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The Crystal Structure of the Rubidium Salt of an Octadecahydroeicosaborate(2−) Photoisomer[1]

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The crystal structure of the rubidium salt of an octadecahydroeicosaborate(2−) photoisomer, $Rb_2B_{20}H_{18}$, has been determined by X-ray diffraction with a single-crystal specimen. The orthorhombic unit cell, space group $Pn2_1a$, with $a = 12.344$ Å, $b = 19.014$ Å, $c = 7.260$ Å, contains four formula units. The calculated density is 1.58 g/cc (by flotation, 1.57 g/cc). The structure was determined by Patterson and Fourier techniques and refined by a full-matrix least-squares procedure to a conventional R of 0.127 for 1175 scintillation-counter data (0.073 for the 935 nonzero data). The noncentric nature of the space group was demonstrated by the measurement of anomalous dispersion effects. The anion consists of two capped square antiprismatic B_{10} polyhedra joined by a pair of hydrogen bridges, one between each pair of equatorial four-rings, such that the result has an approximate 2/m (C_{2h}) point symmetry. A list of 13 possible isomers covering reasonable choices of bridge positions is presented together with their point symmetries.

Introduction

In the past few years, there has been considerable interest in the reactions of the $B_{20}H_{18}{}^{2-}$ ion, and proposals have been made for the probable structures of the products.[3−10] The structure of the parent ion has been established[6,7] as a pair of capped square antiprismatic B_{10} polyhedra connected by a pair of three-center bonds which join the 1–2 edge of one polyhedron to the 2′ position of the other and the 1′–2′ edge of the second to the 2 position of the first.[11]

Recently, Hawthorne and Pilling[3] observed the isomerization of $B_{20}H_{18}{}^{2-}$ in acetonitrile solution when exposed to light from a mercury lamp. They predicted that the photoisomer was one of the two possible structures which result when two B_{10} polyhedra are joined by a pair of B–H–B bridges, one between each pair of equatorial four-rings.

This work was undertaken to determine the geometry of the photoisomerization product. The results prove that the geometry is the centrosymmetric (2/m or C_{2h}) alternative of the pair suggested by Hawthorne and Pilling.

Experimental Section

Crystals of the rubidium salt were sent to us by Professor M. F. Hawthorne of the University of California, Riverside, Calif. Part of this material was recrystallized from water by slow evaporation. Two sets of intensity data were recorded from different crystals, one from the original sample and the other from the recrystallized portion.

A small, colorless crystal fragment from the original sample was glued to the end of a Pyrex-glass fiber, with its long direction parallel to the fiber, the instrument ϕ axis, and the a axis of the crystal. Preliminary oscillation and Weissenberg photographs were taken with Cu Kα radiation to find the Laue group, extinction rules, and cell dimensions. More accurate cell dimensions were derived from Bragg angles of the $h00$, $0k0$, and $00l$ reflections measured with a manual General Electric XRD-5 apparatus using molybdenum radiation and a Zr filter at the receiving slit. The components of the α doublet were resolved ($\lambda(K\alpha_1)$ 0.70926 Å). The same apparatus was used to measure intensities of 1153 independent (in the sense of Laue group) reflections, including 283 recorded as zero but not including space group absences. Each reflection was counted for 10 sec with crystal and counter stationary and a large (~3.5°) take-off angle from the X-ray tube anode. Coincidence losses were negligible. For each reflection which was seriously affected by streaking from other orders, individual backgrounds were measured by seeking a minimum on the low 2θ side of the peak; otherwise, the background was taken from a plot of background as a function of 2θ for various values of ϕ and χ. The measurements included reflections to $2\theta = 45°$, or $(\sin \theta)/\lambda = 0.540$. Repeated measurements of several arbitrarily chosen reflections showed systematic trends in which one reflection actually became slightly stronger and others decreased by various ratios, in one case a factor of 2. It is suspected that these changes were caused by a bending or cracking of the crystal induced at least in part by radiation damage. In spite of these inauspicious circumstances, we proceeded with the analysis. When it became evident that the quality of the data was unacceptable, we selected from the recrystallized material a second crystal about 0.11 × 0.06 × 0.05 mm in size and of much better appearance than the first. Cell dimensions and reflection intensities were measured with the same technique as before except that a shutter excluded the X-rays from the crystal except during the actual counting time. The measurements included 1158 Laue-independent reflections, including 240 recorded as zero. The intensities of several reflections which were measured at frequent intervals showed only random fluctuations of the size expected for counting statistics.

Calculations with the partly refined structure permitted identification of reflections which were most likely to show violations of Friedel's rule. Eleven of these and six others of simple indices were selected. Each member of the sets $\pm h$, k, $\pm l$ and $\pm h$, $-k$, $\pm l$ which was observable with the quarter-circle goniometer in this setting (a axis) was counted at least twice for 100 sec. These data gave a total of 1175 intensities (independent in the sense of the point group but including 17 Friedel pairs). Standard deviations of 5% of the intensity or 1 count/sec, whichever was greater, were assigned to all of the raw intensities, ex-

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(7) B. L. Chamberland and E. L. Muetterties, *Inorg. Chem.*, **3**, 1450 (1964).

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(10) A. Kaczmarczyk, R. Dobrott, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U.S.*, **48**, 729 (1962).

(11) Numbering according to R. Adams, *Inorg. Chem.*, **2**, 1087 (1963); see Figure 1.

cept for the anomalous dispersion data, for which standard deviations were estimated from the scatter between measurements made within the sets $k > 0$ and $k < 0$. Weighting factors were derived from these standard deviations as 1 over the square of the resulting standard deviations of the observed structure factors. The calculated absorption coefficient, μ, of 60 cm^{-1}, and the dimensions of this crystal indicate that μs is limited between 0.3 and 0.5, where s is the maximum path length of an X-ray within the crystal. We estimate that the variation in intensities due to absorption is not more than 20% and is distributed in such a way as to be largely absorbed by temperature factors.

Both data sets were corrected for Lorentz and polarization effects, but no corrections were made for absorption or extinction.

Pyroelectricity was indicated by attraction of a crystal to the side of the glass dewar after the crystal was quickly dipped into liquid nitrogen.

Computations were performed on an IBM 7044 with a 32K memory except for final refinements, which were done on a CDC 6600. Fourier syntheses and distance-and-angle calculations were done by Zalkin's (unpublished) FORDAP and DISTAN programs. Our unpublished version of the Ganzel–Sparks–Trueblood least-squares program minimizes the function $\Sigma w(|kF_o| - |F_c|)^2 / \Sigma w |kF_o|^2$, where F_o and F_c are the observed and calculated structure factors, respectively, w is the weighting factor, and k is the scale factor. This least-squares program has been modified to handle anomalous dispersion, and these effects were included in the later refinements. The atomic scattering factors[12] for Rb$^+$ were corrected by $\Delta f' = -0.9$ electron and $\Delta f'' = +3.1$ electrons as the real and imaginary parts of the anomalous dispersion. Scattering factors for boron and hydrogen were also taken from standard tables.[12] The anisotropic temperature factors used have the form: $\exp(-0.25 \Sigma_i \Sigma_j h_i h_j b_i b_j B_{ij})$, $i, j = 1, 2, 3$, where b_i is the ith reciprocal axis.

Results

Four formula units of $Rb_2B_{20}H_{18}$ are contained in the orthorhombic unit cell with dimensions $a = 12.344 \pm 0.007$ Å, $b = 19.014 \pm 0.010$ Å, $c = 7.260 \pm 0.005$ Å. The calculated density of 1.58 g/cc agrees with the value (1.57 ± 0.01 g/cc) obtained by flotation in a mixture of carbon tetrachloride and dibromoethane. These measurements apply to room temperature ($\sim 23°$) and their standard deviations are estimates. The Laue symmetry and observed extinction rules of $0kl$, $k + l \neq 2n$, and $hk0$, $h \neq 2n$, correspond to both the centric Pnma and the noncentric Pn2$_1$a. The positive test for pyroelectricity and the violations of Friedel's rule (presented below) indicate the noncentric Pn2$_1$a, and this choice leads to a successful structure with each atom in the general set of positions: $x, y, z;$ $^1/_2 - x,$ $^1/_2 + y,$ $^1/_2 + z;$ $-x,$ $^1/_2 + y,$ $-z;$ $^1/_2 + x, y,$ $^1/_2 - z$.

Determination of Structure.—The Patterson function calculated from the first data set was consistent with either one rubidium ion in the eightfold Pnma or a pair of nearly centric rubidium ions in the fourfold Pn2$_1$a. The latter was chosen because of the observed pyroelectric effect and the broadening of the Patterson peaks in the a and c directions. Four cycles of least-squares on two slightly noncentric rubidium ions with isotropic temperature factors reduced the R factor for 811 low-angle data of the first set to 0.323 where $R = \Sigma \left| |kF_o| - |F_c| \right| / \Sigma |kF_o|$. The zero coordinate of the y axis in the polar space group Pn2$_1$a was defined by requiring the two rubidium ions to have equal and oppo-

(12) "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 202, 206, 216.

TABLE I

FINAL POSITIONAL AND THERMAL PARAMETERS IN $Rb_2B_{20}H_{18}$

Atom	x	y	z	B^a
Rb(1)	-0.3714 (2)^b	-0.0801 (1)	0.3225 (4)	c
Rb(2)	0.3688 (2)	0.0801 (1)	-0.3299 (4)	c
B(1)	0.039 (2)	0.176 (1)	0.566 (4)	4.4 (6)
B(2)	0.052 (1)	0.219 (1)	0.369 (3)	1.1 (4)
B(3)	0.158 (2)	0.167 (1)	0.457 (3)	2.7 (5)
B(4)	0.069 (2)	0.092 (1)	0.499 (3)	3.0 (5)
B(5)	-0.044 (1)	0.146 (1)	0.407 (2)	0.8 (3)
B(6)	0.140 (2)	0.181 (1)	0.218 (3)	1.8 (4)
B(7)	0.162 (2)	0.091 (1)	0.315 (4)	3.2 (5)
B(8)	0.022 (2)	0.075 (2)	0.275 (4)	4.8 (7)
B(9)	0.000 (2)	0.160 (1)	0.174 (3)	2.3 (4)
B(10)	0.096 (2)	0.111 (1)	0.110 (4)	3.0 (5)
B(1')	0.138 (2)	0.389 (1)	0.400 (3)	2.9 (4)
B(2')	0.095 (2)	0.316 (1)	0.293 (3)	2.8 (5)
B(3')	0.077 (2)	0.405 (1)	0.195 (3)	2.3 (5)
B(4')	0.229 (1)	0.421 (1)	0.239 (2)	0.9 (4)
B(5')	0.241 (2)	0.329 (1)	0.312 (3)	2.4 (4)
B(6')	0.081 (2)	0.330 (1)	0.048 (3)	2.8 (5)
B(7')	0.172 (2)	0.403 (1)	0.005 (4)	3.1 (5)
B(8')	0.287 (2)	0.350 (1)	0.104 (3)	3.1 (5)
B(9')	0.188 (2)	0.284 (1)	0.153 (3)	4.0 (5)
B(10')	0.204 (2)	0.318 (1)	-0.062 (3)	3.2 (5)
H(1)^d	0.019	0.197	0.717	1.2
H(3)	0.229	0.187	0.556	1.2
H(4)	0.064	0.054	0.631	1.2
H(5)	-0.136	0.150	0.463	1.2
H(7)	0.238	0.053	0.286	1.2
H(8)	-0.017	0.022	0.214	1.2
H(9)	-0.051	0.177	0.040	1.2
H(10)	0.116	0.089	-0.041	1.2
H(1')	0.117	0.412	0.550	1.2
H(3')	0.003	0.445	0.217	1.2
H(4')	0.267	0.475	0.295	1.2
H(5')	0.297	0.309	0.437	1.2
H(6')	0.008	0.309	-0.047	1.2
H(7')	0.173	0.440	-0.128	1.2
H(8')	0.378	0.344	0.046	1.2
H(10')	0.225	0.295	-0.212	1.2
H(2-2')	0.027	0.285	0.403	1.2
H(6-9')	0.210	0.215	0.114	1.2

^{a} The units are Å.^{2} ^{b} The number in parentheses is the standard deviation in the least significant digit as derived from the least-squares matrix. ^{c} The anisotropic temperature factors for Rb(1) are: B_{11}, 4.1 (2); B_{22}, 2.5 (2); B_{33}, 5.6 (2); B_{12}, 0.7 (1); B_{13}, 1.4 (1); B_{23}, 0.3 (1); and for Rb(2) are: B_{11}, 4.3 (2); B_{22}, 3.1 (2); B_{33}, 3.8 (2); B_{12}, -0.7 (1); B_{13}, -1.1 (1); B_{23}, 1.1 (1), where the units are Å.^{2} ^{d} H(1) is on B(1) and similarly. H(2–2') and H(6–9') are the two bridging hydrogens. No standard deviations are given for the positional parameters since these are assumed positions.

site y coordinates in this and all subsequent refinements. A Fourier synthesis phased on the rubidiums was calculated and various choices of peaks refined as boron atoms on a cut-and-try basis. In these trials, the appearance of a large temperature factor was taken as an indication of a poor choice of atomic position. After several trials, a difference Fourier was calculated on the basis of the two rubidium ions and 16 borons which had been "found" ($R = 0.297$, all data). This difference Fourier indicated that the rubidium ions were rather badly anisotropic. The same 16 borons plus four more selected from the difference Fourier were refined with the rubidium ions allowed anisotropic temperature factors. R dropped to 0.233 with two

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $Rb_2B_{20}H_{18}$

K	FOB	FCA
H,L= 0, 0		
2	70	69
-2	69	65
4	243	233
6	197	204
8	185	186
10	95	84
12	181	184
14	79	73
-14	76	71
16	40	43
18	70	70
-18	68	68
20	64	60
H,L= 0, 1		
1	38	33
-1	36	32
3	171	166
-3	171	165
5	138	136
7	71	72
9	128	131
11	80	80
13	0	18
15	76	78
17	77	69
19	12	14
H,L= 0, 2		
0	133	138
2	88	85
-2	88	86
4	24	34
6	136	130
8	77	75
10	38	38
12	78	75
14	49	50
16	0	16
18	54	49
H,L= 0, 3		
1	22	19
3	21	14
5	15	18
7	33	34
9	27	23
11	0	6
13	0	7
15	29	23
17	17	15
H,L= 0, 4		
0	42	43
2	12	22
4	9	18
6	33	33
8	23	18
10	10	11
12	15	7
14	39	37
16	0	12
H,L= 0, 5		
1	34	32
3	88	90
5	43	44
7	18	18
9	63	60
11	54	54
13	0	12
15	27	36
H,L= 0, 6		
0	71	67
2	41	42
4	28	29
6	75	74
8	44	41
10	17	28
12	54	49
H,L= 0, 7		
1	20	26
3	52	55
5	29	29
7	32	30
9	37	38
H,L= 1, 1		
0	51	53
1	40	39
-1	46	45
2	66	64
3	92	92
-3	86	85
4	29	31
5	52	54
6	70	69
7	24	24
8	42	41
9	61	60
10	25	24
11	38	39
12	43	42
13	13	15
14	14	21
15	27	32
16	11	3
17	27	24
18	20	20
19	0	4
20	12	19
H,L= 1, 2		
0	129	135
1	60	65
2	68	68
3	113	114
4	54	55
5	71	73
6	115	113
7	49	45
8	51	55
9	77	82
10	17	18
11	53	52
12	71	72
13	22	18
14	58	59
15	59	61
16	16	17
17	45	42
18	39	43
19	0	7
H,L= 1, 3		
0	124	129
1	63	65
2	75	77
-2	71	73
3	132	135
-3	138	140
4	65	65
5	66	69
6	105	104
7	38	41
8	57	58
9	99	101
10	31	28
11	57	57
12	78	81
13	31	28
14	37	41
15	48	53
16	20	19
17	42	42
-17	38	38
18	30	40
H,L= 1, 4		
0	88	92
1	37	37
2	44	47
3	81	82
4	40	40
5	58	59
6	87	88
7	31	31
8	51	49
9	79	82
10	32	32
11	31	37
12	55	55
13	22	20
14	30	35
15	37	36
16	12	12
17	32	32
H,L= 1, 5		
0	62	60
1	31	33
2	16	18
3	47	49
4	37	44
5	29	37
6	33	33
7	0	12
8	27	26
9	42	45
-9	38	39
10	15	9
11	27	29
12	32	30
13	12	15
14	0	20
15	32	30
H,L= 1, 6		
0	11	6
1	0	3
2	11	11
3	0	15
4	21	24
5	11	19
6	15	21
7	16	13
8	0	6
9	11	14
10	12	13
11	0	5
12	0	11
13	0	10
H,L= 1, 7		
0	12	8
1	12	9
2	0	10
3	0	10
4	0	13
5	12	6
6	0	5
7	0	8
8	12	7
9	18	9
H,L= 2, 0		
0	4	2
1	18	16
2	109	98
3	196	196
4	30	27
5	139	135
6	17	16
7	66	66
8	17	15
9	115	117
10	27	14
11	121	116
12	31	21
13	16	15
14	14	12
15	116	112
16	24	9
17	78	81
18	16	8
19	27	20
20	0	11
H,L= 2, 1		
0	279	302
1	37	36
2	101	99
3	27	28
4	114	107
5	6	10
6	203	198
7	0	9
8	112	112
9	8	4
10	76	73
11	9	4
12	126	123
13	24	24
14	60	59
15	0	7
16	22	22
17	19	11
18	60	60
19	0	2
20	50	50
H,L= 2, 2		
0	6	13
1	62	58
2	9	7
3	131	128
4	7	9
5	58	57
6	17	17
7	49	48
8	11	13
9	84	83
10	0	4
11	46	47
12	13	18
13	26	29
14	0	4
15	44	53
16	0	4
17	16	23
18	0	9
19	0	9
H,L= 2, 3		
0	44	37
1	10	13
2	11	11
3	8	7
4	21	20
5	0	3
6	16	15
7	12	16
8	28	26
9	9	16
10	13	13
11	19	22
12	25	27
13	0	6
14	0	6
15	0	4
16	0	10
17	12	7
18	21	25
H,L= 2, 4		
0	8	3
1	29	31
2	15	11
3	55	54
4	26	22
5	15	21
6	0	2
7	0	9
8	0	13
9	40	44
10	0	9
11	40	42
12	0	10
13	16	15
14	0	2
15	16	24
16	0	6
17	25	26
H,L= 2, 5		
0	77	76
1	0	5
2	41	41
3	24	24
4	24	29
5	20	24
6	75	75
7	10	10
8	39	39
9	11	6
10	15	21
11	11	6
12	40	38
13	0	4
14	42	41
15	17	14
H,L= 2, 6		
0	0	4
1	28	32
2	0	7
3	64	64
4	0	6
5	36	36
6	11	5
7	22	19
8	0	1
9	59	54
10	0	4
11	36	35
12	0	3
H,L= 2, 7		
0	55	53
1	0	8
2	23	24
3	0	9
4	24	25
5	0	6
6	34	38
7	0	2
8	28	28
H,L= 3, 1		
0	96	99
1	44	47
2	34	35
3	56	59
4	16	18
5	51	51
6	87	95
7	28	26
8	44	47
9	61	58
10	30	30
11	24	27
12	36	37
13	0	9
14	32	32
15	33	33
16	0	5
17	20	19
18	23	28
19	0	1
H,L= 3, 2		
0	119	122
1	75	73
2	64	66
3	144	146
4	65	63
5	39	45
6	75	79
7	23	27
8	58	56
9	89	89
10	20	20
11	64	67
12	67	69
13	33	33
14	21	25
15	43	48
16	0	5
17	35	36
18	32	33
19	0	4
H,L= 3, 3		
0	118	120
1	53	51
2	51	55
3	74	78
-3	76	82
4	30	31
5	59	61
6	103	104
7	21	24
8	68	68
9	71	71
10	23	23
11	43	45
12	66	65
13	0	2
14	58	56
15	51	51
16	12	8
17	34	35
18	41	39
H,L= 3, 4		
0	69	69
1	36	37
2	45	48
3	94	98
4	32	36
5	57	55
6	75	75
7	43	42
8	31	31
9	65	67
10	15	22
11	41	41
12	49	49
13	19	15
14	30	26
15	53	54
16	17	14
17	28	31
H,L= 3, 5		
0	46	48
1	17	17
2	35	31
3	49	49
4	30	25
5	28	23
6	50	53
7	29	29
8	11	22
9	32	35
10	22	25
11	20	16
12	29	34
13	0	8
14	0	11
15	22	27
H,L= 3, 6		
0	24	22
1	11	17
2	19	20
3	0	12
4	0	14
5	0	7
6	11	7
7	11	8
8	0	6
9	0	14
10	13	14
11	0	2
12	0	11
H,L= 3, 7		
0	17	9
1	17	17
2	17	8
3	0	9
4	12	6
5	12	7
6	21	19
7	12	15
H,L= 4, 0		
0	198	204
1	21	21
2	127	120
3	26	29
4	112	105
5	27	25
6	195	197
7	43	42
8	83	87
9	47	42
10	69	69
11	13	12
12	111	113
13	20	8
14	50	51
15	15	12
16	11	13
17	0	4
18	60	61
19	0	4
H,L= 4, 1		
0	16	19
1	85	86
2	40	37
3	184	187
4	12	12
5	108	105
6	17	21
7	49	51
8	14	13
9	121	119
10	27	19
11	98	98
12	27	24
13	10	18
14	0	16
15	100	98
16	0	2
17	53	51
18	0	13
19	0	15
H,L= 4, 2		
0	79	79
1	10	9
2	39	38
3	7	12
4	33	33
5	14	8
6	78	79
7	0	6
8	50	47
9	13	11
10	36	33
11	0	12
12	53	52
13	21	17
14	28	28
15	11	5
16	0	9
17	0	5
18	42	40
H,L= 4, 3		
0	8	5
1	18	23
2	0	8
3	38	38
4	22	24
5	12	12
6	0	2
7	18	21
8	29	33
9	16	22
10	14	13
11	0	9
12	0	11
13	15	19
14	0	2
15	0	11
16	0	2
17	12	1
H,L= 4, 4		
0	44	38
1	13	16
2	37	39
3	0	8
4	23	21
5	31	27
6	53	56
7	0	3
8	32	24
9	0	10
10	0	12
11	11	9
12	25	21
13	11	14
14	29	23
15	0	7
16	12	9
H,L= 4, 5		
0	14	7
1	45	47
2	17	15
3	58	52
4	20	22
5	23	23
6	10	14
7	0	11
8	0	10
9	53	48
10	0	5
11	41	39
12	0	5
13	0	19
14	0	1
H,L= 4, 6		
0	69	66
1	0	6
2	41	39
3	11	15
4	20	29
5	11	4
6	65	66
7	0	6
8	41	37
9	12	8
10	0	17
11	0	9
H,L= 4, 7		
0	0	7
1	17	20
2	12	12
3	45	40
4	0	6
5	17	21
6	0	8
H,L= 5, 1		
0	41	43
1	25	30
2	34	35
3	70	74
4	30	28
5	21	20
6	33	34
7	20	24
8	26	25
9	32	34
10	0	1
11	40	38
12	36	33
13	0	7
14	18	21
15	29	30
16	0	4
17	20	25
18	12	14
H,L= 5, 2		
0	87	94
1	29	32
2	46	45
3	58	60
4	16	16
5	50	50
6	93	95
7	21	21
8	65	67
9	60	59
-9	62	62
10	27	29
11	36	34
12	58	57
13	0	10
14	48	46
15	39	39
16	0	7
17	24	25
18	33	31
H,L= 5, 3		
0	80	82
1	44	47
2	55	55
3	129	133
4	45	45
5	64	63
6	87	87
7	63	61
8	32	37
9	86	87
10	25	29
11	44	48
12	56	52
13	22	22
14	28	28
15	55	58
16	12	9
17	35	38
H,L= 5, 4		
0	100	106
1	44	45
2	30	32
3	47	49
4	42	41
5	19	23
6	52	47
7	14	16
8	51	49
9	47	45
10	15	12
11	35	33
12	61	57
13	16	12
14	27	29
15	27	30
H,L= 5, 5		
0	25	21
1	0	11
2	15	22
3	39	37
4	10	16
5	32	36
6	34	34
7	22	22
8	22	19
9	41	41
10	16	14
11	12	17
12	24	21
13	12	9
H,L= 5, 6		
0	11	10
1	11	10
2	11	7
3	16	11
4	0	13
5	12	7
6	0	8
7	0	15
8	0	3
9	0	10
10	12	5
H,L= 5, 7		
0	0	1
1	0	5
2	0	6
3	0	2
4	0	14
5	0	5
H,L= 6, 0		
0	19	27
1	93	90
2	42	40
3	146	144
4	26	23
5	114	115
6	22	23
7	52	49
8	25	18
9	149	144
10	42	39
11	68	73
12	23	20
13	24	23
14	31	31
15	83	83
16	12	5
17	49	49
18	0	5
H,L= 6, 1		
0	142	149
1	27	29
2	66	67
3	29	30
-3	32	34
4	72	71
5	8	14
6	93	95
7	0	8
8	70	69
9	33	40
10	31	29
11	14	17
12	84	84
13	0	12
14	33	39
15	0	7
16	0	7
17	0	12
18	50	50
H,L= 6, 2		
0	0	10
1	41	40
2	48	47
3	85	89
4	19	23
5	47	50
6	14	14
7	45	42
8	34	33
9	58	57
10	14	20
11	40	41
12	24	21
13	0	11
14	19	20
15	49	52
16	0	7
17	21	23
H,L= 6, 3		
0	13	10
1	0	4
2	0	4
3	9	5
4	16	20
5	0	2
6	14	18
7	0	4
8	14	7
9	18	11
10	0	16
11	0	1
12	0	12
13	11	8
14	0	1
15	0	2
16	0	10
H,L= 6, 4		
0	0	9
1	22	19
2	22	20
3	10	11
4	0	4
5	27	28
6	10	13
7	10	15
8	11	13
9	29	28
10	11	9
11	20	15
12	12	10
13	0	10
14	0	8
15	18	11
H,L= 6, 5		
0	49	44
1	0	2
2	43	45
3	15	15
4	29	29
5	15	11
6	69	61
7	0	4
8	30	29
9	12	7
10	12	10
11	12	5
12	39	39
H,L= 6, 6		
0	20	17
1	35	34
2	0	8
3	56	53
4	0	10
5	24	23
6	17	15
7	24	22
8	0	9
9	35	32
H,L= 7, 1		
0	50	49
1	21	21
2	37	37
3	38	37
4	19	19
5	18	18
6	49	50
7	13	16
8	27	25
9	17	23
10	0	4
11	18	20
12	29	34
13	16	6
14	34	34
15	0	22
16	0	11
17	0	16
H,L= 7, 2		
0	53	55
1	40	38
2	36	36
3	96	99
4	24	21
5	58	58
6	60	63
7	47	44
8	28	31
9	73	73
10	21	21
11	24	34
12	29	33
13	16	18
14	20	21
15	40	36
16	0	9
H,L= 7, 3		
0	67	65
1	27	32
2	29	31
3	45	42
4	32	34
5	22	22
6	45	48
7	0	9
8	59	57
9	37	35
10	0	7
11	35	34
12	60	59
13	0	9
14	36	37
15	21	24
H,L= 7, 4		
0	38	39
1	23	25
2	29	35
3	75	75
4	29	31
5	46	51
6	50	50
7	28	35
8	19	18
9	57	57
10	11	10
11	33	28
12	29	29
13	0	8
H,L= 7, 5		
0	43	42
1	22	24
2	16	20
3	11	17
4	19	20
5	0	15
6	32	30
7	0	9
8	17	22
9	17	26
10	21	19
11	12	11
H,L= 7, 6		
0	0	6
1	12	8
2	0	13
3	0	14
4	0	15
5	0	5
6	0	8
7	0	11
H,L= 8, 0		
0	105	107
1	20	16
2	68	70
3	37	32
-3	37	36
4	60	53
5	34	33
6	93	92
7	24	21
8	65	65
9	31	35
10	18	17
11	26	19
12	83	79
13	11	7
14	44	41
15	12	12
16	0	10
H,L= 8, 1		
0	20	22
1	41	45
2	23	25
3	86	89
4	0	11
5	61	63
6	24	22
7	47	46
8	20	26
9	74	75
10	11	23
11	39	37
12	19	19
13	11	7
14	24	22
15	59	60
16	0	4
H,L= 8, 2		
0	76	84
1	16	15
2	21	29
3	0	16
4	31	35
5	0	7
6	47	44
7	0	9
8	42	43
9	0	13
10	11	17
11	11	6
12	54	52
13	0	7
14	0	19
15	0	10
H,L= 8, 3		
0	10	3
1	10	15
2	38	39
3	10	13
4	0	12
5	0	8
6	0	7
7	19	15
8	11	14
9	11	9
10	16	17
11	0	5
12	0	5
13	0	9
14	12	8
H,L= 8, 4		
0	24	19
1	0	3
2	28	23
3	19	18
4	22	23
5	0	3
6	21	26
7	11	13
8	11	12
9	12	5
10	0	16
11	0	4
12	21	20
H,L= 8, 5		
0	20	16
1	26	27
2	16	12
3	42	38
4	12	9
5	37	32
6	17	16
7	21	18
8	0	8
9	42	39
H,L= 8, 6		
0	41	37
1	0	3
2	21	21
3	0	7
4	18	18
H,L= 9, 1		
0	33	36
1	37	39
2	31	31
3	41	40
4	0	12
5	10	15
6	21	17
7	0	8
8	15	14
9	41	37
10	0	5
11	20	18
12	20	17
13	12	14
14	12	16
H,L= 9, 2		
0	50	52
1	10	17
2	37	38
3	35	37
-3	40	43
4	27	23
5	21	20
6	47	50
7	15	7
8	46	41
9	35	31
10	11	8
11	16	18
12	41	43
13	0	11
14	30	32
H,L= 9, 3		
0	35	42
1	37	36
2	18	22
3	69	74
4	24	21
5	46	46
6	43	40
7	35	35
8	16	16
9	58	56
10	12	11
11	29	31
12	24	24
H,L= 9, 4		
0	52	49
1	11	16
2	27	27
3	28	25
4	23	22
5	16	15
6	48	44
7	17	14
8	34	30
9	21	21
10	12	14
H,L= 9, 5		
0	0	10
1	0	10
2	0	17
3	29	31
4	12	10
5	21	18
6	0	16
7	18	13
H,L=10, 0		
0	40	35
1	46	46
2	21	27
3	86	83
4	26	25
5	44	40
6	26	25
7	31	33
8	25	14
9	59	60
10	20	8
11	33	37
12	17	20
13	21	17
H,L=10, 1		
0	63	67
1	0	7
2	41	42
3	21	20
4	30	30
5	19	21
6	68	66
7	11	8
8	45	43
9	16	14
10	20	15
11	12	16
12	45	49
13	0	2
H,L=10, 2		
0	0	10
1	11	12
2	0	6
3	36	30
4	15	14
5	25	24
6	16	12
7	16	17
8	23	23
9	20	25
10	0	7
11	0	10
12	0	13
H,L=10, 3		
0	16	24
1	0	12
2	11	4
3	0	2
4	11	14
5	16	9
6	12	5
7	0	4
8	0	13
9	0	5
10	0	11
11	12	5
H,L=10, 4		
0	0	7
1	12	14
2	0	10
3	20	18
4	0	11
5	17	14
6	0	8
7	0	4
8	12	4
H,L=10, 5		
0	30	29
1	0	9
2	12	14
3	0	16
H,L=11, 1		
0	11	5
1	0	7
2	22	23
3	19	11
4	11	3
5	0	13
6	32	30
7	12	7
8	17	21
9	17	12
10	0	7
11	12	7
H,L=11, 2		
0	30	20
1	32	39
2	11	11
3	52	50
4	0	11
5	23	19
6	17	19
7	0	21
8	0	10
9	32	30
10	12	4
H,L=11, 3		
0	44	44
1	0	8
2	26	29
3	24	26
4	24	20
5	0	14
6	48	43
7	0	9
8	28	32
H,L=11, 4		
0	12	18
1	17	15
2	0	12
3	33	34
4	0	6
H,L=12, 0		
0	45	47
1	12	6
2	20	22
3	17	13
4	20	18
5	24	26
6	43	41
7	0	6
8	28	24
H,L=12, 1		
0	20	26
1	26	27
2	17	9
3	50	49
4	0	16
5	24	23
6	0	17
7	21	15
8	18	14
H,L=12, 2		
0	17	21
1	0	13
2	17	17
3	12	5
4	12	12
5	21	19
6	25	28
7	12	11
H,L=12, 3		
0	0	4
1	0	10
2	12	9
3	0	8
4	0	6
H,L=13, 1		
0	0	4
1	12	10
2	0	6
3	28	23

of the new borons going to large temperature factors. It was suddenly seen that sixteen of the eighteen "good" borons were arranged in pairs about a pseudo-center (local, noncrystallographic inversion center) and that the addition of two more borons in positions pseudo-centric to the remaining pair produced two capped square antiprisms which had a pair of short equatorial–equatorial distances between them. Two anisotropic rubidium atoms and these twenty borons refined to $R = 0.218$ on all 1153 data of the first set.

An empirical correction for absorption and for degradation of the crystal was attempted, but R was not significantly reduced. The possibilities of disorder in the orientation of the boron structure, of being in the wrong space group, and of having the rubidium atoms "trapped" in the wrong places by false minima were all investigated without improving the agreement.

It was at this time that the second data set was taken and the first set discarded. The structure found from the first data set immediately refined to $R = 0.158$ on the 1158 data of the second set. An inspection of the observed and calculated structure factors revealed a systematic error in the second data set caused by the scattering of the irradiating X-ray beam off a telescope into the counter near a particular value of θ. When the affected data were removed by deleting all data with $(\sin \theta)/\lambda \geqslant 0.50$, R dropped to 0.114 on 925 data.

All of the data in the neighborhood of the systematic error (40–45°, 2θ) were retaken with a lead sheet shielding the counter from the spurious X-rays, and other data showing large disagreements were remeasured to check for errors such as misset angles and mispunched cards. At this time, the seventeen reflections were selected and examined for anomalous dispersion effects. These data showed that the wrong alternative had been chosen for the polarity. When the structure was inverted as required, a refinement of two anisotropic rubidium ions and twenty borons, including anomalous dispersion, gave an R of 0.136 on the 1175 data of the corrected second set. Another difference Fourier showed peaks ranging from 0.78 to 0.46 electron/Å^3 in reasonable positions for all eighteen hydrogens. Only eight nonhydrogen peaks larger than 0.46 electron/Å^3 were not explainable by such things as

TABLE III

VALUES OF $(|F(+)| - |F(-)|)/0.5(|F(+)| + |F(-)|)$

FOR $Rb_2B_{20}H_{18}{}^a$

h	k	l	Obsd	Calcd
1	1	1	−0.13	−0.15
9	3	2	−0.13	−0.14
1	17	3	0.11	0.10
1	9	5	0.10	0.14
6	3	1	−0.10	−0.12
8	3	0	−0.10	−0.11
1	3	1	0.06	0.07
5	9	2	−0.05	−0.07
1	2	3	0.05	0.05
0	1	1	0.05	0.03
1	3	3	−0.04	−0.03
0	14	0	0.04	0.03
3	3	3	−0.03	−0.04
0	18	0	0.03	0.03
0	2	0	0.01	0.01
0	2	2	0.	−0.01
0	3	1	0.	0.01

^{a} $F(+)$ and $F(-)$ are the structure factors for h, k, l and $h, -k, l$, respectively.

pile-up of errors near the rubidium ion or ill-fitting borons (*e.g.*, a peak midway between two boron positions). Many attempts at refining the hydrogen positions under various restrictions produced various degrees of agreement, various unacceptable temperature factors and boron–hydrogen distances, and much

In the no-hydrogen case the final R was 0.133 on all 1175 data and 0.079 on the 935 nonzero data. In the last cycle, no parameter shifted by more than 0.04 of the standard deviation calculated for it from the least-squares matrix.

In the case which included hydrogens, the final R was 0.127 on all 1175 data and 0.073 on the 935 non-zero data. In the last cycle, no parameter shifted by more than 0.03 of its standard deviation. The standard deviation of an observation of unit weight, defined as $[\Sigma w(|kF_o| - |F_c|)^2/(u - v)]^{1/2}$, where u is the number of data and v is the number of independent parameters refined, was 1.73. The root-mean-square difference in boron positions between the two refinements is 0.05 Å, and the greatest difference is 0.11 Å.

The results of the refinement which included hydrogen are believed to be more accurate on the basis of better agreement and smaller scatter in both the boron temperature factors and in boron–boron distances. All results presented hereafter refer to the refinement on the corrected second data set which included hydrogens. The final positional and thermal parameters are presented in Table I, while Table II lists the observed and calculated structure factors. Observed and calculated values of the function

$$(|F(+)| - |F(-)|)/0.5(|F(+)| + |F(-)|)$$

TABLE IV

DISTANCES^a IN $Rb_2B_{20}H_{18}$

Apex–ring	Å	Intra-ring	Å	Inter-ring	Å
B(1)–B(2)	1.66 (3)	B(2)–B(3)	1.77 (3)	B(2)–B(6)^c	1.72 (3)
–B(3)	1.67 (3)	B(3)–B(4)	1.82 (3)	B(6)–B(3)	1.78 (3)
–B(4)	1.70 (3)	B(4)–B(5)	1.87 (3)	B(3)–B(7)	1.77 (3)
–B(5)	1.64 (3)	B(5)–B(2)	1.85 (3)	B(7)–B(4)	1.76 (3)
B(10)–B(6)	1.64 (3)	B(6)–B(7)	1.86 (3)	B(4)–B(8)	1.76 (4)
–B(7)	1.73 (4)	B(7)–B(8)	1.78 (3)	B(8)–B(5)	1.85 (4)
–B(8)	1.65 (4)	B(8)–B(9)	1.80 (4)	B(5)–B(9)	1.80 (3)
–B(9)	1.58 (3)	B(9)–B(6)	1.80 (3)	B(9)–B(2)	1.91 (3)
B(1')–B(2')	1.68 (3)	B(2')–B(3')	1.86 (3)	B(2')–B(6')	1.80 (3)
–B(3')	1.70 (3)	B(3')–B(4')	1.93 (3)	B(6')–B(3')	1.79 (3)
–B(4')	1.73 (3)	B(4')–B(5')	1.83 (3)	B(3')–B(7')	1.82 (3)
–B(5')^b	1.82 (3)	B(5')–B(2')	1.83 (3)	B(7')–B(4')	1.88 (3)
B(10')–B(6')	1.73 (3)	B(6')–B(7')	1.82 (3)	B(4')–B(8')	1.82 (3)
–B(7')	1.73 (3)	B(7')–B(8')	1.88 (3)	B(8')–B(5')^b	1.66 (3)
–B(8')	1.70 (3)	B(8')–B(9')	1.79 (3)	B(5')–B(9')^b	1.58 (3)
–B(9')	1.70 (4)	B(9')–B(6')	1.76 (3)	B(9')–B(2')^c	1.65 (3)

Across bridges	Å
B(2)–B(2')	1.98 (3)
B(6)–B(9')	2.10 (3)

^{a} These distances are not corrected for thermal motion. The terminal digits in parentheses are the standard deviations as estimated from the least-squares matrix in units of 0.01 Å. However, we feel that the root-mean-square deviations from the averages given in the text of ∼0.05 Å are a better measure of the accuracy of these distances. ^{b} Evidence that B(5') is displaced from its "true" position. ^{c} Pairs of borons in the same B_{10} unit which are involved in hydrogen bridges.

frustration. The structure was finally refined in two ways: with no hydrogen included and with each hydrogen in a calculated position 1.2 Å from its boron (∼1.3 Å in the case of the two bridging hydrogens) and constrained to "ride"[13] on its boron. All hydrogens were also required to have the same temperature factor. Both refinements were done with the weighting scheme described.

(13) Each B–H unit was refined as a rigid, nonrotating body.

where $F(+)$ and $F(-)$ are structure factors for $k > 0$ and $k < 0$ are tabulated in Table III for the seventeen anomalous dispersion data. The agreement of magnitudes and signs clearly establishes the noncentric space group and is strong evidence of the correctness of the structure.

Discussion.—The structure of the photoisomeric $B_{20}H_{18}{}^{2-}$ anion found in this study is shown in Figure 1. This structure is the more symmetric one of the two
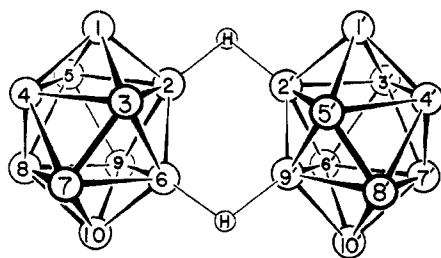
Figure 1.—$B_{20}H_{18}{}^{2-}$ photoisomer (terminal hydrogens omitted for clarity).

TABLE V

ANGLES[a] IN $Rb_2B_{20}H_{18}$

Angle, B–B–B numbers	Deg Unprimed	Primed	Angle, B–B–B numbers	Deg Unprimed	Primed
2 1 3	64	67	6 2 9	59	61
3 1 4	65	68	6 3 7	63	61
4 1 5	68	62	7 4 8	61	61
5 1 2	68	63	8 5 9	59	67
6 10 7	67	63	2 6 3	61	62
7 10 8	63	66	3 7 4	62	63
8 10 9	68	63	4 8 5	62	63
9 10 6	68	62	2 9 5	60	69
e-a-e av	66 ± 2°		e-e'-e av	61 ± 2°	
1 2 3	58	57	3 2 6	61	59
1 2 5	55	62	5 2 9	57	54
1 3 2	58	56	2 3 6	58	59
1 3 4	58	57	4 3 7	59	60
1 4 3	57	55	3 4 7	59	57
1 4 5	55	61	5 4 8	61	54
1 5 2	56	55	2 5 9	63	57
1 5 4	58	57	4 5 8	57	63
10 6 7	59	58	2 6 9	66	55
10 6 9	55	58	3 6 7	58	60
10 7 6	54	58	3 7 6	58	59
10 7 8	56	56	4 7 8	60	58
10 8 7	60	57	4 8 7	60	61
10 8 9	54	58	5 8 9	59	55
10 9 6	57	60	2 9 6	55	64
10 9 8	58	58	5 9 8	62	59
a-e-e av	57 ± 2°		e-e-e' av	59 ± 3°	
2 1 4	102	101	3 2 2'		115
3 1 5	101	97	9 6 9'		116
6 10 8	100	99	2 2' 5'		112
7 10 9	103	94	6 9' 6'		110
Av 100 ± 3°			Av 113 ± 3°		
2 3 4	93	88	5 2 2'		155
3 4 5	88	89	7 6 9'		154
4 5 2	89	92	2 2' 3'		157
5 2 3	90	91	6 9' 8'		153
6 7 8	88	89	Av 155 ± 2°		
7 8 9	93	86	6 2 2'		93
8 9 6	89	95	2 6 9'		86
9 6 7	90	89	2 2' 9'		91
			6 9' 2'		91
Av 90 ± 2°			Av 90 ± 3°		

[a] Standard deviations for these angles as calculated from the least-squares matrix are ~1.5°, but we feel that the given root-mean-square deviations from the averages show that ~2.5° would be nearer the truth.

possibilities postulated by Hawthorne and Pilling.[3] The anion has an approximate 2/m (C_{2h}) point symmetry. A calculation of the deviations of the anion from perfect 2/m symmetry gave a root-mean-square deviation of 0.07 Å (excluding B(5'); see below). We feel that this is nearly, if not entirely, within the ac-

curacy of the determination. Thus the noncentric nature of the space group is a result of an unsymmetrical arrangement (Figure 2) of symmetric pieces. We assign no significance to the handedness found for the particular sample from which the data were obtained and would expect another crystal to have an equal chance of having either handedness.
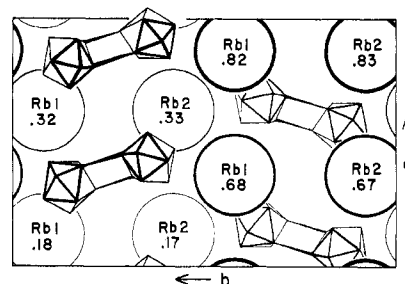

Figure 2.—One unit cell of $Rb_2B_{20}H_{18}$ seen down the c axis (hydrogens omitted). Numbers on Rb ions are z coordinates as decimal fractions of c; the centers of the B_{20} units are approximately at $z = 1/4$ and $z = 3/4$.

An examination of the boron–boron distances given in Table IV shows that B(5') is apparently mislocated in a position too far from the apex and too close to the opposite equatorial ring. We do not understand how this effect arises but did exclude B(5') from the calculation of the deviations of the anion from 2/m symmetry and from the calculations of average boron–boron distances.

The average of 15 apical–equatorial distances (excluding B(1')–B(5')) is 1.68 ± 0.04 Å and the average of 28 equatorial–equatorial distances (excluding B(5')–B(8'), B(5')–B(9'), and the interbridging boron distances) is 1.82 ± 0.05 Å. The shortened interbridging boron distances average 1.68_5 ± 0.05 Å and the B–B distances across the B–H–B bridges average 2.04 ± 0.09 Å. The errors quoted are root-mean-square deviations. The increase in calculated bond distances due to thermal motion is estimated to be 0.02 Å, or about half a standard deviation. These averages may be compared with those found[14] for the cuprous salt of $B_{10}H_{10}{}^{2-}$ which are 1.73 ± 0.02 Å for apical–equatorial distances, 1.86 ± 0.03 Å for distances within the equatorial rings, and 1.81_5 ± 0.01_5 Å for distances between equatorial rings.

The two rubidium ions are nearly centrically located, as can be seen from the table of atomic coordinates. The distance between one rubidium ion and the invert ($\bar{1}$) of the other's position is 0.062 ± 0.008 Å. The rubidium–hydrogen distances are normal for van der Waals contacts. The average of the eight shortest Rb–H distances (four on each rubidium) is 2.8 Å, and the shortest single distance is 2.6 Å. The minimum boron–rubidium distance is 3.3 Å.

The $B_{20}H_{18}{}^{2-}$ ion described above is not the only one which might be constructed by joining two B_{10} polyhedra with two B–H–B bridges involving adjacent borons in each B_{10} unit. There are thirteen isomers

(14) R. Dobrott and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 1779 (1962).

Table VI

Possible $(B_{10}H_8)<\genfrac{}{}{0pt}{}{H}{H}>(B_{10}H_8)^{2-}$ Isomers

No.[a]	Bridge locations[b]	Pairs linked[c]	Point group[d]
1	1–2′, 2–1′	A–A	$2/m = C_{2h}$
2	1–1′, 2–2′	A–A	$mm2 = C_{2v}$
3	2–3′, 3–2′	E–E	$mm2 = C_{2v}$
4	2–2′, 3–3′	E–E	$2/m = C_{2h}$
5	2–2′, 6–9′	E′–E′	$2/m = C_{2h}$
6a	2–2′, 6–6′	E′–E′	$222 = D_2$
6b	2–2′, 9–9′		
7a	1–2′, 2–3′	A–E	$1 = C_1$
7b	1–3′, 2–2′		
8a	1–2′, 2–6′	A–E′	$1 = C_1$
8b	1–2′, 2–9′		
9a	2–2′, 3–6′	E–E′	$1 = C_1$
9b	2–2′, 3–9′		

[a] The a–b pairs are enantiomers. [b] Reference 11. [c] A denotes an apex–equatorial pair, E denotes a pair in the same equatorial ring, and E′ denotes a pair which has one member in each ring. [d] In Hermann–Mauguin and Schoenflies notations, respectively.

which may be so constructed, five of which are symmetric and the remaining eight of which form four enantiomorphic pairs. Other isomers involving bridging to nonadjacent atoms were not considered because of the drastic crowding of the pair of B–H groups which lie between any such nonadjacent pair. The thirteen isomers are listed in Table VI, together with the point groups to which they belong and an indication of which pairs of atoms in each polyhedron are involved in the hydrogen bridges. The isomer found in this investigation is the fifth listed in Table VI, while no. 1 was proposed[10] for the structure of the parent $B_{20}H_{18}^{2-}$ ion before it was shown[6,7] to be linked by a pair of B–B–B three-center bonds rather than hydrogen bridges. Hawthorne and Pilling mention[3] "the formation of unidentified metastable intermediates" in the thermal reversion of the photoisomer studied here to the parent ion. Thus it may be that some or all of the isomers discussed here also exist.

Structure of Gadolinium Sesquisulfide

By C. T. PREWITT and A. W. SLEIGHT

The structure of Gd_2S_3 has been solved and refined by least-squares procedures to an R of 0.019 using 540 nonequivalent reflections collected with a counter diffractometer. Crystals were grown in a GdI_3 melt at 1200°. The crystals are orthorhombic with $a = 7.339$ Å, $b = 15.273$ Å, $c = 3.932$ Å, $D_m = 6.14$ g cm^{-3}, $D_x = 6.187$ g cm^{-3} for $Z = 4$, and space group Pnam. Two kinds of nonequivalent gadolinium atoms are present in Gd_2S_3. One is surrounded by a monocapped trigonal prism of sulfur atoms while the other gadolinium atom is in a bicapped trigonal prism of sulfur atoms. This structure is found for rare earth sesquisulfides from La through Dy and probably also for Pu_2S_3.

Introduction

Very little structural information has been available on rare earth sesquisulfides. (Rare earths will be considered to be La through Lu plus Y and Sc.) The structure of Sc_2S_3, determined by Dismukes and White,[1] is related to the NaCl structure. Apparently, this structure exists for certain rare earth sesquiselenides and sesquitellurides[2,3] but not for any other rare earth sesquisulfide.

According to Flahaut,[4] there are five possible structures for the rare earth sesquisulfides other than that of Sc_2S_3. Two rare earth sulfides, Yb_2S_3 and Lu_2S_3, have the corundum structure.[5] Five—Dy_2S_3, Y_2S_3, Er_2S_3, Ho_2S_3, and Tm_2S_3—have a monoclinic structure. Sesquisulfides from La through Tb can have a defect

Th_3P_4-type structure which actually exists over a range of compositions. In addition, Flahaut[4] stated, mainly on the basis of powder patterns, that there are two unknown structures which are referred to as α and β types. A comparison of the powder pattern of Nd_2S_3 reported by Picon, et al.,[6] with a powder pattern of our Gd_2S_3 crystals indicated that our crystals are of the general α-sesquisulfide structure type. Since this structure has been found for sesquisulfides of La through Dy[7] and also for Pu_2S_3[8] and since suitable single crystals were prepared for the first time, an investigation of the Gd_2S_3 structure was undertaken.

Experimental Section

Synthesis.—Crystal sponge gadolinium metal (99.9%) was obtained from the Lunex Co. Sulfur was 99.999%, and iodine was reagent grade resublimed. The three reactants were sealed

(1) J. P. Dismukes and J. G. White, *Inorg. Chem.*, **3**, 1220 (1964).

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(4) J. Flahaut, M. Guittard, M. Patrie, M. P. Pardo, S. M. Golabi, and L. Domange, *Acta Cryst.*, **19**, 14 (1965).

(5) J. Flahaut, L. Domange, and M. Pardo, *Compt. Rend.*, **258**, 594 (1964).

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