Table IX
Overlap Populations and Energies for o-$B_{10}H_{10}C_2H_2$ and Methyl Derivatives

Bond	o-$B_{10}H_{10}C_2H_2$	1-Methyl derivative o-$B_{10}H_{10}C_2H(CH_3)$	1,2-Dimethyl derivative o-$B_{10}H_{10}C_2(CH_3)_2$
C(1)–C(2)	0.645	0.612	0.575
C(1)–B(3)	0.419	0.405	0.435
C(1)–B(4)	0.559	0.534	0.523
C(2)–B(3)	0.419	0.449	0.438
C(2)–B(7)	0.559	0.554	0.520
B(3)–B(4)	0.299	0.338	0.299
B(3)–B(7)	0.299	0.263	0.292
B(3)–B(8)	0.400	0.366	0.328
B(4)–B(5)	0.338	0.375	0.372
B(4)–B(8)	0.482	0.450	0.475
B(4)–B(9)	0.410	0.371	0.362
B(7)–B(8)	0.482	0.509	0.480
B(7)–B(12)	0.410	0.404	0.362
B(8)–B(9)	0.435	0.454	0.444
B(8)–B(12)	0.435	0.427	0.446
B(9)–B(12)	0.383	0.369	0.346
C(1)–methylC(1)		0.912	0.916
C(2)–methylC(2)			0.918
$\Sigma\epsilon_i$	−114.502	−127.743	−140.984
KE^a	326.607	365.396	404.182
HFMO^b	−0.382	−0.381	−0.378

^{a} Kinetic energy in atomic units. ^{b} Highest filled molecular orbital in atomic units.

electrophilic attack on o-$B_{10}C_2H_{12}$ and its C-methyl derivatives.

Overlap populations (Table IX) are reasonable except for the values for C–CH_3 bonds of 0.91 to 0.92, which are to be compared with 0.71 for alkanes.[12] Of course, bond distances do not support partial double-bond character in these C–CH_3 bonds, so we believe that the problem is associated with the K value[8] for $2p\pi$–$2p\pi$ overlap. Perhaps this same problem produces the lowered C–C overlap as carborane is methylated. Even so, the B–C overlap populations seem to be unaffected by this symptom, which may be cured when self-consistent field results are available on more appropriate model compounds. Values are also given in Table IX for $\Sigma\epsilon_i$, for the kinetic energy, and for the eigenvalue of the highest filled molecular orbital as an estimate of the vertical ionization potential.

Experimental and theoretical studies of these types are being carried out for other carboranes.

(12) M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.* **88**, 2367 (1966).

Contribution from the Department of Chemical Engineering,
University of Texas, Austin, Texas

The Crystal Structure of Neodymium Tritelluride[1]

By B. K. Norling and H. Steinfink

The crystal structure of $NdTe_3$ has been determined from h0l and 0kl electron density projections and by a least-square refinement of these structure factors. All other reported lanthanide tritellurides are isostructural with it. The crystal is orthorhombic, pseudo-tetragonal, with $a_0 = b_0 = 4.35$ A and $c_0 = 25.80$ A, space group Bmmb, with four molecules per unit cell. All four crystallographically independent atoms are in position 4(c), 0, $1/4$, z, of Bmmb. The z parameters are 0.8306 (Nd), 0.0705 (Te), 0.4294 (Te), and 0.7047 (Te). The structure is closely related to that of $LaTe_3$. The lanthanide atoms in both structures have identical coordination. The $NdTe_3$ structure may be viewed as a stacking of $NdTe_2$ unit cells with additional Te layers between cells and with alternate cells shifted by $a_0/2$.

Introduction

The rare earth lanthanides form a series of isostructural compounds of composition $LnTe_3$. Pardo, *et al.*,[2] report that Chirazi first prepared $CeTe_3$ by allowing $CeCl_3$ to react with H_2 and Te. The product consisted of $CeTe_2$ and golden, easily cleavable flakes. Carter[3] showed that these crystals had 1:3 stoichiometry, and he prepared also the tritellurides of La and Pr. He noted that their X-ray powder patterns were identical except for small differences in their cell parameters and from a single-crystal pattern of a disordered $LaTe_3$ crystal deduced that it was tetragonal, $a = 4.38$ A, $c = 26.10$ A, with 3 formula weights in the cell. Ramsey, *et al.*,[4] prepared $LaTe_3$ from the elements and obtained very good, ordered, single-crystal X-ray patterns. The diffraction photographs could be indexed on a tetragonal cell, with four formula weights in the unit cell, but nonspace-group extinctions were observed: *i.e.*, if $h + k = 2n + 1$, then reflections with all values of l were present; if h and k were both even, then $l = 2n$ were present; and if h and k were both odd, $l = 2n$

(1) Research sponsored by Air Force Office of Scientific Research, Office of Aerospace Research, U. S. Air Force, Grant No. 806-65, and by National Institute of Health training grant in crystallography, 5T1DE 120-03.

(2) M. Pardo, O. Gorochev, J. Flahaut, and L. Domange, *Compt. Rend.*, **260**, 1666 (1965).

(3) F. N. Carter, "Metallurgy of Semiconductor Materials," Interscience Publishers, Inc., New York, N. Y., p 260.

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

+ 1 were present only. The tetragonal appearance and nonspace-group extinctions can be explained on the basis of twinning of an orthorhombic pseudo-tetragonal, B-centered unit cell by reflection across (110). Haase[5] and Lin[6] prepared ErTe₃ and NdTe₃, respectively, and in both instances the diffraction photographs showed orthorhombic symmetry with $a = b$ and extinctions which were consistent with space group Bmmb. The most extensive list of lanthanide tritelluride lattice parameters was published by Pardo, *et al.*[2] The compounds were all isostructural although their crystal structure was unknown. We prepared single crystals of untwinned NdTe₃ and investigated its crystal structure.

Experimental Section

The specimens were prepared by direct reaction of the elements in evacuated Vycor tubes. The methods of preparation have been previously described.[6] The best crystal which was finally chosen for analysis came from a reacted stoichiometric 1:3 mixture. It was a thin, distorted trigonal prism measuring approximately $40 \times 37 \times 5 \mu$. The maximum path length of about 55 μ results in a maximum linear absorption $\mu_1 L = 11.8$ for Cu Kα and 1.54 for Mo Kα radiation. The crystal was mounted perpendicular to the cleavage plane (001) so that the c axis was parallel to the spindle axis of the X-ray camera. The $h0l$ and $0kl$ reflections were recorded on a precession camera using Mo Kα radiation, and the intensities were read by visual comparison with a standard scale. The intensities were corrected for Lorentz and polarization factors, but no absorption corrections were applied. The $hk0$ and $hk3$ reflections were recorded using a Weissenberg camera, but these data were used solely to confirm the space group. The systematic extinctions hkl where $h + l = 2n + 1$ and $hk0$ where $k = 2n + 1$ were consistent with space groups Bmmb, Bm2₁b, or B2mb. The nonstandard orientation was chosen to facilitate comparison of the structure of NdTe₃ to the related structure of LaTe₂. The unit cell dimensions are $a = b = 4.35$ A, $c = 25.80$ A; the measured density of 7.0 g/cm³ places 4 formula weights in the unit cell. The structure was solved from an examination of the $h0l$ and $0kl$ Patterson projections. With the parameters derived from these projections, structure factors were calculated for the centrosymmetric model, and the essential correctness was confirmed by the agreement between observed and calculated amplitudes and by the appearance of the electron density maps. Refinement was carried out by a least-square procedure using a weighting factor of $(F_o)^{-2}$ for 120 reflections. All atoms lie in the special position 4(c), 0, ¼, z, at the intersection of two mirror planes in Bmmb. The final value of the discrepancy coefficient, $R = ||\Sigma F_o| - |F_c||/\Sigma|F_o|$, is 0.125, and Table I shows the atomic coordinates, anisotropic temperature factors, and their standard deviations, for this structure; Table II lists the observed and calculated structure factors.

Discussion of Structure

The unit cell contains 12 planar layers each consisting of one kind of atom; however, the separation between the neodymium and tellurium layers is 0.9 A so that they can be considered as one puckered layer. The structure can thus be described as consisting of four puckered layers and four densely packed tellurium layers with the sequence of layers along the c axis being Te, Nd–Te, Nd–Te, Te, Te, Nd–Te, Nd–Te, Te.

The NdTe₃ structure is closely related to the LaTe₂

(5) D. J. Haase, H. Steinfink, and E. J. Weiss, *Inorg. Chem.*, **4**, 541 (1965).
(6) W. Lin, H. Steinfink, and E. J. Weiss, *ibid.*, **4**, 877 (1965).

TABLE I

FINAL COORDINATES,[a] ANISOTROPIC TEMPERATURE FACTORS, AND STANDARD DEVIATIONS[b]

Atom	z	B_{11}	B_{22}	B_{33}
Te(1)	0.0705 (3)	0.016 (6)	0.020 (5)	0.0005 (1)
Te(2)	0.4294 (3)	0.015 (5)	0.023 (5)	0.0004 (1)
Te(3)	0.7047 (3)	0.013 (5)	0.026 (5)	0.0004 (1)
Nd	0.8306 (3)	0.010 (3)	0.013 (4)	0.0002 (1)

[a] $x = 0$ and $y = 0.2500$ for each atom. [b] Numbers in parentheses are standard deviations in the least significant figure.

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR NdTe₃

H	K	L	F_o	F_c	H	K	L	F_o	F_c
0	0	2	68	-59	1	0	1	65	52
0	0	4	155	-98	1	0	3	87	-76
0	0	6	118	-86	1	0	5	88	-54
0	0	8	476	-555	1	0	7	239	230
0	0	12	192	201	1	0	9	262	-289
0	0	14	260	248	1	0	11	114	117
0	0	16	120	115	1	0	13	130	117
0	0	18	90	64	1	0	15	229	-269
0	0	20	185	-196	1	0	17	204	222
0	0	22	295	-301	1	0	19	54	-54
0	0	24	180	124	1	0	21	99	-85
0	0	28	143	134	1	0	23	113	124
0	0	30	221	226	1	0	25	81	-52
0	0	32	157	-145	2	0	0	418	629
0	1	2	109	63	2	0	2	58	-34
0	1	4	187	-145	2	0	4	101	-73
0	1	6	232	271	2	0	6	79	-59
0	1	10	191	-216	2	0	8	580	-459
0	1	14	196	212	2	0	12	172	168
0	1	16	216	-262	2	0	14	201	205
0	1	18	129	151	2	0	16	105	96
0	1	20	45	50	2	0	18	78	58
0	1	22	121	-182	2	0	20	157	-171
0	1	24	92	85	2	0	22	250	-264
0	2	0	459	-613	2	0	24	130	112
0	2	2	54	30	2	0	28	134	118
0	2	4	96	74	2	0	30	167	204
0	2	6	73	57	2	0	32	138	-130
0	2	8	516	488	3	0	1	41	36
0	2	12	159	-189	3	0	5	77	-56
0	2	14	208	-197	3	0	7	177	180
0	2	16	103	-94	3	0	9	191	-193
0	2	18	54	-59	3	0	11	94	97
0	2	20	146	170	3	0	13	103	87
0	2	22	230	255	3	0	15	188	-205
0	2	24	111	-108	3	0	17	189	172
0	2	28	118	-116	3	0	19	49	-40
0	2	30	193	-196	3	0	21	66	-57
0	2	32	121	-127	3	0	23	97	101
0	3	2	56	-60	3	0	25	76	-42
0	3	4	38	32	4	0	0	306	592
0	3	6	102	88	4	0	4	47	-47
0	3	8	164	-181	4	0	8	284	-282
0	3	10	138	149	4	0	12	115	114
0	3	14	143	-151	4	0	14	175	130
0	3	16	175	181	4	0	16	79	62
0	3	18	111	-108	4	0	18	50	45
0	3	22	101	98	4	0	20	113	-113
0	4	0	60	-65	4	0	22	205	-187
0	4	4	518	551	4	0	24	95	87
0	4	8	289	-253	4	0	26	36	-37
0	4	12	113	115	5	0	7	105	102
0	4	14	155	111	5	0	9	123	-125
0	4	16	54	55	5	0	11	50	58
0	4	20	117	-117	5	0	13	48	56
0	4	22	178	-164	5	0	15	147	-158
0	4	24	79	76	5	0	17	110	113
0	5	6	102	104	5	0	21	50	-48
0	5	10	101	-88					
0	5	14	92	69					
0	5	16	111	-116					
0	5	18	66	59					

structure discussed by Wang, *et al.*,[7] and the two structures are compared in Figure 1. The NdTe₃ structure may be visualized as a stacking of slightly distorted NdTe₂ unit cells having an additional tellurium layer between adjacent cells, with alternate cells shifted by $a_0/2$. The Nd coordination in NdTe₃ is identical, except for a small difference in bond length, with that in NdTe₂. The interatomic distances in NdTe₃ and LaTe₂ are compared in Table III.

The phase NdTe₂ displays a solid-solution region, with the other terminal composition near NdTe₁.₇, and the tellurium deficiency results from the removal of Te from the pure tellurium layers, *i.e.*, those equivalent to the Te(1) and Te(2) layers in the NdTe₃ structure.[7] Since the conductivity of NdTe₂ is the highest of the solid-solution series, it was concluded that the pure tellurium layers account for most of the metallic behavior of the compounds. The apparent radius of tellurium in the pure tellurium layers of NdTe₃ is 1.538 A, which is near the accepted metallic radius of 1.60 A for 12-fold coordinated tellurium. From Figure 1 it is clear that NdTe₃ contains twice as many tellurium

(7) R. Wang, H. Steinfink, and W. F. Bradley, *ibid.*, **5**, 142 (1966).
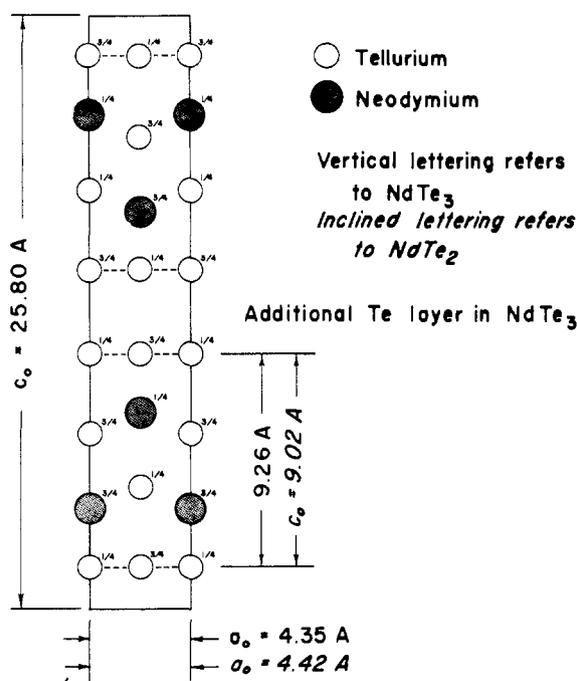
Figure 1.—A comparison of the structures of NdTe₃ and NdTe₂ in the *h0l* projection.

Figure 2.—Te(1) or Te(2) coordination polyhedron; distances are shown in A.

TABLE III

A Comparison of Interatomic Distances
in NdTe₃ and LaTe₂

Interatomic distances, A	NdTe₃		LaTe₂[7]
Te(1)–Te(1)	4.240	± 0.010	ne[a]
Te(2)–Te(2)	4.350	± 0.010	ne
Te(3)–Te(3)	3.862	± 0.010	4.009
Te(1)–Te(2)	3.076	± 0.010	3.187
	4.240	± 0.010	ne
Te(1)–Te(3)	4.089	± 0.010	4.036
Te(2)–Te(3)	4.089	± 0.010	4.033
Nd–Nd	4.350	± 0.009	4.507
Nd–Te(1)	3.353	± 0.010	3.381
Nd–Te(2)	3.353	± 0.010	3.381
Nd–Te(3)	3.208	± 0.009	3.293
	3.246	± 0.009	3.260

[a] ne: no equivalent interatomic distance reported for LaTe₂.

Figure 3.—Te(3) coordination polyhedron; interatomic distances are shown in A.

atoms in the pure tellurium layers as does NdTe₂. It might be concluded, as a first approximation, that lanthanide tritellurides should exhibit twice the metallic character of lanthanide ditellurides. Although this assumption depends on a structural analogy which ignores detailed differences in bonding within the pure tellurium layers, it is supported by experiments. Ramsey[8] measured the resistivities of similarly processed samples of LaTe₂ and LaTe₃. Over the range −50 to +270°, the resistivity of LaTe₃ ranged from about 0.3 to 0.7 of that of LaTe₂.

There are essentially only two types of tellurium and one type of neodymium present. Te(1) and Te(2) have identical coordination polyhedra. Each Te(1 or 2), Figure 2, is surrounded by six nearest neighbors, at 3.076 A (4 Te) and at 3.353 A (2 Nd), forming an ir-

regular prism. The other tellurium atoms in Figure 2 cannot be considered as bonded to the central Te atom. The remaining third of the tellurium atoms, Te(3), Figure 3, are each surrounded by five nearest neighbors at 3.208 A (4 Nd) and 3.246 A (1 Nd), forming a nearly regular pyramid; the other atoms shown are considered as nonbonded because of the large interatomic distances. Each neodymium, Figure 4, is surrounded by nine near neighbors at 3.208 A (4 Te), 3.256 A (1 Te), and 3.353 A (4 Te). The nearest Nd–Nd approach is 4.35 A, and these distances are parallel to the a_0 and b_0 axes.

The bond numbers may be calculated from Pauling's equation for intermetallic compounds

$$D(n) = D(1) - 0.600 \log n$$

where $D(n)$ is the observed bond distance for bond number n, n less than 1.0 for intermetallic compounds,

(8) T. H. Ramsey, H. Steinfink, and E. J. Weiss, *J. Appl. Phys.*, **36**, 548 (1965).
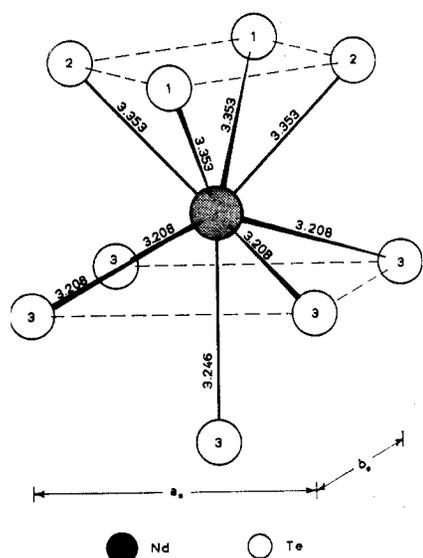
Figure 4.—Neodymium coordination polyhedron; interatomic distances are in A.

two atoms involved. Pauling's values of $R(1)$ for neodymium and tellurium are 1.637 and 1.37 A, respectively.[9] The bond numbers and corresponding valences are summarized in Table IV. It should be noted that the calculated valence for the "metallic-covalent" tellurium atoms is considerably less than the formal valence for Te^{2-}.

TABLE IV

BOND DISTANCES, BOND NUMBERS, AND VALENCES

Central atom	Coordinating atom	$D(n)$	n	Σn (valence)
Nd	4 Te(3)	3.208	0.462	
	1 Te(3)	3.246	0.399	
	4 Te(1 and 2)	3.353	0.265	3.307
Te(1 and 2)	4 Te(1 or 2)	3.076	0.275	
	2 Nd	3.353	0.265	
	2 Te(3)	4.089	0.006	
	4 Te(1 and 2)	4.240	0.003	1.654
Te(3)	4 Nd	3.208	0.462	
	1 Nd	3.246	0.399	
	4 Te(3)	3.862	0.014	
	4 Te(1 and 2)	4.089	0.006	2.323

and $D(1)$ is the empirically determined single-bond distance, the sum of the single-bond radii, $R(1)$, of the

(9) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 403.

Crystallographic Evidence for Nonequivalent Ligand Fields in Tantalum Subchloride

BY R. D. BURBANK

Robin and Kuebler have interpreted the electronic spectra of the polynuclear subhalides of tantalum of general formula $Ta_6X_{14} \cdot 7H_2O$ in terms of a distorted polynucleus in which two Ta at the apices of an elongated tetragonal bipyramid approach a valence of $+3$ while four Ta in the equator of the bipyramid approach a valence of $+2$. An X-ray structure analysis of $Ta_6Cl_{14} \cdot 7H_2O$ crystals is consistent with this interpretation. The crystals are trigonal, most probable space group $P\bar{3}1m$, with $a = 9.36$ A, $c = 8.80$ A, and one unit of composition per unit cell. The structure, which is both disordered and subject to faulting, contains an elongated bipyramidal polynucleus. One type of ligand field is provided for two Ta along the axis of elongation, and a second type of ligand field is provided for the remaining four Ta. The polynucleus combines with twelve Cl to form a $Ta_6Cl_{12}{}^{2+}$ complex ion. The complex ion combines with two Cl ions and four H_2O to form a $Ta_6Cl_{14} \cdot 4H_2O$ unit. The $Ta_6Cl_{14} \cdot 4H_2O$ units occur in layers which alternate with layers of three H_2O to yield the over-all composition of $Ta_6Cl_{14} \cdot 7H_2O$. The observed structural disorder appears to be built into the crystal during the course of crystal growth in order to permit a maximum of hydrogen bonding throughout the crystal.

Introduction

In a recent study of color and nonintegral valence Robin and Kuebler[1] have concluded that there is a fundamental difference between the niobium and tantalum subhalides. The compounds have the general formula $M_6X_{14} \cdot 7H_2O$ where M = Nb or Ta and X = Cl, Br, or I. The central building block in these compounds is the polynuclear complex ion $M_6X_{12}{}^{2+}$. Vaughan, Sturdivant, and Pauling[2] determined the structures of the ions $Nb_6Cl_{12}{}^{2+}$, $Ta_6Br_{12}{}^{2+}$, and $Ta_6Cl_{12}{}^{2+}$ in

(1) M. B. Robin and N. A. Kuebler, *Inorg. Chem.*, **4**, 978 (1965).
(2) P. A. Vaughan, J. H. Sturdivant, and L. Pauling, *J. Am. Chem. Soc.*, **72**, 5477 (1950).

ethanol solutions using X-ray diffraction. Within the limitations imposed by the experimental technique, the scattering was satisfactorily explained by a model of cubic symmetry. The metal atoms are situated at the corners of an octahedron whose edges are $\sim$2.9 A long. The halide atoms are on the radial perpendicular bisectors of the octahedral edges with a metal to halogen distance of $\sim$2.4 A.

In the octahedral model of the $M_6X_{12}{}^{2+}$ ion, the metal atoms are all in equivalent ligand fields within the complex and the formal valence at each metal atom is $+2\frac{1}{3}$. However, if the symmetry is lower than octa-