tion. Special thanks are due also to the directors and staffs of the data processing centers who made their facilities available to us. These include Mrs Jeanette Sieg, formerly of the Pittsburgh Board of Education, Mr William B. Kehl of the University of Pittsburgh, Mr William Milburn of the Mellon Bank and Trust Company, and Dr E. B. Weinberger of the Gulf Research Laboratories. We also gratefully acknowledge the generosity of Dr Heinz W. Sternberg who supplied the dicobalt octacarbonyl used in this research.

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The Crystal Structure of Boron Trifluoride Dihydrate

BY W.-B. BANG AND G. B. CARPENTER

Metcalf Research Laboratory, Brown University, Providence 12, *Rhode Island, U.S.A.*

(*Received* 1 *July* 1963 *and in revised form* 7 *August* 1963)

The crystal structure of boron trifluoride dihydrate has been determined at 3 °C by X-ray diffraction. The crystals belong to the monoclinic space group $P2_1/c$ and have cell dimensions

$$a=5{\cdot}606,\ b=7{\cdot}438,\ c=8{\cdot}683\ \text{Å};\ \beta=90{\cdot}45°.$$

$BF_3.2H_2O$ appears to have a structure with one water molecule bonded to boron to form the molecular addition compound $F_3B.OH_2$; the other water molecule links these together by means of hydrogen bonds. However, the ionic formulation $[H_3O]^+[BF_3OH]^-$ cannot be entirely excluded by the diffraction evidence.

Introduction

The early observation by Klinkenberg & Ketelaar (1935) that the X-ray diffraction pattern of $BF_3.2H_2O$ is very similar to those of NH_4BF_4 and NH_4ClO_4 suggested that the former compound is isomorphous with the latter compounds, and so is probably a hydronium salt in the solid. The presence of H_3O^+ and BF_3OH^- in the liquid was indicated by the conductometric measurements of Greenwood & Martin (1951). It would then be interesting to compare the pattern of hydrogen bonding here with those in other hydronium salts such as H_3OCl (Yoon & Carpenter, 1959) and H_3OClO_4 (Lee & Carpenter, 1959). On the other hand, Ford & Richards (1956) concluded from nuclear magnetic resonance studies that in slowly crystallized boron trifluoride dihydrate the water molecules are present in molecular complexes. The present structure determination was undertaken to ascertain the true nature of this substance and to investigate the hydrogen bonding pattern. Additional details of this work are presented in a thesis by one of us (Bang, 1963).

Experimental

Boron trifluoride dihydrate, prepared by introducing boron trifluoride gas into water and subsequent fractional crystallization, was sealed in Pyrex glass capillaries. Crystals were grown and preserved in the capillaries by cooling with a stream of cold nitrogen. Crystallization was initiated by touching the capillary lightly with a piece of solid carbon dioxide. By partial melting and refreezing, a satisfactory crystal was obtained; it was used for all diffraction measurements. The $b+c$ direction was along the capillary axis.

A series of precession photographs was prepared with Zr-filtered Mo radiation. The crystal was held at about 3°C, just 3° below the melting point, in order to minimize the formation of frost on the sample and the possibility of the crystal cracking inside the capillary. Both zero and upper layers were recorded for five orientations; for each layer, exposures of 6 hours and of $1\frac{1}{2}$ hours were recorded. Relative intensities were estimated by visual comparison with a standard scale. The 572 observed reflections were placed on a common scale by the method of Rollett & Sparks (1960), the duplicates were averaged, and 191 independent structure factor magnitudes were extracted. This is not quite half of those accessible within the volume of reciprocal space surveyed, but the difficulty of growing and preserving satisfactory crystals of this material would make it very time-consuming to obtain more data.

Unit cell and space group

The crystal was found to be monoclinic, although nearly orthorhombic, and to belong to the space group $P2_1/c$. Unit-cell dimensions were determined from measurements of relatively high-angle diffraction spots on precession photographs of several layers, by means of a least-squares procedure. The resulting dimensions are $a=5{\cdot}606$ (0·003), $b=7{\cdot}438$ (0·006), $c=8{\cdot}683$ (0·005) Å, and $\beta=90{\cdot}45$ (0·12)°; the quantities in parentheses are the estimated standard deviations from the normal equations of the least-squares treatment, and so measure random errors only.

The density calculated from these data for 4 molecules per cell is 1·74 g.cm^{-3}; this is consistent with the value 1·62 g.cm^{-3} measured pycnometrically for the liquid.

Determination of the structure

Despite the lower symmetry of crystalline boron trifluoride dihydrate relative to hydronium perchlorate (Lee & Carpenter, 1959), these substances were assumed to be approximately isomorphous as implied by the suggested isomorphism with ammonium perchlorate. This gave a trial structure with some atoms at $x=\frac{1}{4}$, the locus of a mirror plane for hydronium perchlorate which is not present in boron trifluoride dihydrate. This structure was refined by a combination of Fourier and least-squares methods to a conventional discrepancy index of 17·2%. At this point the refinement had become very slow, although it had not completely converged, and some of the interatomic distanecs and temperature parameters seemed unlikely. Consequently it appeared that the previous trial structure was not a satisfactory starting point for refinement, although, from the qualitative similarity of the structure factors to those of hydronium perchlorate, it seemed unlikely that it could be very far from correct. A slightly revised trial structure was therefore formulated, differing chiefly in having the boron atom shifted to the other side of the $x=\frac{1}{4}$ plane from the position to which it had moved in the preceding refinement. A sequence of least-squares refinement cycles, with the introduction of anisotropic temperature parameters for atoms other than boron at an advanced stage, reduced the conventional discrepancy index ultimately to 8·6% for the observed reflections only.

Even with this fully refined structure, it was not possible to distinguish between oxygen and fluorine atoms on the boron atom by structure factor calculations. The same discrepancy was obtained for either choice for atom 4, the one which other structural evidence indicated to be oxygen. The temperature parameters were slightly more consistent with atom 4 identified as oxygen.

It proved to be impossible to locate hydrogen atoms directly and unambiguously by difference synthesis since the background fluctuations were as large as peaks thought to represent hydrogen atoms.

The final atomic coordinates and thermal parameters are listed in Table 1. There the quantities in parentheses are the standard deviations estimated from the diagonal elements of the least-squares normal equations matrix; they are thus somewhat optimistic. The temperature parameters are those in the expression

$$\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{23}kl+\beta_{31}lh)\right].$$

The temperature factor was restricted to the isotropic form for the boron atom; consequently the off-diagonal parameters are exactly or very nearly zero.

The observed and calculated structure factors are listed in Table 2. The atomic scattering factors used were that of McWeeny (1951) for boron and those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for oxygen and fluorine.

During the course of the refinement, several different programs and computers were used; the program LSII of Senko & Templeton (1957) for the IBM 650, the program ORXLS of Busing & Levy (1959) for the IBM 704, and the program BXLS of Carpenter (1963) for the IBM 7070 computer.

Description and discussion of the structure

The structure of boron trifluoride dihydrate is illustrated schematically in Fig. 1. The general features are similar to those of hydronium perchlorate (Lee & Carpenter, 1959) except that the latter has mirror planes at $x=\frac{1}{4}$ and $\frac{3}{4}$ passing through the roughly tetrahedral groups of atoms. The details, however, lead to a rather different interpretation.

Table 1. *Atomic parameters* ($\times 10^4$) *for* $BF_3 \cdot 2H_2O$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{23}	β_{31}
F(1)	2656(5)	651(4)	3069(4)	300(10)	178(7)	161(6)	−91(16)	−110(9)	122(15)
F(2)	2651(6)	1134(5)	5676(4)	282(12)	282(8)	153(6)	152(18)	173(12)	−2(14)
F(3)	4026(6)	3279(4)	4030(4)	303(12)	208(7)	140(6)	−117(16)	3(11)	−4(14)
O(4)	9910(6)	2703(5)	4140(4)	186(15)	154(8)	156(7)	113(18)	−40(13)	28(16)
O(5)	7472(7)	3168(5)	6642(4)	334(15)	198(9)	104(6)	41(19)	−30(12)	−78(17)
B(6)	2439(12)	1845(9)	4262(8)	237(21)	134(15)	98(12)	0	0	0

Table 2. *Observed and calculated structure factors for boron trifluoride dihydrate*

hkl	F_o	F_c
002	173	162
004	298	-351
006	128	-148
008	127	-142
011	160	-171
012	266	276
013	-40	4
014	224	242
015	105	-109
016	-50	-22
017	87	96
018	129	-131
020	450	-424
021	127	-113
022	214	-204
023	372	392
024	224	225
025	171	165
026	118	120
027	126	-112
028	-70	5
031	182	-179
032	139	-122
033	266	250
034	344	-360
035	-70	-12
036	-60	22
037	-60	-57
038	-70	33
040	83	-94
041	109	-112
042	-60	-57
043	-60	-16
044	-60	-3
045	-70	-2
046	-80	28
047	-70	64
048	-70	13
051	171	181
052	92	106
053	81	-92
054	75	-75
055	-70	-8
056	-80	29
060	-60	17
061	87	-71
062	-60	20
063	-60	-2
064	75	-71
065	-60	8
066	-70	-11
071	-70	-7
072	-70	38
073	-70	-18
074	71	59
100	-30	-37
102	490	467
-102	333	-381
104	297	-306
-104	307	372
110	320	-349
111	89	-86
-111	-40	16
112	189	-192
-112	292	265
113	268	269
-113	251	-266
114	60	61
-114	-60	47
115	100	90
-115	-60	-11
116	238	225
-116	158	-162
117	-60	-21
-117	-80	31
120	132	-120
121	283	270
-121	414	-391
122	177	-176
-122	83	81
123	246	-256
-123	-50	51
124	90	-94
-124	128	129
125	71	64
-125	92	-95
126	-80	50
-126	-70	0
127	-60	-37
-127	109	101
130	322	-375
131	193	-202
-131	319	334
132	62	-51
-132	190	-190
133	121	-121
-133	63	55
134	70	-64
-134	68	-45
135	-70	55
-135	124	-125
136	-80	-22
-136	-70	21
137	-70	-30
140	139	163
141	-60	70
-141	-70	11
142	121	106
-142	64	40
143	-60	37
-143	63	38
144	-60	7
-144	111	-116
145	-60	32
-145	-60	-48
146	-80	-38
-146	77	-81
147	-80	-48
148	-70	-6
150	-70	-25
151	113	74
-151	70	-80
152	157	210
-152	-60	-23
153	96	-89
-153	103	98
154	-80	34
-154	111	102
155	83	-90
-155	95	87
156	122	-114
160	-80	-96
161	-80	40
-161	-80	13
162	-80	38
-162	-80	-116
163	-70	-36
-163	79	92
164	136	112
-164	-80	-28
165	-70	50
-165	-80	-36
166	-70	29
-166	74	56
171	-70	17
172	-70	-71
-172	-70	-34
173	-70	11
-173	-80	3
200	510	-493
202	-70	-43
-202	425	372
204	56	-50
-204	-50	8
206	-70	-62
-206	-60	-135
210	253	249
211	235	231
-211	294	298
212	434	420
-212	266	262
213	138	-129
-213	85	62
214	-60	9
-214	-50	216
215	-60	-33
-215	-60	30
216	83	-109
-216	-60	24
217	-80	-70
220	221	-213
221	358	321
-221	177	158
222	58	28
-222	123	-116
223	87	-85
-223	51	-50
224	64	65
-224	-70	-47
225	154	-180
-225	-60	-22
226	-70	41
227	-70	18
-227	-70	31
230	-50	19
231	-50	-8
-231	227	-235
232	152	-150
-232	111	-121
233	-60	-11
-233	251	-255
234	126	140
-234	148	120
235	181	169
-235	166	148
236	-70	13
-236	-70	-23
237	-70	61
238	-70	10
-238	-70	35
240	194	211
241	151	-140
-241	-60	30
242	88	84
-242	67	79
243	160	-149
-243	205	-218
244	-70	-35
-244	-70	-38
245	-70	18
-245	-80	-65
246	87	-87
-246	83	-64
250	48	-43
251	-70	-30
-251	-70	28
252	-60	-78
-252	-70	-15
253	-80	19
-253	85	77
254	156	125
-254	-70	74
255	-70	-78
-255	78	-88
260	-80	-25
-261	100	100
262	-60	-58
-262	-60	-7
-263	-80	70
264	-80	31
-264	86	65
271	-70	-53
-271	-80	-28
272	-70	-31
-272	-80	-30
300	279	287
302	-60	37
-302	96	95
304	193	188
306	106	-101
310	-60	-7
311	87	78
-311	93	-95
312	169	179
-312	-60	56
313	70	-43
-313	70	81
314	158	138
-314	-60	-22
315	69	-48
-315	-60	-11
316	94	-90
-316	-70	48
317	-70	16
-317	-70	9
320	112	-112
321	316	-281
-321	335	342
322	64	-66
-322	62	-69
323	209	205
-323	-60	-23
324	80	78
-324	-70	5
325	85	77
-325	-60	-8
326	-70	63
-326	-60	57
327	-80	46
330	201	194
331	-60	-2
-331	91	-93
332	98	-96
-332	-70	-12
333	67	-54
-333	106	118
334	78	-71
-334	96	-94
335	-70	-55
-335	80	87
336	-70	19
-336	-70	-16
340	-70	40
341	-70	29
-341	182	-142
342	74	-72
-342	94	84
343	74	-78
-343	-70	-33
344	87	-89
-344	72	54
345	78	-94
-345	115	93
346	-80	-11
-346	-90	-11
350	88	104
351	-70	37
-351	-70	59
352	-70	8
-352	102	93
353	114	112
-353	98	-118
354	-80	-2
-354	-80	42
355	-80	50
-355	111	-86
360	-60	-25
361	-70	-28
-361	-80	18
362	-80	3
-362	-70	-23
363	-60	59
-363	-70	-22
370	-60	-50
371	-70	-48
-371	-80	6
381	-70	-15
-381	-80	-1
400	296	339
402	83	-71
-402	-70	76
404	148	-134
-404	-60	69
406	-80	6
-406	-70	-36
410	-70	51
411	122	-143
-411	-60	-77
412	-70	-12
-412	-70	-38
413	-70	18
-413	-70	10
414	-70	6
-414	-70	69
415	-70	32
-415	-60	-23
416	-80	1
-416	-70	52
420	67	-57
421	-70	-35
-421	169	-166
422	-60	28
-422	-70	-120
423	-70	9
-423	-70	52
424	73	67
-424	-70	29
425	-70	35
-425	-70	62
430	71	-78
431	-70	37
-431	-70	50
432	-70	-58
-432	-70	-44
433	-60	75
-433	-70	45
434	110	-124
-434	154	-162
435	102	-82
-435	-80	-67
440	-70	14
441	-70	-5
-441	-80	29
442	-70	24
-442	-70	-1
443	72	68
-443	78	76
444	-70	-20
-444	-70	-30
445	-70	37
-445	-80	-22
450	-70	-6
451	-70	31
-451	-70	48
452	112	110
-452	-80	73
453	-70	-54
-453	-80	-10
461	-80	-29
462	-70	-24
-462	-60	7
463	-70	-24
-463	-60	19
464	-70	-6
-464	-90	-2
500	-70	70
502	96	97
-502	-80	10
504	116	-133
-504	-70	32
510	-70	-33
511	-70	38
-511	-60	72
512	-80	73
-512	113	141
513	-70	19
-513	-80	-66
514	-70	63
-514	-70	95
520	97	-102
521	130	123
-521	-80	-50
522	-70	-45
-522	-80	-9
523	-80	-17
-523	-80	55
524	-80	16
-524	-80	63
525	-70	-13
-525	-70	-19
526	-60	31
-526	-70	28
530	77	-85
531	113	-96
-531	-80	-23
532	-80	-38
-532	-80	-64
533	-70	4
-533	-80	-10
534	-70	-7
-534	-80	-4
535	87	84
-535	-80	22
542	-80	34
-542	-70	20
543	-70	-33
-543	-80	-43
544	-80	14
-544	-80	-22
550	-60	-7
551	-60	40
-551	-60	4
552	-60	13
-552	-60	-51
553	-75	-43
-553	-90	29
600	91	-99
602	-60	14
-602	-60	5
611	-70	42
-611	-70	13
612	-70	26
-612	-70	14

The values are $10|F|_o$ and $10F_c$ for the model with atom 4 identified as oxygen.
For $|F|_o$ a minus sign indicates an upper limit for an unobserved reflection.

The important interatomic distances and angles are given in Table 3. Standard deviations are about 0·01 Å for distances, about 1·0° for angles. The atoms are labelled to correspond to Fig. 1; these labels are supplemented where necessary by a three-digit code (t_a, t_b, t_c) giving the translations along the *a*, *b*, and *c* axes which specify a particular adjacent unit cell.

Of the four bonds around a boron atom, that to atom 4 is much longer than the others. (This long bond was produced repeatedly by the least-squares refinement despite misguided attempts to force it to become shorter.) This length of 1·565 is comparable to the average value of 1·585 Å reported for B–N distances in three amine–boron trifluoride addition compounds (Hoard, Geller & Owen, 1951), since distances to oxygen should be a little shorter than those to nitrogen. This B–O distance is somewhat longer than the 1·50 ± 0·06 Å in $F_3B.O(CH_3)_2$ reported by Bauer, Finlay & Laubengayer (1945). No other examples of B–O bonds in similar environments seem to have been reported.

Although the other three bonds to boron differ among themselves by significant amounts, their average 1·370 Å is just the expected value for a B–F bond (Pauling, 1960), is essentially that observed (average 1·39 Å) in the amine–boron trifluorides referred to above, and is much less than the value 1·43 Å found in BF_4^- ion (Pendred & Richards, 1955). It is also less than the value 1·43 Å reported for $F_3B.O(CH_3)_2$ referred to above, but the uncertainties

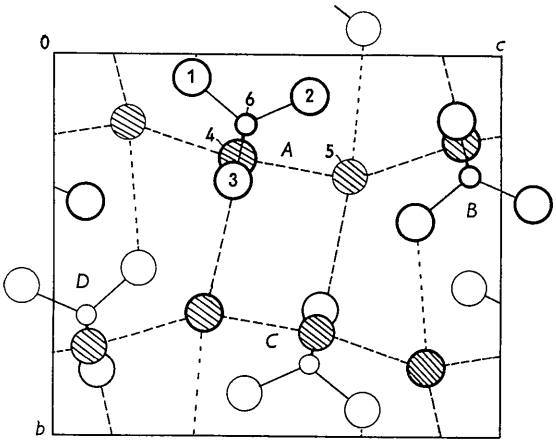

Fig. 1. The structure of boron trifluoride dihydrate viewed along *a*. The small circles are boron atoms, the larger open circles are fluorine atoms, and the shaded circles are oxygen atoms. Heavily outlined atoms lie near $x=\frac{1}{4}$ or $\frac{5}{4}$, lightly outlined ones near $x=\frac{3}{4}$ or $-\frac{1}{4}$.

Table 3. *Bond lengths and angles in* $BF_3.2H_2O$

Dimensions in the $F_3B.OH_2$ molecule

B–F(1)	1·368 Å	B–F(2)	1·340 Å
B–F(3)	1·402	B–O(4)	1·565
O(4)–B–F(1)	107·4°	O(4)–B–F(2)	106·7°
O(4)–B–F(3)	104·6	F(3)–B–F(2)	112·0
F(3)–B–F(1)	109·2	F(2)–B–F(1)	115·8

Coordination of the H_2O molecule

O–*A*(000)4	2·59 Å	O–*A*(000)4	2·64 Å
O–*C*(000)3	2·84	O–*C*(0$\bar{1}$0)1	2·85
O–*A*(000)2	2·97		

A(000)4–O–*B*(000)4	112·1°
B(000)4–O–*C*(000)3	123·2
B(000)4–O–*C*(0$\bar{1}$0)1	72·2
B(000)4–O–*A*($\bar{1}$00)3	162·0
A(000)4–O–*C*(000)3	96·1
A(000)4–O–*C*(0$\bar{1}$0)1	87·6
A(000)4–O–*A*($\bar{1}$00)3	107·0

in that electron diffraction study make a discussion of little value.

The pattern of bond lengths found in the present work — B–F shorter than in BF_4^-, B–O rather long — suggests the addition compound $F_3B.OH_2$ with atom 4 being oxygen, rather than the ion BF_3OH^-. The other oxygen atom, atom 5, must then represent simply water of hydration. This conclusion agrees with that of Ford & Richards (1956). However, the ionic alternative cannot be entirely excluded on the basis of the diffraction evidence.

These general conclusions receive support by the observed pattern of hydrogen bonds. Most conspicuous are the hydrogen bonds of lengths 2·59 and 2·64 Å linking $F_3B.OH_2$ and H_2O molecules together into infinite chains along the *c* axis; these are shown dashed in Fig. 1. The angles at both oxygen atoms, atoms 4 and 5, are reasonable. The next longer interatomic distances are those of 2·84 and 2·85 Å from the water molecule (atom 5) to fluorine atoms 3 and 1, respectively; these run approximately along the *b* axis. The bond angles made by the first are reasonable, those by the second rather unlikely. Both cannot represent hydrogen bonds because they are approximately collinear. The bond length B–F(3) is relatively long; it may be lengthened by participating in a hydrogen bond. Accordingly, the first is tentatively considered as a hydrogen bond and shown dashed in Fig. 1.

Although, in the final difference synthesis, the hydrogen atoms are no higher than random background fluctuations, there are such peaks near the interatomic distances considered to be hydrogen bonds, one near oxygen 4 and two near oxygen 5. The other hydrogen atom which should be bonded to oxygen 4 appears not to be engaged in hydrogen bonding; here too a small peak occurs in a plausible location.

All other interatomic distances are appreciably longer than the sums of the appropriate van der Waals radii.

This work was supported in part by the Office of Naval Research. The least-squares calculations were carried out in part at Harvard University with the help of Professor Lipscomb and Mr. Dobrott, in part at the Computation Center at the Massachusetts Institute of Technology, and in part at the Computing Laboratory at Brown University.

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