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The Crystal Structure of Pyridinium Tetracosabromoantimon(III)triantimon(V)ate, $(C_5H_5NH)_6Sb^{III}Sb^V{}_3Br_{24}$[1]

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Pyridinium tetracosabromoantimon(III)triantimon(V)ate, $(C_5H_5NH)_6Sb^{III}Sb^V{}_3Br_{24}$, crystallizes as intensely deep red acicular crystals in the orthorhombic space group *Cmcm* ($D_{2h}{}^{17}$) with unit cell parameters $a = 17.474 \pm 0.004$, $b = 23.697 \pm 0.006$, and $c = 16.390 \pm 0.006$ Å. The observed and calculated densities are 2.7 ± 0.2 and 2.824 ± 0.002 g/cm^3, respectively. The structure was refined by least-squares methods to a final conventional R index of 0.074 using three-dimensional X-ray diffraction counter data. Three crystallographically independent pyridinium cations, one $Sb^{III}Br_6{}^{3-}$, and two independent $Sb^VBr_6{}^-$ anions form an asymmetric unit. All three anions exhibit slight deviations from octahedral (O_h) symmetry. One of the $Sb^VBr_6{}^-$ ions forms nearly linear $\cdots Br{-}Sb^V{-}Br\cdots Br{-}Sb^V{-}Br\cdots$ chains extending along the c direction of the unit cell. The other two ions, $Sb^VBr_6{}^-$ and $Sb^{III}Br_6{}^{3-}$, form nearly linear $\cdots Br{-}Sb^V{-}Br\cdots Br{-}Sb^{III}{-}Br\cdots$ chains extending along the a direction of the unit cell. The two chains are nonintersecting. Bromine$\cdots$bromine contacts along both chains are quite short, being 3.243 ± 0.007 Å within the former chain and 3.486 ± 0.007 Å within the latter; both are considerably shorter than the anticipated 3.90-Å van der Waals radius sum. All cations are oriented such that the plane of each ring is nearly parallel to the unit cell c axis and essentially normal to one or more of the many $Br\cdots Br$ contacts. The derived $Sb^V{-}Br$ and $Sb^{III}{-}Br$ bond lengths, corrected for thermal effects assuming rigid-body libration of the ions, average 2.546 ± 0.011 and 2.799 ± 0.007 Å, respectively. A brief comparison of these bond lengths is made with other related structures.

Introduction

This paper describes another in a series of $R_xSb_yX_z$ (R = cation; X = Cl, Br, I) structures. Those previously reported include $(NH_4)_4Sb^{III}Sb^VBr_{12}$,[5,6] $Rb_4Sb^{III}Sb^VBr_{12}$,[7] $(C_6H_7NH)_2Sb^VBr_9$,[8] $(C_5H_5NH)_5Sb^{III}{}_2Br_{11}$,[9] and $(C_5H_5NH)Sb^{III}Cl_4$.[10] We now wish to report the results of a detailed single-crystal structure determination of another pyridinium analog, one containing Sb(III) and Sb(V), $(C_5H_5NH)_6Sb^{III}Sb^V{}_3Br_{24}$. This material is intensely colored, appearing deep red to black, within the full temperature range from its melting point (201–202°) down to the temperature of liquid nitrogen (−173°). This coloration is unlike that of the 2-, 3-, and 4-methylpyridinium derivatives, $(C_6H_7NH)_2SbBr_9$, which are similarly intensely colored at their melting points (range 116–38°) and room temperature but are bright orange to red at −173°.[11] It was the purpose of the present investigation to compare this structure with that of the 2-methylpyridinium derivative previously reported[8] and to relate differences in structure with differences in their charge-transfer absorption. These antimony halide complexes afford good model systems for the study of weak interactions in the solid state; also the geometry of possible Sb(III) moieties is of considerable interest, especially in relation to the effect of the lone pair. The study augments two previous single crystal structure investigations of the Sb(III)–Sb(V) systems,[5–7] as well as three structure determinations of ionic antimony halides with $C_5H_5NH^+$ as a cation.[9,10,12] Physical and chemical properties of this material and other intensely colored $R_xSb_yBr_z$ complexes synthesized with quaternary ammonium cations and saturated and unsaturated heterocyclic amines have already been discussed.[5,11]

Experimental Section

Preparation.—The salt was prepared by treating 1.0 ml of pyridine with a solution of 2.50 g of antimony tribromide and 0.5 ml of liquid bromine in 10 ml of warm concentrated hydrobromic acid (48%). The black crystalline precipitate was filtered by vacuum filtration through a sintered-glass funnel, rinsed with a small amount of cold, concentrated hydrobromic acid (48%), and dried on a porous porcelain plate in a desiccator containing concentrated sulfuric acid as the desiccant and a small partial pressure of bromine vapor.

Single crystals suitable for the X-ray investigation were prepared by recrystallizing the raw material from 2–3 ml of hot, concentrated hydrobromic acid (48%) containing 1–2 drops of concentrated sulfuric acid and 1–2 drops of liquid bromine, following a procedure described elsewhere.[8,11]

Anal. Calcd for $(C_5H_5NH)_3Sb_2Br_{11}$: C, 13.22; N, 3.08; H, 1.33; Sb, 17.87; Br, 64.50. Calcd for $(C_5H_5NH)_3Sb_2Br_{12}$: C, 12.49; N, 2.91; H, 1.26; Sb, 16.88; Br, 66.46. Found: C, 13.17; N, . . . ; H, 1.64; Sb, 16.64; Br, 63.7.

Crystal Data.—Pyridinium tetracosabromoantimon(III)triantimon(V)ate, $(C_5H_5NH)_6Sb^{III}Sb^V{}_3Br_{24}$ (formula weight 2885.48) crystallizes in the orthorhombic space group *Cmcm* ($D_{2h}{}^{17}$); lattice parameters at 23° are $a = 17.474 \pm 0.004$, $b = 23.697 \pm 0.006$, and $c = 16.390 \pm 0.006$ Å; $V = 6787 \pm 6$ Å^3 ($23 \pm 3°$); $d_{obsd} = 2.7 \pm 0.2$ g/cm^3 (by flotation) and $d_{calcd} = 2.824 \pm 0.002$ g/cm^3 for $Z = 4$ formula units of $(C_5H_5NH)_6Sb_4Br_{24}$ per unit cell. The color is jet black (reflected light) to deep red (transmitted light from very thin sections of the crystal); the crystal habit is acicular, elongated along the c direction.

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The crystal symmetry was determined from Weissenberg and precession photographs which yielded systematic extinctions (hkl, $h + k = 2n + 1$, and $h0l$, $l = 2n + 1$) consistent with the space groups $Cmc2_1$ ($C_{2v}{}^{12}$), $C2cm$ ($C_{2v}{}^{16}$), and $Cmcm$ ($D_{2h}{}^{17}$). Intensity statistics strongly favored the centrosymmetric space group as the correct choice,[13] later confirmed by the successful refinement of the derived structure. The lattice parameters were determined by a least-squares fit[14] to weighted high-angle copper Kα_1 (λ 1.54050 Å) and Kα_2 (λ 1.54434 Å) reflections measured from $hk0$ and $0kl$ Weissenberg zones calibrated with superimposed aluminum powder lines ($a_0 = 4.0330$ Å). The Nelson-Riley extrapolation function was employed in the refinement. Indicated errors in the cell parameters are 2σ.

Collection and Reduction of X-Ray Intensity Data.—Complete three-dimensional X-ray diffraction intensity data were taken at room temperature with zirconium-filtered molybdenum Kα radiation from a crystal 0.373 mm long and of cross section 0.076 × 0.138 mm (c^*, a^*, and b^*, respectively). The crystal was mounted in a 0.3-mm thin-walled Lindemann glass capillary with the needle axis (unit cell c axis) coincident with the ϕ axis of the diffractometer. A Siemens diffractometer equipped with a scintillation detector and pulse height discriminator was used with the moving-crystal, moving-counter measurement technique (θ, 2θ coupling) and a 3.5° takeoff angle. The receiving aperture size selected to minimize extraneous background was 5.0 mm wide by 5.0 mm high. The counter angle, 2θ, was scanned over 2° at a speed of 2°/min. Background counts of 12 sec were taken at each end of the 2θ scan. All scans were recorded on a chart recorder to provide visual evidence for the existence of observed reflections, proper peak shape, reflection centering in 2θ, and nonoverlap of adjacent reflections. A total of 3255 independent reflections were measured within the range $2\theta \leq 50°$. Equivalent reflections were not measured. Typical background counts at 10, 20, 30, 40, and 50° 2θ were 37, 8, 4, 3, and 2 counts/sec, respectively. Three standard reflections were measured periodically as a check on electronic and crystal stability and a 5% increase in intensities was observed throughout the 60-hr recording period. The alignment of the crystal was checked on a daily basis for ϕ independence at $\chi = 90°$ and adjusted when necessary.

The mosaicity of the crystal was examined by means of a narrow-source (takeoff angle 0.5°) 2θ-scan technique at $2\theta < 11°$. In this region, the 2θ-scan and ω-scan techniques yield comparable results.[15] Widths at half-maximum for three typical strong noncoplanar reflections ranged from 0.09 to 0.16° θ.

The raw intensity of each reflection was corrected for background, Lorentz, polarization, and absorption effects and for the slight increase in intensities as monitored by the reference reflections. Transmission factors were calculated by the program ACACA.[16] Because of the large linear absorption coefficient ($\mu = 164.3$ cm^{-1}) and the variation in μR (0.7–1.2) with the variation in the needle radius R, refined[17] crystal dimensions normal to the needle axis, rather than those obtained by optical measurement, were used in the absorption correction. Pursuant to this refinement, the shape, or profile, of the needle cross section was first carefully examined by measuring the intensity of a strong low-order $00l$ reflection, in this case 004, at $\chi = 90°$ in 15° intervals of ϕ from 0 to 360°. These intensities were used to prepare a plot of I_n/I_{av} *vs.* ϕ, where I_n (corrected for background) was the intensity at $\phi = n$ and I_{av} was the average intensity over the full range of ϕ. By systematically adjusting the shape and optically measured crystal thickness, a "best fit" of the transmission factor curve A_n/A_{av} with that of I_n/I_{av} plotted against ϕ was obtained by defining the crystal as an ellipsoidal cylinder with *minor* diameter 0.0844 mm and *major* diameter 0.1494 mm. The maximum deviation in F_o from the mean, defined as $100(|F_{max} - F_{min}|/F_{av})$, for the 24 independent measurements of the 004 reflection was subsequently reduced from 29.8% with no applied correction to only 1.2% with this correction. The new cross section was further tested on the 008 reflection for 24 values of ϕ and found to be satisfactory. The calculated ratio of the minimum and maximum transmission factors for the full set of three-dimensional data was 0.397. Effects of secondary extinction proved not to be a major problem and so no such correction was applied.

The estimated error in each intensity measurement was calculated by the expression[18] $\sigma(I) = [C_T + 0.25(t_c/t_b)^2(B_1 + B_2) + (pK)^2]^{1/2}$ where C_T is the total integrated peak count obtained in a scan time t_c, B_1 and B_2 are the background counts each obtained in time t_b, and $K = C_T - 0.5(t_c/t_b)(B_1 + B_2)$. The value of p was selected as 0.06. Each $\sigma(I)$ was then corrected for Lorentz, polarization, and absorption effects. The estimated standard deviation in each F_o was calculated by the expression $\sigma(F_o) = [(I + \sigma(I)]^{1/2} - |F_o|$, a function based on the finite difference method.[19] These standard deviations were used during the least-squares refinements to weight the observed structure factors. A total of 1421 reflections were observed above the background level of which 1173 had $F_o{}^2 \geq \sigma(F_o{}^2)$. Those with $F_o{}^2 < \sigma(F_o{}^2)$ were considered as unobserved and thus omitted from the refinements.

Solution and Refinement of the Structure

Preparation of this salt was first reported by Petzold in 1933.[20] The empirical formula was given as $R_3Sb_2Br_{12}$ (R = pyridinium). Analysis of our material indicated two plausible formulas, $R_3Sb_2Br_{11}$ and $R_3Sb_2Br_{12}$, with calculated densities, based on 8 formula units/unit cell, of 2.667 ± 0.002 and 2.824 ± 0.002 g/cm^3, respectively. Our observed density was 2.7 ± 0.2 g/cm^3.

The data were sharpened using the method of Jacobson, *et al.*,[21] and a sharpened three-dimensional Patterson function was computed.[22] Analysis of the Patterson–Harker sections and subsequent Fourier syntheses revealed three crystalographically independent $SbBr_6$ octahedra compatible with space group $Cmc2_1$ and $Cmcm$. Bond length calculations indicated the presence of trivalent and pentavalent antimony in the ratio 1:3. Careful analysis of the trivalent anion through refinement procedures in the space group $Cmc2_1$ ruled out disordered $Sb^{III}Br_5{}^{2-}$ in which the lone pair

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(13) (a) H. Lipson and W. Cochran, "The Determination of Crystal Structures," G. Bell and Sons, London, 1957, pp 32–41; (b) L. Guggenberger, "WSTAT, A Fortran Crystallographic Intensity Statistical Analysis Program," Experimental Station, E. I. du Pont de Nemours and Co., Wilmington, Del., 1967.

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(15) T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1966.

(16) (a) B. J. Wuensch and C. T. Prewitt, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **122**, 24 (1965); (b) C. T. Prewitt, "ACACA, A Fortran Polyhedral Absorption Correction Program," Experimental Station, E. I. du Pont de Nemours and Co., Wilmington, Del., 1966.

(17) Initial dimensions of the air-sensitive crystal were obtained by optical measurement with a 100× microscope while the crystal was in the capillary and therefore tend to be less reliable than those obtained without the interfering refraction problems arising from the capillary walls and crystal adherent. The method described here was devised to get around these problems. It has been successfully applied to a number of crystals and found to result in meaningful improvements in the values of the transmission factors.

(18) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

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

(20) W. Petzold, *Z. Anorg. Allg. Chem.*, **215**, 92 (1933).

(21) R. A. Jacobson, J. A. Wunderlich, and W. N. Lipscomb, *Acta Crystallogr.*, **14**, 598 (1961).

(22) In addition to various local programs for the IBM 7074 and CDC 1604 computers, programs used in the solution and refinement of this structure were Fitzwater, Benson, and Jackobs' Fourier program, Guggenberger's FOUR Fourier program, Ibers and Doedens' NUCLS crystallographic least-squares group-refinement program, Busing and Levy's ORFFE function and error program, and Johnson's ORTEP thermal ellipsoid plotting program.

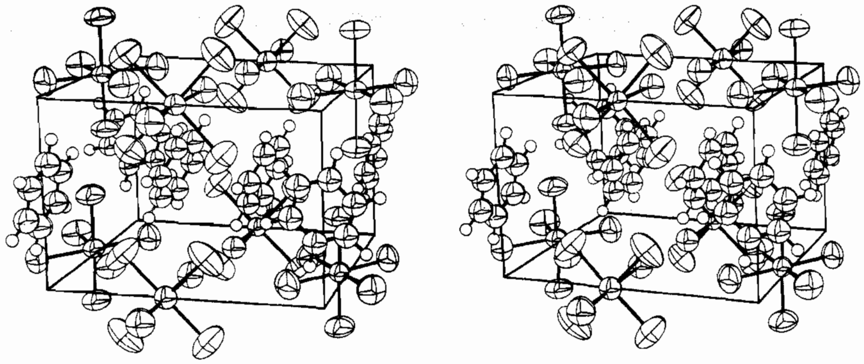

Figure 1.—A stereographic view of the packing of ions in crystals of $(C_5H_5NH)_6Sb_4Br_{24}$. The view depicts the contents of one-eighth the unit cell (two asymmetric units). Ellipsoidal boundaries of the atoms (except carbon and hydrogen) are at the 80% probability level.

of electrons might occupy at random the four possible octahedral sites on a mirror plane. The structure was therefore assumed to be $6C_5H_5NH^+ \cdot Sb^{III}Br_6^{3-} \cdot 3Sb^{V}Br_6^-$. A series of additional three-dimensional electron density syntheses (F_o and $F_o - F_c$) and isotropic least-squares refinements led to the location of all cations. A final difference map revealed that all electron density had now been accounted for and that the empirical formula, $(C_5H_5NH)_6Sb_4Br_{24}$, had been established, confirming Petzold's original analysis.

The structure was refined by using a full-matrix, least-squares procedure. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, respectively, and w is the weight defined as $1/\sigma^2(F_o)$. Atomic scattering factors for neutral atoms tabulated by Hanson, *et al.*,[23] were used. Anomalous parts of the Sb and Br scattering factors were obtained from Templeton's tabulation[24,25] and were included in the calculated structure factors.[26] All initial Fourier syntheses and least-squares refinements were carried out in the noncentrosymmetric space group $Cmc2_1$ to avoid any assumptions about extra mirror symmetry, but after all constituent ions had been identified and trial least-squares results evaluated, it became apparent that the more probable space group was *Cmcm*. A subsequent statistical analysis of the intensities[13] further indicated the presence of a center of symmetry.

Initially a fully isotropic refinement in *Cmcm* was carried out with the pyridinium rings constrained to D_{6h} symmetry using the least-squares group refinement procedure described by La Placa and Ibers.[27] In this refinement C–C and C–H distances of 1.376 and 0.98 Å, respectively, were assumed. Owing to the cavity-like environment in which the cations were situated, ordered nitrogen positions were considered highly unlikely and so no such ordering was assumed; all ring atoms were treated as carbon. The C–C bond length was taken as a weighted average of two C–N lengths, 1.340 Å each,[28] and four C–C lengths, 1.394 Å each, assuming nitrogen statistically occupied one-sixth of each ring position. It is now fairly well established that carbon–hydrogen distances obtained by X-ray diffraction techniques are systematically shorter than those determined from spectroscopic, electron diffraction, or neutron diffraction studies.[29,30] Accordingly, the C–H bond length of 0.98 Å, rather than the spectroscopically determined value of 1.084 (5) Å for an aromatic carbon–hydrogen bond,[31] was used.[32] Each ring was assigned a single, variable isotropic thermal parameter and six variable positional parameters.[27] The origin of the internal system was taken at the ring center with a_3' normal to the ring and a_1' intersecting a vertex. This initial refinement of the rings together with the other atoms, each of which was assigned a variable isotropic thermal parameter, converged rapidly to R values of $R_1 = \Sigma||F_o| - F_c||/\Sigma|F_o| = 0.129$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2} = 0.075$.

A difference map based on the preceding isotropic refinement provided evidence for anisotropic thermal motion of the heavy atoms which seemed physically reasonable, and ellipsoidal thermal parameters were introduced for antimony and bromine. Analysis of mean $w\Delta^2$ ($\Delta = |F_o| - |F_c|$) as functions of $|F_o|$ and $(\sin\theta)/\lambda$ at this point revealed a trend in which the weak reflections were being slightly underweighted and the weights were subsequently modified to remove this dependency.

Convergence was reached with $R_1 = 0.074$ and $R_2 = 0.061$. The corresponding values for all 1421 reflections were $R_1 = 0.100$ and $R_2 = 0.078$. The final standard deviation for an observation of unit weight (*i.e.*, the "error of fit") was 1.20, where the "error of fit" is defined by $[\Sigma w(|F_o|^2 - |F_c|^2)^2/(n - m)]^{1/2}$ with n being the number of observations (1173) and m the number of

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[23] H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).

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

[25] For Mo Kα radiation the real and imaginary dispersion corrections, $\Delta f'$ and $\Delta f''$, for atomic scattering factors are -0.6 and 2.0 for antimony and -0.3 and 2.6 for bromine, both at a $(\sin\theta)/\lambda$ value of 0.0.[24] The effects on the atomic scattering factors caused by these values are considered to be moderately significant.

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[28] B. Bak, L. Hansen-Nygaard, and J. Rastrup-Anderson, *J. Mol. Spectrosc.*, **2**, 361 (1958).

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[30] B. Dawson, *Aust. J. Chem.*, **18**, 595 (1965).

[31] L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, **No. 18**, S18s (1965).

[32] See, for example: (a) V. R. Magnuson and G. D. Stucky, *Inorg. Chem.*, **8**, 1427 (1969); (b) M. R. Churchill and F. R. Scholer, *ibid.*, **8**, 1950 (1969).

TABLE I

FINAL POSITIONAL, THERMAL, AND GROUP PARAMETERS FOR $(C_5H_5NH)_6Sb_4Br_{24}$

Atom	Position	x^a	y	z	$\beta_{11}{}^b$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Iso equiv B,^{c} Å^2
Sb(1)	8g	0.22100 (20)	0.01773 (15)	0.25*^{d}	300 (13)	157 (6)	245 (12)	−1 (10)	0*	0*	3.27
Sb(2)	4c	0.0*	0.28391 (20)	0.25*	179 (19)	149 (10)	387 (25)	0*	0*	0*	3.23
Sb(3)	4c	0.0*	0.25334 (10)	0.75*	179 (17)	128 (10)	300 (22)	0*	0*	0*	2.76
Br(1)	8g	0.11683 (38)	0.09191 (26)	0.25*	412 (30)	286 (16)	571 (36)	133 (18)	0*	0*	5.86
Br(2)	8g	0.12443 (39)	−0.06194 (25)	0.25*	399 (29)	267 (15)	579 (35)	−83 (17)	0*	0*	5.70
Br(3)	8g	0.32997 (39)	−0.05483 (24)	0.25*	384 (27)	220 (14)	558 (34)	94 (16)	0*	0*	5.21
Br(4)	8g	0.32143 (41)	0.09421 (25)	0.25*	542 (33)	235 (15)	563 (37)	−118 (18)	0*	0*	5.99
Br(5)	16h	0.22121 (25)	0.01785 (18)	0.40448 (20)	517 (18)	319 (9)	258 (14)	10 (14)	−28 (14)	17 (12)	5.42
Br(6)	8g	0.14504 (30)	0.28170 (23)	0.25*	180 (20)	250 (13)	476 (29)	12 (14)	0*	0*	4.31
Br(7)	8f	0.0*	0.20916 (28)	0.36026 (46)	336 (25)	358 (17)	808 (44)	0*	0*	278 (22)	6.94
Br(8)	8f	0.0*	0.36035 (28)	0.35771 (47)	305 (26)	401 (19)	782 (46)	0*	0*	−318 (23)	7.05
Br(9)	8g	0.15928 (30)	0.24687 (23)	0.75*	203 (19)	233 (13)	430 (27)	−3 (15)	0*	0*	4.11
Br(10)	8f	0.0*	0.17461 (26)	0.87718 (46)	315 (26)	336 (16)	746 (42)	0*	0*	224 (21)	6.47
Br(11)	8f	0.0*	0.33738 (24)	0.86916 (41)	342 (27)	302 (15)	528 (34)	0*	0*	−128 (17)	5.55

Group	Position of centroid	$x_c{}^e$	y_c	z_c	δ	ϵ	η	Group B,^{b} Å^2
Ring 1	16h	0.2532 (12)	0.1674 (5)	0.4959 (14)	1.641 (18)	−2.609 (20)	−1.169 (15)	7.4 (4)
Ring 2	4a	0.0*	0.0*	0.5*	3.14159*	2.893 (38)	−1.57080*	7.9 (10)
Ring 3	4b	0.5*	0.0*	0.5*	−1.57080*	3.14159*	−1.768 (34)	9.7 (12)

[a] Numbers in parentheses in all tables and in the text are estimated standard deviations occurring in the least significant digit of the parameter. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The β 's and their estimated standard deviations have been multiplied by 10^5. [c] Calculated from the anisotropic thermal parameters and unit cell parameters by the equation $B \sim {}^4/_3(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + 2\,\beta_{12}ab\cos\gamma + 2\beta_{13}ac\cos\beta + 2\beta_{23}bc\cos\alpha)$: W. C. Hamilton, *Acta Crystallogr.*, **12,** 609 (1959). [d] An asterisk denotes a parameter fixed by symmetry. [e] x_c, y_c, z_c are fractional coordinates of the ring centers. The angles δ, ϵ, η (in radians) are those described elsewhere: ref 27; R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4,** 773 (1965). [f] Group B is the isotropic thermal parameter for the entire pyridinium cation.

TABLE II

DERIVED POSITIONAL PARAMETERS FOR GROUP ATOMS IN $(C_5H_5NH)_6Sb_4Br_{24}{}^a$

Atom	Position	x	y	z
		Ring 1		
C(1)	16h	0.2143	0.1881	0.4294
C(2)	16h	0.2923	0.1808	0.4257
C(3)	16h	0.3312	0.1600	0.4923
C(4)	16h	0.2921	0.1466	0.5625
C(5)	16h	0.2140	0.1540	0.5662
C(6)	16h	0.1751	0.1747	0.4996
H(1)	16h	0.1866	0.2029	0.3820
H(2)	16h	0.3202	0.1903	0.3757
H(3)	16h	0.3868	0.1548	0.4897
H(4)	16h	0.3198	0.1318	0.6099
H(5)	16h	0.1861	0.1444	0.6162
H(6)	16h	0.1195	0.1799	0.5022
		Ring 2		
C(7)	8f	0.0	0.0143	0.4186
C(8)	8f	0.0	0.0559	0.4772
C(9)	8f	0.0	0.0416	0.5586
H(7)	8f	0.0	0.0245	0.3607
H(8)	8f	0.0	0.0957	0.4610
H(9)	8f	0.0	0.0712	0.6003
		Ring 3		
C(10)	8f	0.5	0.0114	0.4077
C(11)	16h	0.4318	0.0057	0.4588
H(10)	8f	0.5	0.0194	0.3590
H(11)	16h	0.3832	0.0098	0.4295

[a] Only positions of the crystallographically independent atoms are indicated, though entire rings were included in the refinement. Average estimated standard deviations ($\times 10^4$) in parameters not fixed by symmetry: C, $\sigma(x) = 16$, $\sigma(y) = 11$, $\sigma(z) = 19$; H, $\sigma(x) = 22$, $\sigma(y) = 17$, $\sigma(z) = 25$.

variables (95). On the final cycle the shift in each positional, thermal, and group parameter averaged 0.004 times its own σ. A final difference synthesis revealed no peaks greater than 0.3 e$^-$/Å^3, consistent with good refinement. The largest peaks in this map were associated with the ring carbon atoms, positioned as to suggest slight rotational disorder of the cations about their ring normals.

The final positional, thermal, and group parameters derived from the last cycle of least-squares refinement are presented in Table I, along with the associated standard deviations in these parameters as estimated from the inverse matrix. The positional parameters of the ring carbon atoms, which may be derived from the data in Table I, are presented in Table II. Root-

TABLE III

FINAL ROOT-MEAN-SQUARE THERMAL AMPLITUDES OF VIBRATION (Å) IN $(C_5H_5NH)_6Sb_4Br_{24}$

Atom	Min	Med	Max
Sb(1)	0.183 (4)	0.211 (4)	0.216 (5)
Sb(2)	0.166 (9)	0.206 (7)	0.230 (8)
Sb(3)	0.166 (8)	0.191 (7)	0.202 (7)
Br(1)	0.208 (10)	0.279 (9)	0.319 (8)
Br(2)	0.224 (9)	0.281 (9)	0.296 (8)
Br(3)	0.203 (9)	0.276 (8)	0.284 (8)
Br(4)	0.222 (9)	0.277 (9)	0.319 (9)
Br(5)	0.186 (5)	0.283 (5)	0.302 (7)
Br(6)	0.166 (9)	0.254 (8)	0.267 (7)
Br(7)	0.226 (8)	0.228 (9)	0.401 (9)
Br(8)	0.217 (9)	0.218 (8)	0.416 (9)
Br(9)	0.177 (8)	0.242 (8)	0.258 (7)
Br(10)	0.221 (9)	0.233 (8)	0.378 (8)
Br(11)	0.230 (8)	0.230 (9)	0.324 (8)

TABLE IV

OBSERVED AND CALCULATED STRUCTURE FACTORS (IN ELECTRONS × 10) FOR $(C_5H_5NH)_6Sb_4Br_{24}$[a]

H	K	FO	FC
**** L = 0 ****			
0	4	8954	8489
0	6	4157	4228
0	8	938	1219
0	12	4567	4502
0	16	1409	-1611
0	22	1498	-1537
0	26	3060	-3077
1	3	3714	3836
1	7	3360	-3278
1	9	1400	-1374
1	11	4068	4076
1	13	1923	-2318
1	19	1155	-1158
2	2	12610	-12685
2	4	4673	-4796
2	6	1552	-1526
2	8	2768	-2954
2	10	2668	-2992
2	12	1233	-1059
2	14	1197	1238
2	24	2243	2196
2	28	1217	1313
3	1	3728	-3174
3	3	2620	-2986
3	5	1034	-1194
3	7	7518	-7471
3	9	1171	-1350
3	13	2890	-2755
3	19	1562	1711
3	23	1302	1513
4	0	12459	11528
4	2	1918	-1715
4	4	4070	3970
4	6	13593	13361
4	8	3944	3920
4	16	933	-1008
4	22	1902	-1715
5	3	6912	6695
5	5	10732	10752
5	7	3988	3885
5	9	3155	2990
5	11	2750	2616
5	13	2002	-2235
5	19	1511	-1802
5	21	1672	-1662
6	0	16850	16649
6	2	11945	-11766
6	6	2867	-3155
6	8	2099	-1856
6	10	4313	-4110
6	18	1458	1215
6	20	1594	1639
6	24	1716	1462
7	1	5699	-5605
7	3	2973	-2638
7	5	5744	-5741
7	7	4556	-4801
7	9	3543	-3528
7	11	2596	2473
7	13	2449	-2350
7	17	1853	1716
7	21	1502	1437
8	0	11294	11189
8	2	4813	-4777
8	4	1516	1521
8	6	924	932
8	14	1539	1479
8	16	936	-976
8	22	940	-731
9	1	9040	8998
9	3	6472	6463
9	5	2874	2822
9	7	1892	-2008
9	11	3283	3389
9	25	1565	-1296
10	0	7665	7868
10	2	1331	-1317
10	4	1887	-1922
10	6	3801	3805
10	16	1237	-766
11	1	6316	-6412
11	3	3207	-3073
11	5	962	636
11	7	3412	-3022
11	13	1393	-1469
12	0	5598	5379
12	2	6811	-6721
12	10	2857	-2819
13	3	2243	2693
13	5	1935	2102
13	7	1640	1828
13	11	2093	2283
13	13	1683	-1348
14	0	6866	7384
14	2	3109	-3368
14	4	3568	3585
14	6	2852	3234
14	8	2068	1958
14	20	1163	-794
15	3	1062	571
15	5	1256	-1282
15	7	1220	-1659
15	9	1642	-1840
15	11	1038	1029
16	0	2143	2057
16	2	2539	-2536
16	4	2601	-2804
16	8	1451	-1732
17	5	1122	880
17	11	1083	616
18	0	4780	5291
18	4	1347	1420
20	0	1554	1580
20	2	2840	-3517
**** L = 1 ****			
0	4	3711	-3469
0	6	1985	1913
0	8	1292	-1059
0	10	1218	-1502
0	12	10315	-10565
0	14	7152	-7179
0	16	3314	-3359
0	22	1490	-1288
1	9	1911	1986
1	11	6922	-7094
1	13	5208	5317
1	15	4661	-4590
1	17	1383	1598
1	19	954	-818
1	21	1329	1049
2	2	2679	2769
2	4	1256	1751
2	8	2571	2853
2	10	3539	3688
2	12	4898	5063
2	14	3113	3046
2	16	2698	2830
2	18	1267	1491
2	24	1334	1470
3	3	1402	1243
3	5	939	678
3	7	5829	5771
3	9	2515	2429
3	13	3083	3232
3	19	1687	1705
4	4	1952	-1770
4	6	8616	-8365
4	8	3223	-3058
4	10	3416	-3279
4	18	2044	-2237
4	20	2190	-2275
4	22	1458	-1527
5	1	1195	1292
5	5	3437	-3668
5	7	5825	-5797
5	9	2910	-2726
5	11	5292	-5370
5	13	5514	5539
5	15	2868	-3029
5	17	1432	-1478
5	19	3065	-2956
5	21	1199	-945
6	2	2179	2564
6	6	3648	3832
6	8	908	1638
6	10	2925	2944
6	12	1335	-1424
6	18	1483	1310
6	24	1013	1154
7	3	1768	1434
7	5	3262	2698
7	7	2774	2786
7	9	5370	5109
7	11	3200	-3486
7	13	7593	7490
7	15	1146	-1435
7	17	4319	4482
7	21	1585	1908
8	2	1486	1589
8	4	980	-947
8	8	1117	-1113
8	12	1076	-1156
9	1	2334	-1953
9	5	1327	-1655
9	7	2135	2226
9	9	1022	-1150
9	11	5632	-5541
9	13	2334	-2523
9	15	4823	-4807
9	17	1744	-1709
10	2	1024	-917
10	6	2087	-2488
10	8	1564	1598
10	10	948	-848
10	14	1353	-1498
11	1	1648	1539
11	9	2200	2281
11	13	5738	5779
12	2	1090	1289
12	6	1018	637
12	10	1691	1880
13	5	956	-925
13	7	2061	-2428
13	11	4251	-4307
13	13	3149	3369
13	15	2195	-2614
13	19	1737	-1648
14	4	1930	-1568
14	6	1024	-1002
14	8	2965	-3082
14	18	1341	-1242
14	20	943	-629
15	3	1822	2018
15	7	1923	2026
15	11	1444	-1622
15	13	1463	1478
15	15	1236	-1160
16	8	1368	1741
16	16	1233	1324
17	13	1283	971
18	12	1396	-930
18	14	1265	-1441
19	3	1597	-1206
19	11	1577	-1656
**** L = 2 ****			
0	0		-16382
0	4	5966	-5892
0	6	13201	13292
0	8	1419	-1310
0	12	844	-887
0	20	1122	-1324
0	22	1081	882
0	26	2338	2395
1	3	2525	-2790
1	5	2637	2565
1	7	2168	-2331
1	9	1725	1850
1	11	3145	-3029
2	2	8179	8108
2	4	2095	1784
2	10	1548	1345
3	7	1522	1782
3	13	1245	1296
3	19	1151	-1293
4	0	5236	4852
4	2	3056	2879
4	4	1870	-1797
4	6	5146	-5058
4	8	3482	-3815
4	10	740	-639
4	22	1367	1235
5	1	5809	5460
5	5	3814	-3623
5	7	5427	-5198
5	19	1356	1160
5	21	1204	967
6	0	8877	-8516
6	2	5468	5295
6	4	3980	-3992
6	6	6429	6289
6	8	1786	-1703
6	10	1856	1807
6	20	1444	-1642
6	26	1574	995
7	1	1896	1930
7	5	5250	4746
7	9	2595	2984
7	11	2239	-2277
7	21	1144	-999
8	0	5978	-5552
8	2	3608	3338
8	4	2122	-1871
8	14	1494	-1300
9	1	4630	-4737
9	3	2585	-2652
9	5	1981	2030
9	7	1927	1609
9	9	1233	1294
9	11	1985	-1879
10	10	1344	-935
11	1	3694	3729
11	3	1101	1218
12	0	2735	-2505
12	2	3897	3912
12	4	2161	-2085
12	6	2124	2016
12	8	1545	-1303
12	10	1692	1873
13	1	1280	1153
13	3	1530	-1388
13	7	2535	-2783
13	11	1297	-1521
13	19	1026	663
14	0	2011	-2185
14	2	3056	3179
14	4	2891	-3108
14	8	1226	-1872
15	5	1307	1642
15	9	1628	1923
16	4	1133	1400
16	6	1123	1160
18	0	2278	-2428
18	4	1011	-1331
20	2	2238	2461
**** L = 3 ****			
0	4	2001	1790
0	6	11287	-11497
0	10	2812	-2985
0	12	4901	4853
0	14	3219	3266
0	20	3227	-3086
0	22	1271	930
1	1	1274	1253
1	5	3299	-3190
1	7	4113	4378
1	9	3592	-3658
1	11	2775	2449
1	15	2086	2009
1	17	3364	-3024
1	19	2041	2010
1	21	1403	-1502
2	4	871	762
2	6	1446	1371
2	8	2717	2526
2	10	1295	-1625
2	14	1767	-1663
2	16	1395	-1335
2	18	1234	1679
2	20	1255	-1590
3	5	1315	-1525
3	9	1194	-1294
3	13	2771	2824
4	6	1236	1437
4	8	2782	2748
4	12	3339	-3215
4	14	1788	-1855
4	16	992	-1125
4	18	1967	2002
4	22	1395	1328
5	1	1400	-1075
5	5	1568	-1639
5	7	7037	6929
5	9	1350	-1287
5	13	2987	-2990
5	15	806	-666
5	17	1180	-1104
5	19	3486	3288
6	4	990	1101
6	6	4533	-4830
6	8	2258	1951
6	10	1875	-2022
6	12	2882	2936
6	18	961	511
6	20	2101	-2053
7	1	1268	1281
7	5	2667	-2473
7	7	3005	3256
7	9	3367	-3072
7	11	3304	3355
7	13	1158	-1390
7	15	1461	1606
7	17	3836	-3739
7	19	1530	1336
8	4	1098	830
8	6	2309	-2294
8	8	2417	2283
8	10	1208	-1670
8	12	1238	1318
8	20	1439	-1596
8	22	1014	960
9	1	1547	1771
9	5	2406	-2207
9	7	1547	-1481
9	9	1727	-1968
9	13	3674	3729
9	15	1687	1716
10	2	1174	1540
11	3	1419	1539
11	7	3466	3682
11	9	1405	-1331
11	11	1262	-1238
11	13	1436	-1478
12	6	1066	-985
12	10	1325	-1583
13	7	2808	3230
13	9	1560	-1615
13	11	1456	1644
13	13	1788	-1854
13	17	1798	-1853
13	19	2238	1941
14	4	1209	1145
14	8	2826	3173
14	14	1128	-1002
14	18	1861	1254
15	3	1665	-1408
16	6	1077	-963
17	3	1092	788
19	7	1564	1436
19	9	1506	-1356
**** L = 4 ****			
0	0	9735	4625
0	2	1421	1691
0	4	5884	5939
0	6	13976	-14209
0	8	883	709
0	10	804	-609
0	12	1051	1375
0	20	1592	1554
0	26	1896	-1840
1	1	1075	1283
1	3	1045	1216
1	5	6081	-6206
1	7	5018	5135
1	9	4050	-4042
1	11	851	884
2	0	8814	-8761
2	2	1121	1462
2	4	4599	4511
2	6	4355	-4369
2	8	2128	2298
2	12	1250	-1244
2	16	933	1098
3	1	2383	2284
3	5	3437	-3561
3	7	3403	3323
3	9	1858	-2120
3	11	1376	-1514
3	17	849	-794
3	19	1150	1274
4	0	13625	-137[illegible]
4	2	1427	1254
4	4	3741	3580
4	6	1312	-1256
4	8	3777	3819
4	10	1072	1045
4	12	1289	-1410
4	18	1234	-1259
4	22	900	-777
5	1	4066	-3846
5	7	7638	7711
5	9	1456	-1570
6	0	2939	2342
6	2	1323	-1211
6	4	5565	5704
6	6	8240	-8539
6	8	1961	1855
6	10	1340	-1354
6	14	1182	-1114
6	20	1434	1466
7	3	1574	1229
7	5	5926	-5643
7	7	4577	4595
7	9	3310	-3299
7	11	882	1095
7	21	1281	1236
8	0	2444	-2181
8	4	3959	3811
8	6	5787	-5523
8	8	1636	1122
9	1	4813	4735
9	3	1270	1482
9	5	4610	-4436
9	7	1288	1073
9	9	2480	-2580
9	21	1046	590
10	0	4566	-4668
10	2	2781	3039
10	6	2667	-2989
10	10	1491	1295
11	1	1980	-1987
11	3	1135	-785
11	7	3047	3203
12	0	1285	-1175
12	4	3502	3600
12	6	3698	-3707
12	8	1909	1755
12	10	1190	-1205
13	1	999	-914
13	5	1706	-1807
13	7	4263	4114
13	9	1155	-1167
13	19	1262	-640
14	0	1140	-1484
14	2	1265	-1362
14	4	3596	3862
14	6	1909	-1802
14	8	2069	2108
15	5	2568	-2508
15	7	1606	1585
15	9	2194	-2282
16	2	1095	1122
16	6	2354	-2264
18	4	1702	1697
18	6	1790	-1906
19	7	1334	1229
20	2	1085	-1485
20	4	1541	1543
**** L = 5 ****			
0	4	3893	-4026
0	6	6391	6691
0	8	2502	-2750
0	12	7912	-7935
0	14	4606	-4767
0	16	1668	-2021
0	18	1881	-1922
0	20	2258	2262
0	22	1301	-1132
1	3	1098	-1127
1	5	2245	2219
1	7	3377	-3740
1	9	2536	2600
1	11	1208	-1395
1	15	2565	-2484
1	17	3166	3228
1	19	2267	-2283
2	6	4197	4391
2	8	1095	-1194
2	10	2252	2303
2	12	4192	4035
2	14	2415	2458
2	16	1994	2177
2	20	1796	1962
3	5	2726	2551
3	7	841	768
3	9	2364	2309
3	11	3649	3709
3	13	2709	-2432
3	15	893	780
3	17	1567	1542
3	21	931	541
4	4	2573	-2558
4	6	2242	-2329
4	8	4384	-4183
4	10	2191	-2025
4	12	900	958
4	18	3524	-3393
4	22	1701	-1359
5	1	1372	1801
5	3	1483	-1593
5	7	7241	-7533
5	9	846	-1093
5	13	808	672
5	15	1119	-1136
5	19	3887	-3795
5	21	1114	-595
6	4	1054	-1105
6	6	6650	6673
6	8	1624	-1311
6	10	2131	2240
6	12	1072	-1116
6	16	956	743
6	20	1795	2158
7	5	4019	3565
7	9	4371	4353
7	13	1645	1935
7	15	884	-594
7	17	5182	5032
7	19	1376	-1062
7	21	1297	1610
8	4	1636	-1615
8	6	3634	3427
8	8	3134	-2759
8	18	1298	-1302
8	20	1350	1488
9	1	1103	-1055
9	3	1017	-471
9	11	1423	-1396
9	13	5005	-5152
9	15	2737	-2889
10	2	1312	-1368
10	4	1117	-1248
10	14	1186	-647
10	18	1031	-1109
11	1	1876	1718
11	3	1362	-946
11	5	1231	1430
11	7	1722	-2126
11	9	1906	2032
11	11	2426	2928
11	13	1867	1795
11	17	1439	1407
12	6	2509	2643
12	10	1078	1455
12	12	1076	1046
12	14	1198	556
12	18	1311	-717
12	20	1118	1013
13	3	1453	-1042
13	7	3258	-3508
13	11	1801	-1625
13	15	1793	-1507
13	17	2265	1734
13	19	1909	-2164
14	4	1516	-1808
14	8	3419	-3547
15	3	1068	1500
15	17	1125	1296
16	6	1758	1924
16	16	1243	1150
19	9	1127	1079
**** L = 6 ****			
0	0	18851	-19961
0	2	4860	-5168
0	4	10241	-10458
0	6	3790	4419
0	8	2587	-2636
0	10	1243	-1329
0	12	3333	-2920
0	22	1223	956
0	24	1230	812
0	26	2247	2224
1	1	2196	-2197
1	3	2002	-2036
1	5	2950	3067
1	7	3840	-3834
1	9	1566	1791
1	11	1252	-1358
1	19	1456	1319
2	0	9092	9097
2	2	6528	6824
2	4	1755	1635
2	6	4764	4716
2	8	1813	2030
2	10	1686	1564
2	16	1203	-636
2	24	1321	-1337
3	1	1932	1504
3	3	3315	3208
3	5	3768	3921
3	9	1800	1969
3	11	1068	1040
3	23	1382	-1207
4	2	2715	-2270
4	4	5741	-5775
4	6	6268	-6147
4	8	3933	-3666
4	10	1436	-1621
4	14	1354	1358
4	18	1160	929
4	20	1115	1216
4	22	1163	1106
5	1	1270	-797
5	3	4116	-3936
5	5	4178	-4372
5	7	7671	-7659
5	9	1339	-1308
5	19	2410	1875
5	21	1114	946
6	0	3279	-2856
6	2	4730	4700
6	4	3249	-3173
6	6	7010	6982
6	10	1698	1783
7	1	4052	3775
7	3	3312	3366
7	5	7556	7471
7	9	4008	3884
7	17	1314	-1218
7	21	1729	-1544
8	0	2821	-2463
8	4	3635	-3400
8	6	1186	1818
9	1	7681	-7512
9	3	4318	-4317
9	7	1756	-1827
9	11	1312	-1497
10	2	1751	-1573
10	4	1313	-655
10	20	1136	-1071
11	1	4367	4386
11	3	3052	2990
11	5	1736	1687
12	2	3308	3292
12	4	1899	-1972
12	6	3126	3264
12	10	1751	1619
12	14	1468	1043
13	3	1660	-1725
13	7	3693	-3814
13	11	1103	-1008
13	19	1213	1059
14	0	2343	-2474
14	2	1278	1167
14	4	4148	-4141
14	8	1769	-1763
15	5	2351	2236
15	9	1521	1820
16	4	1337	1285
16	6	1866	1960
16	8	1403	1201
18	0	2462	-2119
18	4	1965	-2041
**** L = 7 ****			
0	4	4108	4142
0	6	2828	-2938
0	8	3006	2774
0	10	3021	3050
0	12	7164	7211
0	14	5760	5906
0	16	2725	2860
0	18	1004	1202
1	3	813	644
1	5	752	623
1	7	882	757
1	11	3718	3933
1	13	2394	-2408
1	15	4048	4025
1	17	2121	-2086
2	2	1498	-2111
2	6	2906	-2965
2	8	2540	-2516
2	10	2620	-2870
2	12	4798	-4751
2	14	2800	-3043
2	16	3101	-3012
2	18	962	-866
2	20	1257	-1268
3	3	863	-1034
3	7	4277	-4221
3	9	1691	-1775
3	11	1446	-1434
3	13	1849	-1856
3	17	938	-1109
3	19	951	-1210
4	4	2665	2541
4	6	4283	4077
4	8	3772	3646
4	10	4096	3889
4	18	2356	2393
4	20	1317	1602
4	22	1195	1033
5	1	2076	-2273
5	3	1464	1432
5	5	2921	3229
5	7	4498	4819
5	9	2500	2770
5	11	3096	3313
5	13	2509	-2438
5	15	3145	3157
5	19	2575	2715
6	2	1702	-1786
6	6	4761	-4603
6	8	1112	-938
6	10	1683	-1698
6	18	1089	-598
7	1	1265	-1210
7	3	1531	-1282
7	5	2041	-2236
7	7	2798	-2426
7	9	4235	-4173
7	13	5554	-5418
7	17	4442	-4500
7	21	1746	-1512
8	4	1643	1489
8	6	1239	-1426
8	8	1199	1426
9	5	1825	1988
9	9	1585	1680
9	11	3493	3688
9	13	3304	2991
9	15	4400	4260
10	4	1255	971
10	10	1543	1347
10	14	1053	1270
11	1	2133	-2110
11	9	2037	-1991
11	11	1620	-1844
11	13	3548	-4057
11	17	1332	-1294
12	2	1305	-970
12	6	1564	-1565
13	3	1125	998
13	7	1940	2160
13	11	2516	2892
13	13	1733	-1822
13	15	2204	2464
13	19	1777	1508
14	4	1599	1714
14	8	2822	2857
14	18	1319	1268
15	3	1464	-1537
15	7	1717	-1516
16	6	1202	-1390
16	8	1335	-1297
**** L = 8 ****			
0	0	17177	17918
0	2	1599	-1876
0	4	4190	3979
0	6	3309	-2843
0	12	2616	2691
0	16	961	-1248
1	3	1737	2078
1	5	777	-787
1	11	2276	2283
1	19	1165	-878
2	0	2321	1850
2	2	7811	-7634
2	4	2421	-2533
2	6	1129	1041
2	8	1715	-1777
2	10	2198	-2153
2	24	1215	1182
3	1	1302	-1076
3	7	2831	-2887
3	13	1316	-1495
3	19	1350	863
4	0	1945	1775
4	2	2212	-2085
4	4	1726	1771
4	6	5307	5425
4	8	1983	1989
4	12	1030	779
4	16	1131	-822
5	1	1898	-1887
5	3	2264	2153
5	5	3864	3776
5	7	2597	2481
5	9	1454	1470
5	11	855	878
5	13	1107	-1269
5	21	1082	-1032
6	0	9291	9030
6	2	6899	-6518
6	6	2226	-2001
6	8	1001	-587
6	10	2459	-2567
6	12	1139	1243
6	18	1242	889
6	20	1393	1006
7	1	2202	-2404
7	5	3775	-3409
7	7	1114	-1556
7	9	1674	-1645
7	11	1502	1491
7	13	1101	-1422
7	17	1149	1046
8	0	6515	6170
8	2	3508	-3421
8	6	994	542
8	16	969	-830
9	1	4189	4052
9	3	2990	2909
9	7	1350	-1245
9	11	1715	1581
10	0	3352	2693
10	6	1356	1329
11	1	3258	-3209
11	13	992	-838
12	0	3622	3781
12	2	4253	-4298
12	10	1996	-2026
12	20	1012	635
13	3	1844	1561
13	7	1466	1432
13	11	1362	1256
14	0	3414	3322
14	2	2160	-2553
14	4	2251	2326
14	6	1253	1153
14	8	1286	1142
16	0	1295	1372
16	2	1576	-1437
16	4	1748	-1469
18	0	2906	2930
**** L = 9 ****			
0	6	3543	3454
0	8	1096	1141
0	10	1054	1244
0	12	2542	-3459
0	14	2420	-2525
1	9	1876	1955
1	11	3810	-3960
1	13	3554	3787
1	15	2484	-2508
1	17	989	1078
1	21	980	876
2	6	2028	-2029
2	10	939	720
3	7	2121	1822
3	11	1391	-1408
3	13	1463	1471
3	15	1331	-858
3	19	1051	869
4	6	3089	-2952
4	12	1653	1594
4	20	1171	-1083
4	22	1070	-708
5	7	1622	-2211
5	11	2050	-2030
5	13	4712	4535
5	19	1060	-1288
6	6	987	1335
6	10	1355	1216
6	12	1188	-1534
7	9	1445	1910
7	11	3656	-3811
7	13	3627	3709
7	15	1355	-1896
7	17	1744	1898
9	7	2173	2112
9	11	2038	-2219
9	15	1759	-2134
10	6	1337	-1129
10	8	1289	1200
11	9	1008	833
11	13	2919	2984
12	10	1060	876
13	11	2160	-2374
13	13	2428	2647
13	15	1547	-1446
14	8	1652	-1392
15	3	1570	1161
15	7	1142	876
15	11	1513	-1266
**** L = 10 ****			
0	0	10348	-9804
0	2	2677	2765
0	6	4988	5289
0	10	1525	1396
0	14	1060	-981
0	20	1551	-1285
1	3	1514	-1380
1	5	1172	1284
1	9	1064	1161
1	11	1813	-1622
2	0	2185	-2393
2	2	1514	1713
2	4	989	-914
2	6	902	-1052
2	8	1058	-1259
3	3	1211	-1045
3	7	1148	1279
3	19	1079	-999
4	0	1230	975
4	2	2543	2735
4	6	2462	-2159
4	8	1692	-1530
4	10	937	615
5	1	3924	3286
5	5	1091	-1514
5	7	946	-1079
5	13	928	831
6	0	6739	-6114
6	2	2483	2789
6	4	1889	-2068
6	6	2486	2651
6	10	936	1458
7	3	1602	-1682
7	5	1320	1203
7	9	971	931
7	11	1360	-1687
8	0	3501	-3475
8	2	2074	2261
8	10	1082	526
8	14	1280	-1129
9	1	1654	-1468
9	3	1362	-1073
9	5	1362	1194
9	7	1585	1795
9	9	1119	867
9	11	1128	-1141
10	0	1672	-1314
10	4	1283	1045
11	1	1159	1487
12	0	2272	-2333
12	2	2019	2023
12	4	1286	-1376
12	10	1132	1171
14	0	1705	-1886
14	2	2023	2281
14	4	1441	-1299
**** L = 11 ****			
0	6	1803	-1862
0	10	1104	-983
0	12	4472	4395
0	14	1840	2107
1	1	1279	1177
1	5	1674	-1682
1	7	1607	1959
1	9	1667	-1642
1	11	2238	2327
1	17	1018	-914
2	10	1483	-1622
2	12	1015	-1051
2	16	1064	-905
3	5	1388	-1465
3	9	1177	-1426
4	6	2613	2458
4	8	1381	1238
4	22	1168	967
5	7	3283	3578
5	11	1226	1415
5	13	1507	-1562
5	19	1652	1755
6	6	2083	-1686
6	10	1653	-1608
6	12	1231	1398
7	5	2165	-2144
7	9	2262	-2513
7	11	1453	1555
7	13	2192	-1963
7	17	1853	-1998
8	10	1327	-949
9	1	1777	1434
9	11	1430	1670
9	13	1735	1681
9	15	1395	1272
11	13	1573	-1594
12	10	1089	-1153
13	7	1938	1869
13	11	1558	1649
14	8	1662	1613
**** L = 12 ****			
0	0	8297	8416
0	2	2670	2432
0	4	6335	4942
0	6	2947	-2812
0	8	2152	2174
1	1	986	863
1	3	1090	1113
1	5	1165	-915
1	7	1744	1903
1	9	1445	-1462
1	11	1406	1244
2	0	5025	-4796
2	2	3295	-2979
2	4	913	-1041
2	6	3234	-3499
3	3	1455	-1477
3	5	1717	-1704
3	9	1514	-1625
4	0	1210	-1012
4	2	1825	1898
4	4	3340	2979
4	6	1489	1534
4	8	2395	2722
4	10	1148	1280
4	18	984	-1236
5	1	1144	478
5	3	2055	1986
5	5	2247	2369
5	7	3673	3679
6	2	2726	-2226
6	4	1337	1455
6	6	4257	-3966
7	1	2442	-2269
7	3	1750	-1728
7	5	3627	-3509
7	9	2399	-2557
8	4	1388	1756
8	6	1535	-1818
9	1	3854	3549
9	3	2632	2302
9	7	1491	1157
10	2	1347	1249
11	1	2172	-2344
11	3	1339	-1594
12	2	1612	-1734
12	6	2410	-2195
13	7	2270	1968
14	4	2568	2343
15	9	1791	-1214
**** L = 13 ****			
0	4	2502	-2565
0	6	1146	1003
0	8	2396	-2913
0	10	1610	-1551
0	12	3936	-3973
0	14	2716	-3155
0	16	1798	-1874
0	18	2180	-1240
1	3	1121	-878
1	5	921	787
1	7	1258	-1812
1	11	928	-1206
1	15	1151	-1263
1	17	1195	1240
1	19	1472	-1233
2	4	908	579
2	6	1997	2099
2	8	1286	1280
2	10	2215	2536
2	12	2318	2511
2	14	2210	2181
2	16	1943	1850
2	20	1506	1461
3	5	1776	1478
3	7	1082	901
3	9	1571	1471
3	11	1748	1813
3	17	1067	1063
4	4	1341	-1689
4	6	1646	-1867
4	8	2772	-2636
4	10	1798	-1809
4	16	1089	-726
4	18	1876	-1639
5	3	1443	-1390
5	7	3389	-3797
5	9	1509	-1346
5	11	1317	-1450
5	19	2500	-2102
6	6	2490	2612
6	10	1540	1615
7	5	2779	2416
7	9	2654	2861
7	13	1883	2165
7	17	2749	2718
8	8	1235	-1162
9	7	1106	-1057
9	11	1154	-1627
9	13	2733	-2642
9	15	1926	-1868
10	14	948	-604
11	9	1428	1588
11	11	2011	1565
12	6	1652	1084
13	7	1402	-1874
14	8	1856	-1871
**** L = 14 ****			
0	0	5860	-5811
0	2	1747	-1724
0	4	3776	-4200
0	6	1961	1964
0	12	1031	-1103
1	5	917	1000
1	7	1875	-1607
2	0	2512	2636
2	2	3027	3005
2	6	1916	1882
2	10	985	589
2	14	1089	637
3	3	1067	1341
3	5	1523	1446
3	9	1194	1139
4	4	2166	-2374
4	6	1515	-1476
4	8	1208	-1416
5	3	1508	-1359
5	5	1405	-1501
5	7	2900	-2975
6	2	2754	2232
6	6	2546	2896
6	10	944	689
7	1	1362	1476
7	5	2598	2731
7	9	1902	1830
8	4	1334	-1365
9	1	2869	-2807
9	3	1998	-1674
11	1	1575	1672
11	3	1660	1426
11	9	1198	753
12	2	1529	1550
12	6	1344	1373
13	7	1763	-1644
14	0	1290	-983
14	4	1531	-1840
**** L = 15 ****			
0	6	1765	-1885
0	12	1453	1476
0	14	1089	1272
1	1	1083	-659
1	17	1228	-1072
2	12	1084	-1031
5	7	1574	1166
5	13	1253	-989
6	6	1481	-1550
7	9	1421	-1030
7	11	1043	714
7	13	1264	-1340
**** L = 16 ****			
0	0	3688	3578
0	2	1748	-1785
0	6	1721	-1686
1	5	979	-845
2	4	1154	779
5	1	1855	-1099
6	0	2780	2559
6	2	1465	-1383
6	4	1152	1131
8	0	1664	1285
**** L = 17 ****			
0	12	1433	-1074
1	11	1198	-1130
**** L = 18 ****			
0	0	3131	-3562
0	4	1749	-1655
3	7	1018	603
4	0	1495	-1222
6	6	1203	1007
8	0	1569	-1012

[a] Asterisks denote unobserved reflections.

mean-square thermal amplitudes of vibration of the antimony and bromine atoms are given in Table III and a plot of the thermal ellipsoids of all nonhydrogen atoms is shown in Figure 1. The β_{33} components of the ellipsoids (normal to the mirror planes at $z = {}^1/_4$ and $z = {}^3/_4$) are not excessively large and this is further support for the choice of space group *Cmcm*. Table IV lists the observed and calculated structure factors (in electrons × 10).

Description of the Structure

Crystals of $(C_5H_5NH)_6Sb_4Br_{24}$ consist of pyridinium cations and $Sb^{III}Br_6{}^{3-}$ and $Sb^{V}Br_6{}^{-}$ anions, arranged as shown in Figures 1–3. The Sb(III):Sb(V) ratio is 1:3. The packing of ions is such that anions populate levels $z = {}^1/_4$ and ${}^3/_4$ and the cations levels $z = 0$ and ${}^1/_2$. Anions in level $z = {}^3/_4$ are displaced in the y direction by approximately 1 Å relative to those in $z = {}^1/_4$. This displacement forces the cations to tilt (rings I and III) or rotate (ring II) by approximately 14° relative to the unit cell c axis. Each cation is surrounded by two $Sb^{III}Br_6{}^{3-}$ and four or six $Sb^{V}Br_6{}^{-}$ anions.

Dimensions of the anions and associated estimated standard deviations are summarized in Table V. The standard deviations were based on the variance–covariance matrix as obtained from the final cycle of least-squares refinement, using the program ORFFE.[22] Also included in Table V are the Sb–Br bond lengths corrected for thermal effects using the Cruickshank approximation of rigid-body libration.[33] In making this correction, the breadth parameter, q^2, for the peaks was assigned a value of 0.12 Å^2. The magnitudes and orientations of the root-mean-square thermal amplitudes of vibration for Sb and Br depicted in Figure 1 indicate that this rigid-body treatment is a reasonable one. Average bond lengths in each hexacoordinate anion are consistent with those in the related ammonium, rubidium, and 2-methylpyridinium salts, summarized in Table VI. Bond lengths within each anion in the

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(33) (a) D. W. J. Cruickshank, *Acta Crystallogr.*, **9**, 754 (1956); (b) D. W. J. Cruickshank, *ibid.*, **9**, 757 (1956); (c) D. W. J. Cruickshank, *ibid.*, **14**, 896 (1961); (d) C. L. Coulter, P. K. Gantzel, and K. N. Trueblood, ACA Computer Program 232 (UCLAT01), Department of Chemistry, University of California, Los Angeles, Calif., 1961.

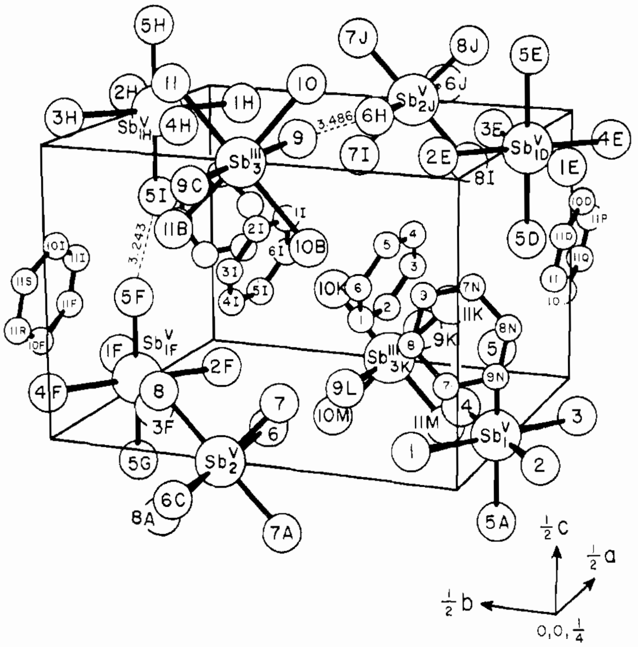

Figure 2.—Crystal structure of $(C_5H_5NH)_6Sb_4Br_{24}$, illustrating the contents of one-eighth the unit cell (two asymmetric units). The view is identical with that in Figure 1. For clarity, pyridinium hydrogen atoms have been excluded. The numbering scheme of all atoms, including those related by symmetry, coincides with that in Tables I, II, and V (footnote *b*).

TABLE V

DIMENSIONS OF THE ANIONS IN $(C_5H_5NH)_6Sb_4Br_{24}$

Atoms	Length, Å Uncor	Length, Å Cor[a]	Atoms[b]	Angle, deg
		(a) $Sb^VBr_6^-$ Anion (Position 8g)		
Sb(1)-Br(1)	2.531 (7)	2.555 (10)	Br(1)-Sb(1)-Br(2)	92.2 (2)
Sb(1)-Br(2)	2.532 (7)	2.547 (10)	Br(1)-Sb(1)-Br(4)	90.1 (2)
Sb(1)-Br(3)	2.566 (7)	2.580 (10)	Br(1)-Sb(1)-Br(5)	90.0 (1)
Sb(1)-Br(4)	2.522 (7)	2.537 (10)	Br(2)-Sb(1)-Br(3)	89.7 (2)
Sb(1)-Br(5)	2.532 (4)	2.544 (6)	Br(2)-Sb(1)-Br(5)	90.1 (1)
			Br(3)-Sb(1)-Br(4)	88.0 (2)
			Br(3)-Sb(1)-Br(5)	90.0 (1)
			Br(4)-Sb(1)-Br(5)	89.9 (1)
		(b) $Sb^VBr_6^-$ Anion (Position 4c)		
Sb(2)-Br(6)	2.535 (5)	2.542 (7)	Br(6)-Sb(2)-Br(7)	89.2 (1)
Sb(2)-Br(7)	2.531 (7)	2.546 (10)	Br(6)-Sb(2)-Br(8)	90.9 (1)
Sb(2)-Br(8)	2.529 (7)	2.545 (10)	Br(7)-Sb(2)-Br(7A)	91.1 (4)
			Br(7)-Sb(2)-Br(8)	90.2 (3)
			Br(8)-Sb(2)-Br(8A)	88.5 (4)
		(c) $Sb^{III}Br_6^{3-}$ Anion (Position 4c)		
Sb(3)-Br(9)	2.788 (5)	2.793 (7)	Br(9)-Sb(3)-Br(10)	87.9 (1)
Sb(3)-Br(10)	2.797 (7)	2.801 (10)	Br(9)-Sb(3)-Br(11)	92.2 (1)
Sb(3)-Br(11)	2.789 (7)	2.809 (10)	Br(10)-Sb(3)-Bf(10B)	96.3 (3)
			Br(10)-Sb(3)-Br(11)	87.4 (2)
			Br(11)-Sb(3)-Br(11B)	88.9 (3)

[a] The estimated standard deviations include an arbitrary uncertainty factor of 1.4 for the rigid-body assumption. [b] Key to symmetry operations in this table, succeeding tables, Figure 2, and the text: (A) $x, y, ^1/_2 - z$; (B) $x, y, 1.5 - z$; (C) $\bar{x}, y, z$; (D) $x, \bar{y}, 1 - z$; (E) $x, \bar{y}, ^1/_2 + z$; (F) $^1/_2 - x, ^1/_2 + y, z$; (G) $^1/_2 - x, ^1/_2 + y, ^1/_2 - z$; (H) $^1/_2 - x, ^1/_2 - y, ^1/_2 + z$; (I) $^1/_2 - x, ^1/_2 - y, 1 - z$; (J) $^1/_2 + x, ^1/_2 - y, ^1/_2 + z$; (K) $^1/_2 + x, ^1/_2 - y, -^1/_2 + z$; (L) $^1/_2 - x, ^1/_2 - y, -^1/_2 + z$; (M) $^1/_2 + x, ^1/_2 - y, 1 - z$; (N) $\bar{x}, \bar{y}, 1 - z$; (P) $1 - x, \bar{y}, 1 - z$; (Q) $1 - x, y, z$; (R) $-^1/_2 + x, ^1/_2 + y, z$; (S) $-^1/_2 + x, ^1/_2 - y, 1 - z$.

pyridinium salt are essentially equivalent within one standard deviation, and deviations of the bond angles from 90° do not exceed 2.2°. One bond, 2.580 (10) Å in length, in the $Sb^VBr_6^-$ ion of Sb(1) and one angle,

TABLE VI

AVERAGE Sb–Br BOND LENGTHS (Å) IN $Sb^VBr_6^-$ AND $Sb^{III}Br_6^{3-}$ IONS[a]

Compound	$Sb^VBr_6^-$	$Sb^{III}Br_6^{3-}$	Ref
$(NH_4)_4Sb_2Br_{12}$[b]	2.552 (10)	2.792 (4)	*d*
$Rb_4Sb_2Br_{12}$[c]	2.550 (47)	2.763 (37)	*e*
$(C_5H_5NH)_6Sb_4Br_{24}$	2.547 (16), 2.544 (2)	2.799 (7)	This study
$(\alpha\text{-}C_6H_7NH)_2SbBr_9$	2.553 (9)	. . .	*f*
Av	2.55 (2)	2.78 (3)	

[a] Bond lengths in the ions in all four structures have been corrected for thermal effects using the Cruickshank approximation of rigid-body libration.[33] The breadth parameter, q^2, was assigned a value of 0.12 Å^2 in each case. Average distances and associated rms deviations were computed from the expressions

$$\bar{x} = \sum_{i=1}^{N} (x_i/\sigma_i^2) \Big/ \sum_{i=1}^{N} (1/\sigma_i^2)$$

$$\sigma(\bar{x}) = \left[\sum_{i=1}^{N} (x_i - \bar{x}^2)/(N - 1)\right]^{1/2}$$

where x_i is an individual observation, σ_i is the corresponding standard deviation, and N is the number of observations. Averages for a given ion include the lengths of all *six* bonds. [b] The corrected bond lengths previously reported[5-7] were based on the Busing–Levy "riding" model, *not* the rigid-body librational model as had been reported. The corrected bond lengths of the independent bonds based on the rigid-body assumption are Sb(V)–Br(1) = 2.560 (8), Sb(V)–Br(3) = 2.541 (7), Sb(III)–Br(2) = 2.789 (8), and Sb(III)–Br(4) = 2.796 (7) Å. [c] The corrected bond lengths of the independent bonds based on the rigid-body assumption are Sb(V)–Br(1) = 2.536 (7), Sb(V)–Br(3) = 2.622 (11), Sb(III)–Br(2) = 2.787 (6), and Sb(III)–Br(4) = 2.716 (6) Å. [d] See ref 6; also footnote *b*, this table. [e] See ref 7; also footnote *c*, this table. [f] See ref 8.

TABLE VII

SELECTED NEAREST-NEIGHBOR C···Br, H···Br, AND Br···Br CONTACTS AND ANGLES

Atoms	Dist,[a] Å	Atoms	Dist,[a] Å
	Carbon···Bromine Contacts		
C(1)···Br(1)	4.09	C(5)···Br(9)	3.85
C(1)···Br(4)	4.14	C(6)...Br(5)	4.11
C(1)···Br(5)	4.06	C(7)···Br(1)	3.90
C(2)···Br(4)	3.57	C(7)···Br(2)	3.95
C(2)···Br(5)	4.07	C(7)···Br(5)	3.87
C(3)···Br(5)	4.14	C(8)···Br(5)	4.14
C(4)···Br(5)	4.19	C(10D)···Br(8I)	3.71
C(4)···Br(5D)	4.12	C(10)···Br(11K)	3.67
C(4)···Br(6H)	3.68	C(11D)···Br(8I)	4.00
C(5)···Br(5)	4.18	C(11)···Br(11K)	4.17
C(5)...Br(5D)	4.10		
	Hydrogen···Bromine Contacts		
H(1)···Br(6)	2.86	H(6)···Br(10B)	2.80
H(2)···Br(4)	3.03	H(7)···Br(1)	3.10
H(2)···Br(9L)	2.48	H(8)···Br(7)	3.06
H(3)···Br(11K)	2.73	H(9)···Br(10B)	2.40
H(4)···Br(3E)	2.85	H(11)···Br(5)	2.77
H(5)...Br(2E)	3.03		
	Bromine···Bromine Contacts		
Br(1)···Br(1C)	4.083 (14)	Br(3F)···Br(8)	3.998 (8)
Br(1)···Br(6)	4.524 (8)	Br(4)···Br(9L)	3.781 (9)
Br(1)···Br(7)	3.893 (8)	Br(4)···Br(11K)	4.022 (7)
Br(2)···Br(2C)	4.348 (14)	Br(5)···Br(5D)	3.243 (7)
Br(2E)···Br(9)	4.424 (8)	Br(6)···Br(9L)	3.486 (7)
Br(2E)···Br(10)	4.025 (8)	Br(7)···Br(10B)	4.381 (10)
Br(3F)···Br(6)	3.898 (8)	Br(8)···Br(11B)	4.510 (10)
Atoms	**Angle, deg**	**Atoms**	**Angle, deg**
Br(5)–Sb(1)–Br(5A)	179.8 (3)	Sb(1)–Br(5)···Br(5D)	164.8 (3)
Br(6)–Sb(2)–Br(6C)	177.6 (3)	Sb(2)–Br(6)···Br(9L)	176.9 (3)
Br(9)–Sb(3)–Br(9C)	173.7 (2)	Sb(3)–Br(9)···Br(6H)	171.9 (3)

[a] Distances and angles do not include a correction for thermal effects of librating anions. The H···Br distances are based on C–H bond lengths of 1.1 Å. Average estimated standard deviations in the C···Br distances are 0.03 Å and those in the H···Br distances are 0.06 Å.

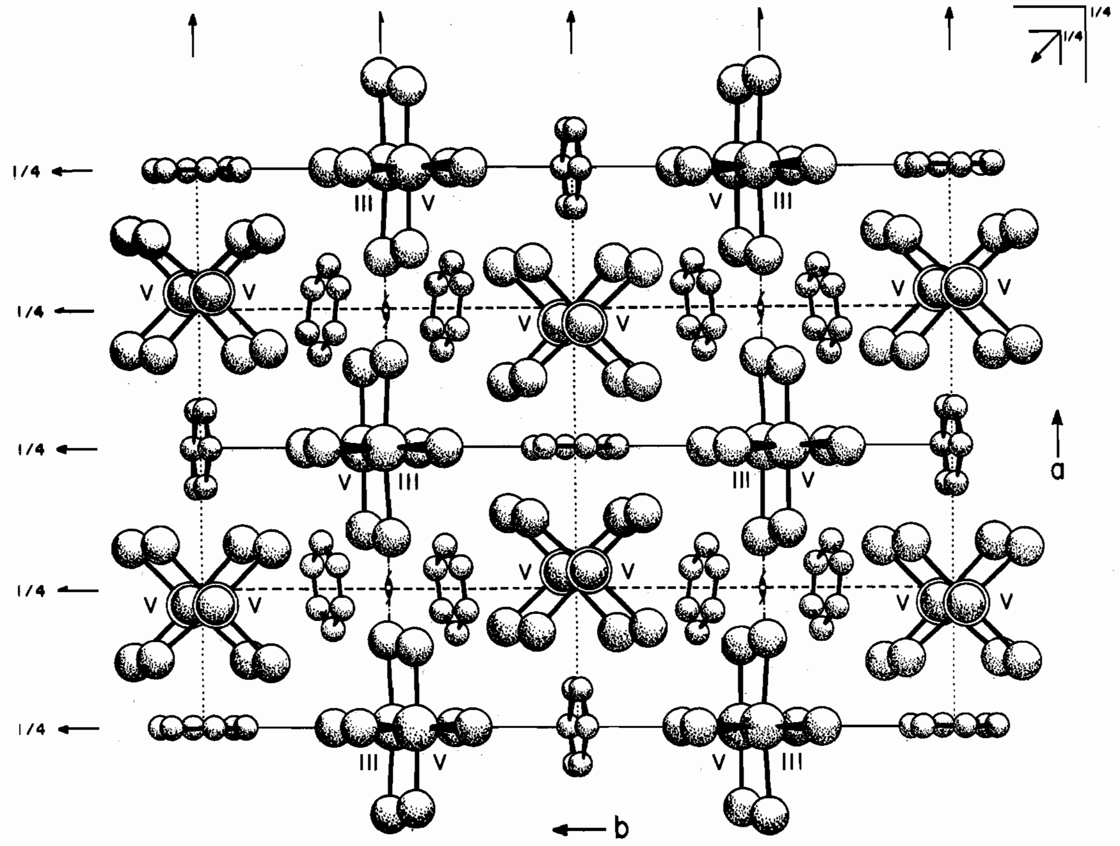

Figure 3.—Crystal structure of $(C_5H_5NH)_6Sb_4Br_{24}$ projected onto the (001) plane. Only the anions in levels $z = {}^1/_4$ and ${}^3/_4$ and the cations in level $z = {}^1/_2$ within the unit cell are shown. For clarity, pyridinium hydrogen atoms have been excluded.

96.3 (3)°, in the $Sb^{III}Br_6{}^{3-}$ ion are the only two exceptions.

Selected nearest-neighbor carbon···bromine and hydrogen···bromine distances are given in Table VII. By comparison with the 3.65-Å[34] sum of the Pauling van der Waals radius of bromine and the half-thickness of the aromatic pyridinium ring, it is evident that no unusual cation···bromine distances along the ring normals are present. The closest approach of any ring is 3.87 Å, the distance of Br(5) from the plane of ring II. Eleven cationic hydrogen···bromine distances less than the Pauling van der Waals radius sums of hydrogen and bromine, 3.2 Å,[34] are present, however. The shortest distance, 2.4 Å, involves H(9) with Br(10B).

Nearest-neighbor interionic bromine···bromine contacts are also listed in Table VII. Two distances significantly shorter than the 3.90-Å van der Waals radius sums are present in the structure. These distances are 3.486 (7) Å between Sb(V) and Sb(III) anions (chain I) and 3.243 (7) Å between neighboring Sb(V) anions (chain II). These distances strongly indicate the presence of weak bonding interactions between these ions. Such short distances, particularly the 3.24-Å distance, would be energetically unfavorable in the absence of some bond formation, indicated as a first approximation by calculation of the interaction energy using the Lennard-Jones potential. Attractive interactions of this type are already known. In solid bromine, for example, intermolecular distances as short as 3.30 Å occur.[35] All Br–Br···Br valency angles are close to 90° or to 180°, as in our case, a structural feature found among all polyhalide complexes except IF_7.[36-38] An even shorter distance, 2.87 Å, has been found between Br_2 molecules and $Sb_2Br_9{}^{3-}$ ions in $[N(CH_3)_4]_3Sb_2Br_{11}$.[39] Also noteworthy is that the interaction along chain I is virtually as short as the Br···Br distance, 3.491 (2) Å, found within the nearly linear $\cdots Br_3{}^- \cdots Sb^VBr_6{}^- \cdots$ chain in $(\alpha\text{-}C_6H_7NH)_2SbBr_9$. This remarkable similarity of the two interactions, summarized in Figure 4, is readily appreciated by considering the structural similarities of the tribromide and $Sb^{III}Br_6{}^{3-}$ ions. First, both ions exhibit similar bonding; expressed in terms of the LCAO–MO treatment, the molecular orbitals may be represented as linear combinations of the outermost p orbitals of the bromine atoms in the normal three-center, four-electron approximation.[9,36,37,40] Second, the external bromines in both ions carry a formal charge of ${}^1/_2-$.

Aromatic molecules are known to form donor–acceptor adducts with such molecules as bromine[41] and carbon tetrabromide.[42] In both cases the distance of bromine from the ring centers is approximately 0.3 Å shorter

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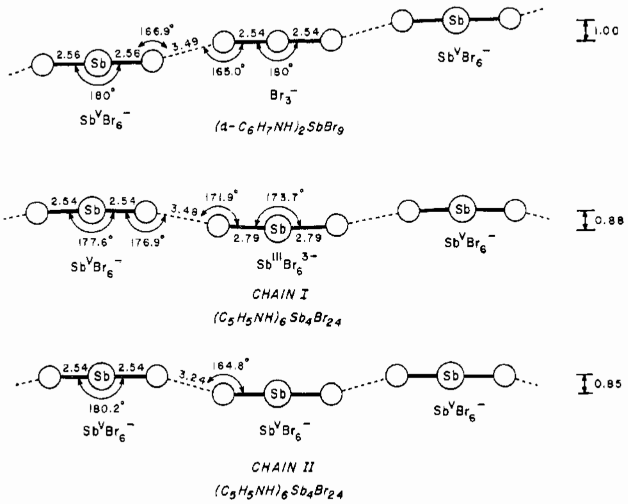

Figure 4.—Schematic representation of the nearly linear anionic chains in $(\alpha\text{-}C_6H_7NH)_2SbBr_9$ and $(C_5H_5NH)_6Sb_4Br_{24}$. Interatomic distances, angles, and the perpendicular displacements of the anionic centers along the chains are indicated.

than the conventional van der Waals distance (3.65 Å). In our material, three cations surrounding the Br · · · Br bond in chain II face bromine atoms. However, all distances exceed van der Waals distances, leading us to conclude that donor–acceptor interactions between the pyridinium cations and the $Sb^VBr_6^-$ anions are very weak or, more likely, nonexistent.

Unlike the deep red 2-, 3-, and 4-methylpyridinium salts which undergo color changes at the temperature of liquid nitrogen,[11] the deep red color of this material is unaffected by a decrease in temperature. This additional absorption by the pyridinium derivative may be ascribed to possible charge-transfer absorption within the anions themselves or to possible intervalence-transfer absorption between the unlike anions.[43] Since the absorption properties of the individual anions are unknown, and in view of the weak bonding between the mixed Sb(III) and Sb(V) moieties, bonding not found in the ammonium and rubidium analogs, the relative importance of intervalence-transfer absorption in this material cannot be fully assessed. Further research in this area is certainly dictated.

Deformation of the $Sb^{III}Br_6^{3-}$ ion from O_h symmetry immediately invites speculation regarding the stereochemical "activity" of a lone pair of electrons. This hexahalide ion is of considerable interest because the valence shell of the central antimony atom contains seven electron pairs of which only six are actually used in bonding. According to the simple valence-shell electron-pair repulsion model of Sidgwick and Powell[44] and Gillespie and Nyholm,[45] lone pairs as well as bonded electron pairs influence the stereochemistry of molecules and ions. It has been shown that for the seven-coordination case more than one arrangement of electron pairs with similar energies is possible.[45b,46–48] Two of these arrangements are exhibited by XeF_6[49] and IF_7.[50–52] The molecule XeF_6, which is formally isoelectronic with the $Sb^{III}Br_6^{3-}$ ion and contains a lone pair of electrons, exists as an irregular octahedron exhibiting a preference toward C_{3v} symmetry, though it is considerably less distorted than predicted solely by the electron-pair repulsion model. The hexahalide ions $SeCl_6^{2-}$, $SeBr_6^{2-}$, $TeCl_6^{2-}$, and $TeBr_6^{2-}$, on the other hand, each exhibit *regular* octahedral structures and therefore constitute definite exceptions to Gillespie's hypothesis;[53–58] similarly, the $SbBr_6^{3-}$ ion in $(NH_4)_4Sb_2Br_{12}$[6] and $Rb_4Sb_2Br_{12}$[7] also exhibits no appreciable deformation. This lack of deformation in the case of the ions may be attributed to ligand–ligand repulsion arising from steric effects of the relatively large chlorine and bromine atoms, forces which are sufficiently strong to prevent virtually any stereochemical influence of the lone pair.[45b] The most prominent deformation of the ion corresponds to a slight opening of a Br–Sb–Br angle to 96.3 (3)°, but there is no associated compression of the remaining four bromine ligands toward the opposite side of the ion. We therefore ascribe the increase in the angle Br(10)–Sb(3)–Br(10B) from 90 to 96.3° primarily to ligand–ligand repulsion introduced by the decrease in the angle Br(9)–Sb(3)–Br(9C) from 180 to 173.7 (3)°, a decrease presumably caused by the weak bond formation between the ions along chain I. Possible weak hydrogen · · · bromine bonding between Br(10B) and H(9) at a distance of 2.4 Å may also contribute to the ion deformation.

Acknowledgments.—Helpful discussions with Drs. L. S. Bartell and D. E. Williams are gratefully acknowledged.

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