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The Crystal Structure of Quinuclidinium Dodecabromoantimon(III)antimon(V)ate-2-Dibromine, $(C_7H_{13}NH)_4Sb^{III}Sb^{V}Br_{12}\cdot 2Br_2$[1]

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Quinuclidinium dodecabromoantimon(III)antimon(V)ate-2-dibromine, $(C_7H_{13}NH)_4Sb^{III}Sb^{V}Br_{12}\cdot 2Br_2$, crystallizes as jet black octahedral crystals in the cubic space group $Fm3m$ $(O_h{}^5)$ with the unit cell parameter $a = 13.873 \pm 0.004$ Å at 24°. The observed and calculated densities are 2.42 and 2.45 g/cm³, respectively. The structure was refined by least-squares methods to a final conventional R index of 0.068 using three-dimensional X-ray diffraction counter data. Unlike $(NH_4)_4Sb^{III}Sb^{V}Br_{12}$ and $Rb_4Sb^{III}Sb^{V}Br_{12}$ (K_2PtCl_6-type structures) in which the Sb(III) and Sb(V) oxidation states are ordered, no ordering of these states was found in the present material. The average anions and threefold disordered bromine molecules form an NaCl-type arrangement with the cations occupying the eight tetrahedral holes at $^1/_4$, $^1/_4$, $^1/_4$, etc. The bromine molecules are aligned parallel with the unit cell axes, thus bridging adjacent anions, but are disordered with respect to these axes. Each cation is aligned with its triad axis parallel with the unit cell triad axis but is statistically disordered such that nitrogen points toward any one of the four surrounding anions. The center of the cation is displaced from the tetrahedral hole by 0.17 Å toward the anion to which nitrogen is pointing. The observed *average* Sb–Br bond length is 2.664 ± 0.008 Å, in excellent agreement with the average (2.665 Å) of known octahedral Sb(III)–Br and Sb(V)–Br bond lengths. The bond length in the Br_2 molecule is 2.32 ± 0.04 Å. The *average* bromine···bromine contact along the linear array ···Br–Sb–Br···Br–Br··· is extremely short, occurring at 3.11 ± 0.02 Å, while the other nearest neighbor Br···Br contacts are 4.43 ± 0.02 Å. The salt is diamagnetic with $\chi = -0.96 \times 10^{-6}$ cgsu at 28°.

Introduction

This paper describes the crystal structure of quinuclidinium[3] dodecabromoantimon(III)antimon(V)ate-2-dibromine, $(C_7H_{13}NH)_4Sb^{III}Sb^{V}Br_{12}\cdot 2Br_2$. It is part of a continuing series of investigations of complex antimony halide anions and the effects of cation size, type, stereochemistry, and charge distribution on the formation and crystallization of these anions. Structures of three mixed ionic antimony(III) and antimony(V) bromide salts have already been reported. Of these, two contain alkali-type ions, *viz.*, the salts $(NH_4)_4Sb^{III}Sb^{V}Br_{12}$[4] and $Rb_4Sb^{III}Sb^{V}Br_{12}$,[5] and the other, $(C_5H_5NH)_6Sb^{III}Sb^{V}{}_3Br_{24}$,[6] contains an unsaturated ring cation. The quinuclidinium structure reported here represents an example of an antimon(III)antimon(V)ate salt containing a saturated ring cation. We felt it would be of considerable interest to determine the structural effects of the use of such a large saturated symmetrical cation.

Experimental Section

Preparation.—The salt was prepared by treating 0.9 g of quinuclidine with a solution of 2.50 g of antimony tribromide and 0.8 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, and dried on a porous porcelain plate in a desiccator containing concentrated sulfuric acid as the desiccant and an atomsphere of air with a small partial pressure of bromine vapor.

Single crystals suitable for the X-ray investigation were prepared by recrystallizing the raw material from hot, concentrated hydrobromic acid following a procedure described elsewhere.[7,8]

Physical Properties.—The crystals are of octahedral habit, resembling those of the alkali (R) salts $R_4Sb^{III}Sb^{V}Br_{12}$. The crystals are virtually jet black in color between room temperature and −173°. As the temperature is elevated above room temperature (in an open melting point tube), the material first reverts to a red solid, beginning at approximately 135° and becoming completely red at 152°. At 168° the red material begins to turn yellow, becoming completely yellow in the range 260–300°. In the absence of a bromine environment at room temperature, the crystals slowly lose bromine, becoming tan.[7]

Magnetic Susceptibility.—A Faraday balance was used to measure the magnetic susceptibility in air at atmospheric pressure at 28°. The substance is diamagnetic with a value $\chi = -0.961 \times 10^{-6}$ cgsu. The observed diamagnetism is slightly greater than that reported for $(NH_4)_4Sb^{III}Sb^{V}Br_{12}$ with $\chi = -0.036 \times 10^{-6}$ cgsu.[9]

Crystal Data.—Quinuclidinium dodecabromoantimon(III)antimon(V)ate-2-dibromine, $(C_7H_{13}NH)_4Sb^{III}Sb^{V}Br_{12}\cdot 2Br_2$ (formula weight 1970.75), crystallizes in the cubic space group $Fm3m$ $(O_h{}^5)$, with the lattice parameter at 24° of $a = 13.873 \pm 0.004$ Å; $V = 2670 \pm 1$ Å³; $d_{\text{obsd}} = 2.42 \pm 0.05$ g/cm³ (by flotation) and $d_{\text{calcd}} = 2.451 \pm 0.001$ g/cm³ for $Z = 2$ formula units per unit cell.

The crystal symmetry was determined from Weissenberg and precession photographs which yielded systematic conditions limiting possible reflections (*hkl* either all even or all odd) consistent with the space groups $F432$, $F\bar{4}3m$, and $Fm3m$. No weak reflections of the type found for $(NH_4)_4Sb^{III}Sb^{V}Br_{12}$ were detected. The lattice parameter was determined by a least-squares fit[10] to 24 weighted copper $K\alpha$ reflections (λ 1.5418 Å) measured from a zero-level Weissenberg zone calibrated with superimposed alu-

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[2] (a) Mobil Research and Development Corp. (b) Ames Laboratory, Iowa State University.

[3] Synonyms for quinuclidine, $C_7H_{13}N$: (a) 1-azabicyclo[2.2.2]octane and (b) 1,4-ethylenepiperidine.

[4] S. L. Lawton and R. A. Jacobson, *Inorg. Chem.*, **5**, 743 (1966).

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

[7] M. L. Hackert, S. L. Lawton, and R. A. Jacobson, *Proc. Iowa Acad. Sci.*, **75**, 97 (1968).

[8] S. L. Lawton and R. A. Jacobson, *Inorg. Chem.*, **7**, 2124(1968).

[9] N. Elliott, *J. Chem. Phys.*, **2**, 298 (1934).

[10] D. E. Williams, "LCR-2, A Fortran Lattice Constant Refinement Program," Report IS-1052, Ames Laboratory, Iowa State University, Ames, Iowa, 1964.

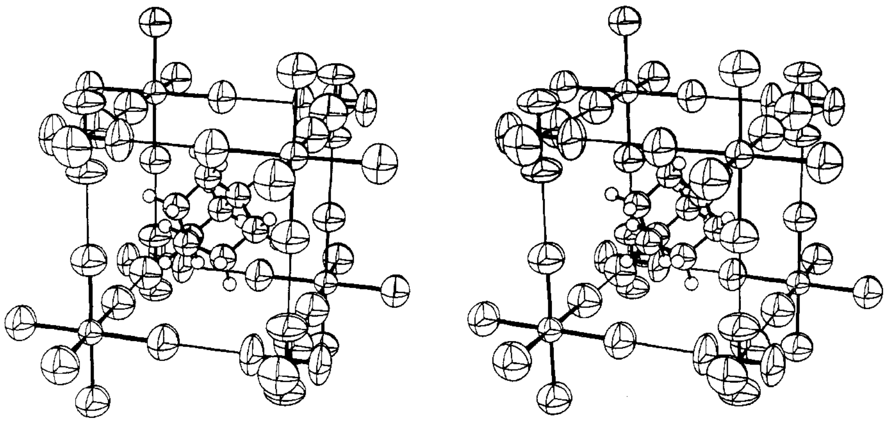

Figure 1.—A stereographic view of the packing of ions and molecules in crystals of $(C_7H_{13}NH)_4Sb_2Br_{12}\cdot 2Br_2$, outlining one-eighth the unit cell. The view corresponds to a right-handed coordinate system with the origin in the front lower left corner with the x axis horizontal. Shown are the $SbBr_6$ anions (Sb(III) and Sb(V) disordered), the disordered Br_2 molecules, and one of four possible orientations of the $C_7H_{13}NH^+$ cation; the nitrogen position lies on the cation triad axis nearest the $SbBr_6$ anion. Ellipsoidal boundaries of the atoms (except carbon and hydrogen) are at the 75% probability level.

minum powder lines ($a_0 = 4.0330$ Å). The indicated error in this parameter is 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 radiation from an octahedral crystal of dimensions 0.157 × 0.157 × 0.157 mm (corner to corner). The crystal was sealed in a 0.2-mm thin-walled Lindemann glass capillary and mounted on the diffractometer with $[110]^*$ coincident with the Φ axis. A General Electric single-crystal diffractometer equipped with an XRD-5 X-ray unit, a scintillation detector, and a pulse height discriminator was used with the moving-crystal, moving-counter measurement technique (θ, 2θ coupling) and a 3.0° takeoff angle. The counter angle, 2θ, was scanned over 3.33° at a speed of 2°/min. Background counts of 40 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, and reflection centering in 2θ. A total of 198 independent reflections were measured within the angular range $2\theta \leq 55°$ of which 70 were observed above the background level. Three strong reflections were measured periodically throughout the recording period as a check on electronic and crystal stability.

The raw intensities of the 27 most intense reflections were initially corrected for background; intensities of the remaining 43 were obtained by integrating the peak area on the recorder trace by means of a compensating planimeter. These planimetered intensities were scaled to the strong reflections by a factor (in counts per unit area) which was derived by planimetering a number of the 27 strong reflections whose integrated intensities from the counter were known. Intensities of all 70 reflections were then corrected for crystal decomposition, Lorentz, polarization, and absorption effects. Transmission factors varied between 0.373 and 0.395, based on a linear absorption coefficient of 137 cm^{-1}. The standard deviation in the intensity of each of the 70 reflections was computed in the usual way[6] using a value of 0.03 for the ignorance factor p. The estimated standard deviation in each structure factor was calculated by the finite-difference method of Williams and Rundle.[11] All 70 reflections observed above the background level satisfied the condition $F_o > 2\sigma(F_o)$ and were therefore used in the refinements.

Solution and Refinement of the Structure.—The structure was solved by normal heavy-atom techniques. Initial coordinates of the antimony and bromine atoms consistent with the conditions imposed by the special positions were readily determined by inspection of an unsharpened three-dimensional Patterson function.[12] These atomic positions generated, through symmetry operations, octahedral $SbBr_6$ anions and molecular bromine, arranged as shown in Figure 1. Subsequent Fourier and difference Fourier syntheses revealed the locations of all eight nonhydrogen atoms in the cation, with each cation occupying a tetrahedral hole in the unit cell. Owing to the absence of superlattice reflections in the reciprocal lattice, the Sb(III) and Sb(V) states cannot be resolved and so each bromine molecule is forced to assume threefold disorder (arising from six identical surrounding $SbBr_6$ anions) and each cation to assume fourfold disorder (arising from four identical surrounding $SbBr_6$ anions). No ordering of the Br_2 molecules or cations is possible in the noncentrosymmetric space groups $F432$ or $F\bar{4}3m$ by virtue of the special position each group occupies. Consequently the centrosymmetric space group $Fm3m$ was selected as best representing the actual structure.

The structure was refined by using a full-matrix least-squares procedure. The function minimized was $\Sigma w\Delta^2$, where $\Delta = |F_o| - |F_c|$, with $|F_o|$ and $|F_c|$ being the observed and calculated structure amplitudes, respectively, and w the weight defined as $1/\sigma^2(F_o)$. Atomic scattering factors for neutral atoms tabulated by Hanson, *et al.*,[13] were used. Anomalous dispersion corrections $\Delta f'$ and $\Delta f''$ for antimony and bromine tabulated by Templeton[14] were applied to the calculated structure factors.[15]

The atomic positions and isotropic thermal parameters of antimony and bromine, along with the scale factor, were refined first, resulting in discrepancy values of $R_1 = \Sigma|\Delta|/\Sigma|F_o| = 0.130$ and $R_2 = (\Sigma w\Delta^2/\Sigma w|F_o|^2)^2 = 0.182$. Contributions of the cation to the calculated structure factors were then included in the refinement. The cation was defined as a rigid body constrained to C_{3v} symmetry, using the least-squares group refinement procedure described by Ibers, *et al.*[16] In this refinement the cation was assigned a single, variable isotropic thermal parameter and six variable positional parameters; C–C and C–N distances of 1.537 and 1.479 Å, respectively, were assumed. This refinement of the cation together with the other atoms and scale factor converged rapidly to $R_1 = 0.084$ and $R_2 = 0.077$.

A difference synthesis based on the preceding isotropic refine-

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

[12] In addition to various local programs for the CDC 1604 computer, programs used in the solution and refinement of this structure were 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.

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

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

[15] J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, **17**, 781 (1964).

[16] S. J. La Placa and J. A. Ibers, *ibid.*, **18**, 511 (1965); R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).

TABLE I

FINAL POSITIONAL, THERMAL, AND GROUP PARAMETERS FOR $(C_7H_{13}NH)_4Sb_2Br_{12}\cdot 2Br_2$

Nongroup Atoms

Atom	Position (occupancy)	x^a	y	z	β_{11}^b	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Iso equiv B,^{c} Å^2
Sb	4a (1)	0*^{d}	0*	0*	49 (4)	49*	49*	0*	0*	0*	3.74
Br(1)	24e (1)	0.1921 (5)	0*	0*	73 (6)	97 (4)	97*	0*	0*	0*	6.82
Br(2)	24e ($^1/_3$)	0.4162 (13)	0*	0*	37 (11)	117 (11)	117*	0*	0*	0*	6.96

Group Atoms

Group	Position of centroid (occupancy)	x_c^e	y_c	z_c	δ	ϵ	η	Group B,^{f} Å^2
Cation	32f ($^1/_4$)	0.2431 (43)	0.2431*	0.2431*	45.0*	180.0*	−144.73*	8.3 (28)

[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 10^4. [c] Calculated from the anisotropic thermal parameters and unit cell parameters by the equation $B \simeq {}^4/_3(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + 2\beta_{12}ab\cos\gamma + 2\beta_{13}ac\cos\beta + 2\beta_{23}bc\cos\alpha)$: 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 degrees) are those described in ref 16. The origin in the internal system was taken at the midpoint of the six carbon atoms which form the propeller blades (those which form bonds with two hydrogen atoms), with a_1' intersecting the nitrogen position and a_3' intersecting the midpoint of a C–C bond which is parallel with the a_1' vector. [f] Group B is the isotropic thermal parameter for the entire quinuclidinium cation.

TABLE II

DERIVED POSITIONAL PARAMETERS FOR GROUP ATOMS IN $(C_7H_{13}NH)_4Sb_2Br_{12}\cdot 2Br_2$

Atom	x^a	y	z	Atom	x^a	y	z
N(1)	1906	1906	1906	H(4)	184	102	306
C(2)	2932	1701	1701	H(5)	102	184	306
C(3)	1701	1701	2932	H(6)	102	306	184
C(4)	1701	2932	1701	H(7)	184	306	102
C(5)	3603	2324	2324	H(8)	401	273	191
C(6)	2324	2324	3603	H(9)	401	191	273
C(7)	2324	3603	2324	H(10)	191	401	273
C(8)	2963	2963	2963	H(11)	273	401	191
H(1)	152	152	152	H(12)	273	191	401
H(2)	306	184	102	H(13)	191	273	401
H(3)	306	102	184	H(14)	337	337	337

[a] Coordinates for carbon have been multiplied by 10^4; those for hydrogen, by 10^3. Symmetry positions occupied by the atoms are as follows: N(1), C(8), H(1), H(14) at 32f (x, x, x, etc.); C(2) through C(7) at 96k (x, x, z, etc.); H(2) through H(13) at 192l (x, y, z, etc.). All occupancies are $^1/_4$.

TABLE III

FINAL ROOT-MEAN-SQUARE THERMAL AMPLITUDES OF VIBRATION (Å) IN $(C_7H_{13}NH)_4Sb_2Br_{12}\cdot 2Br_2$

Atom	Min	Med	Max
Sb	0.218 (6)	0.218 (6)	0.218 (6)
Br(1)	0.266 (1)	0.307 (7)	0.307 (7)
Br(2)	0.190 (28)	0.338 (16)	0.338 (16)

TABLE IV

OBSERVED AND CALCULATED STRUCTURE FACTORS (IN ELECTRONS) FOR $(C_7H_{13}NH)_4Sb_2Br_{12}\cdot 2Br_2$

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
**** L = 0 ****				6	4	3094	3016	11	1	1188	1015	6	6	927	806	10	4	1049	1265
				8	4	940	866	15	1	943	589	10	6	1118	1001	6	6	911	1157
2	0	4494	4416	10	4	2107	2146	3	3	2204	-2148	8	8	1228	-999	10	6	1099	1146
4	0	6784	7162	12	4	1125	1005	5	3	2276	2352	10	10	666	775	10	10	791	847
6	0	5763	6073	14	4	734	573	5	5	4531	4561								
8	0	2130	2086	6	6	2725	2794	7	5	1977	2047	**** L = 3 ****				**** L = 5 ****			
10	0	3508	3526	8	6	852	752	9	5	1634	1528								
12	0	1758	1689	10	6	1922'	1975	11	5	1264	1294	3	3	2902	-2815	5	5	4498	4564
14	0	1164	920	12	6	776	926					7	3	1037	-995	7	5	2270	2380
16	0	982	635	10	8	992	838	**** L = 2 ****				13	3	566	-579	9	5	1642	1768
2	2	3869	3671	10	10	1298	1265					5	5	3257	3220	11	5	1282	1368
4	2	2895	2905					2	2	3395	-2890	7	5	1030	1007	7	7	972	1056
6	2	2433	2354	**** L = 1 ****				4	2	1131	-1003	9	5	728	836	9	7	712	800
8	2	617	465					8	2	1591	-1539	11	5	939	814				
10	2	2090	2066	1	1	2710	2358	10	2	1049	885					**** L = 6 ****			
12	2	960	919	5	1	3978	4033	4	4	695	525	**** L = 4 ****							
14	2	750	489	7	1	1036	1124	8	4	657	-772					6	6	1118	1325
4	4	2963	3114	9	1	1072	937	10	4	1114	1097	6	4	1255	1297	10	6	927	1081

ment revealed pronounced anisotropy in the motions of the bromine atoms, particularly in the bromine molecules. This anisotropy is believed to be primarily an artifact of positional and orientational disorder of the bromine atoms rather than true thermal motions. Further group refinement, in which ellipsoidal thermal parameters were introduced for these atoms, reduced R_1 and R_2 to 0.070 and 0.063, respectively. Fixed contributions for the scattering of the group hydrogen atoms were then added to the structure factors. The C–H and N–H distances were assigned values of 0.98 and 0.94 Å, respectively; the thermal parameters were included in the single variable overall isotropic thermal parameter of the cation.

Convergence was reached with $R_1 = 0.068$ and $R_2 = 0.062$. The final standard deviation for an observation of unit weight, *i.e.*, the error of fit, was 1.08, where the error of fit is defined by $[\Sigma w\Delta^2/(n - m)]^{1/2}$ with n being the number of observations (70) and m the number of variables (10). On the final cycle no shift exceeded 0.0005σ. The relative correctness of the weighting scheme as judged by the variation of mean $w\Delta^2$ with $|F_o|$ and $(\sin\theta)/\lambda$ was satisfactory. The final difference synthesis was featureless, indicating that all electron density had been correctly accommodated. Comparison of the final values of F_o and F_c indicated that a correction for secondary extinction was unnecessary.

The final positional, thermal, and group parameters derived from the last cycle of least-squares refinement are given in Table I, along with the associated standard deviations in these parameters as estimated from the inverse matrix. The positional parameters of the atoms in the cation, which may be derived from the data in Table I, are presented in Table II. Root-mean-square thermal amplitudes of vibration of antimony and bromine are given in Table III. Table IV lists the observed and calculated structure factors.

Discussion

Crystals of $(C_7H_{13}NH)_4Sb_2Br_{16}$ consist of quinuclidinium cations, $Sb^{III}Br_6^{3-}$ and $Sb^{V}Br_6^{-}$ anions, and molecular bromine. Unlike $(NH_4)_4Sb^{III}Sb^{V}Br_{12}$[4] and $Rb_4Sb^{III}Sb^{V}Br_{12}$[5] in which Sb(III) and Sb(V) are ordered, no ordering of these states was found in the present material. The average anions and the disordered bromine molecules occupy, respectively, the sodium and chloride positions in an NaCl-type structure with the cations located in the eight tetrahedral holes at $^1/_4$, $^1/_4$, $^1/_4$, etc. (Figure 1). Presence of tetravalent antimony has been ruled out by the observed diamagnetism of this material at room temperature. The bromine molecules are aligned parallel with the unit cell axes, thus bridging adjacent anions, but are disordered with respect to these axes. The threefold axis of each cation is aligned with the unit cell triad axis, with nitrogen directed toward any one of the four surrounding anions. The center of each cation is displaced from the tetrahedral hole by 0.17 Å toward the anion to which nitrogen is pointing.

The observed Sb–Br bond length is 2.664 (8) Å, in excellent agreement with the average (2.665 Å) of known[6] octahedral Sb^{III}–Br (2.78 Å) and Sb^{V}–Br (2.55 Å) bond lengths. The observed bond length in the Br_2 molecule is 2.32 (4) Å; the apparent lengthening of this bond, relative to that for the molecule in the gaseous state, 2.28 Å,[17] could be the result of donor–acceptor interactions with neighboring anions but might also merely reflect the statistical disorder of Sb(III) and Sb(V).

The *average linear* anion$\cdots Br_2$ contact is quite short, 3.11 (2) Å. By comparison with a normal van der Waals contact of 3.90 Å,[18] this distance is indicative of an attractive interaction between the species. Short Br$\cdots$Br distances (less than 3.5 Å) have been observed in at least five other crystalline materials as well, *viz.*, in crystalline bromine (3.30 Å),[19] PBr_7 ($PBr_4^+\cdots Br_3^-$, 3.14, 3.26, 3.36 Å),[20] $(C_6H_7NH)_2Sb^{V}Br_9$ ($Sb^{V}Br_6^-\cdots Br_3^-$, 3.491 (2) Å),[8] $(C_5H_5NH)_6Sb^{III}Sb^{V}_3Br_{24}$ ($Sb^{V}Br_6^-\cdots Sb^{III}Br_6^{3-}$, 3.486 (7) Å; $Sb^{V}Br_6^-\cdots Sb^{V}Br_6^-$, 3.243 (7) Å),[6] and $[N(CH_3)_4]_3Sb^{III}_2Br_{11}$ ($Sb^{III}_2Br_9^{3-}\cdots Br_2$, 2.87 Å).[21] Owing to statistical disorder in our present material, the preferred orientation of the Br_2 molecule and the localized ordering of Sb(III) and Sb(V) about that molecule can only be postulated. Each molecule is surrounded by six anions, two axially and four equatorially, making a total of ten Br$\cdots$Br contacts. The molecule may bridge (axially) two Sb(III) ions, two Sb(V) ions, or one of each. By analogy with the structure of solid bromine, in which the concept of charge transfer has been invoked to account for the short Br$\cdots$Br contacts,[22] it is proposed that the bromine molecules preferentially bridge Sb(III) ions (electron donors) and are normal to Sb(V) ions (electron acceptors). This arrangement is shown in Figure 2 for four of the six surrounding anions. It is not unreasonable to assume that the energy gained through formation of effective donor–acceptor bonds with Sb(III) ions at 3.02 Å is greater than that gained at 3.25 Å with Sb(V) ions. It is also worth noting that, regardless of which ions are equatorial to Br_2, all eight Br$\cdots$Br contacts per Br_2 molecule always exceed the normal 3.90-Å van der Waals distance, so that the molecules are free to rattle in the octahedral holes, *viz.*, large amplitudes of libration; this could account for the large rms thermal amplitudes of vibration normal to the molecular axis shown in Figure 1. These large rms displacements may also be rationalized in terms of static disorder (a) if the molecular axes of Br_2 are *not* collinear with the unit cell axes but rather are rotated slightly as a result of attractive forces with the Sb(V) ions (in effect, to decrease the $Sb^{V}Br_6^-\cdots Br_2$ distances) or (b) if two dissimilar anions (one trivalent, one pentavalent) occupy equatorial positions trans to one another, thereby forcing a slight translational displacement of the entire Br_2 molecular axis as a result of charge differences and/or bond length differences between the two ions. This latter effect is expected to occur to some extent simply because of the disorder.

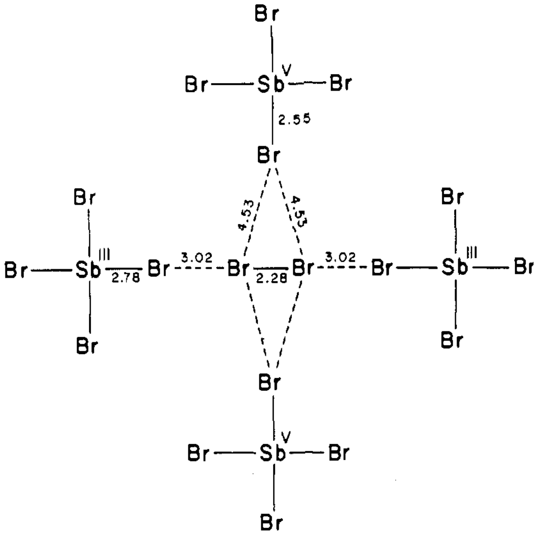

Figure 2.—A schematic representation of the proposed $SbBr_6\cdots Br_2$ interactions in $(C_7H_{13}NH)_4Sb_2Br_{12}\cdot 2Br_2$.

The orientation of the cations within the tetrahedral holes is such that the C–N bonds are parallel with the unit cell edges (and thus the orthogonal Sb–Br bonds) when viewed in projection along the triad axis of the cations. For the *average* structure no Br$\cdots$H distances less than 2.9 Å were found which, being only slightly less than a normal 3.2-Å van der Waals approach,[18] indicate that there are no unusual intermolecular interactions.

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