tals vanishes, and the phosphorescent and thermoluminescent emissions of the untreated crystals change noticeably. These observations indicate that about one in every ten Cd^{2+} ions (each substituted M^{3+} ion has 12 Cd^{2+} nearest neighbors) has to be replaced in order to destroy the "resonance" stabilized state and, hence, the properties dependent upon it.

The following differences observed between $Cd_{1-x}Ca_xF_2$ crystals doped with In^{3+} and Re^{3+} ions can also be considered with the use of the proposed Cd "impurity" level model. Two other observations are valuable. One is the chemical similarity of Cd and In. The second is the relatively high stability of lower oxidation states of In, such as In^{2+} and In^{+}. (Rare earths, on the other hand, are chemically dissimilar to Cd and do not generally form stable lower oxidation states.) The existence of an In^{2+} ion allows for the two activation energies for conduction with In doping and the resulting high-resistivity crystals at 77°K. The low-temperature activation energy, $E_1 = 0.15$ ev, can be identified with the ionization of an electron from an In^{2+} ion into the Cd "impurity" centers (impurity band). Then the high-temperature activation energy, $E_2 = 0.20$ ev, can be attributed to ionization from the Cd centers into the CdF_2 conduction band. This high-temperature energy, E_2, might be larger than that with RE dopants since Cd and In are quite similar chemically. This would tend to lower the "impurity" level in energy, thereby increasing the donor energy, since In could enter into the proposed "resonance" effect.

The increase in broad infrared absorption, in the $Cd_{1-x}Ca_xF_2:In^{3+}$-conducting crystals, with decreasing temperature is also consistent with the formation of lower In oxidation states. As the temperature is lowered, more In^{2+} (and possibly In^{+}) ions are formed. Charge transfer between the "impurity" centers then becomes more favorable, and the absorption increases.

The observation of two thermoluminescent peaks in untreated crystals with In doping also seems to agree with the proposed model. The thermal activation from two states at different energies to the same energy state, say the CdF_2 conduction band, with subsequent yellow to yellow-green emission to a single, terminal, fluorescent level would explain the two identically colored thermoluminescent peaks. Two peaks would be observed above 77°K since electrons would be thermally excited from two levels, the Cd "impurity" and the In^{2+} levels, at two different energies below the conduction band edge.

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CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY,
IOWA STATE UNIVERSITY, AMES, IOWA

The Crystal Structure of Ammonium Hexabromoantimonate, $(NH_4)_4Sb^{III}Sb^{V}Br_{12}$[1]

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A single-crystal X-ray structure analysis of jet black octahedral crystals of ammonium hexabromoantimonate has confirmed the existence of a mixture of trivalent and pentavalent antimony in salts of the type M_2SbX_6 ($M = NH_4^+$, Rb^+, or Cs^+; X = Cl or Br). The crystals of the ammonium salt are tetragonal, space group $I4_1/amd$ (D_{4h}^{19}) with unit cell dimensions $a = 10.66 \pm 0.02$ A and $c = 21.52 \pm 0.02$ A ($c/a = 2.02$). Using three-dimensional scintillation-counter data and a full-matrix anisotropic least-squares analysis, the refinement of all atoms, except hydrogen, has yielded a final unweighted reliability index of 10.5% for 621 observed reflections. Both antimony atoms are six-coordinated and form a distorted K_2PtCl_6 structure in which the ions are arranged in an ordered array with like oxidation states of antimony repeating along the a and b directions in the unit cell but alternating along the c direction. The $Sb^{III}Br_6^{3-}$ ions are undistorted (O_h symmetry), and the $Sb^{V}Br_6^{-}$ ions are distorted (D_{2d} symmetry). The average Sb(III)–Br and Sb(V)–Br bond lengths, corrected for thermal motion assuming rigid-body libration, have been found to be 2.795 ± 0.006 and 2.564 ± 0.006 A, respectively.

Introduction

Crystals of M_2SbX_6 ($M = NH_4^+$, Rb^+, or Cs^+; X = Cl or Br) are jet black, octahedral, and diamagnetic, and have a high specific resistance. The interest in these salts has been largely that of determining by chemical and physical methods the true oxidation state(s) of antimony. In particular, attempts have been aimed at determining whether it is tetravalent or a mixture of trivalent and pentavalent and then attempting to explain the cause of the black color in terms of its oxidation state(s), their distribution in the crystal, and their halogen environment. Studies of these salts in hydrochloric acid solution, such as the spectroscopic studies by Whitney and Davidson[2] and the exchange reactions between antimony(III) and -(V) by Bonner,[3]

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(1) This work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 1826.

(2) (a) J. Whitney and N. Davidson, *J. Am. Chem. Soc.*, **69**, 2076 (1947); (b) J. Whitney and N. Davidson, *ibid.*, **71**, 3809 (1949); (c) N. Davidson, *ibid.*, **73**, 2361 (1951).

(3) N. A. Bonner, *ibid.*, **71**, 3090 (1949).

strongly indicate the probable existence of the mixed oxidation states III and V in the solids. The magnetic susceptibility measurements[4,5] indicate the lack of paramagnetism at room temperature and the resistivity measurements[5] indicate the presence of only tightly bound electrons. The crystal structures of several of these salts have been determined from X-ray powder data of Jensen;[5a] the results indicated that the salts crystallize in a structure isomorphous with K_2PtCl_6, space group Fm3m (O_h^5), thereby indicating that all the antimony atoms, a total of four in each unit cell, are crystallographically equivalent. Through careful X-ray studies of the same compounds by Jensen and Rasmussen,[6] however, several singlet powder lines were successfully resolved into doublets, thereby demonstrating that the crystal symmetry was indeed not cubic but tetragonal, the type of symmetry one might expect from nonequivalent antimony atoms.

An absolute confirmation of the true oxidation state(s) of antimony in these salts is important for three essential reasons: First, tetravalent antimony is virtually unknown. Second, a correct explanation regarding the cause of the black color is possible only when the true oxidation state(s) of antimony and their relative distribution in the crystals are known. Third, if these salts actually contain mixed Sb(III)–Sb(V), then the structures may contain a hexahalogen complex of a nontransition element containing a lone pair of electrons, in this case the complex $Sb^{III}X_6^{3-}$; the effect of the lone pair on both the symmetry and bond distances exhibited by such a complex would be of considerable interest. We therefore decided to investigate the structure of one of these salts, $(NH_4)_2SbBr_6$, using single-crystal X-ray diffraction techniques since not only could possible weak reflections be detected, which might change the space group assignment, but also accurate bond distances could be obtained by this method.

Experimental Section

Preparation.—Ammonium hexabromoantimonate, $(NH_4)_2SbBr_6$, was prepared by a modified method of Ephraim and Weinberg,[7] in which antimony tribromide was allowed to react with ammonium bromide and liquid bromine in a concentrated hydrobromic acid (48%) medium. The antimony tribromide solution was first prepared by dissolving 0.90 g (0.0025 mole) of antimony tribromide in 3 ml of warm, concentrated hydrobromic acid (48%). To this was added 0.49 g (0.005 mole) of solid ammonium bromide. After complete dissolution, 4 drops of concentrated sulfuric acid and 4–5 drops of liquid bromine were added. Upon cooling, brilliant jet black, octahedral crystals precipitated. The mixture was filtered from the mother liquor by vacuum filtration through a sintered-glass funnel and rinsed with cold, concentrated hydrobromic acid (48%) containing a little liquid bromine. The compound was dried on a porous porcelain plate in a desiccator containing sulfuric acid as the desiccant and a small partial pressure of bromine vapor to prevent debromination.

Crystals suitable for the single-crystal investigation were obtained by dissolving a small quantity of the black salt in hot, concentrated hydrobromic acid (48%) so as to form a nearly saturated solution. Drops of concentrated sulfuric acid were then added, with swirling, to the hot solution until about half of the black salt precipitated. The solution was reheated to redissolve the salt, and then a few drops of liquid bromine were added. It was then covered and allowed to cool, undisturbed. Crystallization of the salt was essentially complete within 30 min.

Owing to the moderate instability of the salt in air and its tendency to debrominate, special techniques were used to isolate and mount single crystals in glass capillaries. With the aid of an eye dropper a small portion of the crystals, together with the mother liquor, was withdrawn and spread onto flat filter paper for inspection under a microscope. The mother liquor on the paper served to delay debromination of the salt by allowing sufficient time (approximately 5 to 10 min) to select and mount crystals in open atmosphere. The crystals were mounted and sealed in 0.2-mm glass capillaries whose inner walls were coated with a very thin film of the mother liquor.

Physical and Chemical Properties.—At room temperature the salt crystallizes as jet black octahedra. At liquid nitrogen temperature and at all intermediate temperatures the salt remains jet black in color, indicating that the Pitzer–Hildebrand rule concerning the color of compounds in relation to bond character[8,9] does not apply. It slowly and reversibly debrominates at room temperature (more rapidly at elevated temperatures) to a yellow solid, an observation also noted by Brauer and Schnell.[10] Hydrolysis in distilled water is rapid and results in a white precipitate.

Crystal Data.—Our single-crystal X-ray diffraction investigation revealed that the crystals were not cubic, as reported by Jensen,[5a] but were actually body-centered tetragonal. This fact was initially indicated by the presence of very weak reflections in the reciprocal lattice not belonging to the space group Fm3m (O_h^5), reflections which were disposed in such a manner as to double the length of the c axis and to give rise to a body-centered lattice. In the new lattice these weak reflections occurred only for l odd. The space group, as determined from Weissenberg photographs using Cu Kα radiation, was observed to be $I4_1/amd$ (D_{4h}^{19}). The lattice parameters were calculated from precession photographs using Mo Kα radiation and from measurements in the back-reflection region on a General Electric single-crystal orienter using Cr Kα radiation; they were observed to be $a = 10.66 \pm 0.02$ A and $c = 21.52 \pm 0.02$ A.[11] From the observed density of 3.45 g/cm³, obtained by the flotation method, the number of formula units of $(NH_4)_2SbBr_6$ per unit cell is eight. This gives a value of 3.46 g/cm³ as the calculated density.

Collection and Treatment 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 $0.105 \times 0.108 \times 0.108$ mm (μ 230 cm^{-1}). A General Electric single-crystal orienter equipped with a scintillation counter was used with the moving-crystal–moving-counter measurement technique (θ, 2θ coupling), 4.0° takeoff angle, and a 2.0° diffraction-beam aperture. A 100-sec scan, covering 3.33° in 2θ, was used for each reflection, followed by a repeat scan for background with an ω offset of 2.06. The single-crystal orienter settings were precalculated on an IBM 7074 computer with the program of Williams.[12] A total of 1500 reflections was measured in the molybdenum radiation sphere of radius $(\sin \theta)/\lambda = 0.8072$ ($2\theta = 70°$);

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(4) N. Elliot, *J. Chem. Phys.*, **2**, 298 (1934).

(5) (a) K. A. Jensen, *Z. Anorg. Allgem. Chem.*, **232**, 193 (1937); (b) K. A. Jensen, *ibid.*, **252**, 317 (1949).

(6) A. T. Jensen and S. E. Rasmussen, *Acta Chem. Scand.*, **9**, 708 (1955).

(7) F. Ephraim and S. Weinberg, *Chem. Ber.*, **42**, 4447 (1909).

(8) K. S. Pitzer and J. H. Hildebrand, *J. Am. Chem. Soc.*, **63**, 2472 (1941).

(9) J. Watanabe, M. Atoji, and C. Akazaki, *Acta Cryst.*, **3**, 405 (1950).

(10) G. Brauer and W. D. Schnell, *Z. Anorg. Allgem. Chem.*, **283**, 49 (1956).

(11) These parameters were found to be in remarkable agreement with those reported by Jensen and Rasmussen.[6] Their parameters, calculated from powder photographs taken with a 19-cm Bradley–Jay powder camera, Co Kα radiation, were $a = 7.538$ and $c = 10.760$ A, which, upon conversion to the body-centered tetragonal orientation, become $a = 7.538 \times \sqrt{2} = 10.66$ A and $c = 10.760 \times 2 = 21.52$ A.

(12) D. E. Williams, "Single Crystal Orienter Angles Program SCO-6," Ames Laboratory, Iowa State University, Ames, Iowa.

of these there were 621 reflections detectable above the background, of which 358 were of the *l* even type and 253 of the *l* odd type (the *weak* reflections). Four standard reflections, (800), (920), (440) and (0,0,16), were measured periodically as a check on crystal decomposition. The intensities were found to remain constant within ±3% over the 2-week recording period; decomposition was thus considered negligible. The raw intensities of all reflections were corrected for background, streak, absorption, and Lorentz polarization. The background was obtained from plots of average background *vs.* 2θ. The streak correction, significant for only 78 reflections, was based on a method of Benson,[13] a modification of the method of Williams and Rundle.[14] The individual transmission factors were calculated using the program of Wehe, Busing, and Levy.[15]

Solution of the Structure

The observed space group and cell parameter ratios ($a:b:c$ = 1:1:2.02) indicated that the unit cell was actually two face-centered K_2PtCl_6-type cells stacked one above the other resulting in a cell whose symmetry, and hence repeating units, is the same in two directions but different in the third direction. The manner in which the arrangement differs along this third direction (c axis) was indicated by the symmetry requirements of the space group. For a K_2PtCl_6-type structure, it requires the eight antimony atoms be distributed in *two different* crystallographic positions, four in position (a) and four in position (b)[16] indicating the presence of two types of antimony atoms. The two types were thus assumed to be antimony(III) and antimony(V). The space group positions (a) and (b) are such that like-oxidation states of antimony will repeat along the a and b directions in the tetragonal unit cell but alternate along the c direction; hence, a unit cell which is both body-centered and twice as long in one direction. The cell which results is that shown in Figure 1.

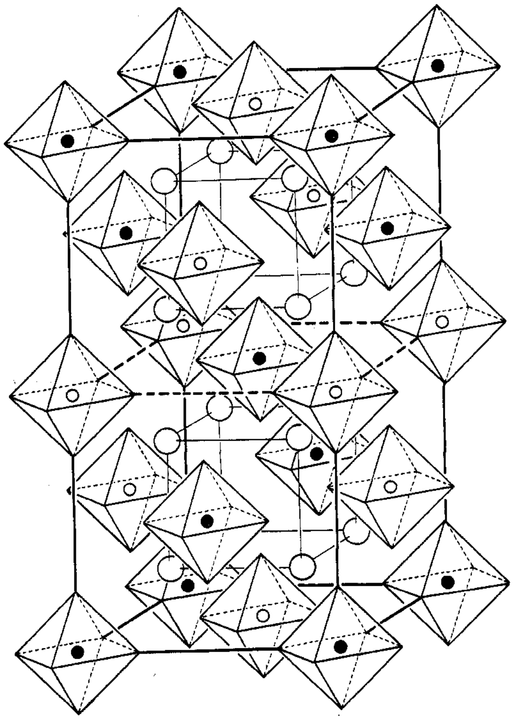

Figure 1.—The unit cell of tetragonal $(NH_4)_4Sb^{III}Sb^{V}Br_{12}$, showing the relative distribution of Sb(III) (small black circles) and Sb(V) (small white circles). Each antimony atom is located at the center of an octahedron formed by six bromine atoms (distortions not shown). The ammonium ions, represented by large white circles, occupy the tetrahedral holes.

In order to proceed in a least-squares refinement of X-ray data belonging to a K_2PtCl_6-type structure containing two nonequivalent metal atoms, it is necessary that the two atoms be distinguished from one another. This was achieved by assigning reasonable bond lengths to Sb(III)–Br and Sb(V)–Br. In this investigation Sb(III) was arbitrarily assigned to position (a) and Sb(V) to position (b), and the positions of the bromine atoms were adjusted accordingly. (A different choice would, of course, merely be equivalent to a shift in the origin.)

Using the least-squares program of Fitzwater,[17] the structure was refined with the center of symmetry at the origin. The Hartree–Fock–Slater atomic scattering factors[18] were used for bromine, antimony, and nitrogen, the bromine and antimony atoms having been corrected for the real contribution of anomalous dispersion.[19] The cation was treated as a nitrogen atom. Using the 621 observed data only, the seven independent atoms were first refined isotropically to an unweighted discrepancy index[20] of 18% and then anisotropically, keeping nitrogen isotropic, to a value of 11%.

TABLE I

AGREEMENT FACTORS[20]

	Type of F_o data	No. of reflections	Unweighted R, %	Weighted R, %
hkl:	all obsd data	621	10.5	9.06
hkl:	*l* even only	369	7.97	7.16
hkl:	*l* odd only	252	19.7	17.5

Refinement of the structure was completed after correcting the calculated structure factors, F_c, for the imaginary part of the anomalous dispersion effect and adjusting the weighting scheme. The weighting scheme was modified by preparing a curve of $\Delta^2\omega$ for n groups of 50 reflections each [where $\Delta^2 = (|F_o| - |F_c|)^2$ and $\omega = (\text{scale factor}/\sigma)^2$] *vs.* $\sin\theta$ and using the equation of the resulting curve to derive a new weighting factor equation which yielded a more constant value of $\Delta^2\omega$.

The final agreement factors are summarized in Table I. Table II lists the final atomic parameters (origin of unit cell at $\bar{4}2m$), corresponding to the orientation in Figure 1; they are 0, $-{}^1/_4$, ${}^1/_8$ from the positions used

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[13] J. E. Benson, Iowa State University, Ames, Iowa, private communication.

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

[15] D. J. Wehe, W. R. Busing, and H. A. Levy, "FORTRAN Program for Single Crystal Orienter Absorption Corrections," ORNL-TM-299, 1962.

[16] "International Tables for X-ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952, pp 245, 246.

[17] D. R. Fitzwater, Iowa State University, Ames, Iowa, private communication.

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

[19] "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 215, 216.

[20] The expressions used to calculate the unweighted and weighted reliability index for the structure as obtained from a cycle of least squares are defined as follows: (i) unweighted reliability index, $R = (\Sigma||F_o| - |F_c||/\Sigma|F_o|) \times 100$; (ii) weighted reliability index, $R = (\Sigma||F_o/\sigma| - |F_c/\sigma||/\Sigma|F_o/\sigma|) \times 100$.

TABLE II[a,b]

(a) Final Atomic Parameters (Origin at $\bar{4}2m$)[c]

Atom	Position	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N	16f	0.2171	0.25*	0.125*	3.57					
Br(1)	16h	0*	0.23796	0.50756	0.01734	0.00420	0.00283	0*	0*	0.00074
Br(2)	16h	0*	0.26069	−0.00073	0.01161	0.00443	0.00264	0*	0*	−0.00209
Br(3)	8e	0*	0*	0.38275	0.01745	0.02155	0.00037	0*	0*	0*
Br(4)	8e	0*	0*	0.12950	0.01029	0.00569	0.00069	0*	0*	0*
Sb(V)	4b	0*	0*	0.5*	0.00365	0.00365	0.00085	0*	0*	0*
Sb(III)	4a	0*	0*	0*	0.00437	0.00437	0.00061	0*	0*	0*

(b) Standard Deviations in Final Atomic Parameters (Origin at $\bar{4}2m$)

Atom	Position	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N	16f	0.0028	...	...	0.71					
Br(1)	16h	...	0.00040	0.00034	0.00066	0.00032	0.00017	...	...	0.00024
Br(2)	16h	...	0.00036	0.00032	0.00041	0.00031	0.00013	...	...	0.00023
Br(3)	8e	...	...	0.00025	0.00178	0.00178	0.00009	...	...	...
Br(4)	8e	...	...	0.00023	0.00082	0.00071	0.00008	...	...	...
Sb(V)	4b	...	...	...	0.00020	0.00020	0.00008	...	...	...
Sb(III)	4a	...	...	...	0.00022	0.00022	0.00007	...	...	...

[a] The isotropic temperature factor and its corresponding standard deviation for nitrogen are listed under the heading β_{11}. [b] The form of the anisotropic temperature factor expression is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$. [c] An atomic coordinate fixed by symmetry is indicated with an asterisk.

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTORS (IN ELECTRONS/4) FOR $(NH_4)_4Sb_2Br_{12}$

H	K	L	|FO|	|FC|
0	2	0	203.7	189.2
0	4	0	345.0	376.3
0	6	0	93.1	97.9
0	8	0	185.1	181.1
0	10	0	38.9	39.2
0	12	0	76.1	74.6
0	14	0	10.8	16.6
0	16	0	29.0	28.7
2	4	0	157.4	152.8
2	8	0	102.4	97.8
2	10	0	9.5	6.9
2	12	0	53.5	51.5
2	14	0	7.0	10.4
2	16	0	23.0	22.7
4	4	0	270.0	282.6
4	6	0	92.6	88.2
4	8	0	152.3	145.8
4	10	0	39.2	38.1
4	12	0	68.5	61.7
4	14	0	18.5	16.8
4	16	0	27.4	24.1
6	8	0	67.0	63.9
6	10	0	6.1	9.5
6	12	0	40.9	36.8
6	16	0	17.8	17.2
8	8	0	89.5	81.7
8	10	0	31.4	32.0
8	12	0	41.6	37.4
8	14	0	15.0	15.4
10	12	0	22.7	21.5
12	12	0	20.8	18.2
0	1	1	9.6	8.5
0	3	1	10.9	12.3
0	5	1	9.8	12.2
0	7	1	29.9	29.3
0	9	1	17.7	14.4
0	11	1	28.4	25.7
0	13	1	13.8	13.8
0	15	1	9.3	15.3
1	2	1	9.0	7.4
2	3	1	24.3	22.9
2	5	1	24.5	26.0
2	7	1	26.4	28.3
2	9	1	25.1	25.0
2	11	1	19.8	20.8
2	13	1	15.8	17.2
2	15	1	15.7	12.3
3	4	1	13.3	12.1
3	6	1	13.0	16.2
4	7	1	22.7	23.5
4	11	1	20.5	20.0
4	13	1	6.8	10.1
4	15	1	9.3	11.9
5	6	1	11.1	11.6
6	7	1	18.7	18.0
6	9	1	7.3	14.2
6	11	1	12.7	12.4
6	13	1	13.3	10.6
7	8	1	14.1	12.6
7	12	1	8.5	4.7
10	11	1	10.4	4.8
0	8	2	11.0	12.6
1	1	2	122.9	98.5
1	3	2	87.8	83.7
1	5	2	69.0	70.9
1	7	2	49.8	52.2
1	9	2	41.8	43.0
1	11	2	30.1	29.0
1	13	2	21.4	23.7
1	15	2	6.6	15.1
1	17	2	5.2	12.1
2	4	2	15.9	7.9
3	3	2	72.9	74.7
3	5	2	63.7	64.5
3	7	2	49.4	50.4
3	9	2	40.5	40.8
3	11	2	26.2	29.1
3	13	2	24.6	22.6
5	5	2	53.7	53.9
5	7	2	42.4	43.5
5	9	2	29.8	33.1
5	11	2	24.9	25.5
5	13	2	20.9	18.6
5	15	2	12.1	14.0
7	7	2	38.5	39.0
7	9	2	31.1	29.5
7	11	2	23.9	24.8
7	13	2	16.9	16.9
7	15	2	15.4	13.7
9	9	2	20.4	20.8
9	11	2	20.4	18.7
11	13	2	5.2	11.4
0	1	3	12.9	8.9
0	3	3	43.4	20.5
0	5	3	26.1	29.2
0	7	3	24.0	24.8
0	9	3	25.3	27.7
0	11	3	15.5	19.1
0	13	3	11.2	18.7
1	2	3	21.7	18.8
1	6	3	12.8	16.2
1	10	3	3.5	11.5
2	3	3	5.2	7.2
2	5	3	28.3	31.3
2	9	3	31.3	31.5
2	13	3	20.0	20.7
3	4	3	9.1	11.2
3	6	3	16.2	10.5
3	14	3	10.2	6.4
4	5	3	18.3	23.4
4	7	3	16.1	17.1
4	9	3	21.0	21.9
4	11	3	6.8	14.0
4	13	3	15.9	14.6
5	6	3	21.3	21.6
5	8	3	11.3	14.0
5	10	3	12.0	11.4
6	9	3	17.4	20.3
6	13	3	16.0	13.5
8	9	3	13.3	11.7
8	13	3	14.6	7.9
0	0	4	218.1	189.3
0	4	4	146.7	150.2
0	6	4	11.1	8.8
0	8	4	88.7	90.4
0	12	4	43.1	43.3
0	14	4	4.5	3.9
0	16	4	12.4	17.6
1	3	4	9.0	5.4
2	2	4	235.9	245.7
2	4	4	24.4	11.1
2	6	4	119.6	121.0
2	8	4	29.1	30.8
2	10	4	38.7	37.9
2	12	4	23.2	27.1
2	16	4	8.8	15.2
4	4	4	120.9	124.7
4	8	4	75.1	76.9
4	12	4	40.3	37.5
4	16	4	16.2	15.7
6	6	4	63.7	63.7
6	8	4	22.2	19.5
6	10	4	20.8	17.4
6	12	4	17.8	18.9
6	16	4	13.8	11.4
8	8	4	47.9	49.0
8	10	4	12.1	10.6
8	12	4	29.4	25.6
10	12	4	14.7	10.7
12	12	4	18.7	14.6
0	1	5	9.4	6.3
0	3	5	24.8	22.9
0	5	5	53.9	27.3
0	7	5	27.0	27.7
0	9	5	26.3	26.4
0	11	5	20.2	21.0
0	13	5	18.2	17.4
1	2	5	9.5	12.9
1	4	5	6.2	8.9
2	3	5	19.3	20.7
2	5	5	11.1	13.9
2	7	5	13.8	15.9
2	9	5	24.8	25.2
2	11	5	12.6	13.1
2	13	5	16.6	18.6
2	15	5	6.9	10.0
3	4	5	10.7	12.6
3	6	5	9.6	4.4
3	10	5	3.8	5.3
4	5	5	22.1	22.9
4	7	5	15.0	19.6
4	9	5	23.2	21.2
4	11	5	16.9	15.7
4	13	5	16.9	13.8
5	6	5	13.6	12.5
5	8	5	14.3	14.2
6	9	5	16.0	17.1
0	2	6	28.3	26.0
0	6	6	16.7	17.6
1	1	6	90.2	78.1
1	3	6	68.7	70.3
1	5	6	63.3	63.2
1	7	6	48.0	49.8
1	9	6	39.9	41.8
1	11	6	27.3	30.1
1	13	6	22.2	23.5
1	15	6	13.8	16.3
2	4	6	16.2	20.0
3	3	6	73.4	65.1
3	5	6	57.2	58.9
3	7	6	45.9	48.5
3	9	6	38.8	39.9
3	11	6	30.5	30.0
3	13	6	23.2	22.5
4	6	6	10.6	14.0
5	5	6	50.0	50.8
5	7	6	41.2	42.7
5	9	6	33.3	33.0
5	11	6	21.8	26.4
5	13	6	17.7	18.7
5	15	6	12.2	14.8
7	7	6	37.2	38.9
7	9	6	31.1	29.7
7	11	6	24.4	25.3
7	13	6	17.7	17.1
9	9	6	20.3	21.3
9	11	6	17.9	19.2
10	12	6	6.9	2.0
11	11	6	17.6	17.5
0	1	7	41.9	28.8
0	3	7	33.7	36.9
0	5	7	12.7	12.7
0	7	7	35.3	35.6
0	11	7	23.2	25.0
0	15	7	8.5	14.6
1	4	7	19.2	24.4
1	8	7	9.7	16.5
2	3	7	15.4	17.0
2	5	7	19.7	17.0
2	7	7	19.2	23.1
2	9	7	14.1	17.4
2	11	7	14.0	18.1
3	4	7	28.4	29.8
3	8	7	15.2	17.4
3	16	7	10.2	2.0
4	7	7	24.2	28.1
4	11	7	21.9	19.4
6	7	7	11.4	14.2
7	8	7	14.6	14.5
0	0	8	380.0	384.9
0	2	8	162.6	154.0
0	4	8	255.8	289.1
0	6	8	89.1	87.9
0	8	8	145.3	149.8
0	10	8	36.5	37.4
0	12	8	61.1	63.9
0	16	8	25.0	25.2
2	2	8	29.0	14.5
2	4	8	122.9	130.1
2	6	8	16.7	11.6
2	8	8	82.5	85.4
2	10	8	8.7	11.8
2	12	8	43.9	45.5
2	14	8	14.8	11.2
2	16	8	18.4	20.3
4	4	8	210.9	225.8
4	6	8	73.9	78.9
4	8	8	117.0	121.9
4	12	8	51.3	53.1
4	14	8	13.4	16.2
4	16	8	20.5	21.2
5	7	8	6.1	10.6
6	6	8	14.5	12.0
6	8	8	54.2	57.0
6	10	8	4.1	12.3
6	12	8	31.8	33.2
8	8	8	69.2	70.1
8	10	8	29.0	29.3
8	12	8	34.5	33.8
8	14	8	15.9	14.4
10	12	8	16.3	19.7
0	1	9	34.2	29.6
0	3	9	17.7	9.1
0	5	9	25.2	25.0
0	7	9	9.2	15.1
0	9	9	14.0	18.0
0	11	9	21.4	18.2
0	13	9	17.5	13.3
0	15	9	8.5	11.7
1	2	9	10.9	9.6
1	4	9	14.0	17.0
2	3	9	7.5	12.6
2	5	9	23.6	23.2
2	7	9	20.3	20.5
2	9	9	22.1	22.3
2	11	9	10.1	16.1
2	13	9	16.3	15.3
3	4	9	6.8	3.0
3	6	9	15.5	11.0
4	5	9	19.5	15.6
4	7	9	7.8	13.3
4	9	9	5.4	12.4
4	11	9	17.3	14.7
6	7	9	14.8	13.6
6	9	9	7.7	13.4
6	15	9	11.3	5.3
7	12	9	11.3	4.9
0	2	10	28.3	30.7
0	6	10	16.4	20.2
1	1	10	91.0	80.3
1	3	10	71.8	70.9
1	5	10	57.0	59.5
1	7	10	45.7	44.8
1	9	10	34.0	34.4
1	11	10	25.0	25.4
1	13	10	18.2	18.1
1	15	10	14.0	14.4
2	4	10	20.2	25.4
2	8	10	17.8	17.3
3	3	10	63.6	64.0
3	5	10	55.9	54.3
3	7	10	43.0	42.8
3	9	10	32.9	32.6
3	11	10	26.2	25.2
3	13	10	20.0	17.4
4	6	10	15.3	16.1
5	5	10	41.7	44.8
5	7	10	34.1	36.5
5	9	10	24.4	26.7
5	11	10	19.2	22.1
5	13	10	13.2	14.5
5	15	10	18.8	13.0
7	7	10	34.9	32.6
7	9	10	25.9	24.1
7	11	10	23.3	21.2
7	15	10	12.6	12.4
9	9	10	21.2	17.1
9	11	10	15.6	16.0
9	13	10	7.1	10.2
10	12	10	8.6	3.2
0	3	11	6.8	7.6
0	5	11	20.4	18.6
0	7	11	15.3	11.5
0	9	11	16.7	19.5
1	2	11	35.2	37.9
1	4	11	9.6	5.6
1	6	11	22.7	27.0
1	10	11	19.0	15.1
2	3	11	24.5	28.6
2	7	11	14.3	11.9
2	9	11	26.0	27.0
2	13	11	21.6	16.7
2	15	11	5.0	5.2
3	6	11	20.8	22.3
3	10	11	11.5	13.9
3	12	11	7.7	1.9
4	5	11	15.2	14.7
5	6	11	24.3	24.4
5	10	11	13.2	12.2
6	7	11	8.5	11.3
0	0	12	119.5	96.8
0	4	12	88.9	85.4
0	8	12	56.8	58.3
0	12	12	28.8	31.0
0	16	12	13.8	13.7
1	7	12	11.5	12.7
2	2	12	129.4	125.6
2	6	12	65.8	67.2
2	8	12	23.5	22.7
2	10	12	20.6	19.9
2	12	12	18.4	21.1
4	4	12	72.1	75.1
4	8	12	50.0	51.0
4	12	12	29.0	27.6
6	6	12	31.5	35.0
6	8	12	16.1	16.2
6	12	12	5.0	15.5
8	8	12	32.4	34.9
8	10	12	14.3	10.0
8	12	12	21.4	20.1
0	3	13	18.3	20.9
0	5	13	11.7	10.1
0	7	13	17.3	22.0
0	9	13	19.3	14.9
0	11	13	11.7	16.1
0	13	13	8.6	11.6
0	15	13	7.2	9.6
1	2	13	21.6	22.2
1	6	13	9.0	5.8
2	3	13	23.8	26.3
2	7	13	11.8	17.7
2	9	13	15.2	13.0
4	5	13	10.1	9.7
4	7	13	17.5	16.2
4	9	13	17.8	12.2
4	11	13	8.8	12.3
4	13	13	8.3	9.6
6	9	13	9.4	10.1
6	13	13	8.4	8.7
8	9	13	6.3	6.7
0	2	14	27.2	28.1
0	6	14	18.4	21.5
0	10	14	6.2	14.6
1	1	14	58.5	47.3
1	3	14	50.6	45.9
1	5	14	44.1	44.1
1	7	14	38.3	39.3
1	9	14	29.0	32.6
1	11	14	27.5	27.5
1	13	14	19.8	18.6
1	15	14	14.6	16.6
2	4	14	20.3	22.6
3	3	14	47.3	44.9
3	5	14	41.3	42.6
3	7	14	37.2	38.6
3	9	14	30.2	31.5
3	11	14	25.2	27.0
3	13	14	18.0	17.9
3	15	14	11.5	16.0
4	6	14	14.2	17.1
5	5	14	34.4	38.5
5	7	14	33.4	34.8
5	9	14	26.7	27.1
5	11	14	21.3	23.9
7	7	14	33.4	32.4
7	9	14	22.8	24.9
7	11	14	23.8	22.5
9	11	14	14.6	17.2
9	13	14	17.1	11.0
0	1	15	42.4	40.2
0	3	15	38.9	40.4
0	5	15	28.6	25.5
0	7	15	27.9	29.8
0	11	15	18.2	17.4
0	15	15	11.8	9.5
1	4	15	30.9	33.5
1	8	15	19.1	20.5
2	5	15	8.6	1.5
2	7	15	4.0	15.3
3	4	15	28.9	33.0
3	8	15	16.0	19.0
3	12	15	8.9	8.2
4	5	15	13.8	22.1
4	7	15	23.2	23.8
4	11	15	12.1	13.7
5	12	15	4.8	7.5
7	8	15	17.4	12.6
0	0	16	197.5	193.2
0	2	16	115.2	101.3
0	4	16	169.0	156.5
0	6	16	65.8	64.7
0	8	16	91.1	89.9
0	10	16	30.6	31.3
0	12	16	42.4	42.7
0	14	16	12.6	14.8
2	2	16	42.1	40.1
2	4	16	88.5	87.6
2	6	16	26.9	28.7
2	8	16	56.3	58.8
2	10	16	11.9	18.5
2	12	16	34.9	33.1
4	4	16	123.8	128.0
4	6	16	54.1	57.6
4	8	16	70.7	75.0
4	10	16	27.4	29.0
4	12	16	36.9	37.3
6	6	16	19.4	22.5
6	8	16	37.9	41.4
6	10	16	19.0	15.7
6	12	16	26.8	25.4
8	8	16	43.1	46.0
8	10	16	23.8	23.4
8	12	16	24.7	23.9
0	1	17	27.9	25.2
0	3	17	10.0	13.5
0	5	17	19.1	20.3
0	11	17	6.9	8.7
1	4	17	19.5	15.2
2	5	17	10.3	17.1
2	7	17	9.7	7.1
2	11	17	4.7	8.0
4	5	17	11.7	12.8
4	9	17	6.3	9.0
6	7	17	9.7	5.2
7	8	17	17.5	5.2
8	9	17	4.7	2.3
0	2	18	21.9	20.6
0	6	18	20.5	14.3
1	1	18	59.1	57.1
1	3	18	56.2	51.1
1	5	18	40.0	41.8
1	7	18	35.1	32.7
1	9	18	21.0	23.0
1	11	18	14.0	19.6
1	13	18	11.5	11.2
2	4	18	17.9	18.2
2	10	18	6.8	3.5
3	3	18	51.7	46.2
3	5	18	39.9	38.2
3	7	18	31.9	30.8
3	9	18	19.6	21.9
3	11	18	20.5	19.1
5	5	18	23.6	31.4
5	7	18	26.8	26.2
5	9	18	9.2	18.5
5	11	18	18.8	16.8
7	7	18	26.4	23.2
7	9	18	21.2	16.8
7	11	18	15.7	15.7
8	10	18	7.0	4.8
0	1	19	8.0	11.0
0	11	19	5.0	1.6
1	2	19	36.2	34.8
1	6	19	23.8	24.1
2	3	19	29.9	29.8
2	5	19	25.8	27.9
2	7	19	18.1	15.6
2	9	19	15.2	16.9
3	6	19	15.2	21.4
5	6	19	13.5	18.7
0	0	20	39.1	36.1
0	2	20	11.6	3.4
0	4	20	38.7	34.7
0	8	20	29.9	28.3
0	12	20	15.7	18.4
2	2	20	46.1	39.0
2	6	20	18.7	19.3
4	4	20	33.6	32.7
4	8	20	28.6	26.0
6	8	20	13.0	12.5
0	1	21	12.7	14.5
0	3	21	10.6	18.6
1	2	21	21.8	18.6
2	3	21	12.4	19.4
4	7	21	8.5	11.2
4	11	21	15.2	8.3
0	2	22	20.8	13.5
0	6	22	8.8	11.2
1	1	22	30.1	25.4
1	3	22	26.3	26.3
1	5	22	30.6	26.8
1	7	22	29.4	26.9
1	9	22	20.7	22.5
1	11	22	22.7	21.7
2	4	22	9.0	11.0
3	3	22	28.8	27.0
3	5	22	26.0	26.9
3	7	22	25.7	26.6
3	9	22	23.4	22.0
3	11	22	25.5	21.0
5	5	22	22.7	25.6
5	7	22	22.8	24.7
5	9	22	15.8	19.9
5	11	22	19.9	18.8
6	8	22	7.4	5.5
7	7	22	21.4	23.5
7	9	22	14.2	18.6
7	11	22	19.7	16.8
9	9	22	21.5	14.5
0	1	23	31.8	33.8
0	3	23	43.0	31.1
0	5	23	22.8	23.6
0	7	23	18.1	19.5
0	9	23	16.1	10.2
0	11	23	14.3	10.7
1	2	23	17.4	14.3
1	4	23	25.6	27.6
1	8	23	18.3	16.0
3	4	23	17.2	25.1
3	8	23	16.8	14.4
4	5	23	13.3	19.5
4	7	23	20.5	15.9
0	0	24	86.5	82.5
0	2	24	58.4	56.2
0	4	24	75.3	69.6
0	6	24	39.5	39.4
0	8	24	45.9	44.8
0	10	24	21.9	22.4
0	12	24	23.3	23.9
2	2	24	37.0	38.6
2	4	24	50.1	49.2
2	6	24	26.0	28.6
2	8	24	32.9	34.8
2	10	24	17.4	17.8
2	12	24	24.0	20.4
4	4	24	44.5	59.0
4	6	24	39.0	35.3
4	8	24	37.3	39.3
4	10	24	19.5	20.5
6	6	24	18.2	22.2
6	8	24	22.9	26.5
8	8	24	24.0	26.3
0	1	25	16.6	15.5
0	3	25	14.9	10.7
0	5	25	16.3	11.6
1	4	25	7.7	9.2
2	5	25	11.1	10.9
2	9	25	11.1	8.3
4	11	25	10.0	2.3
0	2	26	17.5	7.2
1	1	26	32.4	37.2
1	3	26	29.9	33.3
1	5	26	21.0	26.9
1	7	26	20.4	21.3
1	9	26	15.0	14.3
1	11	26	14.1	13.1
2	4	26	11.1	6.6
3	3	26	28.8	30.1
3	5	26	19.1	24.6
3	9	26	9.9	13.6
4	6	26	10.2	4.7
5	5	26	25.1	20.2
0	1	27	18.3	14.5
0	9	27	12.7	7.3
1	2	27	24.6	23.5
1	6	27	18.3	16.1
2	3	27	14.6	21.1
2	5	27	15.2	17.7
0	0	28	16.3	16.0
0	4	28	19.9	15.7
1	2	29	7.9	12.9
1	1	30	14.7	12.7
1	3	30	9.9	14.1
1	5	30	19.6	15.5
1	7	30	20.4	15.8
3	3	30	13.2	15.2
3	5	30	12.0	16.0
3	7	30	13.8	16.7
4	6	30	8.7	2.7
0	3	31	19.0	21.9
1	4	31	10.1	19.5
3	4	31	14.6	17.2
3	6	31	18.6	8.9
0	0	32	27.3	32.0
0	2	32	24.9	26.4
0	4	32	26.3	28.3
2	2	32	18.4	22.8
2	4	32	18.9	23.8
4	4	32	25.8	25.0
0	3	33	11.2	6.5
3	4	33	6.1	3.6

in refining the structure (origin at center). Table III lists the absolute values of the observed and calculated structure factors, where the $F(000)$ used equals one-fourth the $F(000)$ for the absolute scale. As is seen in Table III the l odd reflections are much weaker, in general, than the l even reflections and are therefore much closer to the background level. The errors inherent in their intensities are much larger, thereby leading to a higher agreement factor. In several cases, such as 033, 055, and 017, the background was quite high, contributing to poor agreement between the observed and calculated values of the structure factor.

Description of the Structure

The interatomic distances and angles and their estimated standard deviation are shown in Table IV. The atoms are identified by numbers which refer to 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 the program of Busing,

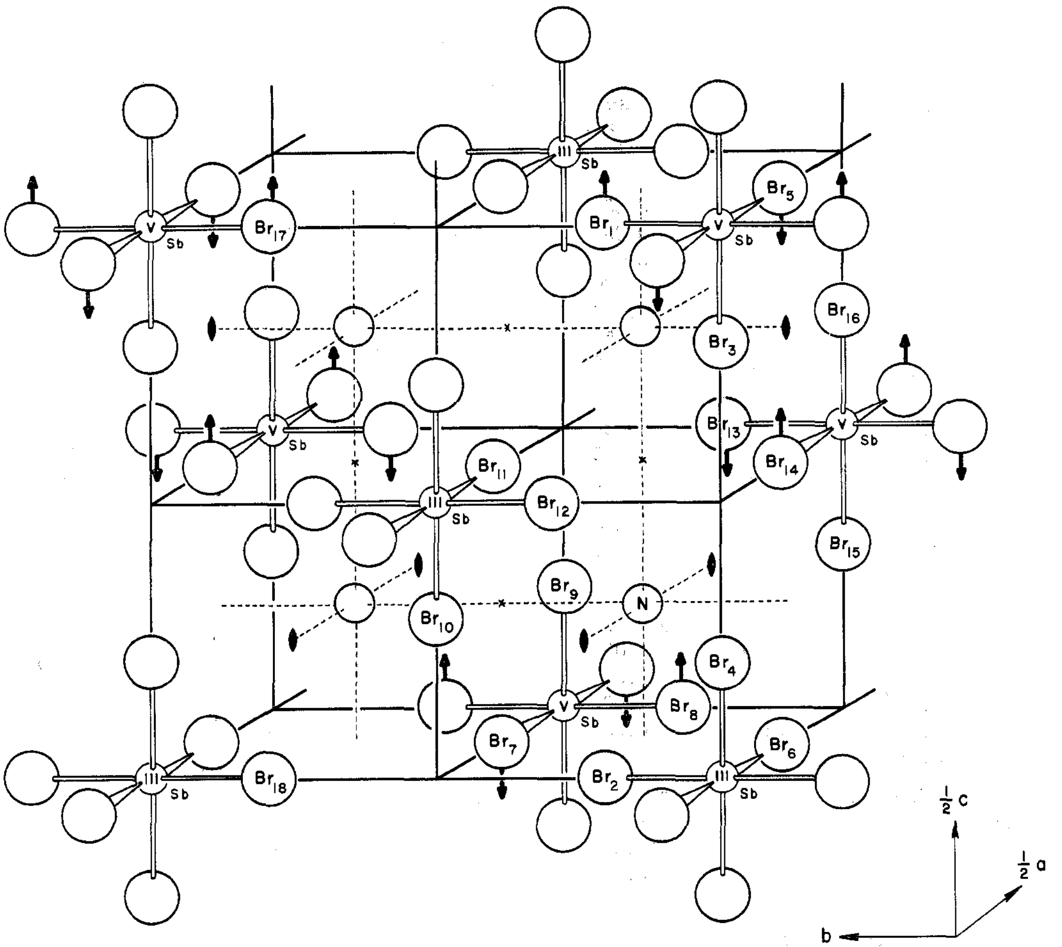

Figure 2.—A portion of the unit cell of $(NH_4)_2Sb^{III}Sb^{V}Br_{12}$, showing the relative distribution of the undistorted $Sb^{III}Br_6^{3-}$ and distorted $Sb^{V}Br_6^-$ anions. The arrows indicate the directions of distortion.

Martin, and Levy[21] in calculating the estimated standard deviations. The third column of Table IV gives distances after correction for thermal motion. Distances between atoms within an anion were corrected for rigid-body libration of the ion about the central antimony atom, as explained below; no other correlation between the motions of the atoms was assumed.

The final parameters show that, within experimental error, the $Sb^{V}Br_6^-$ ion is distorted (Br_e–Sb–Br_a = 93.67 ± 0.15°) and possesses D_{2d} symmetry whereas the $Sb^{III}Br_6^{3-}$ ion is undistorted and possesses O_h symmetry.[22] The mean length of the Sb(V)–Br bond is 2.536 ± 0.006 A and that of the Sb(III)–Br bond is 2.782 ± 0.006 A before correction for thermal motion of the atoms. As is shown in Table V the temperature factors of the bromine atoms show marked anisotropy. The root-mean-square displacement of thermal vibration perpendicular to the Sb–Br bond is about twice as large as that along the bond, the sort of anisotropy which might be expected from an octahedral ion librating about the central atom. The two nonequivalent Sb–Br bond lengths in $Sb^{V}Br_6^-$ and $Sb^{III}Br_6^{3-}$, before correction for thermal motion, differ by 0.019 ± 0.008 and 0.007 ± 0.008 A, respectively; when corrected for thermal motion assuming a librating ion in each case these differences decrease to 0.007 ± 0.008 and 0.001 ± 0.008 A, respectively, thus indicating that this type of correction was a good approximation to reality in this case since significant differences in the bond lengths within each ion are not expected. The corrected mean length of the Sb(V)–Br bond is 2.564 ± 0.006 A, and that of the Sb(III)–Br bond is 2.795 ± 0.006 A.

Each ammonium ion occupies a tetrahedral hole and is thus surrounded by twelve bromine atoms as nearest neighbors. The cation lies on a twofold rotation axis located parallel to the *a* or *b* axis and perpendicular to the *c* axis (see Figure 2); this symmetry element automatically fixes the cation position in the tetrahedral hole in all directions except along the rotation axis itself. The total number of different nearest neighbors is thus six, three from each of the two different neighboring anions. The mean distance between any one of the bromine atoms in the $Sb^{V}Br_6^-$ ion and the ammonium ion with which it is associated is 3.97 A, and the mean distance of the same type but with the $Sb^{III}Br_6^{3-}$ ion is 3.63 A.

Because of the coexistence of two different anions in the same crystal, the van der Waals contacts between the bromine atoms vary over a wide range of values. The mean approach within the $Sb^{V}Br_6^-$ ion is approximately 3.6 A, and within the $Sb^{III}Br_6^{3-}$ ion it is 3.9 A. Since the

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[21] W. R. Busing, K. O. Martin, and H. A. Levy, "OR FFE, a FORTRAN Crystallographic Function and Error Program," ORNL-TM-306, 1964.

[22] Like $Sb^{V}Br_6^-$, the $Sb^{III}Br_6^{3-}$ ion lies on a $\bar{4}2m$ position and thus is not required, by symmetry, to be undistorted.

TABLE IV

INTERATOMIC DISTANCES AND ANGLES AND THEIR ESTIMATED STANDARD DEVIATIONS

Atoms	Distance (uncor), A	Distance (cor), A	Std error, A
Distances and Angles within Anion			
(a) $Sb^{V}Br_6^-$ Ion			
$Sb-Br_1$	2.542	2.566	0.006
$Sb-Br_3$	2.523	2.559	0.005
Br_1-Br_3	3.694	3.739	0.008
Br_1-Br_5	3.602	3.637	0.009
Br_3-Br_5	3.465	3.507	0.006
$Br_1-Sb-Br_3$	93.67°	93.67°	0.15°
$Br_1-Sb-Br_5$	90.23°	90.23°	0.02°
(b) $Sb^{III}Br_6^{3-}$ Ion			
$Sb-Br_2$	2.779	2.795	0.006
$Sb-Br_4$	2.787	2.794	0.005
Br_2-Br_4	3.947	3.963	0.007
Br_2-Br_6	3.930	3.953	0.009
Br_4-Br_6	3.924	3.941	0.007
$Br_2-Sb-Br_4$	90.32°	90.32°	0.13°
$Br_2-Sb-Br_6$	90.002°	90.002°	0.002°
Bromine–Bromine Contacts between Anions (<4.0 A)			
Br_3-Br_{14}	3.881	3.921	0.008
Br_2-Br_7	3.786	3.817	0.008
Br_4-Br_{14}	3.924	3.953	0.008
Br_2-Br_{10}	3.649	3.679	0.007
Br_6-Br_{15}	3.818	3.852	0.008
Bromine–Bromine Nonbonding Distances between Anions along Axes			
Br_1-Br_{17}	5.59	5.62	0.010
Br_3-Br_4	5.450	5.479	0.008
Br_2-Br_{18}	5.10	5.13	0.010
Environment of Cation			
$N-Br_4$	3.53	3.55	0.02
$N-Br_{10}$	3.53	3.55	0.02
$N-Br_2$	3.56	3.58	0.02
$N-Br_{12}$	3.56	3.58	0.02
$N-Br_6$	3.804	3.827	0.007
$N-Br_{11}$	3.804	3.827	0.007
$N-Br_7$	3.933	3.958	0.007
$N-Br_{14}$	3.933	3.958	0.007
$N-Br_8$	3.94	3.96	0.02
$N-Br_{13}$	3.94	3.96	0.02
$N-Br_9$	4.03	4.05	0.02
$N-Br_{15}$	4.03	4.05	0.02

TABLE V

PRINCIPAL COMPONENTS OF THE TEMPERATURE FACTORS

Atom	Principal axis, *r*	Rms amplitude, A	Cosines of angles between the principal axes, *r*, and the unit cell axes		
			a_0	b_0	c_0
Br_1	1	0.150	0.0000	0.9814	0.1922
	2	0.261	0.0000	−0.1922	0.9814
	3	0.316	1.0000	0.0000	0.0000
Br_2	1	0.116	0.0000	0.8944	−0.4472
	2	0.258	1.0000	0.0000	0.0000
	3	0.272	0.0000	0.4472	0.8944
Br_3	1	0.093	0.0000	0.0000	1.0000
	2	0.317	1.0000	0.0000	0.0000
	3	0.352	0.0000	1.0000	0.0000
Br_4	1	0.127	0.0000	0.0000	1.0000
	2	0.191	0.0000	1.0000	0.0000
	3	0.243	1.0000	0.0000	0.0000
Sb(V)	1	0.141	0.0000	0.0000	1.0000
	2	0.145	0.0000	1.0000	0.0000
	3	0.145	1.0000	0.0000	0.0000
Sb(III)	1	0.120	0.0000	0.0000	1.0000
	2	0.159	0.0000	1.0000	0.0000
	3	0.159	1.0000	0.0000	0.0000

contacts within the $Sb^{V}Br_6^-$ ions are much closer than within the $Sb^{III}Br_6^{3-}$ ions, the motions of the individual bromine atoms in the former are probably correlated to a greater extent than in the latter. There appears to be no unusual van der Waals contact of bromine atoms between the two different types of anions; the closest such approach is 3.786 A in the 001 plane and 3.924 A in the 100 and 010 planes.

Discussion

The crystal structure of ammonium hexabromoantimonate, $(NH_4)_4Sb_2Br_{12}$, exhibits several features worth noting. The first regards the stereochemistry of the two anions. The $Sb^{V}Br_6^-$ ion, as might be expected from packing considerations, is distorted. However, the $Sb^{III}Br_6^{3-}$ ion, which contains a lone pair of electrons, appears to be undistorted and exhibits abnormally long bond distances (0.17 A longer than predicted by Pauling's expression $D(n') - D(n) = -0.6 \log (n'/n)$. It has been shown by Gillespie and Nyholm[23] that the stereochemistry of most nontransition element compounds appears to be governed by electrostatic repulsion between pairs of valence electrons, regardless of whether the electron pairs are involved in bonding with ligands or exist as lone pairs. Thus, one would expect an $:XL_6$ complex to exist either as a seven-coordinated structure, with the lone pair occupying one of the seven sites, or as an irregular octahedron. These, however, appear not to be the case for complexes isoelectronic with the rare gas hexahalides. Hexahalide complexes of selenium(IV),[24] tellurium(IV),[25] polonium(IV),[26] and now antimony(III) in this determination have, in each case, been observed to be regular octahedra with the distance between the central atom and the ligands considerably longer than the sum of their normal covalent radii. It has recently been suggested by Urch[27] that, if the *n*s orbital (a_{1g}) of the central atom plays little part in bonding then an extra pair of electrons may be accommodated in the a_{1g} antibonding molecular orbital, without distorting the O_h structure. This, he has pointed out, would decrease the effective electronegativity of the central atom which in turn would allow the *n*d orbitals to be better used in bonding, a fact which is most important for halogens less electronegative than fluorine.

This structure determination does not unambiguously explain the jet black color. A recent study by Day[28] of the solid reflection spectra of several hexahalide complexes containing Sb(III) and Sb(V) has indicated that electron-transfer transitions from the ns^2 or $(n + 1)s^2$

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[23] (a) R. J. Gillespie and R. S. Nyholm, *Quart. Rev.* (London), **11**, 339 (1957); (b) R. J. Gillespie, *Can. J. Chem.*, **38**, 818 (1960); (c) R. J. Gillespie, *ibid.*, **39**, 318 (1961); (d) R. J. Gillespie, *J. Chem. Soc.*, 4672 (1963); (e) R. J. Gillespie, *ibid.*, 4679 (1963).

[24] (a) G. Engel, *Z. Krist.*, **90**, 341 (1935); (b) J. L. Hoard and B. N. Dickenson, *ibid.*, **84**, 436 (933).

[25] (a) E. E. Aynsley and A. C. Hazell, *Chem. Ind.* (London), 611 (1963); (b) I. D. Brown, *Can. J. Chem.*, **42**, 2758 (1964).

[26] (a) K. W. Bagnall, R. W. D'Eye, and J. H. Freeman, *J. Chem. Soc.*, 2320 (1955); (b) K. W. Bagnall, R. W. M. D'Eye, and J. H. Freeman, *ibid.*, 3959 (1955); (c) K. W. Bagnall, R. W. M. D'Eye, and J. H. Freeman, *ibid.*, 3385 (1956).

[27] D. S. Urch, *J. Chem. Soc.*, *Suppl.*, **1**, 5775 (1964).

[28] P. Day. *Inorg. Chem.*, **2**, 452 (1963).

shell of the trivalent ion to the ns^0 shell of the pentavalent ion are responsible for the abnormally deep color. There appear, however, to be no unusual Br–Br distances in $(NH_4)_4Sb_2Br_{12}$ for the electron-transfer paths to take. Further studies on related compounds will therefore be made in an attempt to understand further the structural requirements of charge transfer, assuming this is the cause of the black color.

Acknowledgment.—The authors are indebted to Professor R. E. Rundle, who doubted the existence of the tetravalent state and who correctly predicted, shortly before his death, that, if $(NH_4)_2SbBr_6$ contained mixed Sb(III) and Sb(V) in an ordered array, it would necessarily give rise to weak reflections in the reciprocal lattice and thus render itself amenable to a detailed single-crystal X-ray structure determination.

CONTRIBUTION FROM THE NUCLEAR MATERIALS AND PROPULSION OPERATION,
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Crystal Structure of the Rhombohedral $MO_3 \cdot 3R_2O_3$ Compounds (M = U, W, or Mo) and Their Relation to Ordered R_7O_{12} Phases[1]

BY S. F. BARTRAM

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A complete three-dimensional structure analysis of the complex oxide $UO_3 \cdot 3Y_2O_3$ was carried out using single-crystal data. This structure is characteristic of a large family of rhombohedral compounds containing rare earth oxides and having an oxygen-to-metal ratio of 12:7. Bond lengths and coordination polyhedra for the atoms in this rhombohedral structure are compared with those in other known oxides. The relationship between $U_mY_{7-m}O_{12}$ compositions ($1 < m < 2.0$) and ordered $RO_{1.71}$ phases is shown. Some conclusions are drawn as to their mode of oxidation.

Introduction

The existence of a family of rare earth–group VIb complex oxides has been reported previously.[2] These compounds have the general composition $MO_3 \cdot 3R_2O_3$ (MR_6O_{12}) where M = U, W, or Mo and R = rare earth. They crystallize in a rhombohedral structure which is closely related to the face-centered cubic fluorite structure. In order to clarify the relationship between these structures, single-crystal studies were necessary. A detailed crystal structure analysis was of additional interest because the normally volatile trioxides of U, W, and Mo show exceptional thermal stability in these rhombohedral compounds.

Crystallographic data for the compounds investigated are given in Table I. For the sake of consistency, all dimensions and indices given in the text refer to the hexagonal cell.

TABLE I

CRYSTALLOGRAPHIC DATA FOR RHOMBOHEDRAL PHASES

Compn	Rhombohedral parameters, A		Hexagonal parameters, A			Density, g/cc	
	a_0	α	a_0	c_0	c/a	Obsd	Calcd
UY_6O_{12}	6.530	99° 3′	9.934	9.364	0.943	5.91	6.00
ULu_6O_{12}	6.435	99° 9′	9.797	9.204	0.939	...	9.63
$U_2Y_5O_{12}$	6.568	99° 18′	10.01	9.36	0.935	6.88	6.83
$U_2Y_5O_{13.5}$	6.522	99° 19′	9.943	9.289	0.934	...	7.37

This rhombohedral structure is also characteristic of the ordered $RO_{1.71}$ (R_7O_{12}) phases reported for the oxides of Ce, Pr, and Tb.[3] Results obtained for the complex oxide compounds should be applicable to the ordered intermediate rare earth oxide phases. This point will be amplified in the Discussion section.

Compositional ranges for the existence of the two rhombohedral phases in the U–Y–O system should be somewhat revised from those given before.[2a] Rhombohedral 1 (rhomb 1) can exist from $U_2Y_5O_{12}$ to UY_6O_{12} (55.6 to 75.0 mole % Y_2O_3) and rhombohedral 2 (rhomb 2) occurs from $U_2Y_5O_{13.5}$ to about $U_{1.75}Y_{5.25}O_{13.1}$ (55.6 to 60 mole % Y_2O_3). The ternary phase diagram below 1700° has a two-phase region from 50 to 55.6 mole % Y_2O_3.[2b]

Experimental Section

Crystals of the $UO_3 \cdot 3Y_2O_3$ compound were formed as irregular growths on the surface of material heated in air for several days at 1500°. These crystals were pale yellowish green with no well-developed faces. Although they were very small, one was found from which satisfactory Weissenberg intensity data were collected. This crystal had an average dimension of about 0.04 mm. In spite of its angular shape, it was helpful to apply a spherical absorption parameter of $\mu R = 1.9$ to correct observed intensities for the extremely high absorptivity of this compound.

The chemical composition of these crystals could not be determined directly, but previous work by Chase[4] had conclusively proven the existence of this compound at a mole ratio of $1UO_3$:$3Y_2O_3$ when fully oxidized. Furthermore, X-ray powder dif-

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[1] (1) (a) This paper originated from work sponsored by The Fuels and Materials Development Branch, Division of Reactor Development, U. S. Atomic Energy Commission, under Contract AT (40-1)-2847; (b) presented at The Fifth Rare Earth Research Conference, Iowa State University, Ames, Iowa, Aug 30–Sept 1, 1965.

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[3] (3) (a) D. J. M. Bevan, *J. Inorg. Nucl. Chem.*, **1**, 49 (1955); (b) L. Eyring and N. C. Baenziger, *J. Appl. Phys., Suppl.*, **33**, 428 (1962); (c) N. C. Baenziger, H. A. Eick, H. S. Schuldt, and L. Eyring, *J. Am. Chem. Soc.*, **83**, 2219 (1961).

[4] (4) G. A. Chase, *Acta Cryst.*, **15**, 91 (1962).