Fluoride Crystal Structures. Part XXVI.[1] Bis[difluorobromonium(III)] Hexafluorogermanate(IV)

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Crystals of the title compound are monoclinic, space group $P2_1/c$, a = 5.07(1), b = 13.83(2), c = 6.45(1) Å, β = 116.6(3)°. The structure was solved by the heavy-atom technique and refined by three-dimensional least-squares methods to R 0.087 for 452 visually estimated reflections. The atomic arrangement is consistent with the ionic formulation $[BrF_2]^+{}_2[GeF_6]^{2-}$ but there are strong interactions between the ions through fluorine bridging giving endless chains parallel to the a axis. There is considerable distortion in the octahedral co-ordination of the germanium atom, and the bromine atoms have a distorted square planar co-ordination with two Br–F(terminal) and two Br–F(bridge) distances, means 1.71 and 2.21 Å.

BROMINE trifluoride is amphoteric and can form adducts[2] with strong Lewis acids, such as SbF_5 (ref. 3) or GeF_4.[4] The crystal structure of $BrF_3{\cdot}SbF_5$ has been determined[5] and showed that the adduct is predominantly ionic, although cation–anion interaction occurs through weak fluorine bridges causing distortion of the anion. A controversy existed concerning the structure of the $(BrF_3)_2{\cdot}GeF_4$ adduct. Based on vibrational spectra, Brown and co-workers postulated[4] that it cannot be ionic. Subsequently, Christe and Schack showed[6] that the vibrational spectra do not rule out a predominantly ionic structure containing weak fluorine bridges and/or distorted ions. In view of this controversy and the failure of vibrational spectroscopy to establish unambiguously the nature of $(BrF_3)_2{\cdot}GeF_4$, a crystal structure determination of this adduct appeared most interesting.

EXPERIMENTAL

The preparation of the complex has been described previously.[6] Single crystals were grown by sublimation in a temperature gradient in silica capillaries. The crystals formed as thin plates and most were twinned. One single crystal was sealed in a short length of evacuated silica capillary for the crystallographic investigation. No noticeable decomposition or attack on the silica occurred during data collection.

Crystal Data.—$Br_2F_{10}Ge$, M = 422, Monoclinic, a = 5.07(1), b = 13.83(2), c = 6.45(1) Å, β = 116.6(3)°, U = 404 Å^3, Z = 2, D_c = 3.46, $F(000)$ = 384. Space group $P2_1/c$ (C^5_{2h}, No. 14) from systematic absences. Cu-K_α (λ = 1.541 8 Å) and Mo-K_α (λ = 0.710 7 Å, μ = 148 cm^{-1}) radiations; single-crystal precession and Weissenberg photographs.

D_m was not measured but the volume is consistent with Z = 2, since with 20 fluorine atoms in the unit cell, the volume per fluorine atom is 20 Å^3, identical with that for $[BrF_2]^+[SbF_6]^-$.

Structure Determination.—Integrated intensities were collected about the a axis (layers 0—4kl) by use of Mo-K_α radiation and a Nonius integrating Weissenberg camera. The relative intensities were measured with a photometer

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[1] Part XXV, J. C. Dewan, A. J. Edwards, J. E. Guerchais, and F. Petillon, *J.C.S. Dalton*, 1975, 2295.

[2] L. Stein, in ' Halogen Chemistry,' vol. I, ed. V. Gutmann, Academic Press, New York, 1967, ch. 3.

[3] A. A. Woolf and H. J. Emeleus, *J. Chem. Soc.*, 1949, 2865.

[4] D. H. Brown, K. R. Dixon, and D. W. A. Sharp, *Chem. Comm.*, 1966, 654.

[5] A. J. Edwards and G. R. Jones, *J. Chem. Soc. (A)*, 1969, 1467.

[6] K. O. Christe and C. J. Schack, *Inorg. Chem.*, 1970, **9**, 2296.

of similar design to that described by Jeffery,[7] and structure amplitudes derived for 452 independent reflections by correction for Lorentz and polarization factors.

The structure was solved by conventional Patterson–Fourier techniques, with scattering factors for neutral atoms.[8] Refinement of positional and isotropic temperature parameters, and layer scale factors, was by full-matrix least-squares methods. The function $\Sigma w(|F_o| - |F_c|)^2$ was minimised, initially with unit weights and in the final stages of refinement with $\sqrt{w} = |F_o|/22$ when $|F_o| < 22$ and $\sqrt{w} = 22/|F_o|$ when $|F_o| > 22$. When refinement was almost complete (at R 0.17) an absorption correction was applied, by use of the computer programme ABSCOR, for a crystal, elongated along a with dimensions 0.65 × 0.2 × 0.04 mm. After application of this correction and further cycles of refinement the final R was 0.087. The final parameter shifts were $<0.1\sigma$ and an analysis of the variation of $w\Delta^2$ with increasing $\sin\theta/\lambda$ and increasing fractions of $|F_o|$ was satisfactory. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21546 (4 pp., 1 microfiche),* and the final positional parameters and isotropic temperature factors, with their estimated standard deviations, in Table 1. Interatomic distances and angles are given in Table 2.

TABLE 1

Final atomic positional and thermal parameters, with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	$B/\text{Å}^2$
Ge	0	0	1	2.12(8)
Br	0.3142(5)	0.1357(2)	0.6652(4)	2.34(6)
F(1)	0.0123(38)	0.0350(13)	0.7329(27)	3.03(27)
F(2)	0.7287(41)	0.0953(16)	0.9490(30)	3.86(33)
F(3)	0.2692(38)	0.0839(13)	1.1547(28)	3.38(32)
F(4)	0.5301(40)	0.2143(15)	0.5953(31)	4.48(38)
F(5)	0.0077(41)	0.1782(16)	0.4434(30)	4.13(35)

TABLE 2

Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Distances

Ge–F(1)	1.82(2)	Br–F(4)	1.74(2)
Ge–F(2^{I})	1.83(2)	Br–F(5)	1.69(2)
Ge–F(3)	1.73(2)	Br–F(1)	2.25(2)
F(1) · · · F(3)	2.54(2)	Br–F(2)	2.17(2)
F(1) · · · F(2^{I})	2.54(3)	F(4) · · · F(5)	2.44(3)
F(3) · · · F(2^{I})	2.47(3)	F(1) · · · F(2)	3.37(3)
F(1) · · · F(2^{II})	2.61(3)	F(4) · · · F(2)	2.63(3)
F(1) · · · F(3^{II})	2.49(2)	F(5) · · · F(1)	2.71(3)
F(2) · · · F(3^{II})	2.57(3)		

(*b*) Angles

F(1)–Ge–F(2^{I})	88.5(8)	F(4)–Br–F(5)	90.7(9)
F(3)–Ge–F(2^{I})	87.7(9)	F(1)–Br–F(2)	99.6(7)
F(1)–Ge–F(3)	91.2(8)	F(1)–Br–F(5)	85.9(8)
Ge–F(1)–Br	131.3(9)	F(2)–Br–F(4)	83.8(8)
Br–F(2)–Ge^{III}	135.4(10)		

(*c*) Contacts <3.5 Å

Br · · · F(3)	3.34(2)	F(2) · · · F(3)	3.15(3)
F(1) · · · F(4^{I})	3.32(3)	F(5) · · · F(4^{I})	3.03(3)
Br · · · F(4^{IV})	3.24(2)	F(2) · · · F(4^{IV})	3.11(3)
F(3) · · · · F(4^{IV})	3.18(3)	F(4) · · · F(4^{IV})	3.37(1)
Br · · · F(3^{V})	3.28(2)	F(4) · · · F(3^{V})	3.12(2)
F(5) · · · F(3^{V})	3.02(3)	F(5) · · · F(2^{VI})	3.08(2)
F(5) · · · F(2^{VII})	3.44(3)	F(5) · · · F(4^{VII})	2.89(3)

Roman numerals as superscripts refer to atoms in the positions:

I $-1 + x, y, z$
II $-x, -y, 2 - z$
III $1 + x, y, z$
IV $x, \frac{1}{2} - y, \frac{1}{2} + z$
V $x, y, -1 + z$
VI $-1 + x, y, -1 + z$
VII $-1 + x, \frac{1}{2} - y, -\frac{1}{2} + z$

DISCUSSION

The atomic arrangement is illustrated in Figures 1 and 2. The ionic formulation $[BrF_2]^+{}_2[GeF_6]^{2-}$ gives the best description for the structure, since it is compatible with the nearest neighbours to the bromine and germanium atoms. Thus, the two fluorine atoms, mean distance 1.71 Å from bromine, and the four fluorines 1.82 and two 1.73 Å from germanium, define the ions, with the next-nearest fluorine atoms to bromine, at a mean distance of 2.21 Å, having a significantly weaker interaction.

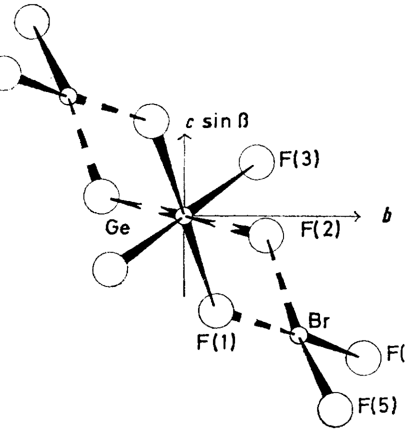

FIGURE 1 The endless chain arrangement shown in projection down [100]

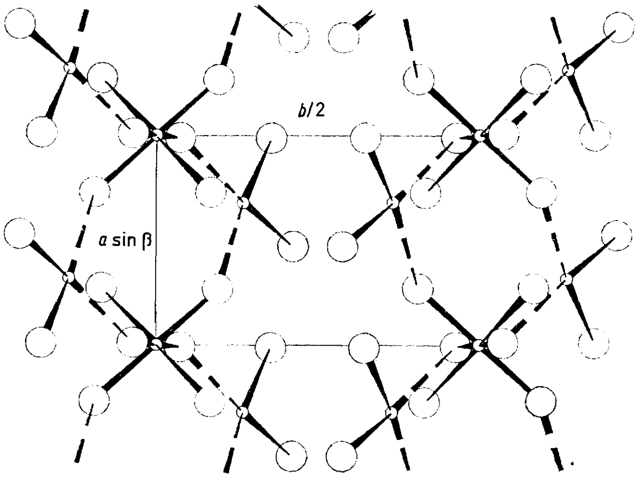

FIGURE 2 Projection of the structure down [001]

The co-ordination around germanium is distorted from octahedral by a lengthening of four coplanar Ge–F bonds involved in bridging to four bromine atoms. The F–Ge–F angles are not significantly different from 90° and the symmetry of the $[GeF_6]$ unit is approximately D_{4h}. This result agrees with the previous conclusions,[4,6] based

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1975, Index issue.

[7] J. W. Jeffery, *J. Sci. Instr.*, 1963, **40**, 494.

[8] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1965, p. 202.

on vibrational spectroscopy, that the compound does not contain octahedral $[GeF_6]^{2-}$ ions.

The two Br–F distances in the BrF_2^+ cation are not significantly different. The mean Br–F distance (1.71 Å) and the F–Br–F angle (90.7°) are very similar to the corresponding values (1.69 Å and 93.5°) found for the cation [5] in $[BrF_2]^+[SbF_6]^-$.

Although the ionic formulation gives an approximate description of the structure, the two extra Br–F distances of 2.17 and 2.25 Å, which complete a distorted square-planar fluorine co-ordination around bromine, represent a significant interaction. Thus, there is a contribution to the structure from the covalently bonded fluorine-bridged arrangement. Since Br in $[BrF_2]^+$ possesses two sterically active electron pairs, this cation can be considered to be pseudo-six-co-ordinated.

The long Br–F contacts from pairs of bromine atoms form bridges between separate $[GeF_6]$ units, to give infinite chains running parallel to the *a* axis, as shown in projection in Figures 1 and 2. The ratio of Br–F(bridge) to Br–F(terminal) is 1.29, significantly less than the value of (1.36) for $[BrF_2]^+[SbF_6]^-$,[5] but slightly larger than that (1.27) for $[BrF_4]^+[Sb_2F_{11}]^-$.[9] This indicates that the covalent interaction increases in the order: $[BrF_2]^+$-$[SbF_6]^- < [BrF_2]^+{}_2[GeF_6]^{2-} \approx [BrF_4]^+[Sb_2F_{11}]^-$. The ratio of the Ge–F(bridge) to Ge–F(terminal) distance (1.05) is very similar to the corresponding Sb–F ratio (1.04) in $[BrF_2]^+[SbF_6]^-$ indicating that the differences in the anion bond lengths are not as good a measure of the strength of the fluorine bridge, and might be influenced by the different number of fluorine bridges involved in the 1 : 1 and 2 : 1 adducts.

We thank Dr T. A. Hamor for his amended versions of the computer programs ORFLS, ORFFE, and FORDAP, the staff of Birmingham University Computer Centre for their assistance, and the Office of Naval Research, Power Branch, for financial support (of K. O. C.).

[5/1063 *Received, 2nd June*, 1975]

[9] M. D. Lind and K. O. Christe, *Inorg. Chem.*, 1972, **11**, 608.