ordinate system ($\vec{X}^i$) defined by suitable cross products of the unit cell vectors $\vec{a}$, $\vec{b}$, $\vec{c}$

$$\begin{aligned} \vec{X}^2 &\equiv \| \vec{b} \\ \vec{X}^1 &\equiv \| \vec{b} \times \vec{c} \\ \vec{X}^3 &\equiv \| \vec{X}^1 \times \vec{X}^2 \end{aligned} \tag{1}$$

such that

$$(X_j) = (\Upsilon^a)(x_j) \qquad 1 \leq j \leq 43 \tag{2}$$

where Υ^a is the (3 × 3) transformation matrix based on the cross-product definitions given in (1) and evaluated by determining the components of the unit cell vectors $\vec{a}$, $\vec{b}$, $\vec{c}$ in the coordinate system $\vec{X}^i$, and $X_j{}^i$ are the coordinates of each atom in this system.

The origin of this coordinate system was then shifted to the copper atom ($X_1{}^i$) and the coordinates, $X'_j{}^i$, of all atoms were recalculated with respect to the new origin

$$X'_j{}^i = X_j{}^i - X_1{}^i \qquad 1 \leq i \leq 3,\ 1 \leq j \leq 43 \tag{3}$$

An internal right-handed orthogonal coordinate system ($\vec{R}^i$) was defined in terms of suitable cross products of the three $\overrightarrow{\mathrm{Cu{-}P}}$ vectors

$$\begin{aligned} \vec{R}^2 &\equiv \| \overrightarrow{\mathrm{Cu{-}P_2}} \\ \vec{R}^1 &\equiv \| \overrightarrow{\mathrm{Cu{-}P_2}} \times \overrightarrow{\mathrm{Cu{-}P_3}} \\ \vec{R}^3 &\equiv \| \vec{R}^1 \times \vec{R}^2 \end{aligned} \tag{4}$$

and the coordinates $R_j{}^i$ of Cu (origin), P_1, P_2, and P_3 in this coordinate system were evaluated. The elements (τ_{ik}) of the transformation matrix Υ^b required to take $\vec{X}^i$ into $\vec{R}^i$ were determined by solving the set of simultaneous equations relating P_1, P_2, and P_3 in the two coordinate systems

$$R_j{}^i = \sum_{k=1}^{3} X'_j{}^k \epsilon \tau_{ik} \qquad 1 \leq i \leq 3,\ 2 \leq j \leq 4 \tag{5}$$

Using the matrix Υ^b, the coordinates of all atoms were expressed in the coordinate system $\vec{R}^i$

$$(R_j) = (\Upsilon^b)(X'_j) \qquad 1 \leq j \leq 43 \tag{6}$$

The net result of these transformations is a set of atomic coordinates, $R_j{}^i$, for $Cu_2(N_3)_2$(diphos)$_3$ which is *independent* of the *lattice*-based coordinate system for the structure.

The fractional coordinates of the copper and three phosphorus atoms, $y_j{}^i$, corresponding to one of the image solutions for $Cu_2(CF_3CN_4)_2$(diphos)$_3$ were then transformed by a series of steps identical with (1) and (2) (*vide supra*) yielding a transformation matrix Υ^c, analogous to Υ^a and a set of positions $Y_j{}^i$ for Cu, P_1, P_2, and P_3. The origin of the coordinate system $\vec{Y}^i$ was then shifted to the copper atom ($Y_1{}^i$) and the coordinates of Cu, P_1, P_2, and P_3 were recalculated in a manner identical with (3) to yield a set of atomic coordinates $Y'_j{}^i$ analogous to $X'_j{}^i$.

The origin of the coordinate system $\vec{R}^i$ was formally made coincident with the origin of the coordinate system $\vec{Y}^i$ and the transformation matrix Υ^d required to superimpose the corresponding phosphorus atoms in the two coordinate systems was evaluated in a manner similar to (5). Using the matrix Υ^d, the coordinates of all atoms of $Cu_2(N_3)_2$(diphos)$_3$ on the internal coordinate system $\vec{R}^i$ were evaluated in the *lattice*-based coordinate system, $\vec{Y}^i$, of $Cu_2(CF_3CN_4)_2$(diphos)$_3$

$$(Y'_j) = (\Upsilon^d)(R_j) \qquad 1 \leq j \leq 43 \tag{7}$$

The origin of this coordinate system was then shifted to the standard origin for the space group ($C2/c$, 000) and the fractional coordinates of all atoms were calculated by applying the inverse of the transformation matrix Υ^c

$$(Y_j) = (\Upsilon^c)^{-1}(Y_j) \qquad 1 \leq j \leq 43 \tag{8}$$

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The Crystal Structure of $[BrF_4{}^+][Sb_2F_{11}{}^-]$

By M. D. Lind* and K. O. Christe

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Crystals of the 1:2 adduct formed by BrF_5 and SbF_5 consist of infinite chains of discrete $BrF_4{}^+$ and $Sb_2F_{11}{}^-$ ions coupled by relatively weak fluorine bridges and, accordingly, should be formulated as $[BrF_4{}^+][Sb_2F_{11}{}^-]$. This is the first direct evidence for the existence of the $BrF_4{}^+$ ion. The crystals are monoclinic with the most probable space group $P2_1/a$, lattice constants $a = 14.19 \pm 0.03$, $b = 14.50 \pm 0.03$, $c = 5.27 \pm 0.01$ Å, $\beta = 90.6 \pm 0.1°$, and four formula units per unit cell; the calculated density is 3.72 g cm^{-3}. The structural parameters were refined by the method of least-squares with visually estimated Weissenberg photographic intensity data. The final value of the conventional agreement index R was 0.14 for 773 reflections having $|F_o|$ greater than $\sigma(|F_o|)$.

Introduction

Previous investigations of solid halogen fluoride adducts have provided evidence that some are predominantly ionic[1-4] and others are predominantly covalent.[5-7] Infrared and Raman spectroscopic studies[4] of the 1:2 adduct[8] formed by BrF_5 and SbF_5 yielded

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equivocal results concerning the nature of this compound because of the large number of possible fundamental vibrations and the low symmetry of the bromine and antimony environments. For the same reasons, the arguments recently presented by Meinert and Gross[9] in favor of the ionic structure are not convincing. To resolve the ambiguity, we have determined the structure from single-crystal X-ray diffraction data. Our investigation was complicated by the marginal stability of the adduct and its tendency to decompose on contact with atmospheric moisture and with glass.

Experimental Section

Preparation of Crystals.—The metal–Teflon FEP vacuum system used and the preparation of $BrF_5 \cdot 2SbF_5$ have been described elsewhere.[4] The single crystals were grown by slow sublimation at 30° in dry N_2. In a dry N_2 glove box, they were transferred to Teflon FEP capillaries, which were subsequently sealed with high melting point Halocarbon wax. A powder X-ray diffraction photograph of crushed single crystals was identical with that of the polycrystalline material from which the single crystals were grown and for which the composition was established by quantitative synthesis.[4]

Crystallographic Data.—Oscillation, Weissenberg, and Buerger precession photographs were obtained with Zr-filtered Mo Kα (λ 0.7107 Å) radiation. These data showed that the crystals have monoclinic symmetry. From the systematic extinctions, $h0l$ with h odd and $0k0$ with k odd, the most probable space group was determined to be $P2_1/a$. The lattice constants, measured from Buerger precession photographs taken at 23°, are $a = 14.19 \pm 0.03$, $b = 14.50 \pm 0.03$, $c = 5.27 \pm 0.01$ Å, $\beta = 90.6 \pm 0.1°$, and $V = 1085$ Å^3. Assuming that the unit cell contains four empirical formula units $BrSb_2F_{15}$ of formula weight 608.4, the calculated density is 3.72 g cm^{-3}. The density of the crystals has not been measured, but the calculated volume per fluorine atom, 18.1 Å^3, is very nearly the value expected for approximately close-packed fluorine atoms.[1,10] For Mo Kα radiation the linear absorption coefficient of the crystals is 9.15 mm^{-1}.

Intensity Data.—The X-ray diffraction intensities were determined from Zr-filtered Mo Kα multiple-film equiinclination Weissenberg photographs by visual comparison with an intensity scale. The specimen was approximately $0.15 \times 0.2 \times 0.4$ mm in dimension with the longest direction nearly parallel to the capillary axis. The axis of rotation was the crystallographic a axis, because it was the axis most nearly aligned with the capillary axis. In each of the reciprocal lattice levels $h = 0$–13, intensities were measured in the range $(\sin \theta)/\lambda \leq 0.65$. A total of 892 independent reflections having intensities above background was measured. Omitted from the intensity measurements were several reflections cut off by the Weissenberg camera beam stop and six reflections too intense to be measured with the intensity scale employed. Within the range of the measurements, there were a large number of reflections too weak to be observed.

After the set of Weissenberg photographs was complete, the $h = 0$ level Weissenberg was repeated to verify that there had been no appreciable decomposition of the crystal. Later, however, the crystal did decompose, and, unfortunately, this happened before its precise shape and dimensions had been recorded; therefore, accurate absorption corrections were impossible, and none was made. We estimate that the errors in intensities caused by absorption are no greater than 8%.

The intensities were reduced to a set of relative structure amplitudes $|F_o(hkl)|$ by application of the appropriate Lorentz–polarization factors and extraction of the square roots.

Determination of the Structure

The four bromine, eight antimony, and sixty fluorine atoms per unit cell are all in the fourfold general positions of space group $P2_1/a$, the equivalent positions of which are $x, y, z;$ $-x, -y, -z;$ $^1/_2 + x, {}^1/_2 - y, z;$ $^1/_2 - x, {}^1/_2 + y, -z$. The asymmetric unit of the structure consists of one $BrSb_2F_{15}$ formula unit or eighteen atoms.

The arrangement of the atoms was deduced from the three-dimensional Patterson function and from the three-dimensional Fourier electron density function calculated with phases determined by the bromine and antimony contributions to the structure factors.

The positional parameters were refined by the method of least squares.[11] The function minimized was $\Sigma w(|F_o| - k_h|F_c|)^2$. A modification of the Hughes[12] weighting procedure was used: for $|F_o| > 100$, $w = 100/|F_o|^2$; for $100 \geq |F_o| > 25$, $w = 1/100$; for $|F_o| \leq 25$, $w = 1/625$. Separate scale factors k_h were used for each of the Weissenberg levels. Scattering factors were those for the neutral atoms given by Cromer and Waber.[13] The real parts of the anomalous dispersion corrections for bromine and antimony given by Cromer[14] were applied, but the imaginary parts were neglected.

The thermal parameters were kept isotropic until the agreement index $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ had decreased to about 0.20, after which the thermal parameters of the bromine and antimony atoms were allowed to become anisotropic. With anisotropic thermal parameters it was necessary to hold at least one scale factor constant; therefore, the scale factors for levels $h = 0$–2 were alternately held constant in successive least-squares cycles. Anisotropic thermal parameters of the fluorine atoms were not determined because of the large number of variable parameters this would entail.

The final values of the parameters are given in Table I. In the final refinement cycle, the largest parameter change was 18% of the estimated standard error in that parameter value and most were much smaller. After convergence, the agreement index R, defined above, was 0.14 for the 773 reflections having $|F_o|$ greater than σ ($=w^{-1/2}$). Including the 119 reflections having $|F_o|$ observable but less than σ, the index R was 0.15. For the full set of 892 data, the weighted agreement index R_w was 0.17, and the standard deviation of an observation of unit weight SIG1 was 1.2. Table II compares the $|F_o|$ values with the F_c calculated from the final parameter values.[15] F_c's were calculated for the reflections too weak to be observed and were found to be satisfactorily small.

TABLE I

POSITIONAL AND THERMAL PARAMETERS AND THEIR ESTIMATED STANDARD ERRORS[a]

	10^4x ($10^4\sigma_x$)	10^4y ($10^4\sigma_y$)	10^4z ($10^4\sigma_z$)	B (σ_B), Å^2
Br	219 (4)	1478 (5)	3015 (10)	2.85[b]
Sb(1)	1510 (4)	6492 (5)	932 (7)	4.29[b]
Sb(2)	3149 (4)	8532 (3)	3945 (9)	3.30[b]
F(1)	997 (30)	613 (28)	4069 (63)	5.06 (1.05)
F(2)	4293 (33)	674 (30)	47 (65)	5.50 (1.14)
F(3)	2837 (34)	1482 (37)	1562 (66)	6.55 (1.22)
F(4)	4191 (31)	2414 (26)	654 (54)	4.70 (1.01)
F(5)	1171 (23)	2525 (19)	4841 (49)	3.21 (0.74)
F(6)	2706 (27)	3450 (26)	3530 (51)	4.15 (0.88)
F(7)	997 (44)	4405 (41)	4796 (92)	7.89 (1.69)
F(8)	4435 (22)	4285 (18)	1386 (43)	2.81 (0.70)
F(9)	2245 (33)	5733 (28)	2641 (68)	5.73 (1.19)
F(10)	806 (53)	6322 (52)	3657 (99)	9.42 (2.17)
F(11)	4049 (34)	6454 (38)	4 (75)	6.55 (1.24)
F(12)	2355 (33)	7615 (27)	2330 (62)	5.07 (1.18)
F(13)	541 (33)	8389 (29)	4292 (62)	5.47 (1.17)
F(14)	3988 (36)	8298 (29)	959 (67)	6.13 (1.36)
F(15)	2480 (26)	9409 (24)	1989 (54)	3.99 (0.85)

	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Br	33 (8)	20 (2)	535 (23)	−1 (3)	−42 (6)	−2 (10)
Sb(1)	78 (9)	38 (2)	366 (13)	−2 (3)	−24 (5)	−3 (7)
Sb(2)	32 (8)	25 (2)	655 (16)	4 (4)	39 (4)	−3 (9)

[a] The β_{ij} are for the expression $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] The isotropic thermal parameters were calculated as $B = 4[V^2 \det(\beta_{ij})]^{1/3}$.

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[15] Table II will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

TABLE III

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (DEG)[a]

		(a) Br Environment			
Br–F(1)	1.76 ± 0.12	F(1)–F(8)	2.62 ± 0.15	F(1)–Br–F(8)	95.5 ± 5.0
Br–F(8)	1.78 ± 0.09	F(1)–F(13)	2.76 ± 0.18	F(1)–Br–F(13)	101.9 ± 5.5
Br–F(13)	1.80 ± 0.12	F(1)–F(11)	2.47 ± 0.17	F(1)–Br–F(11)	84.6 ± 5.9
Br–F(11)	1.91 ± 0.13	F(8)–F(13)	2.62 ± 0.12	F(8)–Br–F(13)	94.0 ± 4.9
Av	1.81	F(8)–F(11)	2.52 ± 0.17	F(8)–Br–F(11)	85.9 ± 5.3
		F(1)–F(5)	2.81 ± 0.14	F(1)–Br–F(5)	88.5 ± 4.5
Br–F(5)	2.24 ± 0.10	Av	2.60	Av	92.4
Br–F(4)	2.49 ± 0.11				
		F(8)–F(4)	2.76 ± 0.14	F(8)–Br–F(4)	78.5 ± 3.9
		F(13)–F(5)	2.81 ± 0.17	F(13)–Br–F(5)	87.3 ± 4.7
		F(13)–F(4)	3.04 ± 0.14	F(13)–Br–F(4)	88.4 ± 4.8
F(1)–Br–F(4)	168.5 ± 4.2	F(11)–F(5)	3.00 ± 0.16	F(11)–Br–F(5)	92.2 ± 5.1
F(8)–Br–F(5)	175.4 ± 3.5	F(11)–F(4)	3.01 ± 0.20	F(11)–Br–F(4)	85.2 ± 5.3
F(11)–Br–F(13)	173.5 ± 6.1	F(5)–F(4)	3.56 ± 0.14	F(5)–Br–F(4)	97.2 ± 3.7
				Av	88.2
		(b) Sb(1) Environment			
Sb(1)–F(3)	1.62 ± 0.12	F(3)–F(2)	2.51 ± 0.20	F(3)–Sb(1)–F(2)	97.7 ± 6.6
Sb(1)–F(2)	1.72 ± 0.14	F(3)–F(9)	2.47 ± 0.16	F(3)–Sb(1)–F(9)	93.9 ± 6.5
Sb(1)–F(9)	1.76 ± 0.13	F(3)–F(4)	2.40 ± 0.19	F(3)–Sb(1)–F(4)	87.1 ± 6.2
Sb(1)–F(10)	1.77 ± 0.18	F(3)–F(12)	2.64 ± 0.16	F(3)–Sb(1)–F(12)	87.9 ± 6.2
Sb(1)–F(4)	1.86 ± 0.11	F(2)–F(9)	2.59 ± 0.20	F(2)–Sb(1)–F(9)	96.3 ± 6.5
Sb(1)–F(12)	2.15 ± 0.12	F(2)–F(10)	2.17 ± 0.22	F(2)–Sb(1)–F(10)	76.8 ± 8.1
Av	1.81	F(2)–F(4)	2.55 ± 0.16	F(2)–Sb(1)–F(4)	90.7 ± 5.5
		F(9)–F(10)	2.28 ± 0.25	F(9)–Sb(1)–F(10)	80.5 ± 8.0
		F(9)–F(12)	2.74 ± 0.18	F(9)–Sb(1)–F(12)	88.4 ± 5.4
F(2)–Sb(1)–F(12)	172.4 ± 6.1	F(10)–F(4)	2.77 ± 0.20	F(10)–Sb(1)–F(4)	99.2 ± 7.8
F(3)–Sb(1)–F(10)	171.5 ± 10.2	F(10)–F(12)	2.98 ± 0.25	F(10)–Sb(1)–F(12)	98.3 ± 7.7
F(9)–Sb(1)–F(4)	172.7 ± 5.8	F(4)–F(12)	2.70 ± 0.20	F(4)–Sb(1)–F(12)	84.5 ± 6.3
		Av	2.57	Av	90.1
		(c) Sb(2) Environment			
Sb(2)–F(6)	1.81 ± 0.10	F(6)–F(5)	2.65 ± 0.14	F(6)–Sb(2)–F(5)	92.5 ± 4.3
Sb(2)–F(5)	1.86 ± 0.09	F(6)–F(7)	2.88 ± 0.22	F(6)–Sb(2)–F(7)	102.7 ± 6.0
Sb(2)–F(7)	1.87 ± 0.18	F(6)–F(15)	2.76 ± 0.13	F(6)–Sb(2)–F(15)	96.3 ± 4.8
Sb(2)–F(15)	1.89 ± 0.10	F(6)–F(12)	2.50 ± 0.13	F(6)–Sb(2)–F(12)	83.5 ± 4.7
Sb(2)–F(12)	1.94 ± 0.12	F(5)–F(7)	2.74 ± 0.18	F(5)–Sb(2)–F(7)	94.4 ± 5.9
Sb(2)–F(14)	2.01 ± 0.13	F(5)–F(12)	2.56 ± 0.17	F(5)–Sb(2)–F(12)	84.8 ± 5.1
Av	1.90	F(5)–F(14)	2.49 ± 0.13	F(5)–Sb(2)–F(14)	80.1 ± 4.5
		F(7)–F(15)	2.73 ± 0.18	F(7)–Sb(2)–F(15)	93.3 ± 5.8
		F(7)–F(14)	2.75 ± 0.20	F(7)–Sb(2)–F(14)	90.3 ± 6.4
F(5)–Sb(2)–F(15)	166.7 [illegible] 4.0	F(15)–F(12)	2.61 ± 0.14	F(15)–Sb(2)–F(12)	86.3 ± 4.4
F(6)–Sb(2)–F(14)	165.6 ± 5.2	F(15)–F(14)	2.74 ± 0.18	F(15)–Sb(2)–F(14)	89.1 ± 4.9
F(7)–Sb(2)–F(12)	173.8 ± 6.3	F(12)–F(14)	2.63 ± 0.19	F(12)–Sb(2)–F(14)	83.5 ± 5.2
		Av	2.67	Av	89.7
		(d) Bridge Bond Angles			
Br–F(4)–Sb(1)	174.1 ± 6.4	Br–F(5)–Sb(2)	170.8 ± 5.0	Sb(1)–F(12)–Sb(2)	173.0 ± 6.4
		(e) Nonbonded Intrachain Distances			
F(1)–F(9)	3.03 ± 0.16	F(2)–F(7)	3.47 ± 0.20	F(8)–F(15)	3.24 ± 0.14

[a] The limits of error are 3 times the computed estimated standard errors.

Discussion of the Structure

Our results show that the crystals consist of infinite chains of discrete BrF_4^+ and $Sb_2F_{11}^-$ ions coupled by relatively weak fluorine bridges. Accordingly the compound should be formulated as $[BrF_4^+][Sb_2F_{11}^-]$. This conclusion is based on the interatomic distances[16] in the structure, which are given in Figure 1 and Table III. The two fluorine atoms F(4) and F(5) involved in the Sb-F---Br bridges are bonded strongly to the antimony atoms and only weakly to the bromine atoms. The Sb(1)-F(4) and Sb(2)-F(5) distances are both equal to the average Sb-F bond distance in this structure, 1.86 Å. The Br---F(4) and Br---F(5) distances, 2.49 and 2.24 Å, are very long and indicative of rela-

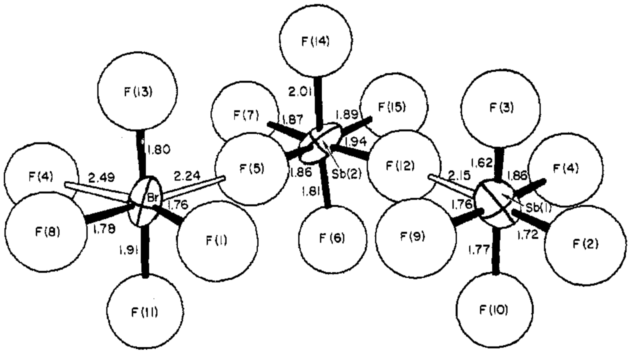

Figure 1.—View in perspective of a segment of the chain structure of $[BrF_4^+][Sb_2F_{11}^-]$ crystals (prepared by the computer program of C. K. Johnston, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965).

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[16] Computed with the program of W. R. Busing, K. O. Martin, and H. A. Levy, Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

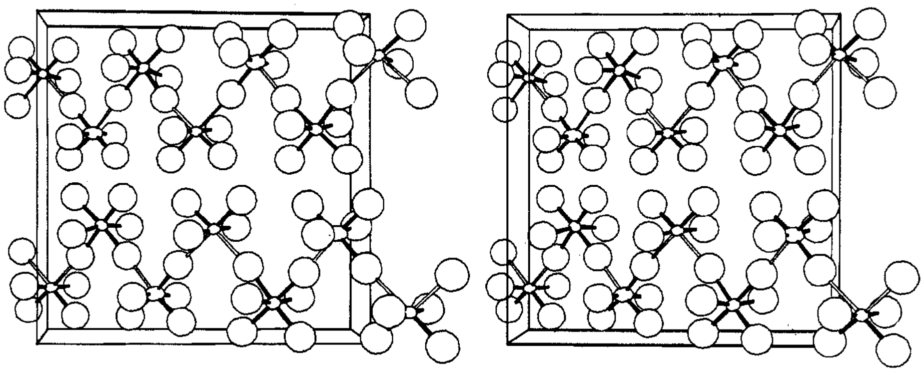

Figure 2.—Stereoscopic view to show the packing arrangement in $[BrF_4^+][Sb_2F_{11}^-]$ crystals (prepared by the computer program of C. K. Johnston, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965). The viewing direction is normal to the 001 planes.

tively weak bonding compared with the other four Br–F bond distances, which average 1.81 Å; this difference is substantially greater than the limits of error in the distances, which are given in Table III. The results rule out the alternative possibility of an essentially covalent structure with strong fluorine bridges.

The bromine atom has four strongly bonded fluorine ligands, F(1), F(8), F(11), and F(13). Including the free electron pair on the bromine atom, the BrF_4^+ structure might be described as a distorted trigonal bipyramid with F(1), F(8), and the free pair occupying the three equatorial positions. Part of the cause for the distortion from an ideal trigonal bipyramid appears to be the presence of the two additional, more remote fluorine ligands, F(4) and F(5), which belong to two neighboring $Sb_2F_{11}^-$ groups. This results in a coordination number of 7 for the bromine atom. For this coordination number, the most likely structures are either a puckered pentagonal bipyramid or an octahedron distorted by having the seventh ligand (the free electron pair) above one of the triangular octahedral faces. As can be seen from Figures 1 and 2 and Table III, the face is that formed by F(4), F(5), and F(11). This results in F(11) being bent toward F(1) and F(8). The free electron pair of the bromine atom is probably not directed at the center of the octahedral face but is probably much closer to the F(4)–F(5) edge because of its greater distance from the bromine atom; thus, the coordination polyhedron approaches a puckered pentagonal bipyramid. This pseudoheptacoordinate structure of BrF_4^+ closely resembles that found by Edwards and Jones[17] for SeF_3^+ in $[SeF_3^+][Nb_2F_{11}^-]$.

The geometry found for BrF_4^+ is in good agreement with that reported for the isoelectronic SeF_4.[18] Gaseous SeF_4 has bond angles of 169 and 100° for the axial and equatorial bonds, respectively, compared to 173 and 96° for BrF_4^+. The deviation of the bond angles of SeF_4 from those of an ideal trigonal bipyramid is due to the nonbonded electron pair being more diffuse than the bonded one, causing an increased repulsion. The equatorial and axial bonds of BrF_4^+ and SeF_4 show a similar difference in average length (0.085 *vs.* 0.089 Å, respectively), although the experimental BrF_4^+ values are statistically rather insignificant because of the relatively large error limits. As expected, the bond distances in BrF_4^+ are somewhat smaller than those found[3] for the BrF_4^- anion, 1.89 Å.

The $Sb_2F_{11}^-$ ion has the expected fluorine-bridged structure in which each antimony atom is surrounded by an irregular octahedral array of fluorine atoms with one fluorine atom shared by the two antimony atoms. However, the structure of the $Sb_2F_{11}^-$ ion reported here differs somewhat from that reported previously for this ion.[2] The essential difference is the pronounced asymmetry of the Sb---F–Sb bridge in the present case. The Sb(1)---F(12) distance of 2.15 Å indicates a relatively weak bond compared with the other Sb–F bonds in the structure; the difference is well outside the limits of error in the distances. Consistent with the long Sb(1)---F(12) distance, the other Sb(1)–F distances, on the average, are considerably shorter than the Sb(2)–F distances; the former average 1.75 Å, while the latter average 1.90 Å. For comparison, in $[XeF^+][Sb_2F_{11}^-]$ the two Sb–F bridge bonds were found to differ by less than twice the estimated standard error, and the average Sb–F bond distances of the two antimony atoms were found to be very nearly the same.[2] Our results suggest that the $Sb_2F_{11}^-$ ion consists of an SbF_6^- ion and an SbF_5 molecule coupled by a moderately strong fluorine bridge. This view is also supported by the finding[19] that, with excess of SbF_5, SbF_6^- forms not only $Sb_2F_{11}^-$ but also higher polymeric anions $[Sb_nF_{5n+1}^-]$ and that the additional SbF_5 molecules can be removed stepwise by controlled pyrolysis.[20]

The fluorine bridges which couple the BrF_4^+ and $Sb_2F_{11}^-$ ions are formed by cis fluorine atoms F(4), F(5), and F(12). Neglecting the differences in bond distances described above, the cis-fluorine-bridged chain structure of $[BrF_4^+][Sb_2F_{11}^-]$ crystals resembles that proposed[19,21] for liquid SbF_5 and for $[Sb_nF_{5n+1}^-]$ ions in solutions. The nature of the fluorine bridges in the $[BrF_4^+][Sb_2F_{11}^-]$ crystals appears to be very similar to that described for $[BrF_2^+][SbF_6^-]$ crystals, which were found to consist of infinite chains of discrete BrF_2^+ and SbF_6^- ions coupled by weak cis fluorine bridges.[1] In $[BrF_4^+][Sb_2F_{11}^-]$ the Br---F–Sb and Sb---F–Sb bond angles are considerably nearer 180° than are the analogous bridge bond angles in $[BrF_2^+][SbF_6^-]$ and

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$[XeF^+][Sb_2F_{11}^-]$. In $[BrF_4^+][Sb_2F_{11}^-]$ the atoms Br, Sb(1), Sb(2), F(1), F(2), F(4), F(5), F(7), F(8), F(9), F(12), and F(15) are all within 0.3 Å of being coplanar; their common plane is very nearly parallel to the 201 planes. This near coplanarity extends the whole length of any given chain. The planes of adjacent chains (see Figure 2) are parallel but are spaced *c*/2 or *c* apart along the *c* direction. The closest approaches of fluorine atoms bonded to different bromine and antimony atoms within the chains are 3.03, 3.24, and 3.47 Å, all of which are substantially greater than twice the van der Waals radius of fluorine.

The chains are approximately close packed. There is no bridging between chains. The minimum interchain F---F separation is 2.72 Å, which is approximately twice the van der Waals radius of fluorine. The minimum interchain Br---F and Sb---F distance is 3.56 Å, which is approximately the value expected for the sums of the van der Waals radii of the atom pairs.

In summary, this is the first direct evidence for the existence of the BrF_4^+ cation. Although the present experimental data do not allow very precise determinations of bond lengths and angles, valuable information about the structure of this interesting adduct was obtained.

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The Crystal and Molecular Structure of the Tetranuclear Metal Cluster Complex Copper(I) *O,O'*-Diisopropylphosphorodithioate, $Cu_4[(i\text{-}C_3H_7O)_2PS_2]_4$

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Copper(I) *O,O'*-diisopropylphosphorodithioate, $Cu_4[(i\text{-}C_3H_7O)_2PS_2]_4$, crystallizes as light yellow prisms in the orthorhombic space group $P2_12_12_1$ with unit cell parameters $a = 11.283 \pm 0.006$, $b = 12.380 \pm 0.004$, and $c = 33.825 \pm 0.008$ Å. The observed and calculated densities are 1.55 ± 0.02 and 1.556 ± 0.002 g/cm³ (for $Z = 4$ molecules/unit cell), respectively. A full-matrix anisotropic–isotropic least squares refinement has resulted in a discrepancy index of 0.072 using three-dimensional X-ray diffraction counter data. The crystal structure is comprised of discrete tetrameric molecules, each containing a central tetrahedron of copper atoms. Chelated to this tetrahedron through sulfur atoms are four $(C_3H_7O)_2PS_2$ ligands, so arranged as to give the molecule a symmetry approaching S_4. One of the sulfur atoms in each ligand bridges two copper atoms almost symmetrically with average distances of 2.256 (9) and 2.272 (16) Å; the other forms a bond with a third copper atom at a distance of 2.272 (9) Å. Each phosphorus atom is thus centered more or less above a face of the copper tetrahedron. Of the six edges of the tetrahedron (the Cu-Cu bonds), the four which are bridged by sulfur average 2.74 (3) Å; the other two edges average 2.950 (6) Å. The two sulfurs in each ligand play different roles in the chelation and this difference is reflected in the lengths of the P–S bonds. Those associated with the Cu–S–Cu bridges average 2.036 (11) Å in length; those bonded to a single Cu are shorter, at 1.972 (8) Å. The average P–O bond length is 1.56 (2) Å, a value entirely comparable to those in previously determined metal phosphorodithioates.

Introduction

Structural investigations of organocopper(I) complexes have shown that the cuprous ion generally adopts a tetrahedral configuration. Recently, compounds containing clusters of four or more copper atoms, entailing coordination numbers greater than 4, have also been reported. These include the copper tetramer, hexamer, and octamer. The tetrameric compounds, *e.g.*, $Cu_4I_4[As(C_2H_5)_3]_4$[1] and $Cu_4[S_2CN(C_2H_5)]_4$[2] display a central tetrahedral configuration of copper atoms. The hexamer, *e.g.*, $Cu_6[SOCN(C_3H_7)_2]_6$,[3] and octamer, *e.g.*, the phenyltrimethylammonium salt of $Cu_8[S_2CC(CN)_2]_6^{4-}$,[4] exhibit a central octahedral and cubic cluster, respectively. Syntheses and characterizations of other copper clusters have also been reported.[5]

As part of a continuing investigation of metal phosphorodithioate complexes, the crystal structure of $Cu_4(dtp)_4$, where dtp = $S_2P(OC_3H_7)_2$, was undertaken. Initial evidence of a tetranuclear copper cluster in $Cu_4(dtp)_4$ was based on vapor pressure osmometry data[6] for benzene solutions at 37°. The present study examines the stereochemistry of this metal cluster complex in the crystalline form and the influence of the dtp ligand on the copper–copper interactions.

Experimental Section

Preparation.—Copper(I) *O,O'*-diisopropylphosphorodithioate was synthesized according to a method previously described.[7] Brittle, light yellow prismatic crystals for use in the X-ray investigation were obtained by recrystallization of the compound from a warm ethanol–acetone mixture.

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