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The Crystal Structure of Thorium Diiodide

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The crystal structure of thorium diiodide, ThI_2, has been determined from counter data by single-crystal X-ray techniques. Thorium diiodide crystallizes in space group $P6_3/mmc$ of the hexagonal system with four formula units in a unit cell of dimensions $a = 3.97 \pm 0.01$ and $c = 31.75 \pm 0.04$ Å and with a calculated density of 7.45 g/cm^3. Least-squares refinement of the structure has led to a final value of the conventional R factor of 0.082 for 200 reflections. The structure consists of four two-dimensionally infinite layers alternating between trigonal-antiprismatic and trigonal-prismatic layers. The coordination polyhedra consist of thorium atoms encompassed by trigonal-antiprismatic polyhedra of iodine atoms in the antiprismatic layers and trigonal-prismatic polyhedra of iodine atoms in the prismatic layers. The coordination polyhedra for both types of layers are linked by the sharing of edges. The Th–I bond distances are 3.22 ± 0.01 and 3.20 ± 0.01 Å in the antiprismatic and prismatic layers, respectively. The results are consistent with a prediction by Clark and Corbett that ThI_2 is not a true thorium(II) salt but should be formulated as $Th^{4+}(I^-)_2(e^-)_2$.

Introduction

The preparation and characterization of pure phases of the lower thorium iodides, in general, and ThI_2, in particular, have been the goal of several investigations. Anderson and D'Eye[1] first reported the preparation of lower halides of thorium, but their preparations produced a mixture of compounds. D'Eye, Ferguson, and McIver[2] obtained a very weak X-ray powder pattern of ThI_2 which they were unable to index. These investigations were hampered by poor-quality metal and unaviodable side reactions with the glass containers.

The first definitive work with regard to the preparation and characterization of ThI_2 was by Clark and Corbett,[3] who prepared pure gold-colored ThI_2 by reaction of high-purity thorium metal with ThI_4 in a tantalum container at about 800°. The low electrical resistance and diamagnetism of ThI_2 led Clark and Corbett to predict that this is not a true thorium(II) salt but a thorium(IV) salt with the extra electrons delocalized in a metallike conduction band.

Scaife and Wylie[4] have reported two modifications of thorium diiodide, α-ThI_2 and β(high-temperature)-ThI_2. They tried to index their powder patterns on the basis of hexagonal cells; however, this, as well as all other attempts at indexing powder patterns of ThI_2, has been doomed to failure because of the large c cell edge. Their β phase corresponds to the material made by Clark and Corbett.

This work started as an attempt to make some sense out of the powder patterns of ThI_2. The observation of a large c cell edge cleared the confusion with regard to the powder patterns but also suggested the presence of a four-layer structure. The crystal structure was then determined to establish the nature of the layer structure and to examine the thorium atom coordination which should demonstrate whether this is a Th(II) or a Th(IV) salt.

Experimental Section

The preparation of thorium diiodide has been described at length by Clark and Corbett.[3] Because of atmospheric reactivity all crysals were handled in a drybox under an inert argon atmosphere. A sample obtained from Corbett in the form of a bole in a glass ampoule was broken open in the drybox and several crysals were knocked off the bole, placed in Lindemann glass capillaries, and sealed in the drybox using a hot wire.

Thorium diiodide crystallizes in a hexagonal cell with cell parameters of $a = 3.97 \pm 0.01$ and $c = 31.75 \pm 0.04$ Å. These parameters were obtained from a least-squares refinement of the reported powder data[3] using the Nelson–Riley extrapolation and weighting the data according to $\tan^2 \theta$. Cell parameters obtained from the diffractometer are essentially the same at 3.96 and 31.76 Å. The calculated density on the basis of four formula units of ThI_2 per cell is 7.45 g/cm^3. The density observed from the dimensions of a pressed pellet was 7.21 g/cm^3.[3] The total number of electrons per unit cell, $F(000)$, is 784. The linear absorption coefficient using Mo Kα (λ 0.7107 Å) radiation is about 500 cm^{-1}; for Cu Kα (λ 1.5418 Å) radiation it exceeds 2000 cm^{-1}. Molybdenum radiation was used in spite of the long c cell edge because there was no analytical absorption correction program available which would correct for the high absorption using copper radiation.

The size of the unit cell as observed on single-crystal photographs enabled us to index the powder patterns reported earlier. The calculated d values and powder intensities for our strongest reflections agree well with patterns reported by Clark and Corbett[3] and Scaife and Wylie.[4] Clearly the reported patterns contain only the strongest lines making the patterns deceptive; also some of the reported lines contain overlapping intensities from several forms of planes. Corbett has indicated in a private communication that lines too weak to measure on his photographs could be identified once their positions were known.

The systematic absences of $hh\overline{2h}l$, $l = 2n$, and $h - k = 3n$, $l = 2n$, observed on single crystal precession and Weissenberg photographs, suggest the possible space groups $P6_3mc$, $P\overline{6}2c$, or $P6_3/mmc$. The $h - k = 3n$, $l = 2n$ condition is not a general one but results from the fact that all atoms are in positions with this limiting condition or else with the limiting condition $hkil$, $l = 2n$. The refinement confirms the centric space group $P6_3/mmc$ as the correct one.

The films show two important features. First, on long exposures some diffuse scattering was observed in the form of streaks emanating from the strong reflections. Generally on the precession photographs the streaks follow the direction of circles passing through the diffraction maxima with the center of the circles being the center of the film. Weissenberg photographs showed some horizontal streaking. The structure solu-

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[1] J. S. Anderson and R. W. M. D'Eye, *J. Chem. Soc. Suppl.*, 244 (1949).
[2] R. W. M. D'Eye, I. F. Ferguson, and E. J. McIver, *Congr. Intern. Chim. Pure Appl., 16^e, Paris, 1957, Mem. Sect. Chim. Minerale*, 341 (1958).
[3] R. J. Clark and J. D. Corbett, *Inorg. Chem.*, **2**, 460 (1963).
[4] D. E. Scaife and A. W. Wylie, *J. Chem. Soc.*, 5450 (1964).

TABLE I

ATOMIC PARAMETERS AND ESD'S FOR ThI_2

Atom	Position	Site symmetry	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Th(1)	2a	$\bar{3}m$	0	0	0	0.0428 (23)	β_{11}	0.00009 (7)	$\beta_{11}/2$	0	0
Th(2)	2c	$\bar{6}m2$	$^1/_3$	$^2/_3$	$^1/_4$	0.0051 (13)	β_{11}	0.00005 (4)	$\beta_{11}/2$	0	0
I(1)	4e	3m	0	0	0.17959 (18)	0.0163 (19)	β_{11}	0.00007 (7)	$\beta_{11}/2$	0	0
I(2)	4f	3m	$^1/_3$	$^2/_3$	0.07128 (20)	0.0331 (26)	β_{11}	0.00014 (7)	$\beta_{11}/2$	0	0

[a] The form of the thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The isotropic equivalents of the anisotropic temperature factors are 1.48, 0.22, 0.61, and 1.23 Å² for Th(1), Th(2), I(1), and I(2), respectively.

tion was carried through without explicitly making use of the fact that diffuse scattering was observed. Second, intensities are weak unless the following conditions are satisfied: $hh2\bar{h}l$, $l = 4n$; $h - k = 3n$, $l = 4n$. In the case of the $000l$ reflections we cannot be certain that any reflections do not satisfy the first condition. We believe that this is a result of the special type of four-layer structure of ThI_2 and that this probably does not indicate any order–disorder phenomena.

The crystal chosen for intensity measurements was a hexagonal platelet of dimensions 0.21 × 0.21 × 0.03 mm. A capillary containing the crystal was placed on a General Electric XRD-5 diffractometer equipped with a pulse height discriminator and scintillation detector. The crystal was mounted so that the $\bar{1}20$ axis coincided with the ϕ axis of the goniostat. The data were measured using zirconium-filtered molybdenum radiation and the θ–2θ scan technique with a takeoff angle of 3°. The diffraction profiles of 328 independent reflections were recorded on a strip chart. The intensities were obtained by planimetering the area above the background for 241 of the chart recordings. The intensities were planimetered to minimize anomalous backgrounds and overlapping from adjacent reflections resulting from the long c lattice parameter. The reflections not planimetered were either very weak or suffered severely from overlap. Forty-one of the planimetered intensities were judged very unreliable because of very high absorption or obvious overlapping as observed on the chart and hence were not included in the refinement. The overlapping contributions from neighboring peaks to a given peak were observed as broad asymmetrical peaks off center with respect to the scan range.

The data were corrected for Lorentz-polarization in the usual way and for absorption using a version of the Busing and Levy absorption correction program[5] for polyhedral crystals adapted for the IBM 7074. Measuring some of the crystal dimensions was difficult, and consequently we feel that the absorption correction is not highly reliable. The calculated transmission factors varied from 0.02 to 0.21. Atomic scattering factors[6] for neutral thorium and neutral iodine were used modified for dispersion by $\Delta f'(\mathrm{Th}) = -6.50$, $\Delta f''(\mathrm{Th}) = 8.50$, $\Delta f'(\mathrm{I}) = -0.55$, and $\Delta f''(\mathrm{I}) = 2.30$.[7] Constant weighting factors were used because the large error contributions from overlap and absorption were hard to account for systematically. Specifically, the sigmas for all reflections were set at 3.0. Ordinary weighting schemes in which the weights vary in some way as a function of the intensities would not account for the largest sources of error in this case and hence would probably not be any better than constant weights. Perhaps a better weighting scheme would vary the weights according to some function of the transmission factors. This is borne out by a cursory glance at those reflections in Table II having the smallest transmission factors (marked by asterisks); clearly these have been poorly corrected for the absorption effect. There is some comfort in the constant weighting approximation in this case since there were no systematic differences in the average values of $w(|F_o| - |F_c|)^2$ in six intervals of $(\sin\theta)/\lambda$ where w is the weighting factor and F_o and F_c are the observed and calculated structure factors, respectively. The function minimized in least squares was $\Sigma w(|F_o| - |F_c|)^2$ using Prewitt's computer program[8] SFLS5.

Structure Determination

Initially we postulated a structure consisting of four cubic close-packed layers, but this structure did not fit all of the peaks in the three-dimensional Patterson map. We were able to obtain a better fit to the Patterson function with a four-layer structure having alternating cubic and hexagonal close-packed layers. The atom placement in the space group is summarized in Table I which gives the final refined parameters. The initial parameters were close to the final ones except that initially the isotropic thermal parameters were assumed as 0.5 and 1.0 for thorium and iodine, respectively.

After four cycles of least squares with isotropic thermal parameters the agreement factor $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ was 0.090. The maximum peaks in the electron density difference map at this point occurred around atom positions and in a manner suggesting anisotropic thermal motion; the maximum heights observed corresponded to about 5% of a Th and 8% of an I atom near these atom positions. There was very little electron density between layers. Four cycles of least squares with anisotropic temperature factors reduced the R factor to 0.082. The electron density difference map was not improved, but the reduction in the R factor is significant at the 0.005 level[9] so that we can reject the hypothesis that all atoms vibrate isotropically; *i.e.*, the refinement with anisotropic thermal parameters should be meaningful. The observed and calculated structure factors are given in Table II where an asterisk is used to denote a reflection not included in the refinement for reasons given earlier. Parameter shifts in the last least-squares cycle were less than 0.1 of their standard deviations.

Discussion

The structure consists of four two-dimensionally infinite layers alternating between cubic close-packed trigonal-antiprismatic layers and hexagonal close-packed trigonal-prismatic layers. The contents of one unit cell are shown in Figure 1a where several atoms from adjacent cells have been added to complete the coordination polyhedra about the Th atoms. Each thorium atom within a layer (a layer being I–Th–I) has six thorium neighbors at a distance equal to a. Each thorium atom in the antiprismatic layers has six iodine neighbors in a distorted octahedral or trigonal-anti-

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(5) W. R. Busing and H. A. Levy, *Acta Cryst.*, **10**, 180 (1957).

(6) H. P. Hansen, F. Herman, J. D. Lea, and S. Skillman, *ibid.*, **17**, 1040 (1964).

(7) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 215.

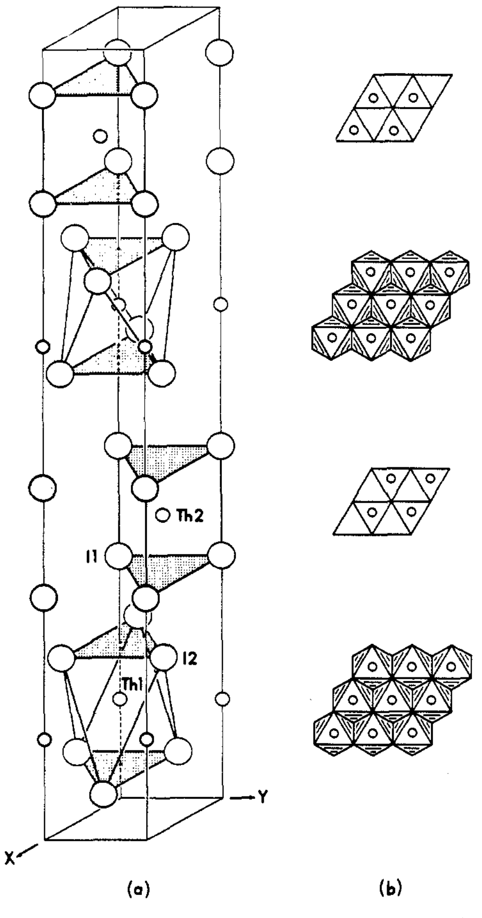
(8) C. T. Prewitt, local unpublished computer program, 1967.

(9) W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965).

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR THORIUM DIIODIDE

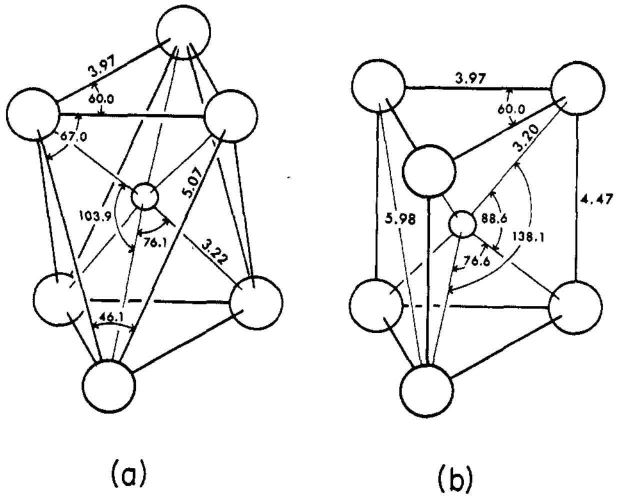
H,K= 0, 0		
4	280	240*
6	16	2*
8	54	46*
10	17	8*
12	617	475*
14	18	2*
16	616	456*
18	97	13*
20	8	19*
22	12	6*
24	207	139*
28	541	416*
32	215	159*
34	22	7
40	277	230*
44	251	243*
H,K= 1, 0		
0	169	160
1	193	193
2	50	47
3	24	24
4	50	51
5	236	240
6	396	435
7	123	120
8	5	17
9	14	13
10	255	259
11	246	245
12	108	101
13	54	54
14	37	40
15	60	56
16	110	110
17	216	216
18	206	198
21	128	98*
22	373	329*
23	211	169*
25	14	10*
26	125	57*
27	259	127*
28	263	98*
29	234	116*
30	65	27*
33	349	137*
34	371	234*
H,K= 1, 1		
0	503	530
4	185	179
6	13	9
8	36	28
10	4	5
12	377	374
16	373	371
24	131	120*
28	432	357*
32	287	139*
40	275	203*
44	242	217*
H,K= 2, 0		
0	133	117
1	159	153
2	43	38
3	28	9
5	208	189
6	342	336
7	105	101
10	205	206
12	83	75
13	54	51
14	45	34
15	52	53
16	90	85
17	181	181
18	166	164
19	8	18
21	97	88
22	284	277
23	155	146
27	106	112
28	104	81
29	112	104
30	11	22*
31	18	10*
32	48	32*
33	173	122*
34	328	203*
35	199	65*
H,K= 2, 1		
0	102	93
1	145	130
2	37	31
4	48	17
5	177	160
6	282	278
7	99	89
8	23	31
10	174	171
11	178	169
12	65	58
14	37	29
15	48	51
16	75	68
17	165	157
18	135	139
19	27	22
20	23	20
21	97	80
22	232	238
23	129	129
27	101	101
29	102	94
31	11	13
32	38	23
33	122	109*
34	208	178*
36	18	25*
H,K= 2, 2		
0	321	313
2	53	44
4	109	114
6	36	19
8	32	14
10	30	24
12	237	233
16	231	236
20	25	16
24	65	65
28	231	241
30	49	43
32	90	99
36	39	13*
H,K= 3, 0		
0	372	364
2	52	38
4	127	129
6	23	16
8	29	16
10	22	19
12	261	268
14	38	41
16	268	271
18	14	31
20	28	16
22	7	9
24	89	93
28	268	272
30	44	39
32	104	110
H,K= 3, 1		
0	67	62
1	105	102
2	39	23
4	42	1
5	139	123
6	205	204
7	76	75
10	128	126
11	135	130
12	43	36
13	39	47
14	38	23
16	51	44
17	120	122
18	100	104
20	38	29
21	80	68
22	171	181
23	98	103
25	28	18
26	35	31
27	79	83
29	72	78
H,K= 3, 2		
0	47	43
1	84	84
2	37	17
3	30	24
4	44	9
5	103	99
6	156	156
7	67	64
8	43	41
10	93	97
11	102	104
12	32	22
13	35	44
14	34	19
16	44	29
17	107	99
18	87	80
21	68	59
22	135	142
23	86	85
H,K= 3, 3		
0	164	173
2	46	53
4	58	69
6	31	24
8	23	13
H,K= 4, 0		
1	67	92
2	35	20
3	32	21
4	39	5
5	117	109
6	185	178
7	73	69
8	47	39
9	37	31
10	110	110
11	117	116
12	29	28
13	26	46
14	36	21
17	108	109
18	82	91
19	28	29
20	28	31
21	63	64
22	154	160
23	100	93
24	39	14
25	23	20
26	42	27
28	39	40
H,K= 4, 1		
0	220	214
4	68	82
6	31	23
8	16	13
10	41	31
12	152	162
14	42	56
16	154	166
18	40	38
20	33	16
H,K= 4, 2		
0	41	26
1	62	66
2	30	12
3	7	27
H,K= 5, 0		
1	65	71
2	28	14
4	37	14
5	81	82
6	123	124
7	46	56
9	28	32
10	74	77
11	84	86
12	27	13



(a) (b)

Figure 1.—View of the crystal structure showing (a) the contents of one unit cell and (b) [001] projections of four cells for each of the four layers in the structure.

prismatic arrangement (Figure 2a). Each thorium atom in the prismatic layers has six iodine neighbors at the apices of a trigonal prism (Figure 2b). Octahedral interstices are formed between the layers.



(a) (b)

Figure 2.—Coordination polyhedra in the (a) trigonal-antiprismatic layers and the (b) trigonal-prismatic layers.

In Figure 1b [001] projections are shown for each of the four layers appearing in Figure 1a; four cells are shown to illustrate the packing within the layers. The coordination polyhedra are linked by the sharing of edges in both types of layers. In the prismatic layers only half of the prisms formed contain thorium atoms. This is expected since putting thorium atoms in every prism formed would place thorium atoms too close together. There are only two pertinent contacts between layers. The first is the perpendicular distance between layers which is 3.44 Å and the second is the shortest interlayer contact distance of 4.13 Å between iodine atoms [I(1)–I(2) in Figure 1a]. Clearly there are no bonding contacts between layers; twinning and stacking faults are to be expected in structures of this type.[10] We have no evidence for crystal twinning but the diffuse scattering observed could very well be due to stacking faults. The structure described here is similar to that reported for TaSe$_2$, except in the TaSe$_2$ structure all of the cations are on the c cell edge.[11] Four-layer polytypes are common in cadmium iodide crystals.[12]

The Th–I distances are 3.22 Å in the trigonal-antiprismatic layers and 3.20 Å in the trigonal-prismatic layers. The distorted octahedra in the antiprismatic layers are elongated along the threefold axis so that the volume of a given octahedron has expanded from 29.5 Å^3 for a regular octahedron of edge a to 41.2 Å^3 found here. The height of a given trigonal antiprism is 4.52 Å with a top edge equal to a and a side edge equal to 5.07 Å. The volume of a given trigonal prism is 30.5 Å^3 with an edge of a and height of 4.47 Å. All of the unique distances and angles are given in Figure 2. The individual calculated standard deviations[13] are 0.01 Å for the bond distances and 0.2° for the angles.

The thermal parameters of the atoms in the antiprismatic layers, Th(1) and I(2), are noticeably large. The thermal motion for these atoms is very anisotropic with normal vibrations [compared to Th(2) and I(1)]

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(10) F. Jellinek, *Arkiv Kemi*, **20**, 447 (1963).

(11) B. E. Brown and D. J. Beerntsen, *Acta Cryst.*, **18**, 31 (1965).

(12) G. C. Trigunayat and A. R. Verma, *ibid.*, **15**, 499 (1962).

(13) Calculations were done using the Busing–Levy function and error program.

in the *c* direction and with large vibrations perpendicular to the *c* direction. Possible explanations for this are systematic errors in the data, fractional occupancy of these layers, partial occupancy of adjacent sites in these layers, and disorder in the form of stacking faults. We can make some comments as to our evaluation of the various alternatives. The fact that both atoms in these layers exhibit the same effect suggests that it is more than just errors in the data. There is no way we can rule out fractional occupancy of these layers. Noteworthy here, however, is the fact that even with partial occupancy of these layers the over-all composition could correspond to ThI_2. The chemical analysis was good with an average $I/Th = 2.01$.[3] We did not refine population parameters for the atoms in the antiprismatic layers because we did not feel justified in assuming temperature factors for these atoms in such a refinement. The electron density difference map seems to discount the possibility of partial occupancy of adjacent sites in these layers. Finally, we feel the presence of stacking faults is probably the best explanation of the effect observed. A layer structure with weak interactions between layers can be easily two-dimensionally disordered. The disorder could appear in our model as large thermal motion perpendicular to *c*. This same disorder could contribute to the diffuse scattering observed.

The Th–I distances found here appear to be equivalent to those found in ThI_4 where they range from 3.13 to 3.29 Å with a mean of 3.20 Å.[14] This indicates the presence of Th^{4+} cores in ThI_2 and supports the Clark and Corbett formulation[3] of thorium diiodide as $Th^{4+}(I^-)_2(e^-)_2$. The extra electrons are presumably extensively delocalized within the layers. The Th–Th distance in thorium metal is 3.60 Å[15] so that the 3.97 Å distance here might be short enough for some Th–Th overlap, but this overlap would be very small. The implication is that the iodine atoms must play a role in accounting for the metallike conduction.[16] Our data are not good enough, especially in the low $(\sin \theta)/\lambda$ range, to differentiate between Th^{2+} and Th^{4+} cores on the basis of atom form factor differences.

In view of the diffuse scattering observed, some static lattice defects have not been explicitly accounted for, but we do not believe these would alter the essential structure features described here. Furthermore, we would expect that different polytypes might be obtained under different reaction conditions or different sample treatment. Scaife and Wylie's α-ThI_2 might be a different polytype in view of the obvious similarities in the powder patterns for their α and β phases. However it is difficult to rationalize their 7.13 Å powder line on the basis of a layered structure with an *a* cell edge similar to that of the β phase.

Acknowledgment.—The authors wish to thank Professor J. D. Corbett for helpful discussions.

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[14] A. Zalkin, J. D. Forrester, and D. H. Templeton, *Inorg. Chem.*, **3**, 639 (1964).

[15] "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958, p s11.

[16] For further discussion of this possibility see J. D. Corbett, R. A. Sallach, and D. A. Lokken in "Lanthanide–Actinide Chemistry," Advances in Chemistry Series, No. 71, American Chemical Society, Washington, D. C., 1968, p 61.

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The Chemistry of Boranes. XXXIII.[1] The Crystal Structure of $Rb_2B_9H_9$

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The crystal structure of $Rb_2B_9H_9$ has been determined from three-dimensional X-ray data collected on a four-circle diffractometer at room temperature. The material crystallizes in the tetragonal space group P4/nmm with two molecules in a cell of dimensions $a = 6.33$ and $c = 11.50$ Å. The structure was refined by least-squares methods to a conventional *R* factor of 0.063. The $B_9H_9^{2-}$ ions consist of discrete triangulated polyhedral units. The individual units lack the complete symmetry of the space group and are disordered so that C_{2v} point symmetry is imposed on the units. The resulting symmetry of the anion cage is idealized D_{3h}. The Rb ion interactions with the polyhedral cage are ionic in nature. Extended Hückel calculations are presented and discussed for the two most plausible $B_9H_9^{2-}$ symmetries (D_{3h} and C_{4v}).

Introduction

The structures of the binary boron hydrides can be characterized as triangulated polyhedra.[2] A characteristic of the highly symmetrical polyhedral borane anions is that individual anion point symmetries change readily with only slight changes in atom positions. For the $B_9H_9^{2-}$ ion the B^{11} nmr spectrum indicated an anion cage with D_{3h} point symmetry,[2] but the X-ray diffraction symmetry of single crystals of $Rb_2B_9H_9$ showed D_{4h} point symmetry suggesting a different structure for the solid state. The crystal structure of $Rb_2B_9H_9$ was determined to establish the solid-state structure of the $B_9H_9^{2-}$ unit and its relationship with the solution structure.

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[1] Paper XXXII: W. H. Knoth, N. E. Miller, and W. R. Hertler, *Inorg. Chem.*, **6**, 1977 (1967).

[2] F. Klanberg and E. L. Muetterties, *ibid.*, **5**, 1955 (1966).