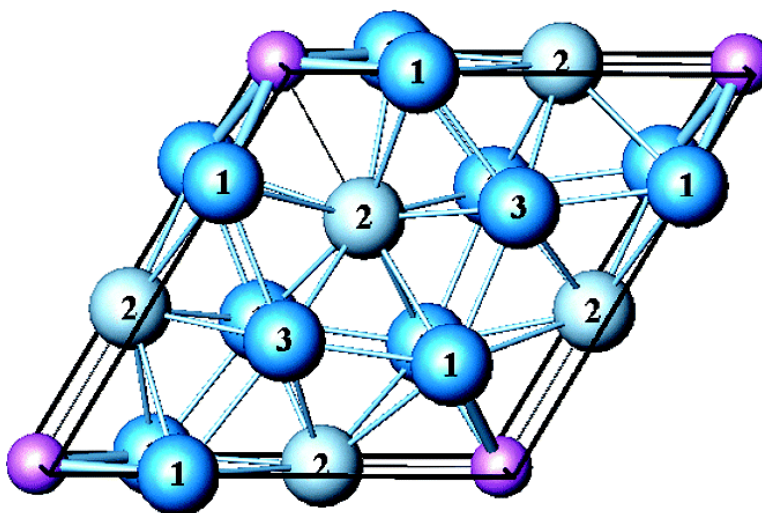


LuTe and LuTe. Novel Substitutional Derivatives of Lutetium Metal

Ling Chen, and John D. Corbett

J. Am. Chem. Soc., **2003**, 125 (26), 7794-7795 • DOI: 10.1021/ja035392z • Publication Date (Web): 10 June 2003

Downloaded from <http://pubs.acs.org> on March 29, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 1 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



Lu₈Te and Lu₇Te. Novel Substitutional Derivatives of Lutetium Metal

Ling Chen and John D. Corbett*

Department of Chemistry, Iowa State University, Ames, Iowa 50011

Received March 31, 2003; E-mail: jcorbett@iastate.edu

In these two unprecedented structure types, simple packing orientations AB... lie normal to complex six (Lu₈Te) or eight (Lu₇Te) repeats of puckered layers in which Te regularly replaces Lu in every third or fourth layer, respectively. Deformations in the latter layers result from strong Lu–Te interactions and size effects. These are the first examples of Lu-rich chalcogenides and are the two most condensed lanthanide chalcogenides known.

Recent investigations have demonstrated a significant relationship between the d-element chemistry of the earliest transition metals, Sc, Y, Ti, especially, and that of the (numerically) metal-rich chalcogenides of the late lanthanides. Yet, so far only a few systems pertain, orthorhombic R₂Te, R = Sc, Gd, Dy, and hexagonal R₆MTe₂, R = Sc, Dy, M = Mn–Ni, Ru, Rh, Os, Ir.^{1–5} There are otherwise no reports of lanthanide chalcogenides more reduced than the simple LnCh phases (NaCl type, Ch = S, Se, Te), perhaps because any earlier investigations were carried out in SiO₂ rather than in the superior Ta or Nb containers. We herein report that this new chemistry extends much farther to the novel compounds Lu₈Te and Lu₇Te and some related phases.

Common structural features of such metal-rich compounds are condensed metal octahedra or trigonal prisms in the form of chains or layers,^{1,6–8} whereas a few examples also show distant relationships with the bcc metals; for example, Ta₂Se⁹ consists of four (100) layers of bcc Ta sandwiched between two square nets of Se, and Hf₃Te₂¹⁰ is a three-layer analogue of Ta₂Se. In these two new, remarkable structure types, Te, a smaller nonmetal and anion-like component, regularly substitutes on particular lattice points of what can be viewed as very distorted hcp Lu metal. The Lu₇Te and then Lu₈Te were synthesized via arc-melting and high-temperature annealing steps from the metal and Lu₂Te₃¹¹ and characterized by single-crystal X-ray diffraction methods as the stoichiometric orthorhombic Lu₇Te and hexagonal Lu₈Te.¹²

Figure 1 gives general overviews of both structures via projections down the short (~3.7 Å) axes, [001] for hexagonal Lu₈Te at the top and [100] for orthorhombic Lu₇Te, bottom. All atoms lie on mirror planes at 0, 1/2, and 1 normal to the views, the lighter colored atoms having the intermediate coordinate of 1/2. The packing along the short axis in both is layered AB... On the other hand, the layers seen in each projection are not classically close-packed but rather are considerably distorted, presumably because of Te substitution on certain lattice sites. Nonetheless, both structures can still be additionally described in a useful way in terms of the sequence of horizontal puckered or wavy layers of atoms along the vertical axis in both parts of Figure 1. These vertical sequences are labeled A, B, C in the conventional way. That in Lu₈Te, top, has the six-layer representation (ABACAB)... [h(hc)₂] as marked, with every fourth layer A or C lying in a mirror plane. The stoichiometry Lu₈Te results from substitution of Te (lavender) for every third Lu in every third layer along [100]. This structure is in fact a new ordered derivative of the Fe₂P type structure (Z = 3)¹⁶ in which the equivalent of P₂ is replaced by Lu₃ (Lu₆TeLu₂). Continuing in this way, we find that Lu₇Te at the bottom of Figure

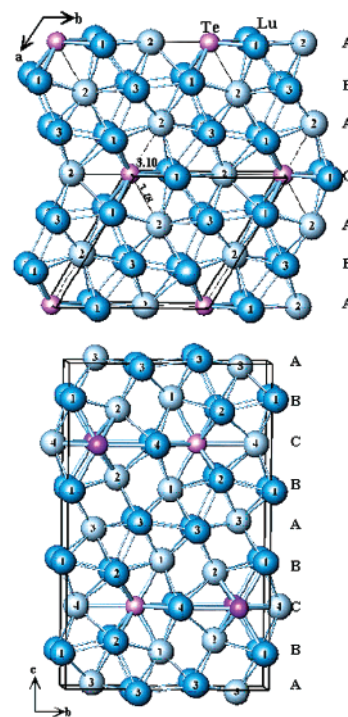


Figure 1. Projection of the structures of hexagonal Lu₈Te (*P* $\bar{6}2m$) (top), and of orthorhombic Lu₇Te (*Cmcm*) (bottom) approximately along the short cell axis (~3.7 Å) in each (\bar{c} , \bar{a} , respectively). Atoms at 0, 1, and 1/2 along that axis are dark and light blue for Lu and purple and lavender for Te, respectively. The six- and eight-layer packing sequences along the vertical axes are labeled.

1 is more complex and distorted. The puckered layers have the relative stacking (ABCBABCB)... [(hc)₄] in an eight-layer sequence along \bar{c} (vertical) in which mirror planes contain the C members. The Te substitutes for every other Lu in every fourth layer to give the stoichiometry Lu₇Te. The two (100) layer types in Lu₇Te are related by the $a/2 + b/2$ centering operation, whereas the two (001) in Lu₈Te are independent.

One would not expect any Te...Te bonding in such electron-rich systems. Rather, these novel reactions can be thought of as introducing smaller periodic Te “defects” and strong polar bonding into the metal, and these produce substantial expansions in two directions in the normal metal. Every atom in these structures has a pair of like neighbors at $\pm c$, 3.687 Å, in Lu₈Te or $\pm a$, 3.742 Å, in Lu₇Te as compared to the repeat (c) of 5.54 Å in the metal.¹⁷ Of course, what are being stacked here are by no means close-packed layers, as is evident in the vertical layering repeats in Figure 1. The tighter binding brought on by these small oxidations of the metal by tellurium is best reflected in the volume increments per atom: Lu, 29.52 Å³;¹⁷ Lu₈Te, 28.73 Å³; Lu₇Te, 28.38 Å³, which amount to decreases of 2.7% and 3.9%, respectively. These occur despite parallel decreases in coordination numbers (below).

Regarding the Te environments, the distances about these atoms

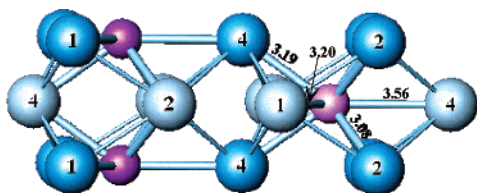


Figure 2. A near-[001] view of slightly more than one cell along \bar{b} (horizontal) of the atoms around the Lu4–Te1 plane at $z = 3/4$ in Lu_7Te (see Figure 1, bottom). This illustrates the close bicapped trigonal prismatic environment around Te along \bar{a} plus the one long Te–Lu4 capping distance.

are also enumerated in the figures. That in Lu_8Te is a regular tricapped trigonal prism, with considerably longer distances to the three capping atoms (lighter black lines), 3.48 Å, than to the six within the trigonal prism, 3.10 Å. The tricapped trigonal prismatic arrangement about Te in Lu_7Te is more distorted, one Te–Lu4 distance along \bar{b} being ~ 0.35 Å longer. The alternating long–short Te–Lu4 distances in the mirror planes at $z = 1/4, 3/4$ can be understood better in terms of the [001] section of this layer shown in Figure 2. With simple planar layering along \bar{a} (vertical), Te is simply too small to lie closer to the third in-plane Lu4. Otherwise, all Te–Lu distances in this figure are fairly regular, 3.08–3.20 Å.

The Te substitutions produce increasingly distorted polyhedra about Lu as well, in particular, in the planes shown in Figure 1. Drawings of all of these polyhedra are contained in the Supporting Information. In Lu_8Te , Lu1 (CN10) is surrounded by a distorted, bicapped square prism that includes two Te; Lu2 (CN11), also with $m2m$ symmetry, is centered in a distorted pentagonal prism with two opposed long edges and a coplanar Te; Lu3 (CN9) in the former P2 site centers a fairly regular tricapped trigonal prism, now with slightly shorter Lu3–Lu1 distances to the capping atoms. The distortions in the lower symmetry Lu_7Te reflect an increased reduction of the practical coordination numbers of the Lu atoms from 12 in the pure metal: Lu1, Lu2, and Lu3 are CN10, bicapped square prismatic, and Lu4 is CN11, monocapped pentagonal prismatic. The Lu1, Lu2, and Lu4 environments cited include one, two, and three Te atoms, respectively. The nearest Lu–Lu distances range over 3.28–3.61 Å in both structures with averages of 3.43 Å in Lu_8Te and 3.45 Å in Lu_7Te . These are relatively comparable to the CN12 value for the metal, 3.48 Å,¹⁸ so the Lu–Lu bonding by this fairly easy measure seems fairly strong. The nine Lu–Te contacts in the two structures average 3.23 and 3.16 Å, respectively, which are reasonably close to a very different measure, 3.24 Å for the sum of crystal radii for Lu^{3+} (CN9) and Te^{2-} .¹⁹ Regardless of their interpretation, the average Lu–Te distance in these compounds is somewhat less than that for Lu–Lu in the 12-coordinate metal, 3.453 and 3.505 Å (6 each), and this fits the appearance that an apparently smaller Te has been inserted. Incidentally, the average Lu–Lu distance about each Lu in Lu_7Te increases about 0.05 Å for each Te present among the near neighbors, reflecting the competition presented by strong Lu–Te bonds. (Data for Lu_8Te are less clear, and the polyhedra are more disparate.)

EHTB calculations for both compounds show, as expected, broad Lu bonding bands that are only partially filled at E_F , and filled Te p levels falling from ~ 2.5 to 5.5 eV below E_F , as has been seen before.^{2–4,20}

The Lu_8Te and Lu_7Te represent novel and remarkable structure types and the most condensed compounds to date among metal-rich binary chalcogenides. Nothing seen before^{2–10,20} has a perceptible relationship to these. Replacement of Lu with the nonmetallic element Te gives stronger metal–nonmetal interactions that lead to the deformation of the close-packed pattern. These

compounds can be viewed as a dilute ordered solution of nonmetal Te in a matrix of very distorted Lu metal, an unprecedented event as far as we are aware and one that forecasts a rich chemistry behind these systems. We have already discovered another unexpected binary compound, $\text{Lu}_{11}\text{Te}_4$,⁵ and an unusual ternary chemistry is expected.

Acknowledgment. This research was supported by the National Science Foundation, Solid State Chemistry, via Grant DMR-01285 and was carried out in the facilities of the Ames Laboratory, U.S. Department of Energy.

Supporting Information Available: Tables of X-ray data collection and refinement results, structural parameters and distances, and coordination polyhedra drawings (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Maggard, P. A.; Corbett, J. D. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1974.
- (2) Herle, P. S.; Corbett, J. D. *Inorg. Chem.* **2001**, *40*, 1858.
- (3) Maggard, P. A.; Corbett, J. D. *Inorg. Chem.* **2000**, *39*, 4143.
- (4) Bestaoui, N.; Herle, S.; Corbett, J. D. *J. Solid State Chem.* **2000**, *155*, 9.
- (5) Chen, L.; Corbett, J. D., unpublished research.
- (6) Simon, A. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1.
- (7) Maggard, P. A.; Corbett, J. D. *Inorg. Chem.* **1998**, *37*, 814.
- (8) Maggard, P. A.; Corbett, J. D. *J. Am. Chem. Soc.* **2000**, *122*, 838.
- (9) Harbrecht, B. *Angew. Chem.* **1989**, *101*, 1696.
- (10) Abdon, R.; Hughbanks, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2328.
- (11) Lu_7Te was prepared first from a pressed pellet of Lu and Lu_2Te_3 by arc-melting in a glovebox. Products obtained directly after the arc-melted button is quenched (on the H_2O -cooled Cu hearth) depend on the Lu:Te proportions loaded and include Lu_7Te , $\text{Lu}_{11}\text{Te}_4$,⁵ and LuTe . Tellurium values were lost from the molten button only slowly, for example, < 2 wt % after two 20-s arc treatments of the loaded composition Lu_7Te_2 . Good crystals of Lu_7Te were obtained after the button was ground, pressed into a pellet, and annealed in a welded Ta container in a vacuum furnace for 48 h at 1300 °C. An intervening Mo sheet substantially reduces the reaction of the products with Ta. Lu_8Te as good monocrystals (plus $\text{Lu}_{11}\text{Te}_4$) is formed in high yield ($\sim 80\%$) from disproportionation of a sample of Lu_7Te at 1200–1000 °C for 2 days to 2 weeks. This phase was also prepared quantitatively from the correct proportions of Lu and Lu_2Te_3 at 1000 °C for 2 weeks. There is no metal-richer phase under these conditions. Similar products are not obtained for La, Pr, Gd, Ho, Tm, Yb. Both phases are visibly stable in air for more than 2 months, although some small unknown crystals were pyrophoric right after arc-melting.
- (12) Single-crystal data were collected at room temperature on a Bruker AXS SMART APEX CCD-based X-ray diffractometer with 20-s frames up to $\theta = 28.2^\circ$. Absorption effects were corrected by SADABS.¹³ The program package confirmed a C-centered condition ($h + k = \text{odd}$), a c -glide along b , and a 2₁ screw axis along c for Lu_7Te , and the mean value of $|E^2 - 1|$ ($= 0.962$) suggested that the structure is centrosymmetric. The highest symmetry space group among three possibilities, $Cmcm$ (a subgroup of that of the metal), gave successful results. All of the atoms were located by direct methods, and the structure was refined with SHELXTL-6.10¹⁴ by full-matrix least-squares on F^2 to anisotropic convergence at $R1 = 2.73\%$, $wR2 (F^2) = 6.52\%$ for $I > 2\sigma(I)$ and 3.09%, 6.66% for all data. The largest peak in the final ΔF map was $4.77 \text{ e } \text{Å}^{-3}$, 0.83 Å from Lu2, and the largest hole was $-2.17 \text{ e } \text{Å}^{-3}$, located 0.68 Å from Lu2.¹⁵ The test for merohedral twinning helped to decide the correct space group of Lu_8Te as the acentric $P62m$. All atom positions were established by direct methods and likewise refined under the twin law without event to $R1, wR2 = 3.28, 6.48\%$ for $I > 2\sigma(I)$ data and 3.67, 6.56% for all data. The largest residual feature was $-2.65 \text{ e } \text{Å}^{-3}$. The atom parameters, interatomic distances, and illustrations of the coordination polyhedra are given for both compounds in the Supporting Information.
- (13) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33.
- (14) SHELXTL6.10; Bruker AXS, Inc.: Madison, WI, 2000.
- (15) Although $\beta\text{-BaCu}_4\text{S}_3$ (Iglesias, J. E.; Pachali, K. E.; Steinfink, H. *Mater. Res. Bull.* **1972**, *7*, 1247) is isopointal with Lu_7Te , the structures are very different. The roles of Lu4 and Te are approximately reversed from those of Ba and S_2 , and infinite copper sulfide sheets between Ba layers run along \bar{c} not \bar{b} and normal to the mirror planes at $z = 1/4$, etc.
- (16) Hyde, B. G.; Henderson, S. *Inorganic Crystal Structures*; J. Wiley: New York, 1989; p 88.
- (17) Beaudry, B. J.; Gschneidner, K. A. In *Handbook of the Physics and Chemistry of the Rare Earths*; Gschneidner, K. A., Eyring, L., Eds.; North-Holland Publishing: The Netherlands, 1978; Vol. 1, p 216.
- (18) Pauling, L. *Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, New York, 1960; p 403.
- (19) Shannon, R. D. *Acta Crystallogr.* **1976**, *32A*, 751.
- (20) Chen, L.; Corbett, J. D. *Inorg. Chem.* **2002**, *41*, 2146.

JA035392Z