w), 1377 (s), 1371 (m), 1222 (s), 1150 (s), 1030 (s), 1002 (s), 742 (m), 730 (m), 689 (w), 645 (w), 641 (w) cm^{-1}. UV−vis.: The compound does not show any absorption maximum from 350 to 750 nm when dissolved in pyridine. Anal. Calcd. for $C_{63}H_{60}HgTe_7N_9Lu_3$: C, 29.5; H, 2.34; N, 4.92. Found: C, 29.3; H, 2.09; N, 4.51. ^1H NMR (NC_5D_5, 40 °C): 8.33(2H), 7.01(m, 3H). Lowering the temperature results in a loss of resolution, with the 8.33 ppm resonance broadening almost into the baseline at −20 °C.

X-ray Structure Determination of 1−3. Data for **1**−**3** were collected on a Bruker Smart APEX CCD diffractometer with graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 100 K. The data were corrected for Lorenz effects and polarization, and absorption, the latter by a multiscan (SADABS)[15] method. The structures were solved by Patterson methods (SHELXS86).[16] All non-hydrogen atoms were refined (SHELXL97)[17] based upon F_{obs}^2. All hydrogen atom coordinates were calculated with idealized geometries (SHELXL97). Scattering factors (fo, f', f'') are as described in SHELXL97. Crystallographic data and final R indices for **1**−**3** are given in Table 1. An Oak Ridge Thermal Ellipsoid Plot (ORTEP) diagram[18] for the common structure of **1**−**3** is shown in Figure 1. Complete crystallographic details are given in the Supporting Information. Significant bond geometries for **3** are given in Table 2, with the

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Table 1. Summary of Crystallographic Details for **1**−**3**

	1	**2**	**3**
empirical formula	$C_{63}H_{60}HgN_9$-Te_7Er_3	$C_{63}H_{60}HgN_9$-Te_7Tm_3	$C_{63}H_{60}HgN_9$-Te_7Lu_3
fw	2538.77	2543.78	2561.90
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	11.8594(7)	11.824(6)	11.7950(13)
b (Å)	13.0332(8)	13.027(6)	13.0179(14)
c (Å)	22.9210(14)	22.901(11)	22.848(3)
α (deg)	94.460(1)	94.404(1)	94.490(2)
β (deg)	93.397(1)	93.036(1)	92.899(2)
γ (deg)	95.581(1)	95.553(1)	95.600(2)
V (Å^3)	3507.4(4)	3493.5(4)	3474.8(7)
Z	2	2	2
D(calcd) (g/cm^{-3})	2.404	2.418	2.449
temperature (K)	100(2)	100(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073
abs coeff (mm^{-1})	8.631	8.870	9.351
$R(F)^a$ [$I > 2\sigma(I)$]	0.0386	0.0481	0.0504
$Rw(F^2)^a$ [$I > 2\ \sigma(I)$]	0.0886	0.0916	0.0794

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

geometries for **1** and **2** not differing significantly, as evidenced by the following ranges of distances to metal atoms (see Table 2 for corresponding standard uncertainty values). Hg−Ln separations range from 3.564 to 3.597(Tm), 3.569−3.598(Er), 3.568−3.599(Lu); Hg−Te distances range from 2.739 to 2.896(Tm), 2.742−2.898(Er), 2.740−2.896(Lu); Ln−Te distances range from 2.975 to 3.053(Tm), 2.985−3.064(Er), 2.964−3.039(Lu); Ln−N distances range from 2.43 to 2.50(Tm), 2.45−2.51(Er), 2.42−2.48(Lu).

Thermolysis of 3. 3 (100 mg) was placed in a quartz thermolysis tube that was sealed under vacuum, and the sample end was placed into a model 847 Lindberg tube furnace. The "cold" end of the tube was held at −196 °C by immersion in liquid nitrogen. The sample was heated to 650 °C at a ramp rate of 20 °C/min, then held at 650 °C for 5 h at which time it was cooled to 25 °C at a rate of 3.5 °C/min. The black powder (40 mg) that was formed at the sample end of the quartz tube was identified as LuTe[19] by X-ray powder diffraction (International Centre for Diffraction Data (ICDD), Powder Diffraction File PDF#00−19−0745). CGMS analysis identified the volatile product as $TePh_2$ ($M^+ = 209$).

Results and Discussion

The telluride clusters $(py)_7Ln_3HgTe_4(TePh)_3$ (Ln = Er(**1**), Tm(**2**), Lu(**3**)) were isolated in high yield by first reducing PhTePh in pyridine with elemental Ln in the presence of Hg, followed by the addition of 2 equiv of elemental Te (reaction 1) and saturation of the solution with hexane.

$$\mathrm{Ln/Hg + PhTeTePh} \xrightarrow{\mathrm{py}} \mathrm{Ln(TePh)_3}$$
$$\xrightarrow{\mathrm{Te}} \mathrm{(py)_7Ln_3HgTe_4(TePh)_3 + PhTeTePh} \qquad (1)$$

Product isolation was successful only for the smaller lanthanides that traditionally adopt 6-coordinate structures. Attempts to prepare the analogous Yb derivative did not give an isolable product, presumably because Te based anions are not sufficiently electronegative to stabilize Yb(III) ions with respect to reductive elimination of PhTeTePh and the formation of Yb(II) products.[13a,d]

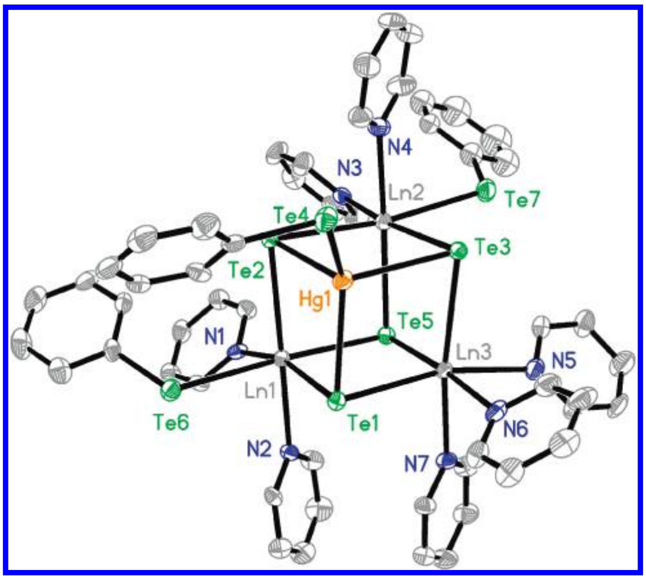

Figure 1. ORTEP diagram of the cubane clusters $(py)_7Ln_3HgTe_4(TePh)_3$ (Ln = Er, Tm, Lu) with thermal ellipsoids drawn at the 50% probability level (for **1**), gray carbon atoms, and the H atoms removed for clarity.

Discrete compounds with Ln−Te bonds are extremely rare, with **1**−**3** being the first examples of isolable Ln−TeR/Ln−Te^{2-} compounds that are not supported by sterically demanding (i.e., Cp*) ligands.[20] Early work in this area focused on the synthesis of Ln−TeR compounds with sterically demanding $Te(2,4,6,tri^iPr-C_6H_2)$[11] or $Te-Si(SiMe_3)_3$[12] tellurolates, with the latter compounds decomposing at room temperature to give $Ln_5Te_3(TeSi(SiMe_3)_9$ clusters that were too unstable to characterize fully. The benzenetellurolate ligand was subsequently introduced[13] and yielded a series of divalent $Ln(TePh)_2$ coordination compounds, but attempts to prepare trivalent benzenetellurolates or stable tellurido compounds were unsuccessful, leading only to the synthesis of polytellurido clusters.[13d]

Low temperature single crystal X-ray diffraction was used to establish that **1**−**3** adopt a cubane arrangement of four M (Hg, 3 Ln) metals connected by triply bridging tellurido ligands. All three compounds are isostructural and so in the following discussion of specific structural details we will refer to the Lu compound, with the Tm and Er compounds showing the same features/trends. In **3**, the Hg(II) ion bonds three tellurido dianions and a terminal tellurolate in what must be described as a distorted tetrahedral environment, with PhTe−Hg-Te angles that range from 103 to 122°. There are three crystallographically unique Ln in the structure, with one, Ln(3), that coordinates three Te^{2-} and three pyridine donors in an octahedral arrangement, and the two others, Ln(1) and Ln(2), that have octahedral geometries composed of three Te^{2-}, two pyridine, and a terminal PhTe ligand. The two chemically similar Ln are not related by crystallographic symmetry.

The cubane motif found for **1**−**3** has been noted with increasing frequency in structural lanthanide chemistry. This

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Table 2. Significant Distances (Å) and Angles (deg) for $(py)_7Lu_3HgTe_4(TePh)_3$

Hg(1)−Lu(3)	3.5985(6)	Lu(1)−Te(6)	3.0233(8)	Lu(3)−N(7)	2.436(7)
Hg(1)−Lu(1)	3.6016(6)	Lu(2)−N(3)	2.434(8)	Lu(3)−N(5)	2.443(8)
Lu(1)−N(1)	2.414(7)	Lu(2)−N(4)	2.455(8)	Lu(3)−N(6)	2.450(8)
Lu(1)−N(2)	2.476(7)	Lu(2)−Te(2)	2.9766(8)	Lu(3)−Te(3)	2.9698(7)
Lu(1)−Te(1)	2.9645(7)	Lu(2)−Te(3)	2.9977(8)	Lu(3)−Te(5)	2.9745(7)
Lu(1)−Te(2)	2.9884(7)	Lu(2)−Te(5)	3.0051(7)	Lu(3)−Te(1)	2.9884(7)
Lu(1)−Te(5)	3.0011(7)	Lu(2)−Te(7)	3.0392(9)		

Te(4)−Hg(1)−Te(1)	122.13(2)	Te(1)−Hg(1)−Lu(1)	53.316(15)
Te(4)−Hg(1)−Te(2)	111.58(2)	Te(2)−Hg(1)−Lu(1)	53.540(15)
Te(1)−Hg(1)−Te(2)	105.68(2)	Te(3)−Hg(1)−Lu(1)	108.517(17)
Te(4)−Hg(1)−Te(3)	103.58(2)	Lu(2)−Hg(1)−Lu(1)	71.863(14)
Te(1)−Hg(1)−Te(3)	105.55(2)	Lu(3)−Hg(1)−Lu(1)	68.643(10)
Te(2)−Hg(1)−Te(3)	107.38(2)	N(1)−Lu(1)−N(2)	79.9(2)
Te(4)−Hg(1)−Lu(2)	126.18(2)	N(1)−Lu(1)−Te(1)	165.57(18)
Te(1)−Hg(1)−Lu(2)	111.436(18)	N(2)−Lu(1)−Te(1)	86.55(17)
Te(2)−Hg(1)−Lu(2)	53.729(16)	N(1)−Lu(1)−Te(2)	94.36(18)
Te(3)−Hg(1)−Lu(2)	54.052(15)	N(2)−Lu(1)−Te(2)	173.88(17)
Te(4)−Hg(1)−Lu(3)	139.16(2)	Te(1)−Lu(1)−Te(2)	99.350(19)
Te(1)−Hg(1)−Lu(3)	53.858(15)	N(1)−Lu(1)−Te(5)	90.32(19)
Te(2)−Hg(1)−Lu(3)	107.750(17)	N(2)−Lu(1)−Te(5)	87.99(18)
Te(3)−Hg(1)−Lu(3)	53.095(15)	Te(1)−Lu(1)−Te(5)	94.126(19)
Lu(2)−Hg(1)−Lu(3)	71.105(11)	Te(2)−Lu(1)−Te(5)	89.97(2)
Te(4)−Hg(1)−Lu(1)	147.48(2)	N(1)−Lu(1)−Te(6)	88.93(19)
N(2)−Lu(1)−Te(6)	88.86(18)	N(3)−Lu(2)−Hg(1)	138.43(19)
Te(1)−Lu(1)−Te(6)	85.88(2)	N(4)−Lu(2)−Hg(1)	90.3(2)
Te(2)−Lu(1)−Te(6)	93.14(2)	Te(2)−Lu(2)−Hg(1)	51.148(15)
Te(5)−Lu(1)−Te(6)	176.85(2)	Te(3)−Lu(2)−Hg(1)	51.447(16)
N(1)−Lu(1)−Hg(1)	144.58(18)	Te(5)−Lu(2)−Hg(1)	85.287(17)
N(2)−Lu(1)−Hg(1)	134.73(17)	Te(7)−Lu(2)−Hg(1)	136.67(2)
Te(1)−Lu(1)−Hg(1)	49.703(15)	N(7)−Lu(3)−N(5)	79.1(3)
Te(2)−Lu(1)−Hg(1)	50.697(14)	N(7)−Lu(3)−N(6)	89.3(3)
Te(5)−Lu(1)−Hg(1)	84.753(16)	N(5)−Lu(3)−N(6)	84.9(3)
Te(6)−Lu(1)−Hg(1)	97.617(18)	N(7)−Lu(3)−Te(3)	169.81(18)
N(3)−Lu(2)−N(4)	92.8(3)	N(5)−Lu(3)−Te(3)	91.10(19)
N(3)−Lu(2)−Te(2)	87.64(19)	N(6)−Lu(3)−Te(3)	92.78(19)
N(4)−Lu(2)−Te(2)	86.8(2)	N(7)−Lu(3)−Te(5)	86.34(17)
N(3)−Lu(2)−Te(3)	170.11(19)	N(5)−Lu(3)−Te(5)	94.03(19)
N(4)−Lu(2)−Te(3)	87.14(19)	N(6)−Lu(3)−Te(5)	175.60(18)
Te(2)−Lu(2)−Te(3)	102.23(2)	Te(3)−Lu(3)−Te(5)	91.515(19)
N(3)−Lu(2)−Te(5)	90.27(18)	N(7)−Lu(3)−Te(1)	90.49(18)
N(4)−Lu(2)−Te(5)	175.6(2)	N(5)−Lu(3)−Te(1)	166.31(18)
Te(2)−Lu(2)−Te(5)	90.12(2)	N(6)−Lu(3)−Te(1)	86.1(2)
Te(3)−Lu(2)−Te(5)	90.375(18)	Te(3)−Lu(3)−Te(1)	99.61(2)
N(3)−Lu(2)−Te(7)	84.87(19)	Te(5)−Lu(3)−Te(1)	94.183(19)
N(4)−Lu(2)−Te(7)	88.1(2)	N(7)−Lu(3)−Hg(1)	138.26(18)
Te(2)−Lu(2)−Te(7)	170.76(2)	N(5)−Lu(3)−Hg(1)	142.21(19)
Te(3)−Lu(2)−Te(7)	85.24(2)	N(6)−Lu(3)−Hg(1)	98.27(18)
Te(5)−Lu(2)−Te(7)	95.32(2)	Te(3)−Lu(3)−Hg(1)	51.232(14)
Te(5)−Lu(3)−Hg(1)	85.188(15)	Lu(2)−Te(2)−Lu(1)	89.72(2)
Te(1)−Lu(3)−Hg(1)	49.630(14)	Hg(1)−Te(3)−Lu(3)	75.673(19)
Hg(1)−Te(1)−Lu(1)	76.981(17)	Hg(1)−Te(3)−Lu(2)	74.501(17)
Hg(1)−Te(1)−Lu(3)	76.512(19)	Lu(3)−Te(3)−Lu(2)	88.583(18)
Lu(1)−Te(1)−Lu(3)	85.994(18)	Lu(3)−Te(5)−Lu(1)	85.589(18)
Hg(1)−Te(2)−Lu(2)	75.123(18)	Lu(3)−Te(5)−Lu(2)	88.355(18)
Hg(1)−Te(2)−Lu(1)	75.764(17)	Lu(1)−Te(5)−Lu(2)	88.937(19)

structural arrangement was originally observed in hydroxide chemistry,[21] with Ln_4OH_4 clusters that were severely distorted from an ideal cubane arrangement because of the tendency of O to use sp^3 orbitals. Cubane structures with Ln_4Se_4 cores[22] and "double cubane" Ln_6S_6 fragments[22,23] were subsequently prepared, and these chalcogenido derivatives were considerably less distorted from an ideal cubic shape relative to their OH analogues, because the S/Se ligands use p orbitals rather than hydroxide sp^3, and so chalcogenido ions naturally form bonds with 90° X−E−X angles. Most recently, there have been descriptions of extremely interesting imido compounds with $Ln_4(NR)_4$ cores that are similar to the OH cubanes in terms of distortions from an ideal cubic structure.[24] While the hydroxides and imido compounds contain seven coordinate Ln, the chalcogenido series have thus far always been found with octahedral Ln.

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The Ln−Te bond lengths in **1**−**3** display classical ionic behavior in the sense that there does not appear to be a directional dependence to the Ln−Te bond length. In ionic systems, Ln−L bond lengths for a given complex have traditionally been predicted by summing the ionic radius of Ln and L.[25] Recently, however, there have been structural reports of mer-octahedral LnX_3Y_3 coordination compounds in which the Ln−X or Ln−E bonds trans to anions are consistently longer than the analogous bonds trans to neutral donors. The effect, first noted in the benzene thiolate compound $(py)_3Yb(SPh)_3$,[26] has since been shown to exist in a range of simple mer-octahedral molecular compounds ((i.e., $(THF)_3LnX_3$ (X = Cl,[27] Br,[28] I[29]) or $(THF)_3Ln(EC_6F_5)_3$ (E = O,[30] S, Se[31]), and similar trends were also noted in the chalcogenido cubane clusters. In both the clusters and the molecular fluorinated chalcogenolates, the bond length inequivalence is more pronounced in the sulfur derivatives than it is in the selenium analogues. This uncharacteristic directional behavior has been treated theoretically, and from the calculations it appears that there is a small but significant covalent interaction between the Ln d orbitals and the p-orbitals on the chalcogen.[31] Unlike these lighter chalcogenido clusters, the bonds in **1**−**3** did not show a consistent directional trend in Ln−Te bond lengths. For the unique $Te(5)^{2-}$ that does not bond to Hg, the Lu(1)−Te(5) bond trans to the anionic TePh is longer than the Lu(3)−Te(5) bond trans to pyridine but shorter than the Lu(2)−Te(5) bond trans to pyridine. Similarly, if we look at the Lu−Te bond distances for the two Lu that coordinate TePh, we find that for Lu(1) the Ln−Te(5) bond trans to the tellurolate is slightly longer than the two Lu−Te bonds trans to pyridine, while for Ln(2), the Lu−Te(2) bond trans to the tellurolate is the shortest of the three $Lu(2)-Te^{2-}$ bonds. The absence of a trans influence in these compounds would be consistent with what one might expect, given the diffuse nature of the anionic electron density, the relative weakness of Ln−Te bonds in general, the fact that the differences in bond lengths are small, and that the bond length differences decrease when S is replaced by Se.

In chalcogenido compounds solid-state and solution structures are not necessarily the same,[32] and diamagnetic lutetium compounds are often invaluable for probing the solution structure. Compound **3** is unfortunately just sparingly soluble in toluene, but is soluble enough in pyridine to attempt a variable temperature ^1H NMR analysis, to establish whether the solid state structure is maintained in solution. Unfortunately, there is only a single set of weak TePh resonances in the ^1H NMR spectrum at room temperature, and while they begin to broaden as the temperature is lowered, they do not resolve before solubility issues preclude an exact determination of solution structure.

The thermolysis chemistry of these compounds was interesting because in the past heterometallic compounds have decomposed thermally to give either phase separated (MSe/Ln_2Se_3) or ternary (Ln_2CdSe_4) solid state materials. Thermal decomposition of a sample of **3** led to the formation of a black solid product, with a clearly defined ring of Hg metal condensing at the cool end of the sealed, evacuated thermolysis tube. This is surprising given the past tendency of Hg tellurolates to deliver HgTe,[33] but reductive elimination of Hg to give RTeTeR[34] has also been observed. Analysis of the non-volatile solid state product by X-ray powder diffraction revealed that LuTe was the only crystalline product (Reaction 2), and a GCMS analysis of the volatile organic products that had condensed in the liquid nitrogen trap showed that $TePh_2$ was the only non-volatile organic product of the reaction.

$$(py)_7Ln_3HgTe_4(TePh)_3 \xrightarrow{\Delta,\ \mathrm{vac}} LnTe + Hg + TePh_2 + ?? \qquad (2)$$

The formation of the mono- rather than sesquitellurides came as no surprise, given that previous experiments with a lanthanide tellurolates such as $Ln(PhNNPh)(TePh)$[35] or the tellurium rich precursors $Ln_4Te(TeTe)_4(TePh)_2$ have already shown that LnTe phases form upon thermolysis.[13d]

Conclusions

Heterometallic lanthanide/main group tellurido clusters can be isolated in high yield, and crystallize as cubane structures with distorted tetrahedral Hg and octahedral Ln coordination environments. Two of the lanthanide ions have octahedral geometries with Ln−Te bonds trans to either py or TePh ligands, and there appears to be no directional influence to the Ln−Te bond length. These compounds decompose at elevated temperatures to give LnTe.

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Supporting Information Available: X-ray crystallographic files in CIF format for the crystal structures of **1**−**3**; complete tables of bond geometries for **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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