TABLE VI

INTERMOLECULAR CONTACTS, TO 3.0 Å[a]

Atom 1	Atom 2	Transformation	Dist, Å
H(15)	H(3)	$-x + 1, y - 1/2, -z + 1/2$	2.47
H(16′)	H(5)	$-x + 3/2, y - 1/2, z$	2.49
H(16)	H(3)	$-x + 1, y - 1/2, -z + 1/2$	2.55
H(19)	H(9)	$-x + 3/2, y - 1/2, z$	2.59
H(20)	H(12)	$-x + 1, -y + 1, -z$	2.60
H(19)	Me(1)	$x + 1, y, z$	2.63
H(20′)	H(9)	$-x + 3/2, y - 1/2, z$	2.64
H(13)	H(8)	$-x + 1/2, y - 1/2, z$	2.71
H(20)	H(11)	$-x + 1, -y + 1, -z$	2.74
H(16′)	H(4)	$-x + 3/2, y - 1/2, z$	2.75
H(15′)	H(5)	$-x + 3/2, y - 1/2, z$	2.76
H(3)	H(4)	$x - 1/2, y, -z + 1/2$	2.79
H(12)	H(12)	$-x + 1, -y + 1, -z$	2.79
H(13)	H(11)	$-x + 1, -y + 1, -z$	2.87
H(20)	C(12)	$-x + 1, -y + 1, -z$	2.88
H(20)	C(11)	$-x + 1, -y + 1, -z$	2.91
H(20)	H(10)	$-x + 3/2, y - 1/2, z$	2.94
H(20′)	H(10)	$-x + 3/2, y - 1/2, z$	2.99

[a] Note that hydrogen atoms of methyl groups have not been included in this computation.

Å for H(15)···H(3) $[-x + 1, y - 1/2, -z + 1/2]$ and carbon···hydrogen = 2.63 Å for H(19)···Me(1) $[x + 1, y, z]$.

Discussion

The present X-ray structural analysis confirms the ground-state stereochemistry of $(C_8H_{12})[(C_6H_5)(CH_3)_2P]_2Ir(CH_3)$ as originally assigned by Shapley and Osborn.[7] On cooling solutions of this complex, the limiting low-temperature ^1H nmr spectrum is first observed at 0°. The coalescence of the cycloocta-1,5-diene vinylic resonances and of the methylenic signals (and other spectral characteristics) observed upon warming the solution can be explained in terms of a series of pseudorotations using the P(1)–Ir, P(2)–Ir, and Me(1)–Ir bonds as pivots (*cf.* scheme 1 of Figure 2 in ref 7).[33] These pseudorotations involve, *inter alia,* the transit of a phosphine ligand into an axial position. Thus, the value of the P–Ir–P angle is an important consideration in the pseudorotation of these pentacoordinate species. It is thus comforting to note that the P–Ir–P angle in (C_8H_{12})(diphos)$Ir(CH_3)$, a species which exhibits fluxional behavior at temperatures as low as −60°, has the extremely low value of ∼85°.[11,34] Furthermore, the equatorial P–Ir–P and P–Ir–A angles are the only angles about iridium that show drastic changes in going from $(C_8H_{12})[(C_6H_5)(CH_3)_2P]_2Ir(CH_3)$ to (C_8H_{12})(diphos)$Ir(CH_3)$.

Subsequent papers in this series will report the crystal structures of further molecules in this class, with particular attention being paid to correlations between fluxional behavior and geometry within the metal coordination sphere.

Acknowledgments.—We thank Professor J. A. Osborn and Dr. J. R. Shapley for providing the sample and for lengthy discussions. S. A. B. gratefully acknowledges the receipt of a National Science Foundation predoctoral fellowship. This research was generously supported by the National Science Foundation (Grant No. GP-26293, to M. R. C.).

(33) Note the pseudorotation is not the only mechanism that explains the detailed features of the temperature-dependent ^1H nmr spectrum of the complex under discussion (*cf.* ref 7). It is, however, the most *probable* mechanism.

(34) The crystal structure of (C_8H_{12})(diphos)$Ir(CH_3)$ has been undertaken. Details will be reported at a later date.

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Molecular Bromine Bridging of $Sb^{III}{}_2Br_9{}^{3-}$ Anions and the Crystal Structure of Tetramethylammonium Nonabromodiantimonate(III)–Dibromine

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Received February 22, 1972

Tetramethylammonium nonabromodiantimonate(III)–dibromine, $[(CH_3)_4N]_3Sb_2Br_9 \cdot Br_2$, crystallizes in space group $P6_3/mmc$ with $a = 9.585$ (5) Å, $c = 22.667$ (3) Å, and $Z = 2$. The observed and calculated densities are 2.55 and 2.48 g/cm³. The 289 independent reflections, significantly above background, were measured on a four-circle diffractometer equipped with a scintillation counter and were used for anisotropic, full-matrix least-squares refinement of the heavy-atom parameters to a conventional $R = 0.137$. The structure contains $Sb_2Br_9{}^{3-}$ anions bridged by Br_2 molecules. The cations as well as the Br_2 molecules are disordered. Only one-third of the terminal bromines are bridged. The $Sb^{III}{}_2Br_9$ moiety consists of two $SbBr_6$ octahedra sharing a face. The Br–Sb–Br···Br–Br···Br–Sb–Br chain is nearly linear. The Br···Br_2 distance is 2.89 (1) Å, which is indicative of important bridging interactions.

Introduction

The crystal structure of tetramethylammonium nonabromodiantimonate(III)–dibromine, $[(CH_3)_4N]_3Sb_2Br_{11}$, was undertaken as part of a series of structure investigations of halo-coordinated antimony compounds.[1−10] Numerous intensely colored compounds of the type $R_xSb_yBr_z$, where R is an aliphatic amine,

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(6) S. L. Lawton, R. A. Jacobson, and R. S. Frye, *Inorg. Chem.,* **10**, 701 (1971).

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(8) J. R. Clark, R. A. Jacobson, and R. G. Baughman, to be submitted for publication.

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aromatic amine, alkali metal, or ammonium cation, have been widely studied since 1901 when Rosenheim and Stellman[11] reported the preparation of $(C_5H_5NH)_2SbBr_7$. The wide variety of related compounds[12] includes $RSbBr_4$, $RSbBr_6$, $RSbBr_7$, R_2SbBr_5, R_2SbBr_6, R_2SbBr_7, R_2SbBr_8, R_2SbBr_9, R_3SbBr_6, $R_2Sb_2Br_7$, $R_3Sb_2Br_{11}$, $R_3Sb_2Br_{12}$, $R_3Sb_2Br_{15}$, $R_2Sb_3Br_{11}$, $R_5Sb_3Br_{14}$, $R_7Sb_3Br_{16}$, and $R\cdot SbBr_3\cdot 3HBr$. The intense dark color common to many $R_xSb_yBr_z$ compounds has been attributed[13] to charge transfer between mixed oxidation states of antimony or to some other charge-transfer phenomena.

In this laboratory a series of structural investigations of antimony halide complexes have been performed to investigate the wide variety of complexes attainable in the solid state by merely varying the cation used and to obtain, if possible, a general description of antimony halide bonding. The role of the lone pair of electrons on antimony(III) and the charge-transfer path in these compounds are also of interest.

The structure determination of a red tetramethylammonium salt was undertaken as a result of preliminary investigations of several intensely colored $R_xSb_yBr_z$ complexes. Two $(CH_3)_4N^+$ salts exist: a black salt which decomposes when exposed to X-rays and a very stable[5] red salt. The stoichiometry of the red form was reported[14] to be $R_3Sb_2Br_{11}$.

Experimental Section

Crystal Data.—Tetramethylammonium nonabromodiantimonate(III)–dibromine, $[(CH_3)_4N]_3Sb_2Br_9\cdot Br_2$, mol wt 1345, crystals are hexagonal of space group $P6_3/mmc$, with $Z = 2$, $a = b = 9.5850$ (5) Å, $c = 22.6667$ (26) Å, temperature ~24°, $d_{\text{measd}} = 2.55$ g/cm³, $d_{\text{calcd}} = 2.48$ g/cm³, Mo Kα (λ 0.7107 Å), and $\mu = 148.6$ cm^{-1}.

The clear red $[(CH_3)_4N]_3Sb_2Br_{11}$ crystals were prepared by the method of Hackert, *et al.*[5] Microscopic examination revealed the sixfold symmetry of the crystals which grew as hexagonal plates with sharply defined faces. As the crystals were found to be air stable, they were mounted on glass fibers. The preliminary Weissenberg and precession photographs exhibited 6/*mmm* Laue symmetry. The following systematic absence was observed: $hh\overline{2h}l$ when $l = 2n + 1$. The Laue symmetry and systematic absence are consistent with the space groups $P6_3/mmc$, $P\bar{6}2c$, and $P6_3mc$. The diffraction pattern was quite weak and numerous reflections were accidentally absent. Four-day precession photographs did not reveal any previously unobserved systematically weak reflections relating to a pseudocell as was found in $Rb_4Sb^{III}Sb^{V}Br_{12}$.[2]

The unit cell parameters and their standard deviations were obtained by a least-squares fit[15] to 13 independent reflection angles whose $+2\theta$ and -2θ centers were determined by a left-right, top–bottom beam splitter technique using a previously aligned Hilger-Watts automated four-circle diffractometer (Mo Kα radiation, λ 0.71069 Å). The calculated density of 2.48 g/cm³ for two molecules per unit cell agrees well with the observed density of 2.55 ± 0.1 g/cm³ which was determined by flotation techniques. To obtain adequate counting statistics, a crystal having approximate dimensions 0.19 × 0.16 × 0.11 mm along the *a*, *b*, and *c* axes, respectively, was used for data collection. Data were collected at room temperature utilizing the Hilger-Watts diffractometer equipped with scintillation counter and employing Zr-filtered Mo Kα radiation. All data within the *hkl* "octant" were recorded within a 2θ sphere of 50°. As nearly all intensities from 40 to 50° 2θ were found to be at background level, $\bar{h}\bar{k}\bar{l}$ and $h\bar{k}l$ equivalent data were recorded within the 2θ sphere of 40°. A total of 2748 reflections were measured using the θ–2θ scan technique with a takeoff angle of 4.5°. Symmetric scans ranged in width from 1.0° in 2θ at low 2θ to 2.0° at large 2θ. The stepping rate was 0.4096 sec/step of 0.02° in 2θ. Stationary-crystal, stationary-counter background counts were measured at each end of the scan for half the time of the scan. Three standard reflections were observed periodically, and these observations indicated that no decomposition occurred during data collection.

The intensity data were corrected for Lorentz–polarization effects and for absorption ($\mu = 148.6$ cm^{-1}). The absorption correction[16] was calculated using ABCOR; the maximum and minimum transmission factors were 0.227 and 0.123, respectively. The estimated error in each intensity was calculated by

$$\sigma_I^2 = [C_T + C_B + (0.03C_T)^2 + (0.05C_B)^2 + (0.10C_I)^2]/A$$

where C_T, C_B, C_I, and A are the total count, background count, net count, and transmission factor, respectively. The quantities 0.03, 0.05, and 0.10 represent estimates for nonstatistical errors in the total count, background count, and absorption correction, respectively. The estimated standard deviation σ_F for each structure factor was calculated using the method of finite differences.[17]

No significant differences could be found between Friedel related pairs of observed structure factors; the lack of apparent anomalous dispersion effects indicates that the space group is probably centric. The equivalent data were then averaged. The estimated standard deviation $\bar{\sigma}_F$ in each averaged structure factor was taken as the root mean square of the individual σ_F's. Of the total 720 independent reflections ($h \geq k \geq 0$) only 286 reflections were considered observed ($\geq 3\bar{\sigma}_F$). The overall internal agreement, $R_F = 0.086$,[18] was not unexpectedly high since there was a large fraction of unobserved reflections. The 286 observed data were used in the least-squares refinement with the reciprocals of $\bar{\sigma}_F^2$ used as weights.

Solution and Refinement of Structure

A Patterson map was computed by a Fourier program written by the author specifically for the hexagonal symmetry. Analysis of the heavy-atom vectors in this map indicated the presence of a center of symmetry, and hence the space group was assumed to be $P6_3/mmc$. An equivalent result was also obtained by a statistical test[19] and was confirmed by successful refinement in this space group. (Attempted refinement in space groups $P6_3mc$ and $P\bar{6}2c$ revealed unusual coupling of thermal and positional parameters.) The Patterson map clearly revealed the Sb_2Br_9 moiety. The two remaining bromine atoms could not be located; however, there was a set of six unique peaks with peak heights corresponding to $^1/_3$(Br–Br) vectors. A structure factor and difference electron density map calculation clearly indicated the presence of a threefold disordered bromine molecule. All heavy-atom positions and isotropic temperature factors were then refined by full-matrix least-squares techniques to a conventional discrepancy factor of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.197$ and a weighted R factor of $wR = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2\}^{1/2} = 0.213$. A difference electron density map indicated appreciable anisotropic thermal motion and diffuse peaks attributable to disordered tetramethylammonium cations. Anisotropic refinement of the heavy atoms lowered R to 0.167 and wR to 0.186. Throughout the refinement the scattering factors for Sb^{3+}, Br^-, C, and N reported by Cromer and Waber[20] were used. Both Sb and Br were modified for the real and imaginary parts of anomalous dispersion.[21] The disordered cations were located by repeated difference map calculations.

The two symmetry-independent cations exhibit site disorder as well as considerable thermal motion. Although the cation

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[14] W. Petzold, *Z. Anorg. Allg. Chem.*, **215**, 92 (1933).

[15] In addition to local programs written at this laboratory, the authors wish to acknowledge the use of ABCOR (Busing and Levy), ORTEP (C. K. Johnson), ORFFE (Busing, Martin, and Levy), a local modification of ORFLS (Busing, Martin, and Levy), and LCR2 (D. E. Williams).

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[17] D. E. Williams and R. E. Rundle, *J. Amer. Chem. Soc.*, **86**, 1660 (1964).

[18] $R_F = \Sigma_{i=1}{}^{720}\Sigma_{j=1}{}^{NE_i}[(|F_{ij} - \bar{F}_i|)^2/\bar{\sigma}_{F_i}{}^2]/[\Sigma_i NE_i\bar{F}_i{}^2/\bar{\sigma}_{F_i}{}^2]$ where NE_i is the number of equivalent data of independent reflection *i*.

[19] E. R. Howles, D. C. Phillips, and D. Rogers, *Acta Crystallogr.*, **3**, 210 (1950).

[20] D. T. Cromer and J. T. Waber, *ibid.*, **18**, 104 (1965).

[21] D. H. Templeton, "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, pp 215, 216, Table 3.3.2C.

TABLE I

CATION PARAMETERS

Cation	Atom[a]	Occupancy	x	y	z	B, Å^2
1[b]	N	$^1/_4$	0.0	0.0	0.237	6.0
	C(1)	$^1/_4$	0.0	0.0	0.170	10.0
	C(3)	$^1/_4$	0.172	0.156	0.25	5.0
2[b]	N	$^1/_4$	0.0	0.0	0.258	5.0
	C(1)	$^1/_4$	0.0	0.0	0.190	10.0
	C(3)	$^1/_4$	0.088	0.176	0.281	7.0
3–4	N	1	$^1/_3$	$^2/_3$	−0.086	10.0
	C(1)	1	$^1/_3$	$^2/_3$	−0.154	10.0
	C(3)	$^1/_2$	0.25	0.50	−0.059	7.0
	C(3)	$^1/_2$	0.424	0.848	−0.063	7.0

[a] N and C(1) lie on the 6_3 axis (cations 1 and 2) or the $\bar{6}$ axis (cation 3 and 4). The remaining three carbons of the cation are related to C(3). [b] Cations 1 and 2 exhibit further disorder due to the mirrors at $z = {}^1/_4$ and $^3/_4$.

models given in Table I were determined through difference map calculations, they could not be satisfactorily refined by least-squares techniques. The models were constrained to represent closely NC_4 tetrahedra with C–N distances ~1.54 Å. The thermal parameters were selected to best fit the electron density map. Inclusion of the cations lowered R to 0.137 and wR to 0.125.

The final difference map revealed no peaks higher than 1.8 e/Å^3. However, diffuse peaks of ~1 e/Å^3 could be seen in proximity to the cations indicating that the cation model only approximately represented the true disorder. The authors feel that further efforts to represent the cation disorder are not warranted. In the last cycle of refinement the largest shift in any parameter was less than 0.01 times its own esd. The final heavy-atom parameters are given in Table II, along with their estimated standard deviations as derived from the inverse matrix.[22] The computer drawings shown throughout the following text were made using ORTEP. Distances, angles, and their standard deviations were calculated by ORFFE using the variance–covariance matrix from the final least-squares cycle.

TABLE II

HEAVY-ATOM POSITIONAL AND THERMAL[a] PARAMETERS AND THEIR STANDARD ERRORS[b] FOR $[(CH_3)_4N]_3Sb_2Br_9 \cdot Br_2$

Atom	Notation	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br^m	12k	0.0573 (9)	$2x$	0.0287 (7)	0.030 (3)	0.021 (3)	0.0042 (6)	$^1/_2\beta_{22}$	$^1/_2\beta_{23}$	−0.001 (1)
Br^t	12k	0.2020 (4)	$2x$	0.0996 (3)	0.033 (1)	0.027 (2)	0.0066 (3)	$^1/_2\beta_{22}$	$^1/_2\beta_{23}$	−0.0033 (5)
Br^b	6h	0.4741 (5)	$2x$	$^1/_4$	0.031 (2)	0.021 (2)	0.0057 (3)	$^1/_2\beta_{22}$	0	0
Sb	4f	$^1/_3$	$^2/_3$	0.1641 (3)	0.0205 (9)	β_{11}	0.0049 (2)	$^1/_2\beta_{22}$	0	0

[a] The form of the anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Estimated standard deviations are given in parentheses for the least significant figures.

Description of the Structure

The unit cell contains two $Sb^{III}{}_2Br_9{}^{3-}$ anions, two bromine molecules, and six cations. The anions throughout the crystal are bridged by Br_2 molecules, forming an infinite three-dimensional network. The important bond distances and angles are summarized in Table III. The molecular bromines are labeled Br^m and the bridging and terminal anion bromines are labeled Br^b and Br^t, respectively. The stereo pair (Figure 1) shows one Br_2 bridge between anions. Each Br^t is a possible bridging site. However, due to the disorder of the Br^m atoms and steric effects each anion is bridged to only two other anions on the average.

The presence of molecular bromine was reported in $(C_7H_{13}NH)_4Sb^{III}Sb^VBr_{12} \cdot 2Br_2$.[10] However, the role of the Br_2 molecule was unclear due to disorder of both Sb octahedra and the Br_2 species. In the tetramethylammonium salt the molecular bromine bond distance is 2.31 (3) Å in good agreement with the Br–Br distance in $(C_7H_{13}NH)_4Sb^{III}Sb^VBr_{12} \cdot 2Br_2$ of 2.32 (4) Å, both of which are possibly lengthened over the crystalline and gaseous bromine distances of 2.28 Å.[23]

The $Sb_2Br_9{}^{3-}$ anion had D_{3h} symmetry. The bond distances and angles are quite similar to those observed in $(C_5H_5NH)_5Sb_2Br_9 \cdot Br_2$.[4] We observe a slight lengthening though of the $Sb–Br^b$ distance (3.04 *vs.* 3.00 Å), a decrease in the Sb···Sb distance (3.89 *vs.* 4.01 Å), and a corresponding decrease in the $Sb–Br^b–Sb$ angle (79.6 *vs.* 83.7°). The $Sb–Br^t$ distance appears unchanged (2.63 Å). The Br–Sb–Br···Br–Br··· chain is nearly linear: $\angle(Br^b–Sb–Br^t)$, 174.0 (3)°; $\angle(Sb–Br^t \cdots Br^m)$, 179.9 (5)°; $\angle(Br^t \cdots Br^m–Br^m)$, 179.4 (6)°. The Br_2 molecule bridges two anions and lies perpendicular to four other $Sb–Br^t$ bonds. The $Br^t \cdots Br_2$ distance along the bridged chain is only 2.89 (1) Å.

The cations filll large holes between the anions. The closest $C \cdots Br(Br^m)$ contact is 3.3 Å. However, most C···Br contacts are ≥3.95 Å, the sum of CH_3 and Br van der Waals radii.[24] A half-cell ($0 \leq z \leq {}^1/_2$) projection onto the *ab* plane is given in Figure 2a while in Figure 2b is shown a projection down the b^* axis onto the *ac* plane. In these figures the large open circles (relative radius 1.5 Å) are the cations located on the mirrors at $z = {}^1/_4$. The large half-open circles are the remaining cations. The small open circles are the bridging anion bromines. The small black circles are the terminal anion bromines. The disordered bromine molecules are omitted in Figure 2a for clarity. The observed disorder and large thermal motion of the cations are probably the result of the lack of directional bonding and the large available volume between anions.

TABLE III

SELECTED DISTANCES AND ANGLES FOR $[(CH_3)_4N]_3Sb_2Br_{11}$[a]

Atoms	Distance, Å	Atoms	Angle, deg
$Br^m–Br^{mb}$	2.31 (3)	$Br^{mb}–Br^m \cdots Br^t$	179.4 (6)
$Br^m \cdots Br^t$	2.89 (1)	$Br^m \cdots Br^t–Sb$	179.9 (5)
$Br^t–Sb$	2.625 (8)	$Br^t–Sb–Br^b$	174.0 (3)
$Br^t \cdots Br^{tc}$	3.77 (1)	$Sb–Br^b–Sb^d$	79.6 (3)
$Sb–Br^b$	3.043 (8)	$Br^b–Sb–Br^{tc}$	93.1 (2)
$Sb \cdots Sb^d$	3.89 (2)	$Br^{tc}–Sb–Br^t$	92.0 (3)
		$Br^{bc}–Sb–Br^b$	83.4 (2)

[a] Estimated standard deviations are given in parentheses for the least significant figures. [b] Symmetry operation $(x, y, z) \rightarrow (\bar{x}, \bar{y}, \bar{z})$. [c] Symmetry operation $(x, y, z) \rightarrow (1 - y, 1 - x, z)$. [d] Symmetry operation $(x, y, z) \rightarrow (x, y, {}^1/_2 - z)$.

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[22] A listing of structure factor amplitudes will appear immediately 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 Street, N.W., Washington, D. C. 20036, by referring to code number INORG-72-2247. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

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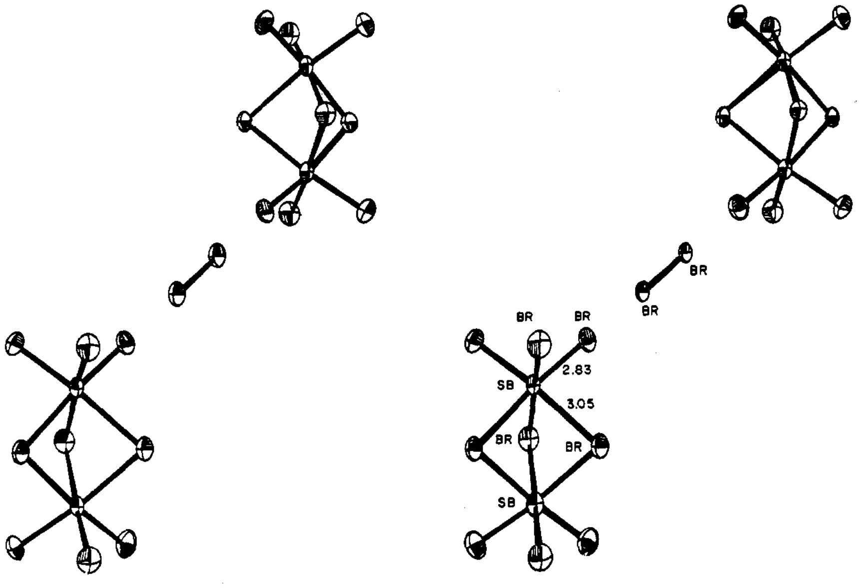

Figure 1.—Molecular bromine bridging of $Sb_2Br_9{}^{3-}$ anions.

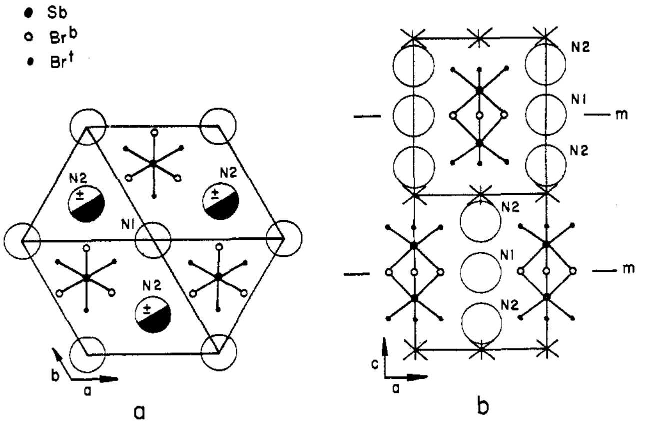

Figure 2.—(a) Projection of half-cell ($0 \leq z \leq 1/2$) contents onto the *ab* plane. (b) Projection of the unit cell down the b^* axis onto the *ac* plane. Br^m atoms lie at the ends of the stick bonds.

Discussion

The shortness of the $Br^t \cdots Br^m$ distance, approximately 1 Å shorter than the sum of bromine van der Waals radii,[24] is indicative of an important interaction between the bromine molecule and the $Sb_2Br_9{}^{3-}$ anions. This distance is 0.13 Å shorter than the 3.02 Å of the proposed $Sb^{III}Br \cdots Br_2$ interaction in $(C_7H_{13}NH)_4Sb^{III}Sb^{V}Br_{12} \cdot 2Br_2$.[10] The shortest reported $Br \cdots Br$ contact (other than in these two Br_2 bridged compounds) is 3.14 Å in PBr_7.[25]

The Br_2 bridge produces a chain of at least 12 atoms. This chain consists of three linear fragments; the eight-atom central fragment includes the molecular bromine. The site disorder of Br_2 prevents us from definitely defining the chain length—some chains may of course be of much longer length. The possibility of a super cell ($a' = 3a$) containing ordered Br_2 molecules cannot be definitely eliminated. However, no evidence was found for its existence.

A black tetramethylammonium salt is known to exist which readily debrominates to form a red solid.[5] This leads one to speculate that the black salt could contain $Sb_2Br_9{}^{3-}$ anions with all Br^t sites saturated with Br_2 bridges.

The bonding of the $Sb^{III}{}_2Br_9{}^{3-}$ anion and the molecular bromine bridge is of some interest. To a first approximation, the bonding in antimony(III) bromide salts can be explained completely through use of p orbitals and multicenter bonds. For example, it has been suggested[4] that the $Sb^{III}{}_2Br_9{}^{3-}$ moiety consists of six three-center four-electron bonds (Br^b–Sb–Br^t). The Sb^{III} lone pair of electrons was assigned to the spherical s orbital. In this structure, electron donation from the "nonbonding" σ^* orbital of Br_2 to $Sb_2Br_9{}^{3-}$ and some lengthening of the Br_2 bond might be expected. Unfortunately, the standard deviations in the bond distances are such that no definite conclusion can be reached in this regard. The shifts in bond distances and angles of the $Sb_2Br_9{}^{3-}$ anion are probably due to crystal-packing forces. The stability of the title compound can be partially attributed to the postulated Br_2 bridge. In addition, this bridging model predicts that $[(CH_3)_4N]_3Sb_2Br_{11}$ should be a semiconductor or a weak conductor.

(25) G. L. Breneman and R. D. Willett, *Acta Crystallogr.*, **23**, 467 (1967).