

same cation through two O atoms, namely  $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$  (Schröpfer, 1973) and  $\text{CdSO}_3 \cdot \frac{3}{2}\text{H}_2\text{O}$  (Kiers & Vos, 1978). Also, in these structures the chelating O—S—O angle is smaller than the other O—S—O angles. Thus, for  $\text{CdSO}_3 \cdot \frac{3}{2}\text{H}_2\text{O}$  average values are  $101.6$  and  $105.5^\circ$  and for  $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$   $101.6$  and  $105.1^\circ$  for chelating and non-chelating O—S—O angles, respectively.

This distortion obviously occurs because of attractive forces between the cation and the O atoms in question.

#### References

- BUGLI, G. & CARRÉ, D. (1980). *Acta Cryst.* **B36**, 1297–1300.  
 DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **A24**, 390–397.

- HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.  
*International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.  
 JOHANSSON, L.-G. & LINDQVIST, O. (1979). *Acta Cryst.* **B35**, 1017–1020.  
 JOHANSSON, L.-G. & LINDQVIST, O. (1980). *Acta Cryst.* **B36**, 2739–2741.  
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.  
 KIERS, C. TH. & VOS, A. (1978). *Cryst. Struct. Commun.* **7**, 399–403.  
 LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* **A30**, 580–584.  
 LINDQVIST, O. & WENGELIN, F. (1967). *Ark. Kemi*, **28**, 179–191.  
 MAGNUSSON, A. & JOHANSSON, L.-G. (1981). *Acta Cryst.* To be published.  
 SCHRÖPFER, L. (1973). *Z. Anorg. Allg. Chem.* **401**, 1–14.

*Acta Cryst.* (1981). **B37**, 1110–1112

## The Structure of Boron Trifluoride Dihydrate, a Redetermination\*

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**Abstract.**  $\text{BF}_3 \cdot 2\text{H}_2\text{O}$ , monoclinic,  $P2_1/c$ ,  $a = 5.562$  (5),  $b = 7.334$  (8),  $c = 8.746$  (8) Å,  $\beta = 90.30$  (8)°,  $M_r = 103.84$ ,  $Z = 4$ ,  $D_x = 1.93$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 0.28$  mm<sup>-1</sup>. Final  $R = 0.056$  for 1194 reflections. With all atoms now directly located and refined the title compound in the solid state at 173 K is firmly established as hydroxytrifluoroboric acid monohydrate,  $\text{BF}_3\text{OH}_2 \cdot \text{H}_2\text{O}$ , as opposed to the ionic alternative, oxonium hydroxytrifluoroborate,  $\text{H}_3\text{O}[\text{BF}_3\text{OH}]$ , which could not be entirely excluded by a previous analysis of the crystal structure [Bang & Carpenter (1964). *Acta Cryst.* **17**, 742–745].

**Introduction.** The title compound was prepared by introducing a stoichiometric amount of boron trifluoride into water. A liquid sample (melting point 279 K; Pawlenko, 1959) was sealed in a thin-walled glass capillary of 0.3 mm diameter. Single-crystal growth was achieved on a diffractometer (Syntex  $P2_1$  with low-temperature attachment LT-1 modified for optimal performance) in a stream of cold nitrogen gas. The space group was determined from axial photographs

and systematic absences. With the crystal at 173 K the positions of 15 high-order reflections used for lattice parameter refinement were measured as well as the intensities of 1567 independent reflections up to  $2\theta_{\text{max}} = 70^\circ$  ( $\omega$  scan, Mo  $K\alpha$ , graphite monochromator). Of these, 1194 with  $|F_o| \geq 3.0\sigma_F$  were classified as observed and used in the structure determination. Starting from the non-H atom parameters of the previous analysis at 276 K (Bang & Carpenter, 1964)† full-matrix least-squares refinement followed by a difference synthesis led to the positions of all H atoms. Refinement of the complete structure, anisotropic for the non-H atoms and isotropic for H (71 parameters), converged at  $R = 0.056$  (0.068) and  $R_w = 0.072$  (0.071) for the observed (all) reflections. The reflections were weighted according to  $1/w = \sigma_F^2 +$

\* Crystal Structures of Acid Hydrates and Oxonium Salts. XIX. A preliminary report has been given (Mootz & Steffen, 1979). For Part XVIII see Mootz, Ohms & Poll (1981).

† With the angle  $\beta$  very close to  $90^\circ$  an axial setting by chance was adopted in the present analysis which is different from that in the previous one. Direct comparability is obtained with an acute angle ( $89.55$  instead of the reported  $90.45^\circ$ ) for the Bang & Carpenter unit cell and all its atomic  $x$  coordinates inverted at  $x = \frac{1}{2}$ , the position of a pseudo mirror of the structure. This, therefore, amounts to the same as starting from the unchanged coordinates and interchanging only the elemental assignments (and symbols) of O(4), called O(1) in the present analysis, and F(3), which was actually done.

Table 1. Atomic parameters with e.s.d.'s from the least-squares refinement in parentheses

Coordinates are multiplied by  $10^4$  for non-H and by  $10^3$  for H atoms. The equivalent isotropic thermal parameters of the non-hydrogen atoms have been calculated from  $B_{eq} = \frac{1}{3}(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + 2B_{12}ab \cos \alpha + \dots)$ .

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}, B$ ( $\text{\AA}^2$ )
B	2570 (3)	1902 (2)	4218 (2)	1.75
F(1)	2358 (2)	654 (2)	3049 (1)	2.50
F(2)	2290 (2)	1162 (2)	5660 (1)	2.80
F(3)	930 (2)	3310 (1)	4001 (1)	2.26
O(1)	5060 (2)	2720 (2)	4121 (1)	2.01
O(2)	7557 (2)	3137 (2)	6660 (1)	1.79
H(1)	580 (5)	284 (4)	489 (4)	4.0 (6)
H(2)	591 (5)	252 (4)	327 (3)	3.5 (6)
H(3)	880 (6)	236 (5)	663 (4)	4.9 (7)
H(4)	825 (5)	418 (5)	672 (3)	4.3 (6)

(0.02F)<sup>2</sup>. Scattering factors were taken from Cromer & Waber (1974). The final atomic parameters are listed in Table 1. The anisotropic thermal parameters\* show no unusual features, the diagonal terms ranging from 1.3 to 4.1  $\text{\AA}^2$ . All calculations were carried out with the program system EXTL (Syntex) on an Eclipse computer (Data General).

**Discussion.** Alternative chemical structures have been considered for boron trifluoride dihydrate in the solid state. They are surveyed in the reports of a phase study of the system  $\text{BF}_3\text{-H}_2\text{O}$  by Pawlenko (1959) and of a previous determination of the crystal structure at 276 K by Bang & Carpenter (1964) based on 191 independent reflections from eye-estimated precession photographs. The higher accuracy of the present analysis with more than six times as many diffractometer data measured at a much lower temperature is evident from the e.s.d.'s of atomic coordinates now reduced by a factor of about four and from the successful location and refinement of the H atoms. In this way the structure is firmly established as that of a true acid hydrate hydroxytrifluoroboric acid monohydrate,  $\text{BF}_3\text{OH}_2\cdot\text{H}_2\text{O}$ , and the ionic alternative of an oxonium salt oxonium hydroxytrifluoroborate,  $\text{H}_3\text{O}[\text{BF}_3\text{OH}]$ , which was not entirely excluded by the previous determination, is ruled out.

Fig. 1 shows the asymmetric unit with its hydrogen-bonded environment and gives interatomic distances and angles, which are not corrected for thermal motion. The three B—F bonds in the acid molecule are of similar length (average 1.383  $\text{\AA}$ ). The fourth bond extending from the tetrahedral B atom, B—O(1), is

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35868 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

much longer at 1.512  $\text{\AA}$ , though not as long as the 1.565  $\text{\AA}$  of the previous analysis. A similar pattern was found in the crystal structures of two other simple trifluoroboric free acids with a three-coordinated O atom, anhydrous  $\text{BF}_3\text{OH}_2$  and  $\text{BF}_3\text{O}(\text{CH}_3)\text{H}$  (Steffen, 1980; Mootz & Steffen, 1979).

The four independent H atoms form three simple hydrogen bonds and a bifurcated one, O(2) being involved in all of them. That this atom is part of a water molecule, as indicated by the H atom positions and indirectly by the long B—O(1) bond (see above), is further supported by the various O...O and O...F distances, which at 2.631 to 3.133  $\text{\AA}$  are rather too long for hydrogen bonding of an oxonium ion. As shown in Fig. 2 the linking of acid and water molecules extends in three dimensions.

The interesting approximate isotypism between the orthorhombic room-temperature form of oxonium per-

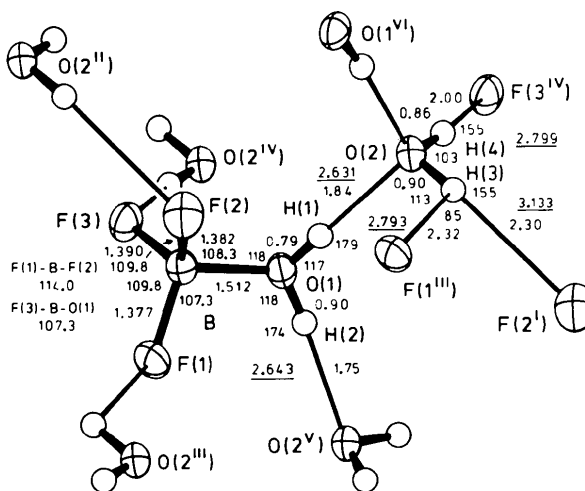


Fig. 1. The asymmetric unit and its hydrogen-bonded environment with interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ ). Distances O...O and O...F in hydrogen bonds are underlined. Thermal ellipsoids correspond to 50% probability (ORTEP II; Johnson, 1976); the uniform radius of the H atoms corresponds to  $B = 1.0 \text{\AA}^2$ . The e.s.d.'s are 0.002 (0.03)  $\text{\AA}$  and 0.1 (2-3) $^\circ$  for distances and angles without (with) H atoms. Symmetry code: (I)  $1 + x, y, z$ ; (II)  $-1 + x, y, z$ ; (III)  $1 - x, -y, 1 - z$ ; (IV)  $1 - x, 1 - y, 1 - z$ ; (V)  $x, \frac{1}{2} - y, -\frac{1}{2} + z$ ; (VI)  $x, \frac{1}{2} - y, \frac{1}{2} + z$ .

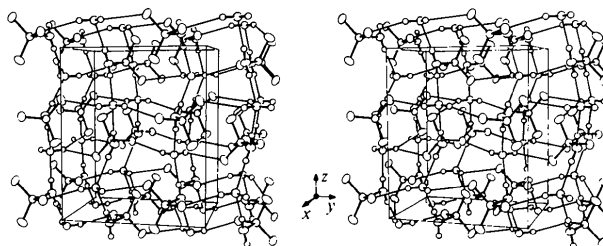
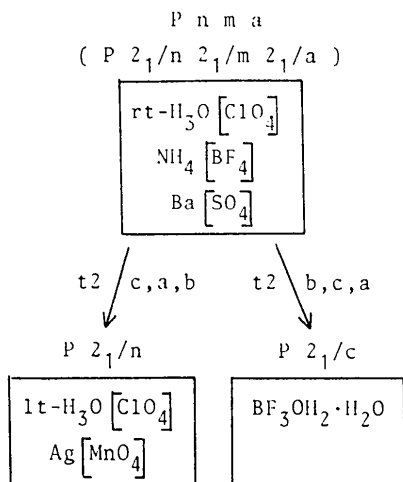


Fig. 2. Stereoplot (ORTEP II; Johnson 1976) of the hydrogen-bonded three-dimensional network.

chlorate (Lee & Carpenter, 1959; Truter, 1961) and the monoclinic title compound, which has already been pointed out by Bang & Carpenter (1964), can be schematically expressed as a group-maximal subgroup relation (Bärnighausen, 1975) as follows:



Included in the scheme are two of the known isotypes (Muller & Ray, 1974) of  $rt-H_3O[ClO_4]$  and the low-temperature form  $lt-H_3O[ClO_4]$  (Nordman, 1962) together with its isotype  $Ag[MnO_4]$  (Boonstra,

1968), which could be recognized as such. A true isotype of  $BF_3OH_2 \cdot H_2O$  could not be retrieved.

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#### References

- BANG, W.-B. & CARPENTER, G. B. (1964). *Acta Cryst.* **17**, 742-745.
- BÄRNIGHAUSEN, H. (1975). *Acta Cryst.* **A31**, S3.
- BOONSTRA, E. G. (1968). *Acta Cryst.* **B24**, 1053-1062.
- CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 71-98. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1976). *ORTEP II*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
- LEE, F. S. & CARPENTER, G. B. (1959). *J. Phys. Chem.* **63**, 279-282.
- MOOTZ, D., OHMS, U. & POLL, W. (1981). *Z. Anorg. Allg. Chem.* In the press.
- MOOTZ, D. & STEFFEN, M. (1979). *Z. Kristallogr.* **149**, 139-141.
- MULLER, O. & RAY, R. (1974). *The Major Ternary Structural Families*, p. 102. Berlin, Heidelberg, New York: Springer.
- NORDMAN, C. E. (1962). *Acta Cryst.* **15**, 18-23.
- PAWLENKO, S. (1959). *Z. Anorg. Allg. Chem.* **300**, 152-158.
- STEFFEN, M. (1980). Dissertation. Univ. of Düsseldorf.
- TRUTER, M. R. (1961). *Acta Cryst.* **14**, 318-319.