of pentaborane generally results in a downfield chemical shift of the attached boron. The only known exception is that of 1-iodopentaborane. The magnitude of the shift for various directly attached substituents is not unusual when compared to other boron systems.[47-52] The upfield shift of the boron diagonally opposite the substituent is mildly surprising, however. It is tempting to attribute this to long-range resonance effects such as are found in substituted benzenes. But considering the complexities inherent in rationalizing chemical shifts in boron compounds,[53] other factors may well be contributing to the observed shift.

^{1}H Nmr (Table II).—The proton magnetic resonance spectra of various substituted pentaboranes reveal several trends: (a) The proton bonded to the apical boron is shifted upfield upon basal substitution, alkyl groups being more effective than the known halogen derivatives. (b) Although it is not possible to resolve all the various kinds of basal terminal hydrogens in certain derivatives, the effect of neighboring substituents is very roughly additive. (c) Upon substitution at the apex the basal protons shift slightly to higher field with alkyl derivatives and slightly to lower field with halogen derivatives. (d) Methyl hydrogens are shifted to lower field in going from an apex to a basal position. All methyl and methylene groups bonded to boron are observed at higher field than in alkanes. This is consistent with observations made on other boron systems.[54-56]

Double resonance of the ^{11}B nuclei resolves the two types of bridge hydrogens in 2-chloro- and 2-bromopentaborane (Figure 1), but because the number of each kind is identical, an absolute assignment is not possible. There are certain inconsistencies in $J_{\text{H-B}}$ and $J_{\text{B-H}}$ for given boron–hydrogen bonds. This is not totally unexpected, since other nuclei in the molecule will couple weakly but with different magnitude to the two nuclei of a given B–H bond.[57]

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The Crystal Structure of Neodymium Monotellurooxide—Nd_2O_2Te

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The crystal structure of Nd_2O_2Te has been determined and refined from powder X-ray diffraction intensity data. The unit cell possesses body-centered tetragonal symmetry with two molecules per unit cell. The lattice parameters are a_0 = 4.032 A and c_0 = 12.80 A. The three crystallographically independent atoms are located in the following positions of space group I4/mmm: 4(e) $\pm(0, 0, z)$, z = 0.341 (Nd); 4(d) $(0, {}^1/_4, {}^1/_4;\ {}^1/_2, 0, {}^1/_4)$ (O); and 2(a) (0, 0, 0) (Te), all plus body-centering translations. One significant feature of this structure is the ninefold coordination exhibited by the lanthanide ion. The magnetic susceptibility measured as a function of temperature gave μ_{eff} = 3.62 BM.

Introduction

The preparation of a family of lanthanide compounds of the general formula R_2O_2Te, in which R is a lanthanide element, has been reported [2-4] Although they listed lattice parameters, they did not report a structure. We suggest a structure compatible with the observed X-ray powder data.

Experimental Section

The olive-green sample we used was prepared by the reaction of calcined sesquioxide with hydrogen and tellurium according to the procedure described by Kent and Eick.[2] From its loss in mass upon oxidation to the sesquioxide, according to

$$Nd_2O_2Te(s) + {}^1/_2O_2(g) \longrightarrow Nd_2O_3(s) + Te(g) \qquad (1)$$

the composition of the oxytelluride was determined to be $NdOTe_{0.50\pm0.01}$.

The density was determined pycnometrically in phenyl chloride, with relatively large quantities of powder. A value of ρ = 7.2 ± 0.1 g/cm^3 was observed and is in good agreement with the theoretical value of 7.15 g/cm^3 and also with the previously re[2] ported[4] value of 6.98 g/cm^3. The result of Kent and Eick (5.17 g/cm^3), which was deduced reproducibly from volume and weight measurements of a compacted cylindrical sample, is in-

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accurate because of voids which develop in the pellet during the compacting. This error leads to incorrect unit cell parameters.

The relative X-ray powder diffraction intensities were measured with a General Electric XRD-5 diffractometer using Ni-filtered Cu Kα radiation. Peak intensities were determined by scanning across the line with accumulation of time and counts while the background was determined from an average of measurements made on either side of the peak. Subtraction of background yielded the integrated intensities. Wherever peaks appeared to overlap, they were grouped together in a single count. The incident beam was not monitored, and fluctuations of the order of 4% over 48 hr were observed for the whole system. An attempt was made to reduce the resulting inaccuracy by determining the intensity of the most intense plane (103) after that of each other plane and subsequently expressing the intensity of every peak relative to this plane. This procedure provided an intensity scale fairly independent of random fluctuations, and a reproducibility of better than 2% of the total observed intensities was achieved.

A careful inspection of the diffraction pattern for Nd_2O_2Te imposed the requirements of tetragonal symmetry indicated in Table I with the following lattice parameters: $a_0 = 4.032 \pm 0.002$ A and $c_0 = 12.80 \pm 0.01$ A. These are in good agreement with previously reported values.[3,4] From our lattice parameters a theoretical density of 7.15 g/cm³ based on two formula units of Nd_2O_2Te per unit cell is calculated, in agreement with the value reported above.

Table I

X-Ray Powder Data for Nd_2O_2Te

H K L	d_{obs}	d_{calc}	I_{obs}	I_{calc}
0 0 2	6.371	6.398	1.0	1.1
1 0 1	3.844	3.846	0.9	1.0
1 0 3	2.931	2.930	100.0	100.0
1 1 0	2.851	2.851	39.8	38.8
1 1 2	2.603	2.604	1.8	1.0
1 0 5	2.161	2.161	10.2	10.8
0 0 6	2.131	2.133		
1 1 4		2.129		
2 0 0	2.017	2.016	19.4	19.4
2 1 1	1.787	1.786	0.6	0.4
1 1 6	1.708	1.708	21.7	20.7
2 0 4		1.706		
1 0 7	1.662	1.665	36.2	35.5
2 1 3		1.661		
0 0 8		1.600	0.0	<0.3
2 1 5	1.466	1.474	14.7	15.0
2 0 6		1.465		
2 2 0	1.427	1.426		
1 0 9	1.342	1.341	6.0	7.0
3 0 1	1.338	1.337		
2 1 7	1.283	1.284	13.8	14.4
3 0 3		1.282		
0 0 10		1.280		
3 1 0	1.276	1.275		
2 0 8	1.252	1.253		
3 1 2		1.250		
3 0 5	1.186	1.190	5.1	5.5
2 2 6		1.185		
3 1 4		1.184		
1 1 10	1.169	1.168		
1 0 11	1.117	1.118	8.3	8.0
2 1 9		1.116		
3 2 1		1.114		
3 1 6	1.095	1.094	17.0	17.1
3 0 7	1.085	1.083		
3 2 3	1.082	1.081		
2 0 10		1.080		
0 0 12	1.067	1.066	1.9	1.0
2 2 8	1.064	1.064		
4 0 0	1.009	1.008	4.7	4.4
1 1 12	0.999	0.999		
3 1 0		0.997		
2 1 11	0.977	0.978	3.5	3.5
3 0 9		0.977		
4 1 1		0.975		
1 0 13	0.954	0.956	12.2	12.2
3 2 7		0.954		
4 1 3		0.953		
2 2 10		0.952		
3 3 0		0.950		
2 0 12	0.943	0.943		
4 0 6	0.912	0.911	8.0	7.4
3 3 4		0.911		
3 1 10	0.902	0.903		
4 2 0		0.902		
3 0 11	0.880	0.880	11.7	12.5
3 2 9		0.879		
1 1 14	0.869	0.870		
3 3 6		0.868		
4 2 4		0.868		
2 1 13	0.865	0.864		
4 1 7		0.862		
2 2 12	0.854	0.854	2.8	3.1
4 0 8		0.853		
1 0 15	0.835	0.835	8.6	10.1
2 0 14	0.833	0.832		
4 2 6	0.831	0.830		

The reported Miller indices and the above lattice parameters suggested a relationship to the K_2NiF_4 structure which is exhibited by other lanthanide phases (*i.e.*, Nd_2CuO_4).[5]

Structure Determination and Results

Various structures were considered as possible solutions by using a Fortran program which calculates the intensity of every possible peak for any atomic arrangement in any space group. A trial and error procedure within the body-centered tetragonal space groups indicated that D_{4h}^{17} (I4/mmm) was the most symmetrical space group which agreed with our observations. The atoms are located in the following positions of this space group

$$(0, 0, 0, {}^1/_2, {}^1/_2, {}^1/_2)$$

$$\begin{array}{lll} \text{Nd} & 0, 0, z;\ 0, 0, \bar{z} & \text{in } 4(e) \\ \text{O} & 0, {}^1/_2;\ {}^1/_2, 0 & \text{in } 4(d) \\ \text{Te} & 0, 0, 0 & \text{in } 2(a) \end{array}$$

The structure was refined using a computer program, first employed to analyze data for $LaCoO_3$,[6] which adjusts the structure parameters to obtain a minimum value for the factor R defined as

$$R = \frac{\sum_{hkl}|I_o(hkl) - I_c(hkl)|}{\sum_{hkl} I_o(hkl)}$$

No weighting scheme was used since data collected by counting and refined on intensities are weighed naturally (*i.e.*, the strongest peak is assumed to have the best accuracy).

The theoretical atomic-scattering factors calculated by Cromer and Waber[7] (Nd^{3+} and Te^0) and Tokonami[8] (O^{2-}) were used. In this refinement, the real and imaginary parts of the anomalous dispersion correction of Cromer[9] were also used by calculating both the A and the B part of the structure factor F.

The calculations yielded the following values for the variable position parameter, z, and the isotropic atomic temperature factors, B: $z_{Nd} = 0.341 \pm 0.001$, $B_{Nd} = 0.36$, $B_{Te} = 1.08$, and $B_O = 1.58$.

A final value of $R = 0.034$ supports convincingly the postulated structure. The calculated and observed intensities are presented in Table I, where $I_c^{hkl} = (1.1 \times 10^{-3})(M)(Lp)F_{hkl}^2$ (M is the multiplicity, Lp is the Lorentz and polarization correction, and F is in electrons). The structure is illustrated in Figure 1 and the resulting bond lengths with their error are listed in Table II.

Table II

Bond Lengths in the Nd_2O_2Te Structure

Bond	Length, A	Bond	Length, A
Nd–O	$4 \times 2.328 \pm 0.010$	O–O	$4 \times 2.851 \pm 0.001$
Nd–Te	$4 \times 3.503 \pm 0.010$		$4 \times 4.032 \pm 0.002$
	$1 \times 4.365 \pm 0.016$	Te–Te	$4 \times 4.032 \pm 0.002$
Nd–Nd	$1 \times 4.070 \pm 0.030$	Te–O	$8 \times 3.782 \pm 0.003$
	$4 \times 3.682 \pm 0.010$		
	$4 \times 4.032 \pm 0.002$		

Discussion

The structure may be considered to consist of eight planar layers, each composed of like atoms. However, two neodymium layers are separated by only 2.33 A with an oxygen layer halfway between—thus these three layers may be considered to be one layer whose composition is Nd_2O_2. Under these conditions the structure would consist of two types of layers—a tellurium layer (A) and the related body-centered tellurium layer (A′), and the $-Nd_2O_2-$ layer (B) and its mirror image (B′). Using these letter designations the structure can then be described as having the packing ABA′B′A along the c axis.

The atomic arrangement of Nd_2O_2Te is somewhat related to the K_2NiF_4 structure since in both cases the large cations occupy similar nine-coordinate positions.

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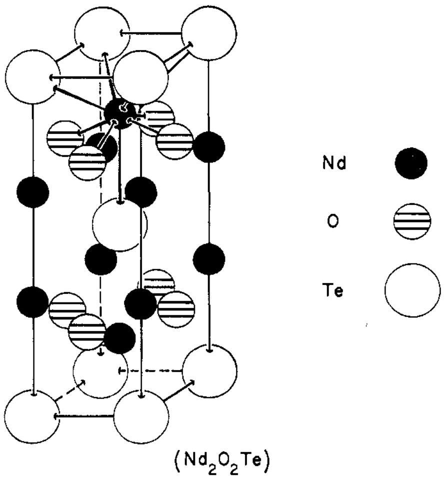

Figure 1.—Structure of Nd_2O_2Te.

They differ, however, in that a large telluride anion is substituted for a small nickel cation and only half as many other anions are present. This deficiency of anions combined with the large size of the telluride ion causes the four oxygen atoms to shift to positions intermediate to those occupied in the K_2NiF_4 structure. The phases Ln_2CuO_4,[5] in which Ln is a lanthanide element, have been reported to be isotypic with K_2NiF_4. In these species the lanthanide ion apparently occupies positions similar to those of the potassium and exhibits ninefold coordination. Since the sizes of the lanthanide and potassium ions are comparable,[10] this similarity seems reasonable.

The lanthanide ion also exhibits ninefold coordination in both lanthanum ditelluride[11] and neodymium tritelluride.[12] A comparison of the coordination of the lanthanide among the three tellurium phases is of interest. In $NdTe_3$ the neodymium is bonded to four telluriums at 3.353 A, four more at 3.208 A, and one at 3.246 A, while in $LaTe_2$ there are four La–Te bonds at 3.381 A, four more at 3.29 A, and one at 3.26 A. This is to be compared to the neodymium coordination in Nd_2O_2Te where there are four Nd–Te bonds at 3.50 A, four Nd–O at 2.33 A, and one long Nd–Te bond at 4.36 A. It can be seen that the presence of the four oxygens has screened the neodymium sufficiently to cause the Nd–Te bonds to be weaker, especially for the single tellurium at the apex of the polyhedra.

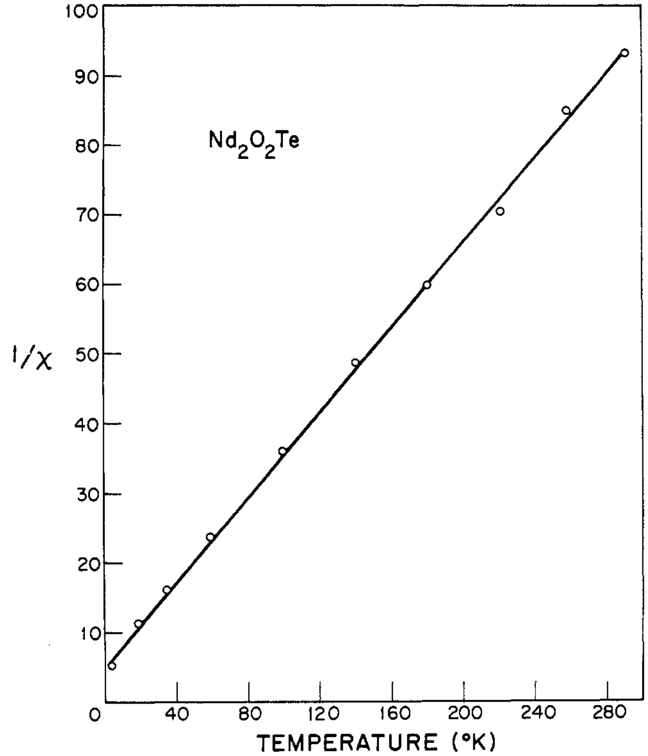

Figure 2.—Inverse molar susceptibility *vs.* temperature for Nd_2O_2Te.

The structure exhibited by the monoseleno oxide,[13] which possesses trigonal symmetry, differs considerably from that of its telluride congener. It also may be described in terms of a layered structure along the *c* axis, consisting of a layer of selenium atoms (A) and two puckered layers of metal–oxygen atoms (B and C) so that the general form may be considered ABCA. The coordination of the metal is seven, in contrast to the value of nine observed in the tellurium-containing species.

The magnetic susceptibility of Nd_2O_2Te was measured as a function of temperature on a vibrating sample magnetometer at a field of 10 koersteds. The results which are presented in Figure 2 give $C_{Nd} = 1.63$ and thus $\mu_{eff} = \sqrt{8C} = 3.62 \pm 0.01$. The theoretical value for Nd^{3+} in the free state is $\mu_{eff} = 3.62$ and the experimental value found for Nd^{3+} in the fluoride NdF_3[14] is $\mu_{eff} = 3.60$. The agreement of these values strongly supports the presence of the Nd^{3+} ion.

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