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## The Crystal Structure of $\text{Rb}_4\text{Sb}^{\text{III}}\text{Sb}^{\text{V}}\text{Br}_{12}$ \*

CAMDEN R. HUBBARD and ROBERT A. JACOBSON

*Abstract.* The crystal structure of rubidium hexabromoantimonate has been determined from three dimensional X-ray data. Eight molecules per unit cell crystallize in the tetragonal space group  $I4_1/amd$  ( $D_{4h}^{19}$ ) with  $a = 10.70$  and  $c = 21.69$  Å. The structure was refined by full matrix least squares with all atoms anisotropic to a discrepancy index,  $R = 0.102$  for 401 independent reflections collected by peak height counter methods. The structure is almost isomorphous with that of  $(\text{NH}_4)_4\text{Sb}^{\text{III}}\text{Sb}^{\text{V}}\text{Br}_{12}$ . Both the  $\text{Sb}^{\text{III}}\text{Br}_6^{-3}$  and the  $\text{Sb}^{\text{V}}\text{Br}_6^{-1}$  ions are distorted from  $O_h$  symmetry and possess  $D_{2a}$  symmetry. These distortions indicate considerable interaction between the  $\text{Sb}^{\text{V}}\text{Br}_6^{-1}$ ,  $\text{Sb}^{\text{III}}\text{Br}_6^{-3}$ , and the  $\text{Rb}^+$  ions.

Antimony halide compounds have been under investigation for many years. Of primary interest have been halide salts of the mixed valence type,  $\text{M}^{\text{III}}-\text{Sb}^{\text{V}}$ , ( $\text{M} = \text{Sb}^{\text{III}}, \text{Bi}^{\text{III}}, \text{In}^{\text{III}}, \text{Tl}^{\text{III}}$ ).<sup>1, 2</sup> These salts are abnormally dark in color indicating a strong absorption of visible light. This was reported to be due an electron transfer from the  $\text{M}^{\text{III}}\text{X}_6^{-3}$  ion to the  $\text{Sb}^{\text{V}}\text{X}_6^{-1}$  ion *via* van der Waals contacts through the halogens and/or the cations.<sup>2-4</sup> Examples of the mixed valence state compounds are  $(\text{NH}_4)_4\text{Sb}^{\text{III}}\text{Sb}^{\text{V}}\text{Br}_{12}$ ,<sup>1</sup>  $\text{Cs}_4\text{Bi}^{\text{III}}\text{Sb}^{\text{V}}\text{Cl}_{12}$ ,<sup>2</sup> and  $(\text{C}_5\text{H}_5\text{NH})_6\text{Sb}^{\text{III}}\text{Sb}_3^{\text{V}}\text{Br}_{24}$ .<sup>3</sup> However, it is possible in some cases to obtain dark antimony salts containing antimony in only one oxidation state; for example, the structure of  $(\text{C}_6\text{H}_7\text{NH})_2\text{SbBr}_9$ <sup>4</sup> has been recently determined and was found to contain  $\text{Sb}^{\text{V}}\text{Br}_6^-$  and  $\text{Br}_3^-$  groups. A review of many of the physical properties of these antimony compounds such as diffuse reflectance spectra, density, melting point, color dependence on temperature, crystal class, method of preparation, etc., is given by M. Hackert et al.<sup>5</sup>

If the proposed charge transfer is to be further investigated, then more structural information on related compounds is needed. An understanding of the effects of packing, bond distances and angles, change of cation, change of halide, etc., will be necessary for complete characterization of these unusual antimony halide compounds.

The configuration of the bromine atoms about the  $\text{Sb}^{\text{III}}$  atom is also of considerable interest since antimony (III) is of  $d^{10}s^2$  configuration. In the  $(\text{NH}_4)_4\text{Sb}^{\text{III}}\text{Sb}^{\text{V}}\text{Br}_{12}$  structure, Lawton found that the  $\text{Sb}^{\text{III}}\text{Br}_6^{-3}$  ion had  $O_h$  symmetry while the  $\text{Sb}^{\text{V}}\text{Br}_6^{-1}$  ion of  $d^{10}s^0$  configuration had  $D_{2a}$  symmetry.

Rubidium also forms a salt with empirical formula  $\text{Rb}_2\text{SbBr}_6$  which is black in color. We decided to carry out a single crystal structural investigation of this compound to determine whether it is essentially isomorphous with the ammonium salt, and if so, what effect the spherically symmetric cation would have on the structure in general and on the symmetry of the  $\text{SbBr}_6$  groups.

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## EXPERIMENTAL

$\text{Rb}_2\text{SbBr}_6$  was prepared by the method of Lawton,<sup>2</sup> a modification of the method of Ephraim and Weinberg.<sup>6</sup> The jet black octahedral crystals were crystallized from conc. HBr (48 percent). Because the crystals were reported to decompose slowly in air, they were placed in thin-walled, Lindemann glass capillaries.

Preliminary investigation using precession and Weissenberg photographs showed that the unit cell is tetragonal with space group  $I4_1/\text{amd}$ . The unit cell parameters at room temperature are  $a = 10.706 \pm 0.003$  and  $c = 21.695 \pm 0.022$  Å. These parameters and their standard deviations were obtained from measurements on a General Electric single crystal orienter using Cr  $K\alpha$  radiation for 16 reflections in two theta range  $45\text{--}118^\circ$  and agree quite well with those reported by Jensen and Rasmussen.<sup>7</sup> The refinement of the lattice constants was carried out using a program of Williams which employs the Nelson-Riley extrapolation function.<sup>8</sup>

In the ammonium salt  $a = 10.66$ ,  $c = 21.52$ , and the space group is  $I4_1/\text{amd}$ . Therefore the assumption that rubidium salt was nearly isomorphous with the ammonium salt seemed quite reasonable. On this basis a calculated density of 4.17 g/cc was obtained assuming eight  $\text{Rb}_2\text{SbBr}_6$  formula units/unit cell.

Using zirconium-filtered molybdenum radiation, X-ray intensity data were collected at room temperature from an octahedral crystal of dimensions  $0.28 \times 0.28 \times 0.30$  mm ( $\mu = 296$  cm<sup>-1</sup>). A General Electric single crystal orienter equipped with a scintillation counter was used employing the peak height measurement technique. The single crystal orienter settings were precalculated by a program of Williams.<sup>8</sup> Only those reflections noticeably above background were measured in the molybdenum radiation sphere of radius  $\sin\theta/\lambda = 0.705$  ( $2\theta = 60^\circ$ ). A total of 473 independent reflections were observed.

The raw intensities for all reflections were converted from peak height data to integrated intensities using the method of Smith and Alexander.<sup>9</sup> This conversion also included a correction for  $K\alpha_1 - K\alpha_2$  splitting. The integrated intensity data were then corrected for background, absorption, decomposition, Lorentz-polarization, and non-characteristic radiation streaking. The background correction was obtained from plots of averaged background versus  $2\theta$  for two different phi values to adjust for the small dependence of background with phi. The streak correction was based on the method of Williams and Rundle.<sup>10</sup> The individual transmission factors were calculated using the program of Wehe, Busing and Levy.<sup>8</sup> Three standard reflections were observed periodically and indicated a slight decomposition of the crystal during the experiment.

## SOLUTION OF THE STRUCTURE

The structure was solved without reference to the ammonium salt. A Patterson map was generated and all atoms were located. From the crystallographic positions of space group  $I4_1/amd$  and the positions determined from the Patterson map, the eight antimony atoms must be distributed in two different crystallographic positions, four in position  $a$ , and four in position  $b$ . The two types were assumed to be antimony (V) and antimony (III). Antimony (V) was arbitrarily assigned to position  $a$ .

A modification of the full matrix least squares program of Busing et al.<sup>9</sup> was used to refine the structure with the center of symmetry at the origin. Hartree-Fock-Slater atomic scattering factors<sup>11</sup> were used for antimony, rubidium, and bromine with corrections for the real and imaginary contributions to anomalous dispersion.<sup>12</sup> The seven atoms were refined isotropically to an unweighted discrepancy index,<sup>13</sup>  $R = 0.190$ . Considerable anisotropic motion was observed for the bromines on an electron density map. The structure was then refined anisotropically to  $R = 0.134$ .

At this point all the reflections were carefully examined for any which may have been measured incorrectly.<sup>14</sup> The four largest reflections were in very poor agreement,  $|F_c| - |F_o| \geq 9\sigma$ . They seemed to be suffering from extinction and were removed from the data set. An additional 41 very weak reflections for which  $F_o < 2\sigma$  were also removed. Another 27 weak reflections for which  $||F_o| - |F_c|| \geq 2|F_o|$  or  $2|F_c|$  were removed as it was felt that these were measured incorrectly. The weighting scheme was then improved by plotting  $\omega\Delta^2$  for ten overlapping groups of about 80 reflections each versus  $F_o$  [ $\Delta^2 = (|F_o| - |F_c|)^2$  and  $\omega = (1/\sigma^2)$ ]. The equation of the above curve was then used to derive an improved set of weights such that  $\omega\Delta^2$  was nearly constant.

The structure was refined for four additional cycles using the remaining 401 reflections ( $\approx 13$  reflections per variable). The average shift in bond length was about 0.01 Å, and the average decrease in the standard deviation as calculated by ORFFE<sup>9</sup> was about 50 percent. Thus the removal of this data found to be in very poor agreement seems to be justified.

The final discrepancy indexes are listed in Table 1 for all data, for  $l$ -even only, and for  $l$ -odd only. The  $l$ -odd reflections would be systematically extinct if both  $SbBr_6$  groups were identical. Hence the  $l$ -odd reflections arise from the differences between the  $Sb^VBr_6^{-1}$  and the  $Sb^{III}Br_6^{-3}$  groups. Figure 1 shows the unit cell and the arrangement of the  $Sb^VBr_6^{-1}$  and  $Sb^{III}Br_6^{-3}$  octahedra.

Table 2 lists the final atomic parameters (origin at  $4m2: 0, -\frac{1}{4}, \frac{1}{8}$  from the origin used in the refinement). These positions correspond

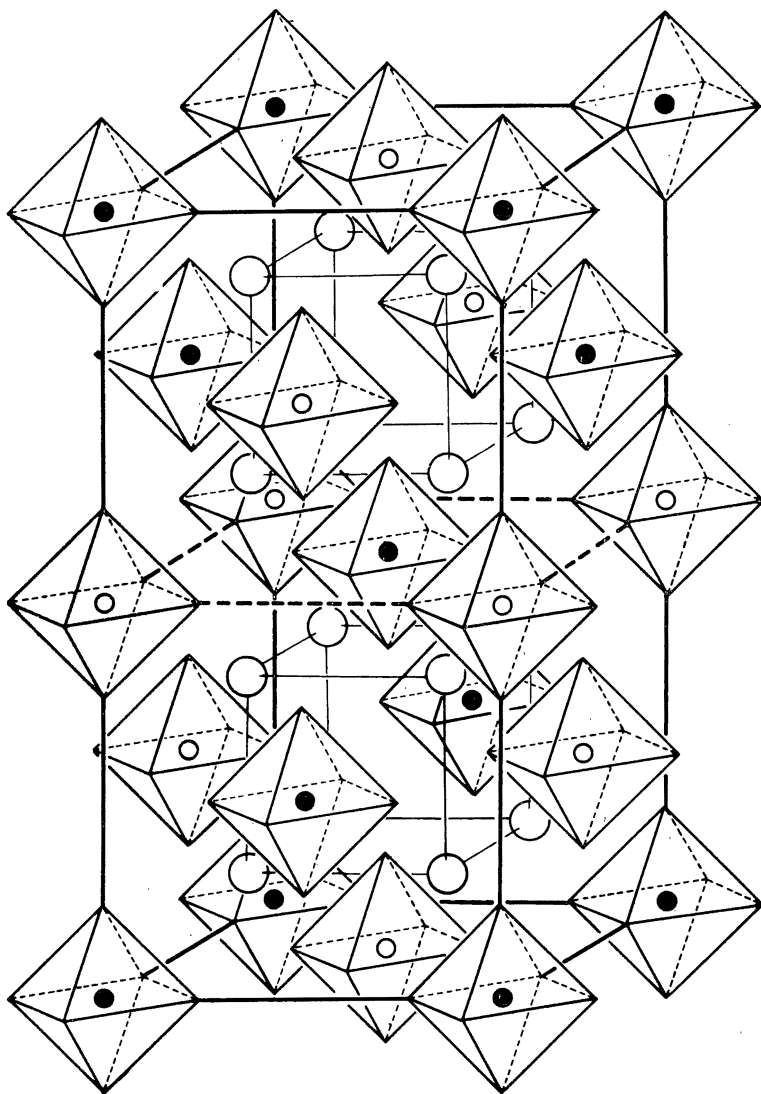


Figure 1. The unit cell of tetragonal  $Rb_4Sb^{III}Sb^VBr_{12}$  showing the alternation of  $Sb^V$  (small black circles) and  $Sb^{III}$  (small white circles) along the  $c$ -axis. Each antimony atom is positioned at the center of an octahedron formed by six bromine atoms. Rubidium atoms are represented by the large white circles. Distortions of the anions are not shown.

to the same orientation as in Figure 2. Table 3 lists the observed and calculated structure factors.

Table 1  
Reliability Index<sup>13</sup> (All Atoms Anisotropic)

Type of $F_{\text{obs}}$ Data	No. of Reflections	Unweighted R	Weighted R
$hkl$ : all data	401	0.102	0.084
$hkl$ : $l$ -even only	235	0.090	—
$hkl$ : $l$ -odd only	166	0.131	—

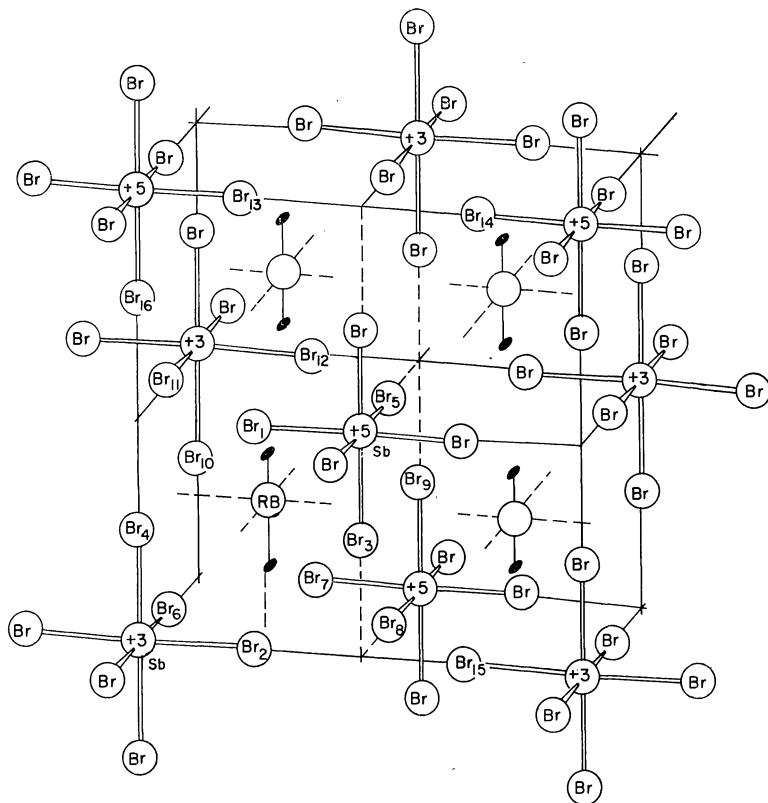


Figure 2. A portion of the unit cell of  $\text{Rb}_4\text{Sb}^{\text{III}}\text{Sb}^{\text{V}}\text{Br}_{12}$  showing the rubidium ions with respect to the relative distribution of distorted  $\text{Sb}^{\text{V}}\text{Br}_6^{-1}$  and  $\text{Sb}^{\text{III}}\text{Br}_6^{-3}$  ions. The  $b$ -axis is across the page,  $c$  vertical, and  $a$  into the page.

#### DESCRIPTION OF THE STRUCTURE

The structure of  $\text{Rb}_4\text{Sb}^{\text{III}}\text{Sb}^{\text{V}}\text{Br}_{12}$  is quite similar to that of the ammonium salt. The existence of weak  $l$ -odd reflections indicates that the two  $\text{SbBr}_6$  groups are indeed different chemical species, presumably  $\text{Sb}^{\text{V}}\text{Br}_6^{-1}$  and  $\text{Sb}^{\text{III}}\text{Br}_6^{-3}$ . The antimony-bromine bond lengths in the rubidium salt are noticeably different than in the ammonium salt along the  $c$ -axis, but are similar perpendicular to the  $c$ -axis. The

**Table 2**  
**Final Atomic Parameters<sup>a</sup>**  
 (Errors in least significant figures in parentheses)

Atom	Pos.	x/a	y/a	z/c	$\beta_{11}^b$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Sb <sup>v</sup>	4a	0* <sup>c</sup>	1/2*	1/4*	45(5)	45(5)*	20(1)	0*	0*	0*
Sb <sup>III</sup>	4b	0*	0*	1/2*	52(6)	52(6)*	16(1)	0*	0*	0*
Br <sub>1</sub>	16h	0*	0.26477(5)	0.25260(3)	183(7)	62(4)	55(2)	0*	0*	-21(3)
Br <sub>2</sub>	16h	0*	0.25970(3)	0.49731(2)	90(4)	45(3)	22(1)	0*	0*	-13(2)
Br <sub>3</sub>	8e	0*	1/2*	0.37013(4)	195(18)	195(18)*	48(3)	0*	0*	0*
Br <sub>4</sub>	8e	0*	0*	0.37502(2)	59(6)	59(6)*	12(1)	0*	0*	0*
Rb	16f	1/4*	0.22294(47)	3/8*	104(6)	91(5)	32(1)	0*	3.6(1.6)	0*

<sup>a</sup>Origin at  $\bar{4}m2$ .

<sup>b</sup> $\beta$ 's  $\times 10^4$ ; the anisotropic temperature factor expression is  $\exp(-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$ .

<sup>c</sup>Asterisk (\*) indicates an atomic parameter fixed by symmetry.





interatomic distances and angles and their estimated standard deviations for both the rubidium and the ammonium salts are listed in Table 4. The atoms are labeled with numbers which identify their location in the unit cell, a portion of which is shown in Figure 2. The complete variance-covariance matrix was used in conjunction with ORFFE<sup>9</sup> in calculating the estimated standard deviations. The anti-mony-bromine bonding distances were corrected for thermal motion using the "riding model" approximation; no other distances were corrected for thermal motion.

**Table 4**  
Interatomic Distances and Angles and Their Estimated Standard Deviations

	rubidium <sup>a</sup>	ammonium <sup>b</sup>
Distance and angles within each anion:		
a) Sb <sup>v</sup> Br <sub>6</sub> <sup>-1</sup>		
Sb — Br <sub>1</sub>	2.553 ± 0.005 Å	2.566 ± 0.006 Å
Sb — Br <sub>3</sub>	2.640 ± 0.008	2.559 ± 0.005
Br <sub>1</sub> — Br <sub>3</sub>	3.585 ± 0.006	3.739 ± 0.008
Br <sub>1</sub> — Br <sub>5</sub>	3.565 ± 0.007	3.637 ± 0.009
Br <sub>1</sub> — Sb — Br <sub>3</sub>	88.72 ± 0.13°	86.33 ± 0.15°
Br <sub>1</sub> — Sb — Br <sub>5</sub>	90.029 ± 0.005°	90.23 ± 0.02°
b) Sb <sup>III</sup> Br <sub>6</sub> <sup>-3</sup>		
Sb — Br <sub>2</sub>	2.787 ± 0.004 Å	2.795 ± 0.006 Å
Sb — Br <sub>4</sub>	2.713 ± 0.004	2.794 ± 0.005
Br <sub>2</sub> — Br <sub>4</sub>	3.843 ± 0.004	3.963 ± 0.007
Br <sub>2</sub> — Br <sub>6</sub>	3.934 ± 0.005	3.953 ± 0.009
Br <sub>2</sub> — Sb — Br <sub>4</sub>	88.80 ± 0.06°	89.68 ± 0.13°
Br <sub>2</sub> — Sb — Br <sub>6</sub>	90.025 ± 0.005°	90.002 ± 0.002°
Environment of cation		
Rb — Br <sub>1</sub>	3.797 ± 0.004 Å	3.96 ± 0.01 Å
Rb — Br <sub>3</sub>	3.997 ± 0.004	3.96 ± 0.02
Rb — Br <sub>5</sub>	4.060 ± 0.005	4.05 ± 0.02
Rb — Br <sub>2</sub>	3.790 ± 0.003	3.83 ± 0.01
Rb — Br <sub>4</sub>	3.658 ± 0.005 Å	3.58 ± 0.02 Å
Rb — Br <sub>6</sub>	3.586 ± 0.003	3.55 ± 0.02
Rb — Br <sub>7</sub>	3.797 ± 0.005	3.96 ± 0.01
Rb — Br <sub>8</sub>	4.06 ± 0.005	4.05 ± 0.02
Rb — Br <sub>9</sub>	3.997 ± 0.004	3.96 ± 0.02
Rb — Br <sub>10</sub>	3.586 ± 0.003	3.55 ± 0.02
Rb — Br <sub>11</sub>	3.658 ± 0.005	3.58 ± 0.02
Rb — Br <sub>12</sub>	3.790 ± 0.003	3.83 ± 0.01
Bromine-bromine contacts between anions (≧ 4.0 Å)		
Br <sub>2</sub> — Br <sub>3</sub>	3.773 ± 0.007 Å	3.818 ± 0.008 Å
Br <sub>2</sub> — Br <sub>8</sub>	3.829 ± 0.004	3.817 ± 0.008
Br <sub>6</sub> — Br <sub>10</sub>	3.781 ± 0.004	3.649 ± 0.007
Br <sub>4</sub> — Br <sub>11</sub>	3.781 ± 0.004	3.649 ± 0.007
Br <sub>3</sub> — Br <sub>8</sub>	3.829 ± 0.004	3.881 ± 0.008
Bromine-bromine non-bonding distances between anions along the axes		
Br <sub>2</sub> — Br <sub>15</sub>	5.145 ± 0.007 Å	5.13 ± 0.01 Å
Br <sub>4</sub> — Br <sub>16</sub>	5.508 ± 0.009	5.479 ± 0.008
Br <sub>13</sub> — Br <sub>14</sub>	5.667 ± 0.010	5.62 ± 0.01

<sup>a</sup>Riding model correction for thermal motion for Sb — Br bonds only.

<sup>b</sup>Rigid body libration correction for thermal motion in ammonium salt for all distances.

The final parameters show that, within experimental error, both the  $\text{Sb}^{\text{V}}\text{Br}_6^{-1}$  and the  $\text{Sb}^{\text{III}}\text{Br}_6^{-3}$  ions are distorted and possess  $D_{2d}$  symmetry. The mean length of the  $\text{Sb}^{\text{V}}-\text{Br}$  bond is  $2.553 \pm 0.005 \text{ \AA}$  perpendicular to the  $c$ -axis and is  $2.640 \pm 0.008 \text{ \AA}$  along the  $c$ -axis. The  $\text{Br}_1-\text{Sb}^{\text{V}}-\text{Br}_3$  bond angle is  $88.72 \pm 0.13^\circ$ . In the ammonium salt all the antimony (V) bromine distances were nearly equivalent and equal to  $2.564 \pm 0.006 \text{ \AA}$ . The same bond angle was  $86.33 \pm 0.15$ . Thus the distortions from  $O_h$  symmetry of the  $\text{Sb}^{\text{V}}\text{Br}_6^{-1}$  ion are quite different in the two salts.

The mean length of the  $\text{Sb}^{\text{III}}-\text{Br}$  bond is  $2.787 \pm 0.004$  perpendicular to the  $c$ -axis and  $2.713 \pm 0.004$  along the  $c$ -axis. The bond angle  $\text{Br}_2-\text{Sb}^{\text{III}}-\text{Br}_4$  is  $88.80 \pm 0.06^\circ$ . In the ammonium salt the  $\text{Sb}^{\text{III}}\text{Br}_6^{-3}$  ion had  $O_h$  symmetry with bond distances of  $2.795 \pm 0.006 \text{ \AA}$ . The rubidium ion occupies a tetrahedral hole formed by four antimony halide groups, two  $\text{Sb}^{\text{V}}\text{Br}_6^{-1}$  and two  $\text{Sb}^{\text{III}}\text{Br}_6^{-3}$ . Three bromine atoms from each of the four groups form the 12 nearest neighbors.

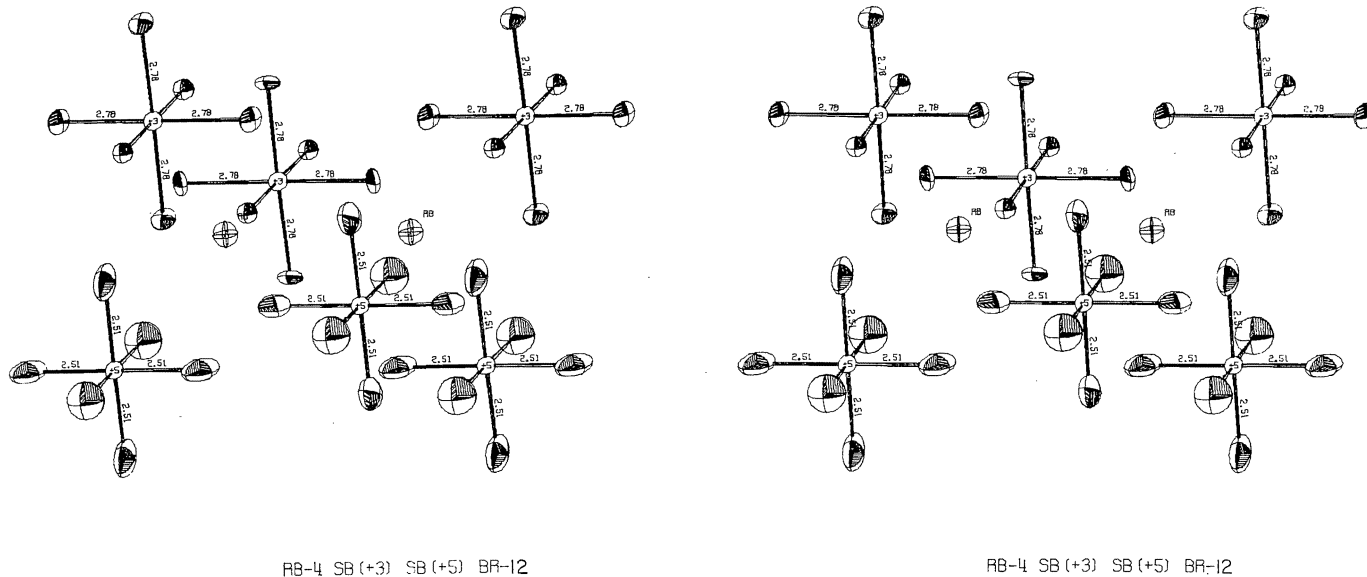
The rubidium ion is fixed by symmetry along the  $c$ -axis, but has some freedom to move in the  $a$ - $b$  plane. The closest distance between any one bromine atom in a  $\text{Sb}^{\text{V}}\text{Br}_6^{-1}$  ion and the rubidium ion is  $3.797 \text{ \AA}$  and the closest distance of the same type with the  $\text{Sb}^{\text{III}}\text{Br}_6^{-3}$  ion is  $3.586 \text{ \AA}$ . The four shortest bromine-bromine distances between different  $\text{SbBr}_6$  groups are  $3.773$  ( $\text{Br}_2-\text{Br}_3$ ),  $3.829$  ( $\text{Br}_2-\text{Br}_8$ ),  $3.781$  ( $\text{Br}_6-\text{Br}_{10}$  and  $\text{Br}_4-\text{Br}_{11}$ ), and  $3.829$  ( $\text{Br}_3-\text{Br}_8$ ). The first two distances are  $\text{Sb}^{\text{III}}\text{Br}_6^{-3} - \text{Sb}^{\text{V}}\text{Br}_6^{-1}$  closest contacts. The third and fourth correspond to the shortest bromine-bromine distances between different  $\text{Sb}^{\text{III}}\text{Br}_6^{-3}$  anions and  $\text{Sb}^{\text{V}}\text{Br}_6^{-1}$  anions, respectively.

Within the  $\text{Sb}^{\text{V}}\text{Br}_6^{-1}$  ion the mean distance between bromines is  $3.61 \text{ \AA}$  and within the  $\text{Sb}^{\text{III}}\text{Br}_6^{-3}$  ion this distance is  $3.90 \text{ \AA}$ . Since the contacts are much closer within the  $\text{Sb}^{\text{V}}\text{Br}_6^{-1}$  ion than in the  $\text{Sb}^{\text{III}}\text{Br}_6^{-3}$  ion, the motions of the individual bromine atoms in the former are probably coupled to a greater degree than in the latter. This coupling will cause librations of the anion and will affect the calculated antimony-bromine bond distances. The difference between the "riding model" correction (as used in this paper) and the "rigid body libration" correction is expected to be small and should not affect the over-all symmetry of each anion.

#### DISCUSSION

The different volumes of the unit cells of  $\text{Rb}_4\text{Sb}_2\text{Br}_{12}$  ( $2,486 \text{ \AA}^3$ ) and  $(\text{NH}_4)_4\text{Sb}_2\text{Br}_{12}$  ( $2,445 \text{ \AA}^3$ ) can be understood assuming that in the ammonium ion the positive charge is partially localized on each of the hydrogen atoms. These localized positive charges, in a fixed orientation, can interact by coulomb attraction with the anions causing a small contraction of the unit cell. This ordering occurs in  $\text{NH}_4\text{Br}$ .<sup>15</sup> In the spherically symmetric rubidium ion localization is not possible.

Figure 3. A stereo pair of a portion of the unit cell showing the special arrangement of the rubidium cations to the antimony halide anions. The *b*-axis is across the page; the *a*-axis is vertical; and the *c*-axis is into the page. The bond distances are uncorrected for thermal motion. The unlabeled distances along the *c*-axis are 2.61 (Sb<sup>V</sup>-Br) and 2.71 (Sb<sup>III</sup>-Br).



Although only small changes in unit cell dimensions are observed, large changes are found in the stereo chemistry of both the  $\text{Sb}^{\text{V}}\text{Br}_6^{-1}$  and  $\text{Sb}^{\text{III}}\text{Br}_6^{-3}$  ions. Neither van der Waal forces nor charge transfer effects through the rubidium ion are possible explanations of the observed distortions. The sum of ionic radii<sup>16</sup> of rubidium and bromide ions, 3.43 Å, is considerably shorter than any observed Rb-Br distance.

Electrostatic effects are a possible explanation for the distortions of the  $\text{Sb}^{\text{III}}\text{Br}_6^{-3}$  ion. Table 4 shows that the average rubidium-bromine distance (3.815 Å) is nearly the same as the nitrogen-bromine distance in the ammonium salt (3.822 Å). Table 4 also shows that the intermolecular bromine-bromine distances between  $\text{Sb}^{\text{III}}\text{Br}_6^{-3}$  anions has increased from 3.649 Å in the ammonium salt to 3.781 Å ( $\text{Br}_6\text{-Br}_{10}$ ) in the rubidium salt, while all other bromine-bromine distances have remained almost constant. The shortening of the  $\text{Sb}^{\text{III}}\text{-Br}$  bond along the *c*-axis reduces the electrostatic repulsion while not affecting the attractions. The net result is a stabilization of the lattice.

The distortion of the  $\text{Sb}^{\text{III}}\text{Br}_6^{-3}$  ion is, therefore, cation and packing dependent. Lawton<sup>3</sup> found the same result in the structure determination of  $(\text{C}_5\text{H}_5\text{NH})_6\text{Sb}^{\text{III}}\text{Sb}_3^{\text{V}}\text{Br}_{24}$ . He concluded that the distortion could not be ascribed to the effect of the lone electron pair and thus to any seven-coordinated type of structure. The increase in Sb-Br distance going from  $\text{Sb}^{\text{V}}$  to the  $\text{Sb}^{\text{III}}$  ion (about 0.2 Å), which is greater than that expected due to the charge difference, suggests the lone pair exists in a spherically symmetric state. This conclusion agrees with the work of Day<sup>2</sup> and with the suggestions of Urch,<sup>17</sup> that a lone electron pair can be accommodated in the  $a_{1g}$  antibonding orbital and not cause distortions from  $O_h$  symmetry.

The distortion of the  $\text{Sb}^{\text{V}}\text{Br}_6^{-1}$  ion might be indicative of charge transfer paths linking the pentavalent antimony bromines along the *c*-axis to the trivalent antimony anions. However, it might also be simply indicative of bromine-bromine repulsions in this ion. These distances are 3.771 Å ( $\text{Br}_2\text{-Br}_3$ ) and 3.829 Å ( $\text{Br}_2\text{-Br}_8$ ). The strength of the former argument is rather weak since these two distances are only 0.13 and 0.07 Å shorter than the sum of two bromide ionic radii (3.90 Å); they are also quite similar to the shortest bromine-bromine distances between like anions. Yet the expansion of the  $\text{Sb}^{\text{V}}\text{-Br}$  bond along the *c*-axis suggests that there is some interaction between the  $\text{Sb}^{\text{V}}\text{Br}_6^{-1}$  ion and its neighbors. No other explanation is apparent to explain the black color, other than the charge transfer which may occur by the paths described above.

#### References Cited

1. S. L. Lawton and R. A. Jacobson. 1966. J. Am. Chem. Soc. 88, 616.
2. P. Day. 1963. Inorg. Chem. 2, 452.
3. S. L. Lawton and R. A. Jacobson. To be published.
4. S. L. Lawton, R. A. Jacobson, and R. S. Frye. To be published.

5. M. L. Hackert, S. L. Lawton, and R. A. Jacobson. *J. Iowa Academy of Sciences* (this issue).
6. F. Ephraim and S. Weinberg. 1909. *Ber. Deut. Chem. Ges.* 42, 4447.
7. A. T. Jensen and S. E. Rasmussen. 1955. *Acta Chem. Scand.* 9, 708.
8. In addition to programs written at this laboratory by Williams and others, other programs used in this study were Johnson's ORTEP to prepare Figures 2 and 3, Busing and Levy's ORFFE to calculate distances, angles, and related errors, Busing, Martin and Levy's ORFLS, modified to allow for correction for the real and imaginary parts of anomalous dispersion, and Wehe, Busing, and Levy's ABCOR to correct for absorption.
9. L. E. Alexander and G. S. Smith. 1962. *Acta Cryst.* 15, 983.
10. D. E. Williams and R. E. Rundle. 1964. *J. Am. Chem. Soc.* 86, 1660.
11. H. P. Hanson, F. Herman, J. D. Lea and S. Skellman. 1964. *Acta Cryst.* 17, 1040.
12. "International Tables for X-ray Crystallography." Vol. III. 1962. The Kynoch Press, Birmingham, England, pp. 215-216.
13. The discrepancy indexes are defined as follows: unweighted  $R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$  and the weighted  $R_w = \frac{\sum w||F_o| - |F_c||}{\sum w|F_o|}$ .
14. For comments on weak reflections which are in error and their influence on positional parameters and standard errors, see C. J. Fritchie, "Proc. of the symposium in X-ray Intensity Measurement." 1965. *Trans Am. Cryst. Assn.* 1, 30.
15. A. F. Wells. 1962. "Structural Inorganic Chemistry," 3rd ed., Oxford Clarendon Press, p. 172.
16. L. Pauling. 1960. "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, p. 514.
17. D. S. Urch. 1964. *J. Chem. Soc., Suppl. I*, 5775.