CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
BRIGHAM YOUNG UNIVERSITY, PROVO, UTAH

High-Pressure, High-Temperature Syntheses of Selected Lanthanide–Tellurium Compounds

BY J. F. CANNON AND H. T. HALL

Received June 23, 1969

Tetragonal LTe_{2-x} ($0 \leq x \leq 0.3$) compounds were synthesized for the following lanthanides with lattice parameters (a_0, c_0) and standard deviations were determined as indicated (values in Å): Y, 4.291 (3), 8.912 (6), Ho, 4.264 (2), 8.872 (4); Er, 4.248 (2), 8.865 (5); Tm, 4.240 (2), 8.831 (4); Lu, 4.222 (1), 8.807 (3). Orthorhombic $LuTe_3$ with lattice parameters (a_0, b_0, c_0) 4.277 (1), 25.137 (6), 4.278 (1) Å was also synthesized. Pressures to 100 kbars with temperatures to 1200° were employed in the studies, and the P–T regions required for synthesis were delineated. The new compounds are extensions of the LTe_{2-x} and LTe_3 series previously reported through Dy for LTe_{2-x} and through Tm for LTe_3.

Introduction

Compounds of the type LTe_{2-x} ($0 \leq x \leq 0.3$) and LTe_3 (L = lanthanides, Sc, Y) have been studied since 1958. The LTe_{2-x} compounds are tetragonal with space group P4/nmm[1] whereas the LTe_3 compounds are orthorhombic (pseudotetragonal) with space group Bmmb.[2,3] The similarity of these two structures has been described by Wang and Steinfink.[4] They show that the essential features of the LTe_3 structure may be constructed by stacking slightly distorted LTe_{2-x} units with alternate cells shifted by $^1/_2 a_0$.

The LTe_{2-x} compounds have been reported[1,3-6] for L = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Yb and those of the LTe_3 type[2,3,7-9] for L = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Y. Pardo, *et al.*,[5] reported that the LTe_{2-x} compounds existed only for L = La–Dy, and Wang and Steinfink[4] mentioned that attempts to prepare $HoTe_{2-x}$ and $ErTe_{2-x}$ resulted in mixtures of the mono- and tritellurides. The latter authors suggested that the formation of LTe_{2-x} and LTe_3 compounds depends on the ionic radius of L. As the ionic radius of L decreases, the Te–Te distance in the basal plane of both types of compounds becomes shorter. When that distance is predicted to be 3.015 Å or less, the compound does not form. A Te–Te distance of 3.015 Å was predicted for $HoTe_{2-x}$ and for $LuTe_3$. Thus LTe_{2-x} compounds for L = Ho, Er, Tm, Lu, Sc and LTe_3 compounds for L = Lu, Sc should not form.

Since Te is more compressible than L, synthesis of the above-mentioned LTe_{2-x} and LTe_3 compounds should become more favorable as the pressure on the reaction mixture is increased. Table I shows a comparison of the L/Te radius ratio under ambient conditions and under pressure. If the L/Te radius ratios in $DyTe_{2-x}$ and $TmTe_3$ represent the lower limits for compound formation, then Table I shows that the application of pressure causes the L/Te radius ratio to become favorable for formation of previously unknown LTe_{2-x} and LTe_3 compounds. Consequently, high-pressure techniques were used in an attempt to synthesize these compounds. Attempts were also made to prepare YTe_{2-x} since it had not been formed previously.

TABLE I
COMPARISON OF L/Te RADIUS RATIOS UNDER AMBIENT AND COMPRESSED CONDITIONS

Element	Metallic covalent radius,[a] Å	Compressed radius,[b] Å	Compressed L/Te radius ratio[c]	Difference[d]	
				LTe_{2-x}	LTe_3
Sc	1.48	1.39	0.97	−0.05	−0.04
Y	1.648	1.488	1.04	+0.02	
Ho	1.632	1.518	1.06	0.04	
Er	1.620	1.507	1.05	0.03	
Tm	1.613	1.500	1.05	0.03	
Lu	1.597	1.485	1.04	0.02	0.03

[a] Determined by extrapolation of the values for the lighter lanthanide metallic covalent radii for the LTe_{2-x} structure from R. Wang, Ph.D. Dissertation, The University of Texas, 1967. [b] Estimation based on data for Sc, Y, and La at 100 kbars from H. T. Hall, *Progr. Inorg. Chem.*, **7**, 1 (1966). [c] Atmospheric pressure Te radius is 1.60 Å, and the compressed Ta radius is 1.43 Å. [d] Difference represents the L/Te radius ratio in column four minus the L/Te radius ratio for $DyTe_{2-x}$ or $TmTe_3$ (1.02 and 1.01 Å, respectively).

Experimental Section

The high pressures and temperatures necessary for this work were generated in the tetrahedral apparatus developed by Hall.[10,11] The sample geometry is shown in Figure 1. After the sample was assembled, the pyrophyllite exterior was painted with a slurry of red iron oxide in methanol and then baked for at least 0.5 hr at 110°.

Synthesis experiments were carried out as follows. The pressure was increased slowly to about 5 kbars and rapidly thereafter to the desired pressure. An electric current was then passed through the graphite heater at a specific wattage for an appropriate time. The sample was then quenched by cutting off the current (cooling to 50 or 60° occurred in about 5 sec) and the pressure was returned to normal. The reaction mixture was removed from its container and X-rayed immediately.

The temperature of each run was determined indirectly from calibration curves of power input (watts) *vs.* temperature.

---

[1] L. Domange, J. Flahaut, M. P. Pardo, A. N. Chirazi, and M. Guittard, *C. R. Acad. Sci.*, **250**, 857 (1960).

[2] T. H. Ramsey, H. Steinfink, and E. J. Weiss, *Inorg. Chem.*, **4**, 1154 (1965).

[3] W. Lin, H. Steinfink, and E. J. Weiss, *ibid.*, **4**, 877 (1965).

[4] R. Wang and H. Steinfink, *ibid.*, **6**, 1685 (1967).

[5] M. P. Pardo, J. Flahaut, and L. Domange, *Bull. Soc. Chim. Fr.*, 3267 (1964).

[6] R. Wang, H. Steinfink, and W. F. Bradley, *Inorg. Chem.*, **5**, 142 (1966).

[7] M. P. Pardo, O. Gorochov, J. Flahaut, and L. Domange, *C. R. Acad. Sci.*, **260**, 1666 (1965).

[8] D. J. Haase, H. Steinfink, and E. J. Weiss, *Inorg. Chem.*, **4**, 541 (1965).

[9] B. K. Norling and H. Steinfink, *ibid.*, **5**, 1488 (1966).

[10] H. T. Hall, *Rev. Sci. Instrum.*, **29**, 267 (1958).

[11] H. T. Hall, *ibid.*, **33**, 1278 (1962).

These curves were prepared[12] by making prototype synthesis runs in which a platinum—platinum–10% rhodium thermocouple was placed. Data were taken at 50-W (about 150°) intervals for pressures of 14, 36, 52, and 69 kbars. Above 450° temperatures are good to ±6% and below 450° to ±8%.

Pressure calibrations[12] were based on Ce (8.1 kbars), Hg (12.2 kbars), Bi I–II (26.5 kbars), Tl II–III (35.4 kbars), Yb I–II (38.2 kbars), and Ba I–II (54.6 kbars) transitions.[13-15] Pressure calibration runs were made at room temperature with the calibration sample surrounded by AgCl. The pressure transitions were reproducible to ±0.3 kbar.

The metals (less than 0.1% lanthanide impurity) were obtained in ingot form from Research Chemicals, Inc., Burbank, Calif. (Ho, Er); Research Chemicals, a division of Nuclear Corp. of America, Phoenix, Ariz. (Sc, Y, Lu); and Alfa Inorganics, Beverly, Mass. (Tm). The Te (99.99+% pure) was purchased in lump form from the American Smelting and Refining Co.

The metal ingots were filed and those filings (≤0.149-mm diameter) that passed a 100-mesh sieve were used. Since the lanthanide metals tend to oxidize, about 100 mg was filed and then used before more filings were made. The Te lumps were crushed and that portion (≥0.074-mm diameter) which did not pass a 200-mesh sieve was used. Appropriate amounts of the metal and tellurium were weighed (to the nearest 0.2 mg) and mixed with a spatula by hand.

Initially, syntheses of the LTe_{2-x} compounds were made using a 1:2 L/Te ratio. Since x tends toward 0.3 for the heavier lanthanides, this resulted in a high LTe_3 impurity in the final product. Because of this, the L/Te ratio was changed to 1:1.7, and the majority of the syntheses were made using this latter ratio.[16-19] Most runs were made for about 60 min, although some were conducted for as short as 5 sec and as long as 348 min. A 60-min synthesis of $HoTe_{2-x}$ at 52 kbars and 1280° was of sufficient duration to give a complete reaction, but syntheses of $HoTe_{2-x}$ at temperatures below 1280° and all syntheses of LTe_{2-x} for L = Er, Tm, Lu, Y resulted in partial reaction, the major impurity being LTe_3. For each run, the synthesis was considered successful if the most intense lines characteristic of the desired compound were present in the X-ray spectrum of the final product.

The LTe_3 syntheses were made using a 1:3 L/Te ratio. Reaction times were varied from 5 to 60 min. In general the X-ray spectra contained lines other than those characteristic of $LuTe_3$. Because $LuTe_3$ decomposes so rapidly, it is difficult to know whether the excess lines resulted from incomplete reaction or decomposition. A successful synthesis was decided on the same basis as the LTe_{2-x} syntheses.

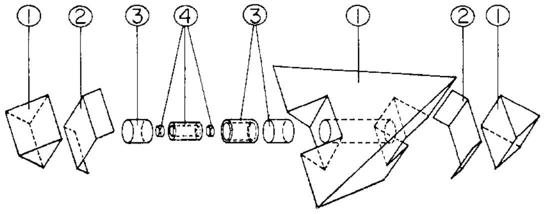

Figure 1.—Tetrahedral sample arrangement: (1) pyrophyllite; the triangular prisms are approximately 0.25 in. wide by 0.25 in. high; the tetrahedron has a 1-in. edge with a hole 0.125 in. in diameter and 0.25 in. long; (2) molybdenum; 0.005 × 0.25 × 0.50 in.; (3) graphite; the end plugs are 0.125 in. in diameter and 0.05 in. long; the tube is 0.125 in. in o.d., 0.086 in. in i.d., and 0.150 in. long; (4) boron nitride; the end plugs are 0.055 in. in diameter and 0.02 in. long; the tube is 0.085 in. in o.d., 0.055 in. in i.d., and 0.150 in. long.

All X-ray work utilized Ni-filtered Cu Kα radiation. The Debye–Scherrer powder camera was 143.2 mm in diameter, and the sample was rotated during exposure. Glass capillaries of 0.5-mm diameter were used to mount the samples. Splitting of the low-angle lines in the X-ray spectra was observed in some of the photographs. This splitting was due to the high absorption of the X-rays by the sample and created no problem. Intensities were visually estimated.

The compounds prepared include L = Ho, Er, Tm, Lu, Y for LTe_{2-x} and $LuTe_3$. Pressures to 100 kbars with temperatures to 1200° were used in attempts to prepare $ScTe_{2-x}$ and $ScTe_3$, but all efforts met with failure.

Results

The pressure–temperature synthesis diagrams for $ErTe_{2-x}$ and $LuTe_3$ are shown in Figures 2 and 3. The general features of the other synthesis diagrams are the same as that of $ErTe_{2-x}$. The main differences are outlined in Table II. As was expected, the minimum pressure requirement for synthesis has an inverse rela-

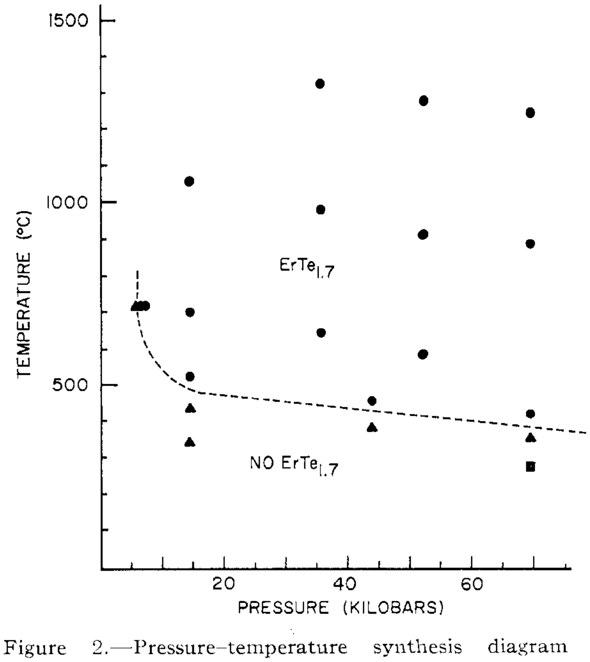

Figure 2.—Pressure–temperature synthesis diagram for $ErTe_{2-x}$ ($x \approx 0.3$): circles, $ErTe_{2-x}$ formation; triangles, reaction but no $ErTe_{2-x}$ formation; square, no reaction.

---

(12) N. L. Eatough, Ph.D. Dissertation, Brigham Young University, 1968.

(13) P. W. Bridgeman, *Proc. Amer. Acad. Arts Sci.*, **62**, 207 (1927).

(14) M. K. Zhokhovskii, V. N. Razuminkhin, E. V. Zolotykh, and L. L. Burova, *Izmer. Tekh.*, **11**, 26 (1959).

(15) R. N. Jeffery, J. D. Barnett, H. B. Van Fleet, and H. T. Hall, *J. Appl. Phys.*, **37**, 3172 (1966).

(16) Russian scientists[17-19] have reported syntheses of compounds of the type L_4Te_7 ($LTe_{1.75}$) for L = La, Pr, Nd. They stated that the L_4Te_7-type compounds have a tetragonal crystal structure similar to, but decidedly different from, the LTe_{2-x} type compounds. The reported space group is P4/mbm with a_0 for L_4Te_7 approximately double the a_0 for LTe_{2-x}. They were unable satisfactorily to index the X-ray powder patterns for L_4Te_7 without using a c_0/a_0 of approximately 1. They also noted that the 003, 111; 212, 114; and 223, 311 unresolved doublets of LTe_{2-x} are well resolved as 003, 221, 422, 224, 443, and 621 lines, respectively, in L_4Te_7.

The LTe_{2-x}-type compounds reported in this paper were indexed on the basis of the lanthanide ditelluride unit cell without difficulty. The X-ray powder data in Table IV show that the unresolved doublets in the front reflection region of the lighter LTe_{2-x} compounds are resolved for these heavier LTe_{2-x} compounds. This is not unexpected, of course, since the c_0/a_0 ratio of LTe_{2-x} increases inversely with lanthanide ionic radius. For these reasons the LTe_{2-x} compounds reported herein are believed to be analogous to the lanthanide ditellurides rather than to the L_4Te_7-type compounds. It is recognized, however, that the evidence is not conclusive and that a single-crystal structural analysis would be required in order completely to resolve the question.

(17) A. A. Eliseev, V. G. Kuznetsov, E. I. Yarembash, and L. I. Antonova, *J. Struct. Chem.* (USSR), **5**, 592 (1964); *Zh. Strukt. Khim.*, **5**, 640 (1964).

(18) K. A. Zinchenko, N. P. Luzhnaya, E. I. Yarembash, and A. A. Eliseev, *Inorg. Mater.* (USSR), **2**, 1506 (1966); *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **2**, 1747 (1966).

(19) A. A. Eliseev, V. G. Kuznetsov, E. I. Yarembash, E. S. Vigileva, L. I. Antonova, and K. A. Zinchenko, *Inorg. Mater.* (USSR), **2**, 1934 (1966); *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **2**, 2241 (1966).

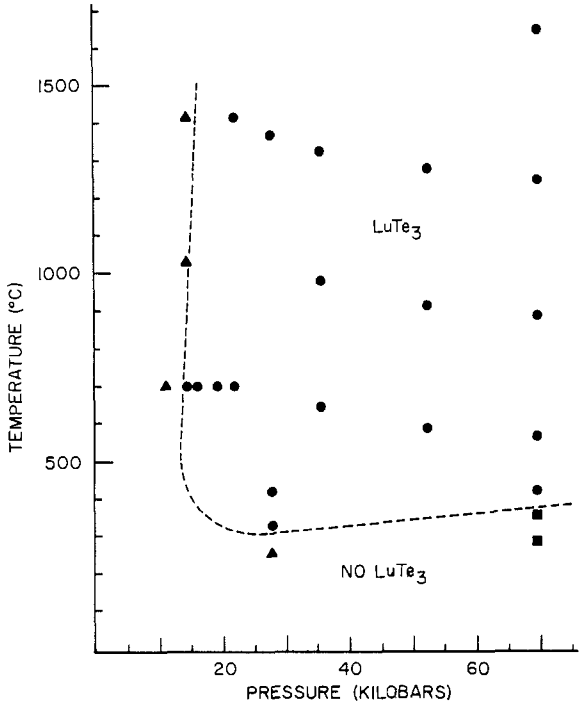

Figure 3.—Pressure–temperature synthesis diagram for $LuTe_3$: circles, $LuTe_3$ formation; triangles, reaction but no $LuTe_3$ formation; squares, no reaction.

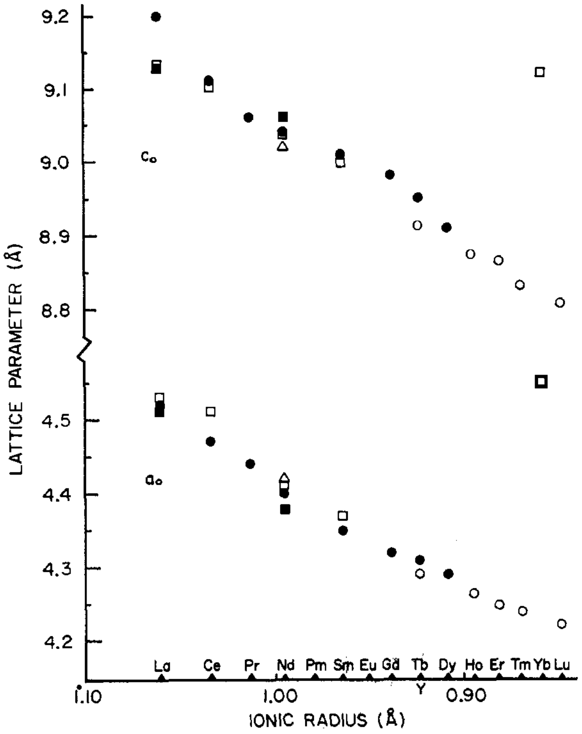

Figure 4.—Variation of lattice parameters with ionic radius for the LTe_{2-x} compounds: filled circles, M. P. Pardo, J. Flahaut, and L. Domange, *Bull. Soc. Chim. Fr.*, 3267 (1964); filled squares, R. Wang, H. Steinfink, and W. F. Bradley, *Inorg. Chem.*, **5**, 142 (1966); open squares, R. Wang, Ph.D. Dissertation, The University of Texas, 1967; open triangles, W. Lin, H. Steinfink, and E. J. Weiss, *Inorg. Chem.*, **4**, 877 (1965); open circles, present work.

tionship to the ionic radius. This indicates that the Te–Te distance in the basal plane is at least partially responsible for the nonformation at atmospheric pressure of the compounds prepared in this study.

TABLE II

MINIMUM PRESSURES AND TEMPERATURES FOR SYNTHESES OF LTe_{2-x} COMPOUNDS

L	L^{3+} ionic radius,[a] Å	Minimum pressure required for syntheses of LTe_{2-x} at 700°, kbars	Minimum temp required for synthesis of LTe_{2-x} at 69 kbars, °C
Y	0.923	3	425
Ho	0.894	3	360
Er	0.881	7	425
Tm	0.869	10	425
Lu	0.848	26	495

[a] D. H. Templeton and C. H. Dauben, *J. Amer. Chem. Soc.*, **76**, 5237 (1954).

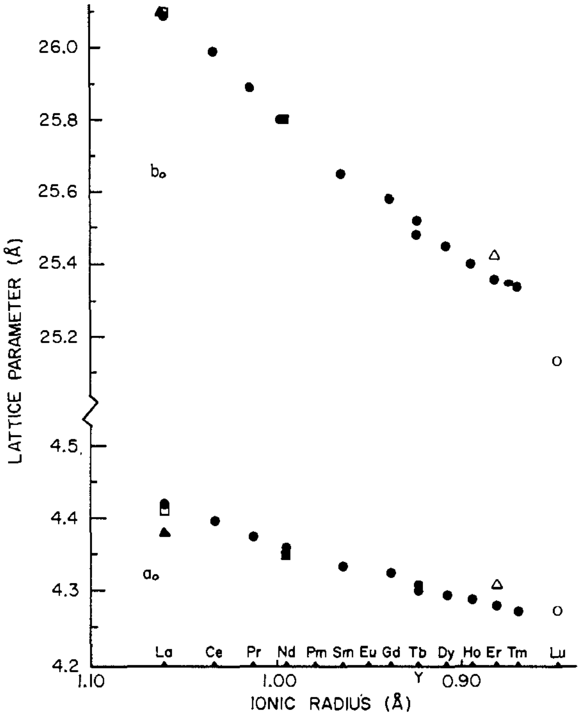

Figure 5.—Variation of lattice parameters with ionic radius for the LTe_3 compounds: filled circles, M. P. Pardo, O. Gorochov, J. Flahaut, and L. Domange *C. R. Acad. Sci.*, **260**, 1666 (1965); filled squares, B. K. Norling and H. Steinfink, *Inorg. Chem.*, **5**, 1488 (1966); filled triangles, W. Lin, H. Steinfink, and E. J. Weiss, *ibid.*, **4**, 877 (1965); open squares, T. H. Ramsey, H. Steinfink, and E. J. Weiss, *ibid.*, **4**, 1154 (1965); open triangles, D. J. Haase, H. Steinfink, and E. J. Weiss, *ibid.*, **4**, 541 (1965); open circles, present work.

TABLE III

LATTICE PARAMETERS

Compound	Unit cell	a_0, Å	b_0, Å	c_0, Å
YTe_{2-x}	Tetragonal	4.291 ± 0.003	4.291 ± 0.003	8.912 ± 0.006
$HoTe_{2-x}$	Tetragonal	4.264 ± 0.002	4.264 ± 0.002	8.872 ± 0.004
$ErTe_{2-x}$	Tetragonal	4.248 ± 0.002	4.248 ± 0.002	8.865 ± 0.005
$TmTe_{2-x}$	Tetragonal	4.240 ± 0.002	4.240 ± 0.002	8.831 ± 0.004
$LuTe_{2-x}$	Tetragonal	4.222 ± 0.001	4.222 ± 0.001	8.807 ± 0.003
$LuTe_3$	Orthorhombic	4.277 ± 0.001	25.137 ± 0.006	4.278 ± 0.001

It may be that the 4f electrons come into play in these syntheses. Gschneidner and Valletta[20] have recently discussed the possibility that 4f electrons participate in bonding in the lighter lanthanide elements and compounds. They suggest that 4f bonding is responsible

---

(20) K. A. Gschneidner and R. M. Valletta, *Acta Met.*, **16**, 477 (1968).

Table IV
X-Ray Powder Data for the New Compounds

YTe_{2-x}

hkl	d_{hkl} (Å) (observed)	d_{hkl} (Å) (calculated)	I_{obs}
0 1 2	3.067	3.091	25
1 1 0	3.006	3.035	15
0 0 3	2.944	2.971	50
1 1 1	2.852	2.873	100
1 1 2	2.494	2.508	100
0 1 3	2.434	2.443	90
0 2 0	2.145	2.146	45
1 1 4	1.791	1.796	30
2 1 2	1.762	1.763	10
0 2 3	1.734	1.739	40
0 1 5	1.642	1.646	30
1 2 3	1.611	1.612	40
2 2 0	1.516	1.517	30
0 1 6	1.400	1.404	35
2 2 3	1.350	1.351	30
1 1 6	1.334	1.334	15
2 1 5	1.305	1.306	35
1 3 2	1.294	1.298	15
1 2 6	1.174	1.175	05
0 3 5	1.113	1.116	30
3 2 3	1.105	1.105	05
3 1 5	1.078	1.080	15
0 4 0	1.069	1.073	10
3 0 6	1.030	1.030	05
2 3 5	0.989	0.990	10
2 1 8	0.964	0.964	35
2 4 0	0.959	0.960	15
1 1 9	0.941	0.941	10
2 3 6	0.930	0.929	15
2 4 3	0.915	0.913	25
4 1 5	0.898	0.899	10
2 2 8		0.898	
4 1 6	0.855	0.852	25

$HoTe_{2-x}$

hkl	d_{hkl} (Å) (observed)	d_{hkl} (Å) (calculated)	I_{obs}
0 1 2	3.044	3.074	35
1 1 0	2.996	3.015	45
0 0 3	2.938	2.957	50
1 1 1	2.833	2.855	100
1 1 2	2.480	2.494	95
0 1 3	2.415	2.430	90
0 2 0	2.123	2.132	70
1 1 4	1.779	1.787	20
2 1 2	1.745	1.752	25
0 2 3	1.722	1.729	35
0 1 5	1.633	1.638	30
1 2 3	1.598	1.603	55
2 2 0	1.503	1.507	25
0 1 6	1.394	1.397	25
2 2 3	1.344	1.343	20
1 1 6	1.327	1.328	20
2 1 5	1.297	1.299	30
1 3 2	1.289	1.290	15
1 2 6	1.168	1.169	35
0 3 5	1.109	1.109	20
3 2 3	1.098	1.098	20
3 1 5	1.076	1.074	10
0 4 0	1.067	1.066	10
3 0 6	1.025	1.025	15
2 3 5	0.984	0.984	30
2 1 8	0.959	0.959	20
2 4 0	0.956	0.953	15
1 1 9	0.937	0.937	20
2 3 6	0.924	0.924	20
2 4 3	0.908	0.907	10
4 1 5	0.894	0.893	25
2 2 8		0.893	
4 1 6	0.849	0.847	25
5 1 2	0.820	0.822	20
2 3 8	0.808	0.809	15
1 3 9	0.797	0.796	20

$ErTe_{2-x}$

hkl	d_{hkl} (Å) (observed)	d_{hkl} (Å) (calculated)	I_{obs}
0 1 2	3.052	3.067	40
1 1 0	2.992	3.004	35
0 0 3	2.946	2.955	25
1 1 1	2.840	2.845	100
1 1 2	2.479	2.487	50
0 1 3	2.422	2.426	50
0 2 0	2.124	2.124	80
1 1 4	1.779	1.783	05
2 1 2	1.747	1.746	35
0 2 3	1.721	1.725	35
0 1 5	1.635	1.636	30
1 2 3	1.596	1.598	50
2 2 0	1.504	1.502	20
0 1 6	1.395	1.396	30
2 2 3	1.339	1.339	10
1 1 6	1.330	1.326	30
2 1 5	1.295	1.296	30
1 3 2	1.285	1.286	10
1 2 6	1.166	1.166	10
0 3 5	1.108	1.106	25
3 2 3	1.094	1.094	15
3 1 5	1.075	1.071	15
0 4 0	1.063	1.062	05
3 0 6	1.023	1.022	05
2 3 5	0.982	0.981	10
2 1 8	0.957	0.957	20
2 4 0	0.949	0.950	10
1 1 9	0.936	0.936	20
2 3 6	0.921	0.921	15
2 4 3	0.905	0.904	20
4 1 5	0.892	0.891	10
2 2 8		0.892	
4 1 6	0.846	0.845	20
5 1 2	0.818	0.819	15
2 3 8	0.804	0.807	20
1 3 9	0.795	0.794	20

$TmTe_{2-x}$

hkl	d_{hkl} (Å) (observed)	d_{hkl} (Å) (calculated)	I_{obs}
0 1 2	3.048	3.058	50
1 1 0	2.988	2.998	30
0 0 3	2.930	2.944	60
1 1 1	2.829	2.839	100
1 1 2	2.470	2.480	90
0 1 3	2.408	2.418	100
0 2 0	2.116	2.120	50
1 1 4	1.776	1.778	10
2 1 2	1.745	1.742	20
0 2 3	1.717	1.720	30
0 1 5	1.627	1.630	50
1 2 3	1.592	1.594	45
2 2 0	1.499	1.499	10
0 1 6	1.390	1.391	40
2 2 3	1.339	1.336	15
1 1 6	1.323	1.321	30
2 1 5	1.292	1.292	35
1 3 2	1.281	1.283	15
1 2 6	1.163	1.163	35
0 3 5	1.104	1.104	20
3 2 3	1.093	1.092	15
3 1 5	1.068	1.068	10
0 4 0	1.060	1.060	05
3 0 6	1.019	1.019	15
2 3 5	0.979	0.979	30
2 1 8	0.954	0.954	20
2 4 0	0.947	0.948	20
1 1 9	0.933	0.933	20
2 3 6	0.920	0.919	15
2 4 3	0.902	0.902	20
4 1 5	0.889	0.889	30
2 2 8		0.889	
4 1 6	0.844	0.843	20
5 1 2	0.818	0.817	15
2 3 8	0.802	0.805	20
1 3 9	0.793	0.792	25

$LuTe_{2-x}$

hkl	d_{hkl} (Å) (observed)	d_{hkl} (Å) (calculated)	I_{obs}
0 1 2	3.026	3.048	20
1 1 0	2.975	2.986	30
0 0 3	2.918	2.936	50
1 1 1	2.818	2.828	70
1 1 2	2.467	2.471	80
0 1 3	2.403	2.410	100
0 2 0	2.108	2.111	45
1 1 4	1.764	1.772	15
2 1 2	1.733	1.735	15
0 2 3	1.712	1.714	30
0 1 5	1.625	1.626	40
1 2 3	1.587	1.588	35
2 2 0	1.492	1.493	20
0 1 6	1.384	1.387	30
2 2 3	1.333	1.331	25
1 1 6	1.317	1.317	25
2 1 5	1.287	1.288	30
1 3 2	1.276	1.278	20
1 2 6	1.159	1.159	30
0 3 5	1.100	1.100	25
3 2 3	1.089	1.088	15
3 1 5	1.064	1.064	15
0 4 0	1.055	1.056	15
3 0 6	1.016	1.016	25
2 3 5	0.976	0.975	35
2 1 8	0.951	0.951	20
2 4 0	0.942	0.944	15
1 1 9	0.930	0.930	30
2 3 6	0.916	0.915	20
2 4 3	0.900	0.899	05
4 1 5	0.886	0.885	35
2 2 8		0.886	
4 1 6	0.840	0.840	20
5 1 2	0.814	0.814	25
2 3 8	0.801	0.802	20
1 3 9	0.790	0.789	30

$LuTe_3$

hkl	d_{hkl} (Å) (observed)	d_{hkl} (Å) (calculated)	I_{obs}
0 8 0	3.124	3.142	80
1 1 1	2.985	3.003	20
1 3 1	2.831	2.845	100
1 5 1	2.581	2.592	40
1 7 1	2.307	2.313	25
2 0 0	2.132	2.138	60
0 0 2		2.139	
0 12 0	2.089	2.095	15
1 11 1	1.819	1.823	25
0 14 0	1.791	1.796	15
0 8 2	1.766	1.768	30
2 8 0		1.768	
2 8 1	1.625	1.634	15
1 13 1		1.629	
2 0 2	1.510	1.512	30
0 12 2	1.493	1.497	10
2 12 0		1.496	
0 14 2	1.375	1.375	10
2 14 0		1.375	
2 8 2	1.361	1.363	25
1 3 3	1.334	1.335	25
3 3 1		1.335	
1 17 1	1.328	1.328	25
1 5 3	1.304	1.306	20
3 5 1		1.306	
1 15 2	1.265	1.261	15
1 7 3		1.266	
3 7 1		1.266	
1 11 3	1.163	1.164	15
3 11 1		1.164	
2 14 2	1.156	1.157	10
0 22 0	1.142	1.143	10
2 6 3		1.141	
3 15 0	1.083	1.086	15
0 20 2		1.084	
2 20 0		1.084	
0 0 4	1.069	1.069	15
4 0 0		1.069	
0 8 4	1.013	1.012	10
4 8 0		1.012	
3 1 3	1.008	1.007	20
0 22 2		1.008	
2 22 0		1.008	
1 17 3	0.999	0.998	20
3 17 1		0.998	
1 25 1	0.954	0.954	50
2 8 4	0.915	0.915	20
4 8 2		0.915	
1 3 5	0.834	0.835	30
5 3 1		0.835	
3 17 3		0.833	
1 29 1		0.833	
1 5 5	0.828	0.828	15
5 5 1		0.827	
1 25 3	0.807	0.807	60
3 25 1		0.807	

for subtle changes in atomic arrangements that occur on progressing through the series of lanthanide metals. They also suggest that 4f influence is present in some lanthanide compounds and point out the important role pressure could have in influencing 4f bonding. In this connection, they propose a test for determining whether or not 4f electrons are contributing to the bonding in a series of lanthanide compounds wherein pressure determines which of two polymorphs will form. If (at constant temperature) increasing pressure is required with increasing atomic number to form one of the polymorphs, then 4f electrons are contributing to the bonding. If increasing pressure is required with decreasing atomic number, then 4f bonding is not involved.

The data in Table II show that the pressure requirement for synthesis varies directly with atomic number. In this case, the boundary exists between the compound and the elements, but this should have the same significance with respect to 4f bonding as a phase boundary between two polymorphs. Since increasing pressure is required to form LTe$_{2-x}$ from the elements with increasing atomic number, it is likely that pressure is causing the 4f electrons of these heavier lanthanides to participate and, in effect, behave more like the higher lanthanides'.

Each of the new LTe$_{2-x}$ compounds is silvery in appearance whereas LuTe$_3$ is gold colored. Both types of compounds are unstable with respect to the elements. X-Ray spectra of HoTe$_{2-x}$ show no decomposition after 15 days but complete decomposition after 80 days. When heated under vacuum, HoTe$_{2-x}$ remained stable at 260° but decomposed at 340°. The shiny gold-colored LuTe$_3$ was observed to lose its gold color after about 5–8 min. Complete decomposition occurred within 2 or 3 days. These compounds were stored in slip-capped plastic vials in the open atmosphere.

Scientists at the Battelle Memorial Institute, Columbus, Ohio, have been investigating the semiconducting properties of lanthanide metals and compounds.[21–24] Some of the LTe$_{2-x}$ compounds (as well as other lanthanide–tellurium compounds) are included in their study. Although no study of the semiconducting properties of these new LTe$_{2-x}$ compounds has been made, it is expected that their properties will be similar to those of the previously known analogs.

X-Ray studies have shown these new compounds to be isostructural with their lower molecular weight analogs. The points in Figures 4 and 5 show that the variation of lattice parameters *vs.* ionic radius follows the pattern set by the previously known analogous compounds. Lattice parameters are shown in Table III. X-Ray powder data are given in Table IV.

Acknowledgments.—We wish to thank the National Science Foundation and the Army Research Office (Durham) for funding this work. J. F. C. also wishes to thank the National Aeronautics and Space Administration for their support of his graduate studies. Assistance rendered by N. L. Eatough, A. W. Webb, L. Merrill, K. Miller, M. D. Horton, and J. H. Hoen is gratefully acknowledged.

(21) J. F. Miller, J. W. Moody, L. K. Matson, and R. C. Himes, Report AD 246 851, Clearinghouse for Federal Scientific and Technical Information, Springfield, Va., 1960.

(22) J. F. Miller, L. K. Matson, J. S. McNulty, and R. C. Himes, Report AD 262 215, Clearinghouse for Federal Scientific and Technical Information, Springfield, Va., 1961.

(23) J. F. Miller, F. J. Reid, L. K. Matson, and R. C. Himes, Report AD 428 091, Clearinghouse for Federal Scientific and Technical Information, Springfield, Va., 1963.

(24) J. F. Miller, F. J. Reid, L. K. Matson, J. W. Moody, R. D. Baxter, and R. C. Himes, Report AD 607 082, Clearinghouse for Federal Scientific and Technical Information, Springfield, Va., 1964.

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
UNIVERSITY OF ARKANSAS, FAYETTEVILLE, ARKANSAS 72701

The Crystal Structure of Dipyridinium(II) Oxytetrachloroselenate(IV), C$_{10}$H$_8$N$_2$H$_2{}^{2+}$SeOCl$_4{}^{2-}$. A Highly Coordinated Selenium Compound[1]

BY BI-CHENG WANG AND A. W. CORDES[2]

Received October 16, 1969

Crystals of dipyridinium(II) oxytetrachloroselenate(IV), C$_{10}$H$_8$N$_2$H$_2{}^{2+}$SeOCl$_4{}^{2-}$, are monoclinic with $a = 26.62$ (1) Å, $b = 14.40$ (2) Å, $c = 15.497$ (9) Å, $\beta = 104.39$ (5)°, $d_{\text{measd}} = 1.81$ (1) g cm^{-3}, and $d_{\text{calcd}} = 1.823$ (4) g cm^{-3}. The space group is C2/c, with two formula units per asymmetric unit. Multiple-film Weissenberg methods yielded 4292 reflections (2731 observed). Full-matrix least-squares refinement included anisotropic temperature factors for Se and Cl and gave an R of 0.098. The structure consists of square-pyramidal SeOCl$_4{}^{2-}$ units hydrogen bonded to the organic cations. The Se–O distances are 1.61 (1) and 1.65 (1) Å, and the Se–Cl distances are 2.525, 2.431, 2.246, 2.244, 2.445, 2.502, 2.980, and 2.990 Å (all ±0.004 Å).

Introduction

Structures of five-bonded selenium provide a bonding situation intermediate between compounds of four or fewer bonds, which are readily interpreted in terms of ordinary molecular geometry treatments,[3] and the structurally anomalous hexahaloselenate dianions.[4] The recent structure of R$^+$SeOCl$_3{}^-$ (R = 8-hydroxyquinolinium[5]) presented a selenium oxychloride ion

(1) Work supported by the Selenium–Tellurium Development Association and the National Science Foundation.

(2) Alfred P. Sloan Research Fellow.

(3) S. C. Abrahams, *Quart. Rev. Chem. Soc.*, **10**, 407 (1956).

(4) H. A. Bent, *J. Chem. Educ.*, **42**, 348 (1965).

(5) A. W. Cordes, *Inorg. Chem.*, **6**, 1204 (1967).