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Some crystal structures of pyridinium salts of haloantimonate anions

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SOME CRYSTAL STRUCTURES OF PYRIDINIUM SALTS OF HALOANTIMONATE ANIONS

by

Spencer Kellogg Porter

A Dissertation Submitted to the
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INTRODUCTION

There has only been a relatively small amount of work done on the preparation of salts containing halo-coordinated antimony anions, and even less is known of the structural chemistry of this type of compound. The primary purpose of this work was to add to this structural chemistry.

Antimony has two common oxidation states, viz. +3 and +5; and there has been some speculation that a +4 state exists. This seems most unlikely after reviewing the work of Jensen and Rasmussen[1] and of Lawton and Jacobson[2]. Jensen and Rasmussen closely examined the lattice constants of some salts that had been previously thought to contain Sb(IV). These crystals had been reported as cubic, but Jensen and Rasmussen found that some of the lines in the powder pattern thought to be singlets were in reality doublets. They then determined the cells to be tetragonal with c/a ratios close to the square root of two. The salts shown to be tetragonal have the formulas: $(NH_4)_4FeSbCl_{12}$, $(NH_4)_2SbBr_6$, Rb_2SbBr_6, and Cs_2SbBr_6.

Lawton and Jacobson did a full three-dimensional x-ray crystal structure analysis of the second of these which proved to have the formula $(NH_4)_4Sb(III)Sb(V)Br_{12}$. This study found

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[1] Jensen, A. T. and S. E. Rasmussen, Acta Chem. Scand., 9, 708 (1955).

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

discrete $SbBr_6^-$ and $SbBr_6^{3-}$ ions each possessing nearly octahedral symmetry. They found antimony-bromine bond lengths of 2.795Å and 2.564Å for antimony(III) and antimony(V) respectively. Thus by showing that two different bond lengths exist in this compound, they showed the co-existence of the two oxidation states.

Some structural chemistry of halo-coordinated antimony compounds has been done with antimony present in only one oxidation state or the other. The structure of antimony(III) chloride has been determined in the vapor phase by microwave spectroscopy[1], and by electron diffraction[2]. This structure has also been determined in the solid state by x-ray diffraction[3]. All of these studies report that the molecule has C_{3v} symmetry. Antimony-chlorine bond distances of 2.325(5), 2.37(2), and 2.36(3)Å were reported from the microwave, electron diffraction, and x-ray studies respectively. The chlorine-antimony-chlorine bond angles reported are (in the same order) 99.5(15)°, 96(4)°, 95.2° (no e. s. d. calculated).

The structure of $(NH_4)_2SbCl_5$ has been studied by x-ray diffraction[4]. In this salt the antimony atom is surrounded by

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[1] Kisliuk, P., J. Chem. Phys., 22, 86 (1954).

[2] Swingle, S. M., A private communication quoted by P. W. Allen and L. E. Sutton, Acta Cryst., 3, 46 (1950).

[3] Lindqvist, I. and A. Niggli, J. Inorg. Nucl. Chem., 2, 345 (1956).

[4] Edstrand, M., M. Inge., and N. Ingri, Acta Chem. Scand., 9, 122 (1955).

five chlorine atoms forming five vertices of a somewhat distorted octahedron, and the sixth position is thought to contain a localized non-bonding pair of electrons. In this anion four of the antimony-chlorine bonds are 2.62Å in length, and the other (opposite the "lone pair") is 2.36Å.

The crystal structure of antimony(V) chloride has been determined at -30°C from an analysis of two dimensional projections of the electron density[1]. Each molecule in the crystal is a trigonal bipyramid with antimony-chlorine (equatorial) distances of 2.29Å and antimony-chlorine (apical) distances of 2.34Å. The distances and geometry found agree well with an earlier vapor phase study by electron diffraction[2].

Antimony(V) chloride is known to form adducts with Lewis bases. One of these, $SbCl_5 \cdot OPCl_3$ has been studied by single crystal x-ray techniques[3]. In this compound the antimony atom is surrounded by six groups in a distorted octahedral fashion, by five chlorine atoms and a $OPCl_3$ group. Another interesting compound $ISbCl_8$ has been studied by x-ray analysis as well. Here each antimony atom is surrounded by six chlorine atoms. However, two of these bridge, that is, they are coordinated to the iodine atom as well. Thus the formula could either be

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[1] Ohlberg, S., J. Amer. Chem. Soc., <u>81</u>, 811 (1959).

[2] Powell, H. M., D. Clark, and A. F. Wells, J. Chem. Soc., 642 (1942).

[3] Lindqvist, I. and C. Branden, Acta Cryst., <u>12</u>, 642 (1959).

written as $ICl_2{}^+SbCl_6{}^-$ or as $ICl_4{}^-SbCl_4{}^+$.[1]

The structure of antimony(III) bromide has been investigated by electron diffraction[2], and was found to have the same symmetry as antimony(III) chloride with bond distances of 2.51(2)Å and bond angles of 97(2)°.

The work of Lawton and Jacobson[3,4] provided the prime incentive for this study. They performed full three-dimensional x-ray crystal structure analyses on two compounds containing both oxidation states of antimony, viz. $(NH_4)_4Sb_2Br_{12}$ (discussed above) and pyridinium 24-bromoantimon(III)-triantimon(V)ate. The latter contained three crystallographically independent anions of the formula $SbBr_6$. Each of these is a distorted octahedron. The antimony(III)-bromine bonds average 2.82Å in length, and the antimony(V)-bromine bonds 2.56Å. Lawton and Jacobson also studied α-picolinium nonabromonantimonate(V). This compound contains $SbBr_6{}^-$ and $Br_3{}^-$ anions. They also performed some preliminary x-ray studies on several other interesting salts as well. Lattice constants were determined and empirical formulas were established by density measurements. The empirical formula types found were $R_3Sb_2Br_{12}$, R_2SbBr_8, and

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[1] Vonk, C. and E. Wiebenga, Acta Cryst., 12, 859 (1959).

[2] Swingle, S. M., op. cit.

[3] Lawton, S. L. and R. A. Jacobson, op. cit.

[4] Lawton, S. L., "Crystal Structures of Some Unusual Antimony Bromide Salts", M. S. Thesis, Iowa State University, 1966.

$R_3Sb_2Br_{14}$.[1] Hubbard and Jacobson have recently determined the crystal structure of $Cs_4Sb_2Br_{12}$ and found it to be isostructural with the ammonium salt.[2]

In the process of attempting to interpret the results of these investigations, it was found that, as noted above, little good structural information was available on salts containing only antimony(III) or antimony(V), particularly on those with organic cations. It was then decided that such a study would be of value.

We also wished to gain some further information on the forces holding these types of crystals together. Previous results pointed to several possibilities. Adducts such as the $SbCl_5 \cdot OPCl_3$ might form and pack into the crystals as such. Ionic crystals could form. With a proper choice of base hydrogen bonds might form through chlorine-hydrogen-nitrogen linkages. Charge transfer paths were thought by Lawton[3] to be important in the mixed oxidation state salts. Finally it was of interest to compare the bond distances and angles to those of similar compounds studied earlier.

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[1] Ibid., p. 67.

[2] Hubbard, C. and R. A. Jacobson, Ames, Iowa, unpublished research, private communication, 1968.

[3] Lawton, S. L., op. cit., p. 120.

THE PREPARATION AND CRYSTAL STRUCTURE DETERMINATION OF PYRIDINIUM TETRACHLOROANTIMONATE(III)

The first task undertaken was to prepare single crystals of a salt made with an organic base and antimony(III) chloride. The first step in the preparation technique was to dissolve $SbCl_3$ in concentrated HCl. The organic base was then added dropwise into the solution at about 75°C. It was found that the presence of a small amount of sulfuric acid seemed to aid crystal formation, and, therefore, a drop of concentrated H_2SO_4 was added. A solid product formed on adding excess base. Heating to 95°C over a steam bath gave a clear solution. This was followed by cooling to room temperature over a period of four to six hours. This procedure was tried with a number of bases, but suitable crystals were seldom obtained. Pyridine gave crystals which had well-formed faces, and accordingly an x-ray study was begun on its derivative.

Several attempts were made to satisfactorily mount one of the well-formed crystals into a thin-walled Lindemann capillary. Since the crystals decomposed in air or water, the best technique proved to be coating the crystal with a layer of petroleum jelly and then sticking the whole mass to the inner wall of the capillary with a thin glass fiber. The capillary was then mounted in picein wax held by a brass collar which in turn was mounted in a goniometer head. This gave a rigid mount that lasted two or three weeks before crystal decomposition and which prevented shifting of the crystal. The crystals used in the x-ray studies were about 0.29x0.22x0.50 mm.

X-ray alignment of the crystal was done by oscillation photographs. To do this it is necessary to have a real major axis of the crystal close to the oscillation axis of the camera. By adjusting the arcs of the goniometer head holding the crystal it is usually possible to bring this major axis into coincidence with the oscillation axis, and obtain parallel row of reflections in the photograph. Each of these rows is a layer in reciprocal space.[1] Three such layers were photographed by the equi-inclination Weissenberg method[2], and the crystal was then moved to a Buerger precession camera. The precession technique photographs reciprocal lattice layers which include the row on the oscillation axis[3], whereas the Weissenberg method gives layers perpendicular to this axis. Thus by a combination of these techniques it is possible to gain the complete x-ray diffraction record without remounting the crystal. Such pictures were used to determine the unit cell of highest symmetry and to find which classes of reflections were systematically absent.

Mirror symmetry was found in the diffraction record in but one direction. Thus the crystals are monoclinic. The first

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[1] Buerger, M. J., X-Ray Crystallography. John Wiley and Sons, Inc., New York, New York, 1942. p. 133.

[2] Ibid., pp. 221 and 252.

[3] Buerger, M. J., The Photography of the Reciprocal Lattice, ASXRED Monography no. 1, The American Society for X-Ray and Electron Diffraction, Cambridge, Mass., 1944. p. 1.

cell chosen has a = 7.48Å, b = 12.83Å, c = 10.59Å and β = 93.4°. This cell is a body-centered one because h+k+l is even for all the observed reflections. Also in the (h·0·l) zone, h is always even for the observable reflections. Reference to Buerger showed that this is indicative of an a glide plane, and that the Laue (diffraction) group is 2/mI_/a.[1] Two space groups, viz. Ia and I2/a were possible. The only difference between these is that the latter contains a center of symmetry while the former does not. Friedel's Law states that it is impossible to tell whether such a center of symmetry is present in the space group, since the x-ray diffraction record is always centro-symmetric[2]. Reference to *The International Tables for X-Ray Crystallography* showed that the cell chosen was non-standard. Accordingly the cell was changed so that the Laue group is 2/mC_/c, giving possible space groups of Cc or C2/c.[3] The new cell has dimensions of a = 12.92Å, b = 12.83Å, c = 7.48Å and β = 122.4°. The matrix used to transform indices is (1 0 1/0 1 0/$\bar{1}$ 0 0).[4] The accurate lattice constants were in fact obtained by very careful alignment on the single crystal orienter of the crystal used for intensity measurements.

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[1] Buerger, M. J., *X-Ray Crystallography*, pp. 83 and 511.

[2] *Ibid.*, p. 55.

[3] *The International Tables for X-Ray Crystallography*, published for the International Union of Crystallography by the Kynoch Press, Birmingham, U. K., vol. 1, pp. 89 and 101. 1952.

[4] Lawton, S. L. and R. A. Jacobson, *The Reduced Cell and Its Crystallographic Applications*. U. S. Atomic Energy Commission Report IS-1141 (Iowa State University, Ames, Iowa) p. 189.

The errors in the lattice constants were estimated from the alignment errors in the line-up procedure (discussed below). The errors were estimated from the widths of the peaks used to align the crystal, and were found to be about 0.02Å for each of the cell edges and about 0.2° in the beta angle.

The density was not measured, but assuming any reasonable value between 2.0 and 2.5 g/cm^3 it was possible to predict that there must be four molecules per unit cell. (It should be noted that in this space group there must be four or some multiple of four molecules per unit cell). The actual calculated density was 2.18 g/cm^3.

The intensity data were taken on a General Electric single crystal orienter equipped with a scintillation counter. To align a crystal on this instrument it is necessary to find the exact location of three non-coplanar peaks. This was done using a procedure modified slightly from that recommended by the manufacturer.[1] The crystal was aligned such that the $(h \cdot 0 \cdot \bar{h})$ row of the C-centered cell was coincident with the spindle axis. Mo K_α radiation was used to measure the intensities of all crystallographically independent reflections in two octants. The appropriate instrument settings for all reflections were calculated by SCO-6.* All reflections with

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[1] Furnas, T. C., Single Crystal Orienter Manual, The General Electric Co., Milwaukee, Wisconsin, c. 1966.

*Williams, D. E., Louisville, Kentucky, SCO-6, A FORTRAN single crystal orienter alignment program, private communication, *ca.* 1965.

$\theta < 30$ were measured. The integrated intensity of each reflection was measured by the moving-crystal moving-counter method.[1] This is sometimes called a theta-two theta scan because the counter and crystal both move in the horizontal plane, but the counter has twice the angular velocity of the crystal. The duration of the scan for each measurement was 100 seconds and 3.33° in two theta, centered on the peak maximum as calculated by SCO-6.

The absolute value of any reflection's structure factor is proportional to the square root of the reflection's corrected integrated intensity. The following paragraphs discuss the necessary corrections and the methods used to make them.

A net intensity must be obtained by subtracting out the background. In this study the background scatter was measured by off-setting omega two degrees from a known peak position and scanning over the same theta-two theta scan. This was done on about 200 peaks with random two theta values. These were plotted as intensity vs. theta, and a best line was drawn through these points. From this plot the background was obtained for each intensity measurement according to its theta value.

Many crystals gradually decompose under exposure to the x-ray beam, and it is necessary to correct for this in order to put all the observed structure factors on the same scale.

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[1] Furnas, T. C., *op. cit.*, p. 96.

Accordingly the intensities of three medium to strong reflections were measured repeatedly throughout the data-taking period. A plot was made of the sum of these intensities vs. time. All the reflections were then corrected by a factor according to the time when its intensity was measured. Total decomposition was less than 8% for the entire data-taking period of about two weeks.

Much of the radiation emitted by even the best x-ray tubes is non-characteristic. The K_β radiation (from an M to K electronic transition) is at a slightly shorter wavelength than the K_α (from an L to K). The amount of this radiation reaching the counter may be decreased by the use of an appropriate filter. The best material for this is the element of one or two atomic numbers less than the target metal. Such a filter has been found to reduce the K_α radiation by about one-third while reducing the K_β by 99%. Since niobium is radioactive, zirconium was used to filter the Mo K_α radiation.

Radiation with wavelengths longer than that of the K_α is called streak radiation after the appearance of photographs it affects. In closely packed reciprocal lattice rows the streak radiation from peaks with a high intensity and low theta will cause an error in the measurement of peaks with a higher theta and the same prime indices. The intensities of three peaks with prime indices were measured as a function of wavelength. To do this one sets the chi and phi settings of the single crystal orienter according to SCO-6. The intensity is then measured at theta values ranging from that calculated by SCO-6 (for the K_α wavelength) to a point (higher theta) where the intensity is equal to the background. Examining the Bragg equation, $n\lambda = 2d\sin\theta$, we can see that increasing theta has the same effect as increasing the wavelength provided that the interplanar spacing (d) is constant. These intensities were corrected by the Lorentz-polarization factor (see later paragraph this section), scaled to a common scale and plotted as intensity vs. wavelength. Every reflection of an order greater than one was then corrected for streaking effects according to its position in the reciprocal lattice row.

Some of the x-ray intensity is always absorbed by the crystal, and it is necessary to correct for this unless the crystal is very small with respect to the ideal size of $2/\mu$ (μ is the linear absorption coefficient)[1]. The linear absorption coefficient was calculated after Buerger[2] using the mass absorption coefficients given by the International Tables[3]. The linear absorption coefficient is 16.7 cm^{-1} for pyridinium tetrachloroantimonate(III). To calculate the total absorption correction for a reflection it is necessary to calculate the total path length (incident beam path from entry face to a

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[1] Buerger, M. J., X-Ray Crystallography, p. 178.

[2] Buerger, M. J., Crystal Structure Analysis, John Wiley and Sons, Inc., New York, New York, 1960. p. 205.

[3] The International Tables for X-Ray Crystallography, vol. 3, p. 162.

point plus diffracted beam path from the point to the exit face) for every point within the crystal. The paths must then be summed. This cannot be done exactly, but a usable approximation can be made using the method of numerical integration of Gauss[1]. This process has been programmed in the FORTRAN program ABCOR[2] which has been modified for the IBM 360 computer by local workers. One can check the convergence of this process by increasing the number of points in the integration until the transmission factors no longer change. This was done and six points proved to be ample. The range in transmission factors was 0.36 to 0.42.

Finally the intensity of each reflection was corrected for Lorentz and polarization effects. The first of these depends on the geometry of the diffraction experiment, and the second on the fact that the scattered beam is polarized. The geometry of the single crystal orienter is such that the "Lp" factor has the same form for all reflections, viz.[3]

$$\mathrm{Lp}\ (\theta) = \frac{1 + \mathrm{Cos}^2\ 2\theta}{\mathrm{Sin}\ 2\theta}$$

The variances in the intensity measurements and the standard deviations of the structure factors were estimated by the

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[1] Margenau, H. and G. Murphy, The Mathematics of Physics and Chemistry, 2nd ed., Van Nostrand and Co., Princeton, New Jersey, 1956, p. 479.

[2] Busing, W. R. and H. A. Levy, Acta Cryst., 10, 180 (1957).

[3] Buerger, M. J., X-Ray Crystallography, p. 55.

finite difference method of Williams and Rundle[1]. In this method

$$\sigma F = \sqrt{\frac{I + \sigma I}{Lp(\theta)}} \quad - \quad |F_{obs}|$$

where σF is the e. s. d. of the structure factor,

I is the corrected intensity,

σI is the e. s. d. of I,

$Lp(\theta)$ is the Lorentz-polarization correction,

and F_{obs} is the observed structure factor.

The variance in the observed intensity is given by

$$\sigma I^2 = C_T + C_B + C_S + (K_T C_T)^2 + (K_B C_B)^2 + (K_S C_S)^2$$

where C_T is total counts,

C_B is background counts,

C_S is streak counts,

and the K's are estimated percentage errors in each measurement.

Experimentation by the author showed that any set of values of the K's between 0.01 and 0.07 resulted in just about the same weighting scheme. K's of zero were not satisfactory because this gave essentially constant weights for all reflections above a certain threshold value of the intensity. The weights of all reflections below this value were very small. The weights ultimately employed in the least squares refinement

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

will be discussed in later paragraphs.

Experimentation by Dr. D. E. Williams (formerly of the Ames Lab) had measured the extent to which the scintillation counter response was not linear with respect to intensity. This correction was made for all reflections, but proved to be small even for the most intense ones.

There were 1,569 crystallographically independent reflections whose intensities were measured, and 1,111 of these were considered to be observed, that is, their corrected intensity was at least twice their estimated standard deviation ($I/\sigma I>2$). All 1,569 reflections were used in the structure determination, but only the "observed" reflections were used in the final refinement.

The general crystallographic Fourier program of Dahm and Jacobson* was used to calculate a three-dimensional Patterson function. The ambiguity of the space group was as yet unresolved, but both possessed a "c" glide plane (x,y,z to $x,\bar{y},\frac{1}{2}+z$). Since the Patterson contains peaks representing all the interatomic vectors, pairs of atoms related by this transformation had vectors in the Harker line ($0,2v,\frac{1}{2}$)[1]. (Conventionally the (x,y,z) of Patterson space is (u,v,w)). Any Patterson

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[1] Buerger, M. J., Vector Space, John Wiley and Sons, Inc., New York, New York, 1959, p. 132.

*Dahm, D. J. and R. A. Jacobson, Ames, Iowa, a FORTRAN program to generate Fourier syntheses for all space groups not containing a diamond glide plane, private communication. ca. 1966.

map contains n(n-1) peaks (apart from the origin) where n is the number of atoms. If a structure is centric, doubling of most peaks will occur, giving fewer separate peaks in the map. An insufficient number of large peaks representing the heavy atom (Sb,Cl) interactions were found for the acentric space group, Cc; therefore, the centric, C2/c, was initially assumed.

The space group C2/c is an eight-fold group, so it was necessary to place the antimony atom in a four-fold special position. The International Tables[1] gave five possibilities. Four of these listed special conditions for reflection, meaning that an atom in the set of special positions would contribute to the structure factors of only those reflections. Since the antimony atom was by far the largest scatterer in the cell, it was a simple matter to check the pattern of large and small intensities and compare it to the special conditions. None of the patterns fit, leaving only the "e" set which placed the antimony atom on the two-fold rotation axis at (0,y,¼) as a possibility. This meant that the anion had to have at least two-fold symmetry as well. The "y" coordinate was estimated from the "v" coordinate of the largest peak in the Harker line discussed above. Another large peak in the Patterson was taken to be an antimony-chlorine vector.

These two atoms were used as input to the full-matrix

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[1] The International Tables for X-Ray Crystallography, vol. 1, p. 101.

least squares program ORFLS[1]. The atomic scattering factors of Hanson and coworkers[2] were used here and throughout the study. The structure factors calculated by ORFLS gave a conventional discrepancy factor (R) of 0.55. (By definition R = $(\|F_o| - |F_c\|)/|F_o|)$. This was well below the value expected for a random centric structure, namely 0.83[3]. An electron density synthesis was made by the program of Dahm and Jacobson using the signs predicted by the structure factor calculation. This map very plainly showed another large peak which was correctly assumed to represent another chlorine atom position. A further structure factor calculation lowered R to 0.23.

A difference synthesis (using $F_{obs} - F_{calc}$) for the Fourier coefficients[4] was done at this time. A difference map shows peaks where atoms exist in the cell but have not been input into the structure factor calculations. These maps also show depressions where atoms have been input, but do not actually exist. The map calculated showed no significant depressions. It also showed that no chlorine atoms remained to be input; this fixed the formula as $(C_5NH_6)^+SbCl_4^-$. The difference map

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[1] Busing, W. R., K. O. Martin, and H. A. Levy, ORFLS, A FORTRAN Crystallographic Least-Squares Program, ORNL-TM-305, (The Oak Ridge National Laboratory, Oak Ridge, Tennessee) 1962.

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

[3] Wilson, A. J. C., Acta Cryst., 3, 397 (1950).

[4] Buerger, M. J., Crystal Structure Analysis, p. 595.

also showed a ring of electron density that appeared to be the cation position.

Since the space group is an eight-fold group and there are only four nitrogen atoms, it followed that they were in special positions. The ring of electron density in the difference map was across the two-fold rotation axis, and a position on this axis was assumed for the nitrogen atom. Accordingly all four independent ring atoms were used in the next structure factor calculation with atoms one and four of the ring on the two-fold axis and R fell to 0.13.

The next step was to vary the individual atomic temperature factors by the full-matrix least squares procedure in ORFLS[1]. The form of these temperature factors is $\exp(-B\sin^2\theta/\lambda^2)$ where B is determined empirically. All of the temperature factors behaved well except for ring atoms one and four. These became very large indicating that in fact no electron density existed at these points. This meant that the two-fold axis had to be bisecting two bonds. This was not possible if one of the six atoms was different from the other five -- unless the structure were disordered. Another possibility was that the two-fold axis did not exist, that is, that the true space group would be the acentric one, Cc.

The possibility of the acentric space group was examined

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[1] Busing, W. R., K. O. Martin, and H. A. Levy, ORFLS, p. 5.

first. In this space group no atoms can be in special positions[1], but it was necessary to fix the origin in the "x" and "z" directions because the space group is polar in those directions. The antimony atom was chosen and put at (0,y,¼) where it had been in C2/c. Least squares refinement was then tried on this structure. The result was divergence rather than convergence, that is the R factor increased with each cycle. Several attempts were made and all the steps in the procedure were rechecked, but the result was always the same. Thus the true space group was C2/c, and the cation is at least two-fold disordered.

The final refinement cycles were done in space group C2/c. The ring was put into the calculations with the two-fold axis bisecting two of the bonds. All three independent atoms were assumed to be carbons. Full-matrix least squares varying the positional parameters and the individual atomic isotropic temperature factors lowered R to 0.072. The weighted discrepancy index, wR was 0.078. (By definition $wR = (w||F_o| - |F_c||)/w|F_o|$, where w is the weight assigned to each measurement).

ORFLS was then used to convert the isotropic temperature factors to anisotropic temperature factors[2], which have the form $\exp(-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl))$. It was necessary to set β_{12} and β_{23} identically to zero for the

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[1] The International Tables for X-Ray Crystallography, vol. 1, p. 89.

[2] Busing, W. R., K. O. Martin, and H. A. Levy, ORFLS, p. 4.

antimony atom because it lies on the two-fold rotation axis[1]. Three cycles of least squares lowered R to 0.038 and wR to 0.041. On the last cycle it was necessary to remove the eleven most intense reflections because they all seemed to be suffering from extinction[2]. On this cycle also a newer version of ORFLS was used that allowed for corrections for the real and imaginary parts of the anomalous dispersion[3,*]. The shifts in the parameters on the last cycles were all negligible with respect to the estimated error obtained from the inverse matrix.

The last step in this study was a check and adjustment of the weighting procedure. A computer program was written and used to "plot" $w(|F_{obs}| - |F_{calc}|)^2$ as ordinate and the corrected intensity as abscissa for all the observed reflections. If the weighting procedure were valid, this cloud of points should have shown no trends, that is, fitted a horizontal least squares line. The "plot" showed almost no trend, but it was necessary to make some slight adjustments in the weights before the desired condition was met.

Two more cycles of full-matrix least squares were run with ORFLS D. Some of the parameters shifted slightly, but always

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[1] Levy, H. A., Acta Cryst., 9, 679 (1956).

[2] Buerger, M. J., Crystal Structure Analysis, p. 196.

[3] Ibid., p. 542.

[*] Williams, D. E., Louisville, Kentucky, ORFLS D, a modification of ORFLS written by M. Neuman, private communication, 1967.

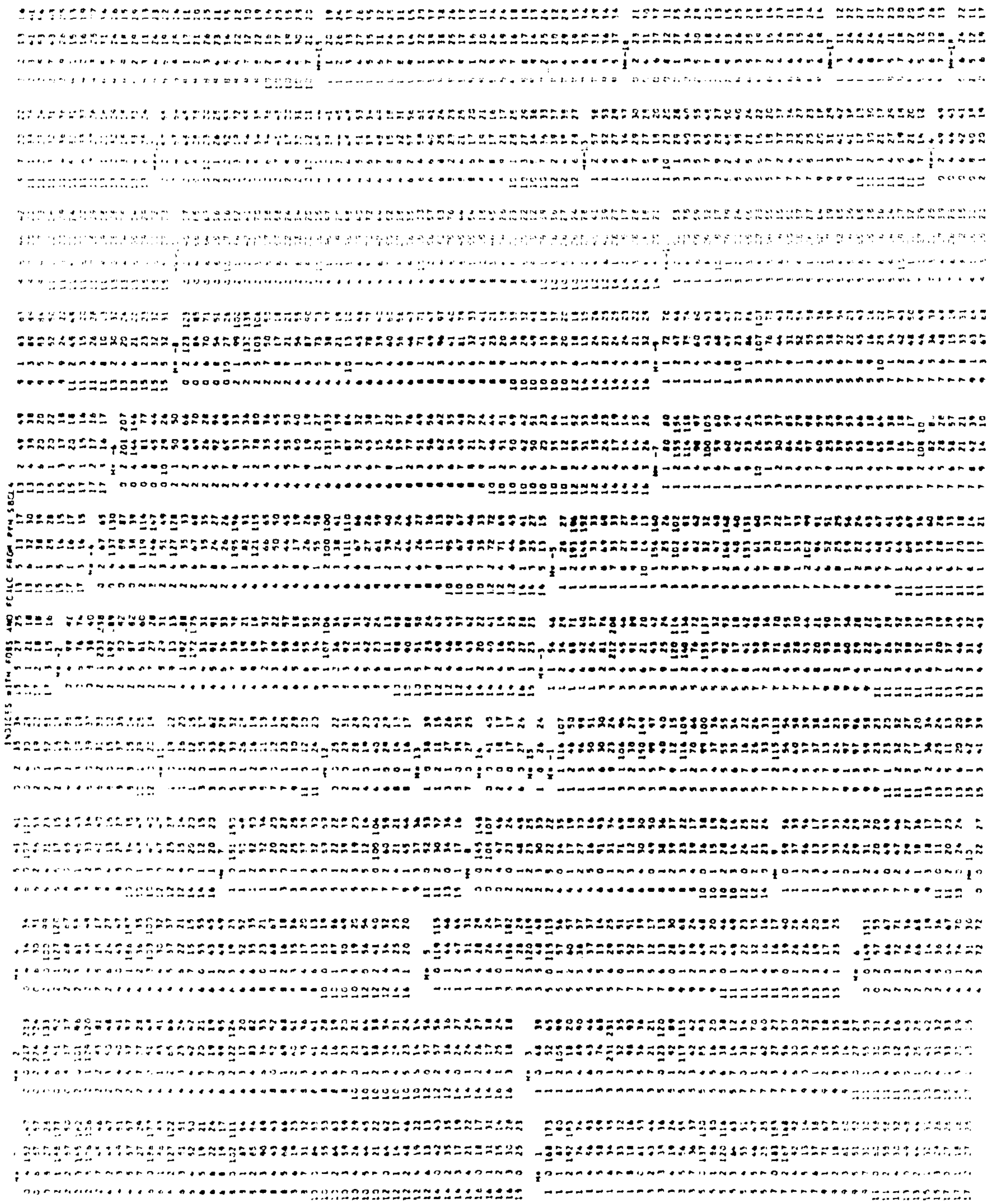
much less than the e. s. d. of the parameter. The least squares converged very rapidly to the same R and wR as before. A list of observed and calculated structure factors of the 1,100 reflections used in the last cycle may be found in Figure 1. A summary of the progress of the structure determination may be found in Table 1.

Table 1. Progress in the solution of the structure of pyridinium tetrachloroantimonate(III)

Atoms included	Temperature factors	R	Notes
Sb, 1 Cl	fixed, isotropic	0.55	from Patterson
Sb, 2 Cl	same	0.23	from e. d. synthesis
all	same	0.13	from difference map
all	varied, isotropic	same	two ring atoms on 2-fold axis, B's high
all	same	divergence	acentric space group
all	same	0.072	centric space group, 2-fold bisecting two C–C bonds in ring
all	varied, anisotropic	0.038	11 reflections discarded
all	same	same	weights adjusted

The final positional and thermal parameters may be found in Tables 2 and 3.

Figure 1. Observed and calculated structure factors from pyridinium tetrachloroantimonate(III)



INDICES WITH FOBS AND FCALC FROM PFM SBCl4

Table 2. Final parameters from pyrindinium tetrachloroantimonate(III)

Atom	x/a	y/b	z/c
Sb	.0(0)	.08082(4)	.25(0)
Cl 1	.1287(1)	.0207(1)	.2305(3)
Cl 2	.1441(1)	-.0870(1)	.1653(2)
C 1	.1154(8)	.5671(11)	.2894(12)
C 3	.0590(9)	.4862(8)	.2698(14)
C 2	.1571(10)	.6653(8)	.2679(15)

Table 3. Thermal parameters from pyridinium tetrachloroantimonate(III), betas are times 10^4[a]

Atom	B	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sb	2.98(4)	63.8(4)	44.1(3)	200.7(12)	0(0)	65.7(6)	0(0)
Cl 1	4.63(7)	102.(1)	72.(1)	311.(4)	-27.(1)	96.(2)	7.(2)
Cl 2	4.69(7)	78.(1)	79.(1)	307.(4)	7.(1)	59.(2)	-26.(2)
C 1	7.11(10)	110.(8)	165.(12)	257.(20)	11.(9)	70.(11)	30.(15)
C 2	6.97(10)	231.(17)	96.(7)	271(24)	65.(8)	103.(21)	20.(12)
C 3	6.55(10)	192.(13)	94.(7)	288.(23)	-48.(7)	127.(17)	-17(11)

[a] The form of the anisotropic temperature factor is $\exp(-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl))$.

THE PREPARATION AND CRYSTAL STRUCTURE DETERMINATION OF PYRIDINIUM HEXACHLOROANTIMONATE(V)

The next project undertaken was to make a chloro-coordinated antimony(V) salt. One solution was made of ten drops of reagent grade $SbCl_5$ in ten ml. of concentrated HCl. Another solution was made of ten drops of pyridine in ten ml. of concentrated HCl. A drop of concentrated H_2SO_4 was added to the first solution (to aid crystal formation) followed by the second solution dropwise at about 75°C. Exactly the same procedure was then used to make crystals as was used to grow the crystals of pyridinium tetrachloroantimonate(III). The largest well-formed crystals obtained were about 0.09x0.09x0.35 mm. A number of attempts were made to grow larger crystals by using a U-tube with a 30°C temperature difference across a sintered glass disk with saturated solution on both sides. No appreciable improvement in size was obtained even after a period of a few days.

Oscillation, Weissenberg, and precession photographs were used once again to obtain lattice constants, the crystal class, and the extinction conditions. The crystals are monoclinic. The only systematically absent reflections are the odd orders in the (0·$\underline{k}$·0) row. Thus, the space group was either $P2_1$ or $P2_1/m$.[1] The density was not measured, but it was possible to

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[1] Buerger, M. J., X-Ray Crystallography, p. 511.

predict four molecules per unit cell by assuming a density close to that of the similar salt done earlier. The actual calculated density was found to be 2.14 g/cm^3 after the formula was fixed.

Using the same crystal as was used to measure reflection intensities, the theta angles of 24 reflections ($40 < \theta < 46^\circ$) were carefully measured on the single crystal orienter with Cu K_{α_1} radiation. The lattice constants were then refined using the FORTRAN program LCR-2.[1] This program uses a least squares technique to fit observed scattering angles to the ones calculated from the lattice constants. The final values (with their standard errors) are $\underline{a}$ = 15.42(3)Å, $\underline{b}$ = 11.66(2)Å, $\underline{c}$ = 7.21(1)Å and beta = 97.31(4)°.

The small crystal size made the reflection intensities weak and necessitated a careful choice of radiation for the intensity measurements. There were two things to be considered in choosing whether Cu K_α or Mo K_α radiation would give the better intensities. The first is that the intensity of the scattered x-rays is proportional to the wavelength to the third power. The other is that the values of the linear absorption coefficient for the different wavelengths are 16.1 cm^{-1} for Mo K_α and 134.8 cm^{-1} for Cu K_α. Thus, the ratio of intensities is given by

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[1] Williams, D. E., LCR-2, A FORTRAN Lattice Constant Refinement Program. U. S. Atomic Energy Commission Report IS-1052, (Iowa State University, Ames, Iowa) 1964.

$$I_{Cu}/I_{Mo}=(1.54/.711)^3\text{exp }(.009\text{x}(-134.8+16.1)) = 3.1$$

where 1.54 and 0.711 are the wavelengths in angstroms and 0.009 the thickness of the crystals in centimeters. On this basis, nickel-filtered Cu K_α radiation was chosen to measure reflection intensities.

The crystal was mounted in a thin-walled Lindemann capillary as had been the crystal of pyridinium tetrachloroantimonate(III). The crystal was aligned such that the $(0\cdot 0\cdot \underline{1})$ row was close to but not coincident with the spindle axis. The intensities were measured on the single crystal orienter using the method described above. In this instance all reflections with theta less than 45° were measured in two octants.

The background correction, the decomposition correction, the absorption correction, and the Lorentz-polarization correction were made in the same way as they had been for the first crystal. The range in transmission factors was 0.27 to 0.36. The streak correction was not made because only six or seven reflections in the entire set would have been affected and none substantially.

There were 1,004 independent reflections measured and again the methods of Williams and Rundle were used to estimate the errors in the corrected intensities and the observed structure factors[1]. In this study all reflections with a corrected intensity 1.67 times its estimated error $(I/\sigma I > 1.67)$ were

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

taken to be observed. There were 863 of these.

A three-dimensional Patterson synthesis was made, again using the program of Dahm and Jacobson. This map was first examined to try to resolve the ambiguity in the space group which was either $P2_1$ or $P2_1/m$. Any peaks resulting from interatomic vectors across the mirror plane would have been found in the (0-v-0) line of the Patterson. However, this line was empty (except for the origin peak). Therefore, the space group could unambiguously be selected as $P2_1$. Since there are only two equivalent positions in this group, there had to be two crystallographically independent antimony positions[1], as there were four antimony atoms per unit cell.

Thus, there had to be four times three or twelve antimony-antimony peaks (excluding the origin) in the Patterson. In the Patterson were found eight peaks large enough to be antimony-antimony peaks. Four of the eight were large enough to be double peaks. Two of the double peaks were in the (u,½,w) Harker plane of the two-fold screw axis. These peak positions were used to obtain the "x" and "z" coordinates of the two antimony atoms. The "y" coordinate of one of these was fixed since the space group is polar in this direction. The other "y" coordinate was fixed by a careful examination of all the vectors. The resulting model was checked by calculating both

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[1] The International Tables for X-Ray Crystallography, vol. 1, p. 79.

positions and heights of all the large peaks in the Patterson. The agreement was excellent.

Structure factors were calculated using ORFLS D and the atomic scattering factors of Hanson and coworkers[1]. The correction for both the real and imaginary parts of the anomalous dispersion was made at this point and in all structure factor calculations in this study. The discrepancy index (R) of 0.48 was slightly better than that expected for a random structure[2]. The phases predicted by the structure factor calculations were used with the observed structure factor magnitudes in an electron density synthesis (again the program of Dahm and Jacobson was used). The positions of eight of the twelve chlorine atoms were evident in this map, and the rest of the structure came easily by further electron density and difference syntheses. The progress of the structure determination is summarized in Table 4.

The individual atomic temperature factors (B's) of the carbon atoms were varied. However, the standard deviations of these parameters were high (on the order of 2Å^2), and the R factor improved very little. Accordingly the average value of 5.6Å^2 was used for all the carbons in the cell. The nitrogen atoms could not be differentiated from the carbons.

The weights were adjusted as had been done for the

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[1] Hanson, H. et al., op. cit.

[2] Wilson, A. J. C., op. cit.

Table 4. Progress in the solution of the structure of pyridinium hexachloroantimonate(V)

Atoms included	Temperature factors	R	Notes
2 Sb	fixed, isotropic	0.48	from Patterson
2 Sb, 8 Cl	same	0.32	from e. d. synthesis
2 Sb, 12 Cl	same	0.23	second e. d. synthesis
plus cations as rigid bodies	same	0.17	difference map
all atoms individually	same	0.13	
same	vary B's of heavy atoms	0.101	
same	heavy atoms anisotropic; C's averaged	0.078	
same	same	0.072	weights adjusted
same	same	0.064	39 weak reflections discarded

pyridinium tetrachloroantimonate(III). This time some of the parameter shifts after the weight adjustment were nearly as large as the e. s. d. of the parameter.

It was apparent that a number of reflections were still in very bad agreement. It was decided to devise a test to discard as much questionable data as possible without appreciably increasing the standard deviations of the parameters. It was thought that perhaps some of the parameters would shift slightly, but that the new parameters (calculated from only the best data) would be more reliable. Therefore, all reflections where the inequalities $1/1.8 < F_{obs}/F_{calc} < 1.8$ did not hold were discarded by a "patch" added to ORFLS D by the author. Almost all of those thusly discarded were quite weak and those with $I/\sigma I$ under two. Some of the parameters did shift but always less than the standard deviation of the parameter. The standard deviations did increase but very slightly. Thirty-nine reflections were discarded by this procedure. The final R factor was 0.062; wR was 0.067. The observed and calculated structure factors for the 824 reflections used in the last cycle are found in Figure 2. (F(000) is 648). The final positional and thermal parameters of this crystal may be seen in Tables 5 and 6.

Figure 2. Observed and calculated structure factors from pyridinium hexachloroantimonate(V)

```
H, K, L, FOBS, AND FCALC FROM PYM, SBCL6-

   H= 0
 0  2 306 291
 0  4 471 466
 0  6  56  54
 1  1 341 346
 1  3 180 187
 1  4  37  45
 1  5 164 180
 2  0 321 329
 2  2 295 301
 2  4 117 119
 2  5  67  67
 3  1  40  36
 3  2  78  78
 3  3  23  31
 3  4  54  52
 4  0  37  31
 4  1  63  64
 4  2 172 172
 4  5  55  57
 5  1 224 225
 5  3 162 162
 5  4  17  25
 5  5 115 103
 6  0 230 234
 6  2  44  55
 6  4 134 131
 7  1 163 165
 7  3  64  55
 7  5 110 119
 8  0 171 153
 8  3  26  36
 8  4 134 113
 9  1  21  33
 9  3  31  38
10  0  39  25

   H= 1
 1  1 158 175
 1  2 120 119
 1  3  93 102
 1  4  36  46
 1  5  50  55
 2  0 327 341
 2  1 209 213
 2  2 306 329
 2  3 118 129
 2  4 111 116
 2  5  62  55
 2  6  59  54
 3  0  23  26
 3  1 256 260
 3  2 261 267
 3  3 236 247
 3  5  68  62
 3  6  87  82
 4  0  67  64
 4  1 158 165
 4  2 352 361
 4  3 139 139
 4  5  68  56
 4  6  68  87
 5  0 155 154
 5  1  69  74
 5  2 164 165
 5  3  32  32
 5  4  75  81
 6  1  70  76
 6  3  55  68
 7  1  37  43
 7  3  46  52
 8  0 145 147
 8  1  56  58
 8  2  28  34
 8  4  94  95
 9  0  61  64
 9  1  83  87
 9  3  89  93
10  0  29  36
10  1  32  48
10  2 108 112

   H= 2
 0  0 222 239
 0  1 422 416
 0  2 155 172
 0  3 153 144
 0  4  45  45
 0  5 154 151
 1  1 173 173
 1  2  94 105
 1  3  37  42
 1  4 116 126
 1  5  60  64
 2  0  51  53
 2  1 192 205
 2  2  69  94
 2  3 131 135
 2  4  28  33
 2  5  59  55
 3  0  21  25
 3  1 133 139
 3  2  81  92
 3  3  38  50
 3  4  22  33
 4  0 172 169
 4  2 125 130
 4  3  55  59
 4  5  50  38
 5  0  79  78
 5  1 120 128
 5  2 233 237
 5  3  38  44
 5  4  59  50
 5  5  42  43
 6  0 195 192
 6  1 183 142
 6  2  57  69
 6  3 123 118
 6  4  81  80
 6  5 118 115
 7  0 312 314
 7  1  97  97
 7  2  63  52
 7  3  25  27
 7  4 187 190
 8  0 111 114
 8  1 137 138
 8  3  53  53
 8  4  41  46
 9  0  22  25
 9  1  20  30
 9  2  36  51
10  2  31  21

   H= 3
 1  0 177 184
 1  1  31  37
 1  3  44  53
 1  4  92  97
 1  5  42  40
 2  0 123 136
 2  1 119 126
 2  3 109 119
 2  4  78  87
 2  5  67  60
 3  0  50  49
 3  1  24  30
 3  2 342 367
 3  4  35  44
 3  6  58 102
 4  1 200 203
 4  3 205 207
 4  5  54  69
 5  0  80  86
 5  1  49  57
 5  2 178 192
 5  3  35  26
 5  4  49  57
 6  0 119 121
 6  1  34  47
 6  2  45  76
 6  4  40  37
 7  0  99 103
 7  1  37  41
 7  2  26  27
 7  4  55  50
 8  0  57  60
 8  1 146 147
 8  3  97  93
 8  4  17  30
 9  0 166 163
 9  2 121 120
10  1 122 123

   H= 4
 0  0 274 255
 0  1  67  45
 0  3  29  35
 0  4 179 172
 0  5 106  96
 1  0 322 340
 1  1  54  51
 1  2  54  56
 1  3  65  71
 1  4 207 209
 1  5  61  56
 1  6  58  63
 2  0 147 151
 2  1 124 127
 2  2 141 136
 2  3  70  78
 2  5  87  91
 3  0 112 113
 3  1  50  59
 3  2  38  36
 3  3  54  61
 3  4  58  69
 3  5  56  53
 4  0  29  34
 4  1  54  62
 4  2 159 167
 4  4  41  52
 5  0 117 120
 5  1 139 139
 5  2  52  61
 5  3 145 147
 5  4  48  45
 5  5  56  54
 6  0 149 155
 6  1 180 179
 6  2 121 120
 6  3 108 101
 6  4  86  83
 7  0 253 259
 7  1  96  95
 7  2  65  63
 7  3  72  75
 7  4 103 102
 8  0  77  75
 8  1 120 122
 8  2  31  47
 8  3  31  44
 9  0  70  75
10  0  40  53

   H= 5
 1  0 157 153
 1  1 159 165
 1  2 109 114
 1  3 109 120
 1  4  21  16
 1  5  95  92
 2  0 299 303
 2  1  28  38
 2  2 195 204
 2  3  55  63
 2  4 137 135
 3  1 224 229
 3  2 119 125
 3  3 195 191
 3  5  97  96
 4  0 112 111
 4  1 122 125
 4  2 271 263
 4  3 105 108
 5  1  82  84
 5  2 176 175
 5  3  59  61
 5  5  48  50
 6  0  52  52
 6  1  75  80
 6  2  22  32
 6  3  49  49
 6  4  35  33
 7  1  67  75
 7  2  31  40
 7  3  29  35
 8  0 146 149
 8  2  31  33
 8  3  34  27
 9  0  16  29
 9  1 116 115
 9  2  40  53
10  0  59  67

   H= 6
 0  0 554 565
 0  1  64  56
 0  2 247 229
 0  3  54  57
 0  4 243 221
 0  5  21  26
 1  0  90  80
 1  1 310 314
 1  2  90  94
 1  3 227 220
 1  5 130 134
 2  0 255 253
 2  2 144 146
 2  3  43  55
 2  4 109 106
 3  0 193 192
 3  1  31  40
 3  2  44  50
 3  3  21  29
 3  4  31  40
 3  5  26  34
 4  0  78  73
 4  1  41  59
 4  2  96  95
 4  3  43  50
 4  4  31  45
 4  5  16  29
 5  0  40  45
 5  1  98 102
 5  2  99  99
 5  3  81  83
 5  4  16  25
 6  0 176 170
 6  2  97  92
 6  4  96  91
 7  0  18  24
 7  1 101 108
 7  3  62  68
 8  0  99  97
 8  2  34  26
 8  3  31  29
 9  0  54  65

   H= 7
 0  5  28  37
 1  0 215 213
 1  1 121 122
 1  2  46  41
 1  3  89  93
 1  4  78  83
 1  5  37  27
 2  0 129 133
 2  1 194 196
 2  2 224 221
 2  3  86  80
 2  4  51  49
 2  5  59  60
 3  0 132 134
 3  1 201 195
 3  2 116 112
 3  3 127 120
 3  4  59  65
 3  5  62  56
 4  0 111 106
 4  1 153 146
 4  2 152 152
 4  3  94  96
 4  4  30  16
 5  0 135 138
 5  1  45  49
 5  2  28  26
 5  3  48  50
 5  4  73  75
 6  0  47  47
 6  2  58  60
 6  3  35  26
 7  2  17  24
 7  3  35  28
 8  0  30  37
 8  2  39  47
 9  0  78  81
 9  1  48  53

   H= 8
 0  0  82  77
 0  1 233 228
 0  3 146 131
 0  4  21  23
 1  0 201 205
 1  1  58  64
 1  2 154 147
 1  4  78  76
 2  0 120 119
 2  1 125 131
 2  2 130 126
 2  3  74  78
 2  4  19  30
 3  1  67  71
 3  2  43  46
 3  3  31  45
 4  0 107 138
 4  1  24  26
 4  2  24  37
 4  3  32  38
 4  4  29  37
 5  0  56  53
 5  1  73  79
 5  2  95  98
 5  3  18  31
 5  4  41  50
 6  0  90  81
 6  1  93  92
 6  3 109 103
 7  0  95  92
 7  1  27  29
 7  2  86  88
 8  0  52  58
 8  1  64  65

   H= 9
 1  0  54  59
 1  2  71  70
 2  0 101  99
 2  1 106 103
 2  2  30  35
 2  3  43  47
 2  4  45  51
 3  0 175 169
 3  1  16  24
 3  2 115 108
 3  4  63  65
 4  0  91  91
 4  1 113 106
 4  3  68  70
 5  0  66  58
 5  1  33  44
 5  2  76  73
 6  0 116 112
 6  1  30  26
 6  2  26  18
 7  0  40  18
 7  2  32  22

   H= 10
 0  0  15  21
 0  1  18  28
 0  2  74  79
 0  3  24  36
 0  4  31  25
 1  0  77  70
 1  1  43  44
 1  2  24  31
 1  3  42  47
 1  4  45  56
 2  0  30  25
 2  1  54  56
 2  2  64  66
 2  3  20  27
 3  0  40  41
 4  0  28  24
 4  1  22  25
 4  2  44  50
 5  0 106 101
 5  1  73  73
 5  2  37  25
 6  0  80  72
 6  1  75  78
 6  2 119 105
 7  0  68  73
 7  1  64  67

   H= 11
 0  0  13  15
 1  0  58  57
 1  1  64  59
 1  3  26  45
 2  0 126 123
 2  2  61  65
 3  1 125 117
 3  2  49  33
 3  3  77  74
 4  0 156 146
 4  1  35  47
 4  2  56  55
 5  1  56  56
 5  2  75  76
 6  1  27  39

   H= 12
 0  0  91  85
 0  1  33  48
 0  2 154 142
 1  0  72  79
 1  1 123 112
 1  2  42  48
 2  0  97  75
 2  2  59  64
 3  0  79  76
 3  1  47  36
 4  0  31  42
 4  1  51  59
 5  0  55  40
 5  1  36  49

   H= 13
 1  0  63  66
 2  0  50  62
 2  1  92  93
 3  0 123 120
 3  1  80  79
 4  0 101  97

   H= 14
 1  0  78  87

   H= -1
 0  2  30  28
 1  1 206 212
 1  2  64  63
 1  3 131 140
 1  4 108 113
 1  5  88  90
 2  1 224 224
 2  2 386 390
 2  3 134 146
 2  4 181 178
 2  5  67  62
 2  6  74  95
 3  1 290 288
 3  2 299 295
 3  3 341 338
 3  4  44  64
 3  5  86  86
 3  6  47  73
 4  1 115 120
 4  2 409 404
 4  3 126 124
 4  4  28  25
 4  5  26  16
 4  6  90 124
 5  1 106 109
 5  2 113 104
 5  3 101 101
 5  4  47  49
 5  5  55  66
 6  1  79  87
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 7  5  31  33
 8  1  17  27
 8  2  23  25
 8  3  19  33
 8  4  82  86
 9  1  61  66
 9  2  32  28
 9  3  69  82
10  2 106 113

   H= -2
 0  1 457 478
 0  2  45  61
 0  3 205 204
 0  4 216 213
 0  5 231 229
 0  6  67  59
 1  1 209 194
 1  2 111 100
 1  3  76  80
 1  4 276 263
 1  5 107 109
 1  6  91  85
 2  1 214 211
 2  2  58  55
 2  3 192 186
 2  4  73  75
 2  5  67  73
 3  1  90  88
 3  2 146 139
 3  3  78  80
 4  2 173 166
 4  3  27  33
 4  4  76  77
 5  1 135 133
 5  3  79  79
 5  4  30  35
 5  5  62  64
 6  1 194 189
 6  2  77  75
 6  3  78  80
 6  4  87  88
 6  5  93 107
 7  1  68  73
 7  4 138 137
 7  5  49  55
 8  1 115 114
 8  3  54  63
 8  4  63  66
 9  1  27  30
 9  2  37  37

   H= -3
 1  1  25  35
 1  3  62  65
 1  4 132 128
 1  5  27  41
 2  1 161 150
 2  2 169 154
 2  3 214 204
 2  5  86  97
 2  6  54  40
 3  2 412 404
 3  3  16  25
 3  4  71  67
 3  5  26  16
 3  6 102 124
 4  1 217 206
 4  3 241 237
 4  5  74  70
 5  1  71  74
 5  2 196 191
 5  4  54  56
 5  5  55  59
 6  1  40  49
 6  3  16  28
 6  4  73  74
 6  5  74  32
 7  1  26  34
 7  2  35  41
 7  4  49  57
 8  1 144 141
 8  3  96  93
 9  2 111 111
10  1 111 109

   H= -4
 0  1 164 157
 0  2  64  67
 0  3  66  68
 0  4 115 117
 0  5 150 151
 1  1  67  63
 1  2  99  94
 1  3  81  74
 1  4 144 134
 1  5  43  50
 2  1 140 132
 2  2 194 185
 2  3  52  57
 2  4 [illegible] [illegible]
 2  5 [illegible] [illegible]
 2  6 [illegible] [illegible]
 3  1 [illegible] [illegible]
 3  3 [illegible] [illegible]
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 4  1 [illegible] [illegible]
 4  2 134 [illegible]
 4  3 [illegible] [illegible]
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 5  1 [illegible] [illegible]
 5  2 [illegible] [illegible]
 5  3 [illegible] [illegible]
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 6  1 [illegible] [illegible]
 6  2 [illegible] 123
 6  3 119 113
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 2  4  95  98
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 3  1 215 207
 3  2 140 141
 3  3 202 197
 3  4 101 100
 3  5  99  94
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 4  2 215 203
 4  3  67  90
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 2  2 112 109
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 3  1  47  44
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 3  5  26  43
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 4  5  46  29
 5  1  96  94
 5  2 136 135
 5  4  46  47
 5  5  47  49
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 6  3  83  89
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 7  3  24  17
 8  1  49  49

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 2  5  54 106
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 3  2  46  53
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 4  1  61  65
 4  2  45  48
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 5  2  37  51
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 5  3  33  50

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 1  2  32  39
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 3  2  55  48
 4  1  77  77

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 0  1 117 128
 1  1  21  37
```

Table 5. Final positional parameters from pyridinium hexachloroantimonate(V)

Atom	x/a	y/b	z/c
Sb a	.0869(3)	.3(0)	.2552(2)
Cl a1	.112(2)	.432(2)	.019(3)
Cl a2	.055(1)	.168(2)	.493(4)
Cl a3	.053(1)	.154(2)	.015(3)
Cl a4	.121(2)	.444(2)	.476(4)
Cl a5	-.055(1)	.358(2)	.212(4)
Cl a6	.236(1)	.242(2)	.291(3)
Sb b	.5881(3)	.1437(2)	.2510(9)
Cl b1	.565(1)	.278(2)	.475(3)
Cl b2	.618(2)	.014(2)	.017(4)
Cl b3	.558(2)	.282(2)	.044(3)
Cl b4	.616(2)	.007(2)	.489(4)
Cl b5	.732(1)	.199(2)	.281(4)
Cl b6	.434(1)	.090(2)	.219(4)
C a1	.192(3)	.696(4)	.238(7)
C a2	.258(3)	.760(4)	.194(7)
C a3	.257(3)	.876(4)	.240(6)
C a4	.170(3)	.925(4)	.277(6)
C a5	.110(3)	.847(4)	.318(7)
C a6	.118(3)	.744(4)	.290(7)
C b1	.701(3)	.524(4)	.239(7)
C b2	.748(3)	.610(4)	.168(6)

Table 5 (Continued)

Atom	x/a	y/b	z/c
C b3	.726(3)	.715(4)	.201(7)
C b4	.645(3)	.749(4)	.251(7)
C b5	.592(3)	.667(5)	.292(7)
C b6	.614(3)	.548(4)	.296(6)

Table 6. Thermal parameters from pyridinium hexachloroantimonate(V), betas are times 10^4[a]

Atom	B	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sb a	4.1(2)	41(2)	105(6)	176(13)	20(3)	9(4)	7(8)
Cl a1	7.4(8)	130(17)	95(20)	241(56)	-29(13)	18(23)	38(26)
Cl a2	5.5(6)	48(7)	142(19)	693(75)	33(9)	102(17)	107(30)
Cl a3	5.5(5)	53(8)	100(17)	227(47)	-2(10)	-7(15)	-120(23)
Cl a4	8.5(9)	107(18)	134(27)	411(80)	8(16)	27(28)	-70(37)
Cl a5	5.9(6)	46(11)	198(30)	453(68)	55(13)	25(21)	3(37)
Cl a6	4.0(5)	24(7)	214(23)	141(38)	29(10)	3(12)	-50(23)
Sb b	4.3(2)	55(3)	54(5)	306(18)	4(3)	47(5)	2(9)
Cl b1	6.1(6)	93(11)	101(19)	170(47)	-13(11)	42(16)	-44(23)
Cl b2	6.4(7)	87(12)	108(24)	477(83)	-36(13)	107(24)	-50(34)
Cl b3	5.4(6)	85(12)	110(19)	333(63)	2(12)	15(21)	12(27)
Cl b4	6.1(7)	122(17)	103(24)	237(62)	-11(15)	59(24)	59(30)
Cl b5	6.5(7)	60(10)	92(16)	560(82)	-3(10)	29(21)	0(29)
Cl b6	6.2(6)	57(9)	159(24)	341(62)	-25(11)	33(18)	-8(32)

[a] The form of the anisotropic temperature factor is $\exp(-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl))$.

THE PREPARATION AND CRYSTAL STRUCTURE DETERMINATION OF PYRIDINIUM NONABROMODIANTIMONATE(III) DIBROMIDE

The final project undertaken as part of this work was the synthesis of a bromide compound using the same reaction that had been used to prepare pyridinium tetrachloroantimonate(III). This reaction and the subsequent formation of crystals was done in the same way as before substituting antimony(III) bromide and concentrated HBr for the original reactants. The bromide crystals were translucent, yellow and well-formed.

Preliminary line-up and unit cell measurements were done in this instance with a precession camera. It became apparent early in the study that one of the reciprocal lattice rows had a very short spacing. Accordingly Cu K_α radiation was used for this work, rather than the shorter wavelength Mo K_α. The extinction conditions were determined from both the precession photographs and three layers of Weissenberg photographs, all from a single mounting of the crystal. For the cell chosen $\underline{h} + \underline{l}$ is even for all observed reflections, and $\underline{k}$ odd is absent in the (0·k·0) row. Thus, the space group was either $B2_1$ or $B2_1/m$.[1] It is always possible to reduce a B-centered monoclinic cell to a primitive one (and halve the volume). The primitive cell constants are $\underline{a}$ = 10.24Å, $\underline{c}$ = 9.5Å and beta = 133.0°.

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[1] Buerger, M. J., op. cit., pp. 83 and 511.

The cell constants were refined in exactly the same way as those of pyridinium hexachloroantimonate(V) had been[1]. The refined values (with standard errors) are $\underline{a} = 18.01(6)$, $\underline{b} = 30.14(9)$, $\underline{c} = 7.82(2)$Å and beta = 95.02(8)°. By assuming a reasonable density between 2 and 2.5g/cm^3 it was possible to predict eight antimony atoms per unit cell. After the formula had been fixed, the density was calculated to be 2.42g/cm^3.

Calculations were made to determine the relative intensities using copper or molybdenum radiation of reflections from these crystals as had been done for the antimony(V) chloride salt. In this instance the ratio of Cu K_α intensities to Mo K_α intensities was about six to one. Furthermore, the very short b* distance would have led to large streak corrections if molybdenum had been used. On the basis of these two facts it was decided to use nickel-filtered Cu K_α radiation for the intensity measurements.

A well-formed crystal about 0.08x0.20x0.40 mm. was mounted in a thin-walled Lindemann capillary with the long direction close to the spindle axis. The single crystal orienter described above was again used to collect intensity data. The crystal was such that the b* direction of the crystal coincided with the shortest diameter. A 100 second theta-two theta scan was used. The background of each peak was measured individually by a 40 second stationary count at both the beginning and end

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[1] Williams, D. E., *op. cit.*

of each scan. The use of this type of background measurement meant that no streak correction was necessary. In this way 1,754 independent reflections were measured whose thetas were less than 45° in two octants.

The data were corrected for decomposition, for absorption, and for the Lorentz-polarization effects as they had been in the other two investigations. The range in transmission factors was 0.10 to 0.27. The methods of Williams and Rundle were again used to estimate errors in the measurements[1]. All reflections where $I/\sigma I$ was greater than 1.67 were judged to be "observed". Only these reflections, 1,435 in number, were used in the solution and refinement of the structure.

A three-dimensional Patterson synthesis was performed using the same general program as before for the IBM 360 computer. In this map the line (0·v·0) contained some large peaks indicating the existence of a mirror plance perpendicular to the "b" axis. If such existed the space group would have to be $B2_1/m$. The interpretation of the Patterson was not as straight-forward as it had been for the other two crystals. The bromine-bromine and antimony-bromine peaks were quite large and not easily distinguished from the antimony-antimony peaks. Since the space group was eight-fold, it was initially assumed that the antimony atom was in the eight-fold general position.

There were two large peaks in the Harker line (0·v·0) of

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[1] Williams, D. and R. Rundle, op. cit.

the mirror plane and both were about the right size for a quadruple antimony-antimony vector. (A quadruple vector is expected for space group $B2_1/m$.) Two reasonable sets of "x" and "z" coordinates were obtained from the largest peaks in the Harker plane (u,½,w) of the two-fold screw axis. It was possible to reduce the four possibilities to two by a careful examination of all the vectors of the antimony-antimony type. Structure factor calculations were made with ORFLS D on the two possibilities. The structure factors of Hanson and co-workers were used here and throughout this study[1]. Corrections were made for the real and imaginary parts of the anomalous dispersion. The better R (of the two) was 0.60 with the antimony atom at (.339, .183, .065) in the unit cell. This single atomic position was used as the beginning model of the structure.

An electron density synthesis was performed using the signs predicted by a structure factor calculation from this model. This map showed several peaks that were nearly the right size to be bromine atom positions. Only one of these was selected for input to the next structure factor calculation. It was the largest of the peaks and was about 2.6Å from the antimony peak. A check of earlier work (see Introduction) showed this to be a reasonable bond distance. This new structure factor calculation only lowered R to 0.56; however, the electron

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[1] Hanson, H., *et al.*, *op. cit.*

density synthesis was very distinct and showed quite clearly an anion of formula Sb_2Br_9. The R factor dropped sharply to to 0.29 when all of these atoms were used to calculate structure factors. This R factor was low enough to indicate that most of the structure had been found.

A difference synthesis was performed at this time. It showed very distinctly a bromine atom that had not been seen before. It was, however, at least 6Å from the nearest antimony atom, and did not appear to be bonded to anything. The R factor dropped to 0.23 when this atom was included, and a new difference synthesis showed that all the antimony and bromine atoms had been accounted for.

Electroneutrality required that each cell have twenty unipositive cations. Since the space group was eight-fold, one of these was required to be on or across the mirror plane. The most recent difference map had shown some areas of electron density that were about the right size and shape to be pyridinium rings. The rigid body refinement feature of ORFLS D was used, assuming each cation to be a regular hexagon 1.36Å on a side. The parameters refined very slowly, finally giving R equal to 0.20.

Each of the ring atom positions was then refined individually from the last positions predicted by the rigid-body refinement. After four cycles of full-matrix least squares the shifts had become much smaller than the standard errors, but the R factor had only dropped to 0.18.

This seemed high for a structure whose positional parameters were correct; the difference synthesis did not show any atom to be out of place. It was thought that the true space group might be $B2_1$. Structure factor calculations, full-matrix least squares, and electron density syntheses were made assuming acentricity. This required forty-three crystallographically independent atoms rather than twenty-four. Several cycles of these procedures gave the following results: (1) the discrepancy index dropped only 0.002, (2) the antimony and bromine positions refined to the centric positions they had occupied, and (3) the carbon atom positions did not refine satisfactorily. This is to say that the shifts in these positional parameters did not become smaller than the estimated error from the inverse matrix even after several cycles. Another attempt was made in the acentric space group by first using the rigid body refinement feature of ORFLS D and later refining the carbon positions individually. The final result was exactly the same as the above. On the basis of these results the true space group was taken to be $B2_1/m$, and this choice was used in the final refinement cycles.

The next step was to vary the temperature factors of the antimony and bromine atoms isotropically. This lowered R to 0.17. The difference synthesis showed considerable anisotropic motion of these atoms, so the temperature factors were converted to anisotropic by ORFLS D and refined. R fell to 0.135.

Next, the isotropic temperature factors of the ring atoms were varied. These behaved very badly and ranged from 4.0 to 15.0Å^2 after refinement. More significantly the program calculated the estimated standard deviations of these parameters to be 2 to 3Å^2, and the discrepancy factor fell by only about 0.001. Thus the refinement of these parameters was not very significant and an average value was used for each ring on the last cycles. These were ring A, 12.1Å^2; ring B, 9.1Å^2; and ring C, 7.0Å^2. Since the temperature factors from ring A were quite high, the entire ring was suspect. Accordingly all these atoms were removed from the calculations, and another difference map was calculated. This showed the ring to be plainly present even if the peak heights were somewhat smaller than was expected. Furthermore the R factor went up slightly on removal of this ring. It was then concluded that the ring in question was actually present but probably somewhat disordered.

The weighting scheme was adjusted in the same way as had been done in the other two crystal structure investigations. There were some very small parameter shifts (always less than one-half the error) and R dropped by 0.002.

As with pyridinium hexachloroantimonate(V) it was obvious that a number of reflections should be discarded. By the same reasoning as was used with this chloride salt, all reflections where $1/1.5<F_{obs}/F_{calc}<1.5$ were retained. As with the other study most of the reflections discarded were the weak ones. The remaining 1,301 reflections were used in four more cycles of full-matrix least squares. Some parameter shifts resulted, but these quickly became very small. The final R factor was 0.109 and the final wR was 0.136. A summary of the structure determination is in Table 7. A list of the observed and calculated structure factors (in electrons/2) is given in Figure 3. The final positional and thermal parameters of this structure can be found in Tables 8 and 9.

Table 7. Progress in the solution of the structure of pyridinium nonabromodiantimonate(III) dibromide

Atoms included	Temperature factors	R	Notes
Sb	fixed, isotropic	0.60	best result from Patterson
Sb, 1 Br	same	0.56	from e. d. synthesis
Sb, 6 Br	same	0.29	second e. d. map
all Sb, Br	same	0.23	difference synthesis
plus cations as rigid bodies	same	0.20	
all atoms individually	same	0.18	
all	same	0.18	try in acentric space group
all	heavy atom B's varied	0.17	
all	heavy atom betas varied	0.135	
all	same	0.109	weights adjusted, 134 badly agreeing weak reflections discarded

Figure 3. Observed and calculated structure factors from pyridinium nonabromodiantimonate(III) dibromide

Table 8. Final positional parameters from pyridinium nonabromodiantimonate(III) dibromide

Atom	x/a	y/b	z/c
Sb	.3370(1)	.1835(1)	.0621(3)
Br 1	.4604(2)	.1362(1)	.0816(6)
Br 2	.2103(3)	.25(0)	.0450(8)
Br 3	.2802(2)	.1334(1)	.2912(6)
Br 4	.3994(3)	.25(0)	.3162(8)
Br 5	.2756(2)	.1323(1)	-.1846(6)
Br 6	.3947(3)	.25(0)	-.1804(7)
Br 7	.1186(2)	-.0058(2)	-.1155(7)
C a1	.578(4)	.25(0)	.096(10)
C a26	.625(4)	.217(2)	.071(11)
C a35	.691(4)	.214(2)	.063(9)
C a4	.722(4)	.25(0)	.030(9)
C b1	.286(2)	-.009(1)	.015(4)
C b2	.328(3)	.025(2)	.086(7)
C b3	.394(3)	.017(2)	.156(7)
C b4	.430(4)	-.023(2)	.165(8)
C b5	.383(4)	-.060(2)	.025(8)
C b6	.311(2)	-.046(1)	-.022(5)
C c1	.019(2)	.172(1)	.094(5)
C c2	.082(3)	.156(2)	.028(7)

Table 8 (Continued)

Atom	x/a	y/b	z/c
C c3	.087(3)	.108(2)	-.009(6)
C c4	.025(2)	.090(1)	.016(5)
C c5	-.036(2)	.102(1)	.065(5)
C c6	-.036(2)	.147(2)	.110(6)

Table 9. Thermal parameters from pyridinium nonabromodiantimonate(III) dibromide, betas are times 10^4[a]

Atom	B	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sb	2.3(1)	26(1)	5(1)	168(5)	-1(1)	-21(2)	1(1)
Br 1	5.2(3)	33(2)	11(1)	362(12)	5(1)	-23(3)	8(2)
Br 2	4.6(3)	29(2)	12(1)	318(15)	0(0)	-23(4)	0(0)
Br 3	5.5(3)	43(2)	13(1)	341(12)	-2(1)	10(4)	20(2)
Br 4	5.0(3)	40(2)	14(1)	237(14)	0(0)	-41(4)	0(0)
Br 5	5.7(3)	41(2)	17(1)	277(11)	-4(1)	-31(3)	-23(2)
Br 6	4.1(3)	35(2)	12(1)	229(13)	0(0)	-12(4)	0(0)
Br 7	6.4(3)	38(2)	19(1)	400(14)	-2(1)	-21(4)	8(2)

[a] The form of the anisotropic temperature factor is $\exp(-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl))$.

DISCUSSION

The most striking feature about this set of three structures is that in each a previously undiscovered geometry has been found, and in each the antimony atom is six-fold coordinated by halogen atoms in a configuration that is distorted octahedral.

All three compounds have in common the fact that there are no halogen to pyridinium cation distances short enough to be taken to be of the hydrogen bonding type. The hydrogen bond distance expected for chlorine-hydrogen-nitrogen is about 3.1Å.[1] Thus we can see that each crystal is held together at least in part by electrostatic forces. A detailed discussion of each structure follows.

Pyridinium Tetrachloroantimonate(III)

Each anion in this crystal is part of an infinite chain (Figures 4 and 5). Each $SbCl_4^-$ group in the chain possesses two-fold symmetry, and, therefore, there are only three independent antimony-chlorine distances. Table 10 is a computation of the important interatomic distances in this crystal. The distance from the antimony to the non-bridging chlorine is 2.380(3)Å which is in good agreement with that found in $SbCl_3$

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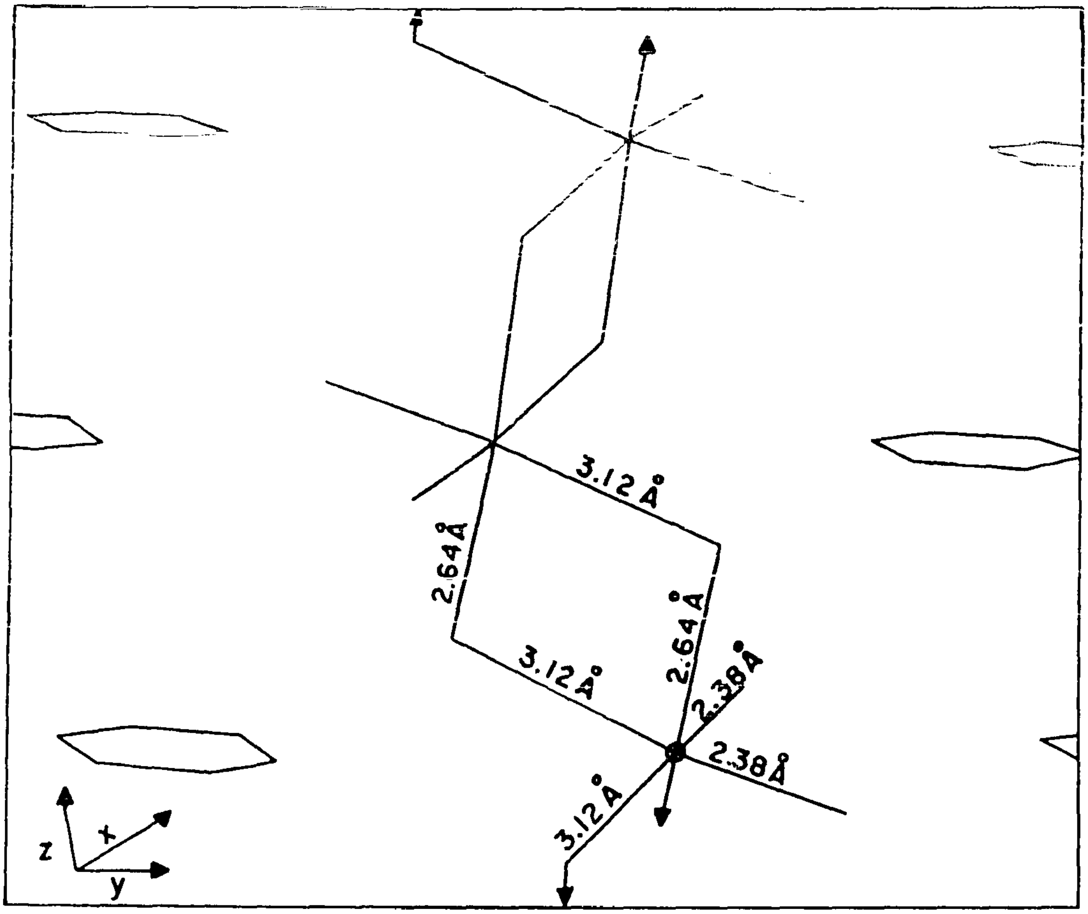
[1] Wells, A. F., Structural Inorganic Chemistry, 3rd ed., Claredon Press, Oxford, U. K., 1962, p. 294.

Figure 4. Part of the structure of pyridinium tetrachloroantimonate(III) showing the infinite chain



THE STRUCTURE OF pyH$^+$ SbCl$_4^-$. THE CIRCLED Sb ATOM IS AT (.0, .081, .25). ALL THE DIFFERENT Sb-Cl DISTANCES ARE SHOWN.

Figure 5. Second view of the infinite chain

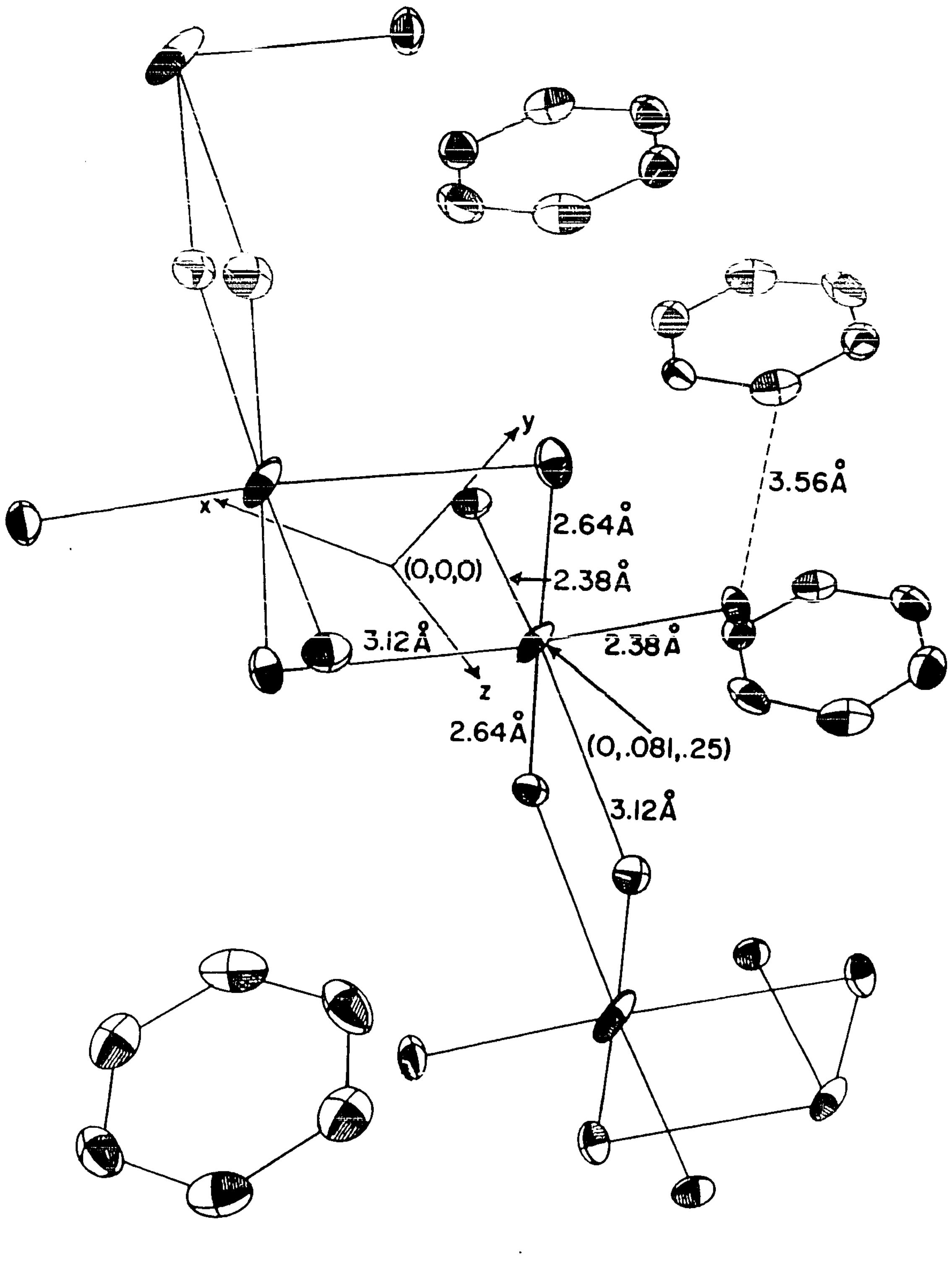

y
x
z
(0,0,0)
2.64Å
2.38Å
3.56Å
3.12Å
2.38Å
(0,.081,.25)
2.64Å
3.12Å

Table 10. Important distances from pyridinium tetrachloroantimonate(III)

Atom 1	Atom 2	Symmetry operation on 2	Distance (angstroms)	D (corr.)[a]
Sb	Cl 1	none	2.380(3)	2.365(3)
Sb	Cl 2	c glide	2.630(9)	2.640(9)
Sb	Cl 2	none	3.126(4)	3.117(4)
C 1	C 2	none	1.34(2)	1.34(2)
C 2	C 2	two-fold	1.33(3)	1.33(3)
C 1	C 3	none	1.35(2)	1.35(2)
C 3	C 3	two-fold	1.37(2)	1.37(2)
Sb	Sb	c glide	4.28(1)	
Cl 1	Cl 1	two-fold	3.49(1)	
Cl 2	Cl 2	two-fold	4.53(1)	
Cl 1	Cl 2	none	3.82(1)	
Cl 1	C 2	none	3.47(1)	
Cl 1	C2	two-fold	3.56(1)	

[a] Averaged over thermal motion (atoms assumed to move independently) as calculated by ORFFE[1].

by x-ray diffraction[2] and electron diffraction[3]. This distance also agrees well with the one short distance in $(NH_4)_2SbCl_5$

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[1] Busing, W. R., K. O. Martin, and H. A. Levy, ORFFE, p. 25.

[2] Lindqvist, I. and A. Niggli, op. cit.

[3] Swingle, S. M., op. cit.

(opposite the non-bonding pair of electrons)[1]. The bridging chlorine is 2.630(9)Å from one antimony atom in the chain and 3.126(4)Å from the next. The shorter of these is in good agreement with the four coplanar bonds found in $(NH_4)_2SbCl_5$. The 3.126Å distance is previously unreported. It is long enough that the bonding interaction is weak. It is however, 0.9Å less than the sum of the van der Waals radii[2], and it is reasonable to assume that a weak bond exists.

The approximate bond order of each of these bonds may be calculated by the Pauling bond order expression for fractional bonds:

$$D(n) = D(1) - 0.6\log(n)$$

where D(n) is the length of the fractional bond of order n, and D(1) is the single bond distance[3]. If we take the single bond distance to be 2.380Å, the 2.630Å bond is of order 0.38 and 3.126Å bond is of order 0.06.

The anion done in this study differs from the similar species done earlier in that there is no obvious place in the space around the antimony atom for a localized non-bonding pair of electrons in the valence shell. The chlorine-antimony-chlorine angles are close to 90°, but there are some that are significantly different. The bond angles are compiled in

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[1] Edstrand, M., M. Inge, and N. Ingri, op. cit.

[2] Pauling, L., The Nature of the Chemical Bond, 3rd ed., Cornell University Press, Ithaca, New York, 1960, p. 260.

[3] Pauling, L., J. Amer. Chem. Soc., 69, 542 (1947).

Table 11. It may be that this lone pair is causing some of this distortion. The angle with the greatest distortion from 90°, is the Cl 2-Sb-Cl 2(c glide) angle. This angle involves the very weak bond of order 0.06, and it maybe that the lone pair is localized in the direction of this bond or near it.

Table 11. Bond angles in pyridinium tetrachloroantimonate(III)

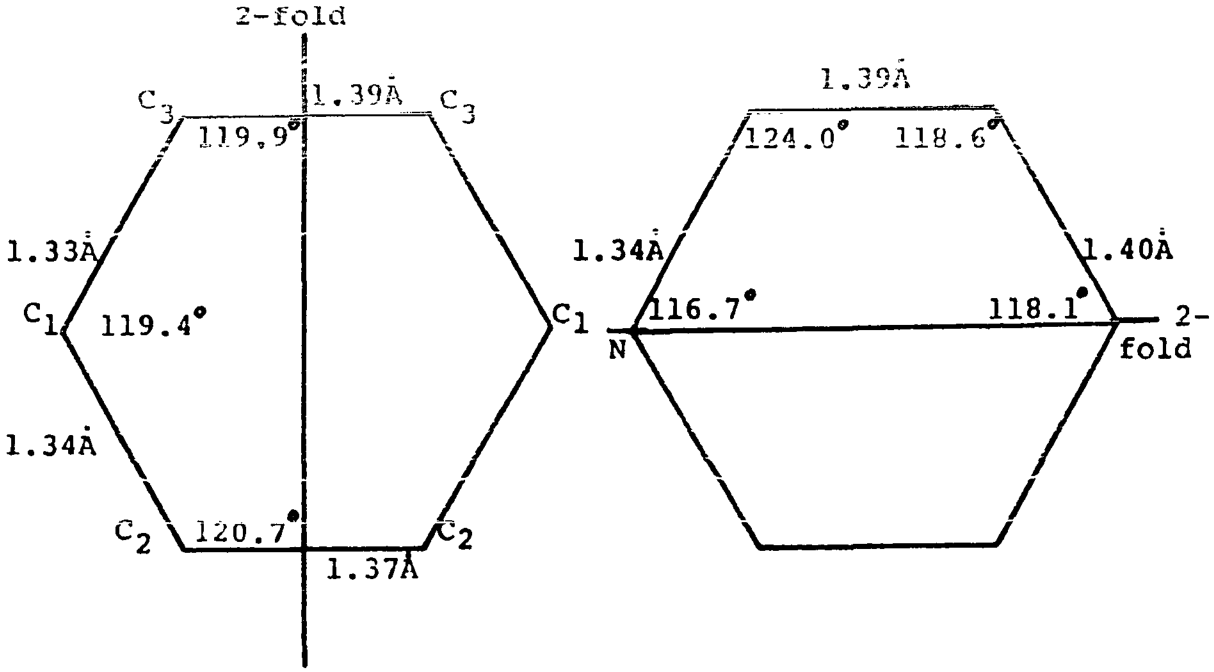
Atom 1	Atom 2	Atom 3	Angle
Cl 1	Sb	Cl 1[a]	94.4(2)
Cl 1	Sb	Cl 2[b]	88.6(2)
Cl 2	Sb	Cl 2[b]	98.0(2)
Cl 2	Sb	Cl 2[a]	92.9(1)
Cl 2	Sb	Cl 1	86.8(1)
Sb	Cl 2[a]	Sb[b]	95.6(2)
C 2[a]	C 2	C 1	120.8(8)
C 2	C 1	C 3	119.5(10)
C 1	C 3	C 3[a]	119.8(7)

[a] Position transformed by the two-fold rotation axis.

[b] Position transformed by the c glide plane.

The ring atom positions refined very well in this structure, but as was discussed above it was impossible to tell which position or positions were occupied by the nitrogen atom on the basis of a time average.

Figure 6 compares the structure of pyridine in the gas phase[1] with the cation in this structure. It is not possible to correlate the one structure with the other and thereby gain information on the nitrogen position. The average bond distance in pyridine is 1.38Å while in this pyridinium ion it is 1.35Å



pyridinium ion in py $SbCl_4$

pyridine

Figure 6. A comparison between the pyridinium cation in pyridinium tetrachloroantimonate(III) and pyridine

Pyridinium Hexachloroantimonate(V)

There are two crystallographically independent anions of of formula $SbCl_6^-$ in this structure. They are both close to

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[1] Schomaker, V. and L. Pauling, J. Amer. Chem. Soc., 61, 1769 (1939).

being regular octahedra, but are significantly distorted. The angles are collected in Table 14. The antimony-chlorine distances are scattered between 2.21(2)Å and 2.44(2)Å (Table 12). The average in anion A is 2.36Å; in anion B it is 2.33Å. Averaging these distances over thermal motion (atoms assumed to move independently) by use of ORFFE[1], these average distances are 2.39Å and 2.34Å respectively.

The standard deviations of the positional parameters are much higher than they were with pyridinium tetrachloroantimonate(III). This was due to the way in which the data were taken. The use of the longer wavelength Cu K_α x-rays meant that the higher orders could not be measured. (The reason for the use of this radiation has been discussed in the section on the solution of this structure.) There is surely a correlation between the highest theta angle of the data taken and the standard deviations of the parameters, just as there is between the highest theta and the resolution of the Fourier syntheses[2]. The standard deviations are small enough that it is probable that the scatter in the bond length really exists. It should be noted that all procedures were checked and rechecked to insure that the methods used were indeed correct and that there was not some systematic error causing this

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[1] Busing, W. R., K. O. Martin, H. A. Levy, ORFFE, A FORTRAN Function and Error Program. ORNL-TM-306 (The Oak Ridge National Laboratory, Oak Ridge, Tennessee) 1962.

[2] James, R. W., Acta Cryst., 1, 132 (1948)

scatter.

This kind of scatter in antimony(V)-chlorine bond lengths has been reported before. Examination of the literature shows a great variety of these distances. As noted earlier antimony(V) chloride has three bonds 2.29Å in length and two of 2.34Å. In $SbCl_5 \cdot OPCl_3$ bond distances of 2.35, 2.32, and 2.33Å are reported[1]. In $ISbCl_8$ distances of 2.26, 2.34, 2.33, 2.41 and 2.44Å are reported for the six chlorine atoms coordinating the antimony atom. The two longest distances are two chlorine atoms that are also coordinated with the iodine atom. The chlorine-iodine distances were 3.00 and 2.85Å respectively[2]. The estimated standard errors in studies to date are high (including this one), and one might speculate as to the existence of three "kinds" of bonds. Most of them appear to be about 2.34Å, a few are between 2.40 and 2.45Å, and finally some are less than 2.30Å.

The standard deviations of the cation atom positions are also quite high compared to those found in pyridinium tetrachloroantimonate(III). Thus it is impossible to make any meaningful comparison of pyridinium rings between the structures. The cations in this structure are probably disordered because they do not fit well into the holes left by the anions. Also, there are not any especially close contacts between

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[1] Lindqvist, I. and C. Branden, _op. cit._

[2] Vonk, C. and E. Wiebenga, E., _op. cit._

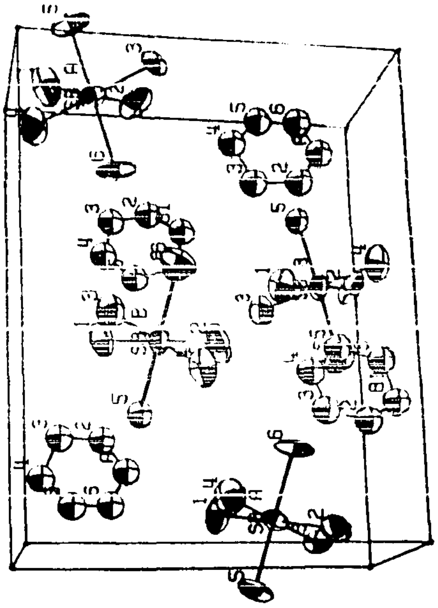
cations and anions. There are no cation-anion distances less than about 3.4Å, which is about 0.3Å greater than the expected hydrogen bond distance. All anion-cation contacts less than 4.0Å are included in Table 13. There is one close chlorine-chlorine distance, viz. Cl a6 to Cl b6 at 3.63Å which is very close to twice the van der Waals radius of chlorine. It does not seem possible to correlate the long (greater than 2.4Å) antimony-chlorine distances according to the proximity of other ions as was done with $ISbCl_8$.

The packing of ions in this structure (Figure 7) is unusual. The cations and anions have not arranged themselves as one would expect for unit point charges of opposite sign. The forces holding these crystals together are no doubt van der Waals and ionic, but because of the complexity of the moieties involved, they are not well understood.

Pyridinium Nonabromodiantimonate(III) Dibromide

This structure too has six-coordinated antimony, but here the distortion from regularity is considerable. The ion $Sb_2Br_9{}^{3-}$ resembles two $SbBr_6$ octahedra sharing a face, but the distortion of the internal angles from 90° is significant. The bond angles of this crystal are compiled in Table 7. The bromine-antimony-bromine angles are (away from the shared face) 91.0° and (toward this face) 80.3° on the average. The ion is shown in Figure 8. It nearly has D_{3h} symmetry with the three bridging bromine atoms on the mirror. (This mirror is coincident with the mirror in the space group, $B2_1/m$, as

Figure 7. The unit cell of pyridinium hexachloroantimonate(V)


Sb
A
B

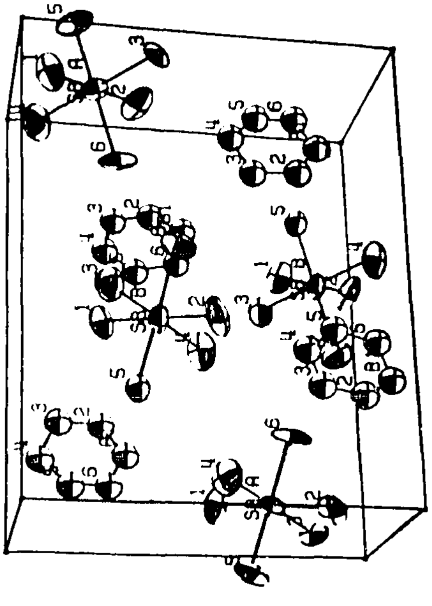

Sb
A
B

Table 12. Antimony-chlorine distances from pyridinium hexachloroantimonate(V)

Atom 1	Atom 2	Distance (angstroms)	D (corr.)[a]
Sb a	Cl a1	2.36(2)	2.39(2)
Sb a	Cl a2	2.40(2)	2.43(2)
Sb a	Cl a3	2.44(2)	2.45(2)
Sb a	Cl a4	2.33(2)	2.36(2)
Sb a	Cl a5	2.28(2)	2.31(2)
Sb a	Cl a6	2.38(2)	2.39(2)
Sb b	Cl b1	2.31(2)	2.33(2)
Sb b	Cl b2	2.36(2)	2.38(2)
Sb b	Cl b3	2.21(2)	2.23(2)
Sb b	Cl b4	2.34(2)	2.36(2)
Sb b	Cl b5	2.29(2)	2.31(2)
Sb b	Cl b6	2.44(2)	2.46(2)

[a] Averaged over thermal motion (atoms assumed to move independently) as calculated by ORFFE .[1]

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[1] Busing, W. R., K. O. Martin, and H. A. Levy, ORFFE, p. 25.

Table 13. Other important distances from pyridinium hexachloroantimonate(V) (All inter-ionic distances less than 4.0A have been included.)

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
C a1	C a2	1.33(5)	C a1	Cl a4	3.64(5)
C a2	C a3	1.39(5)	C a6	Cl a4	3.74(5)
C a3	C a4	1.51(6)	C b1	Cl b3	3.75(5)
C a4	C a5	1.36(6)	C b1	Cl b5	3.83(5)
C a5	C a6	1.23(5)	C b6	Cl b1	3.52(5)
C a6	C a1	1.36(5)	Cl a6	Cl b6	3.63(3)
C b1	C b2	1.38(6)	C b6	Cl b3	3.64(5)
C b2	C b3	1.30(6)	Cl a5	Cl b5[a]	3.87(3)
C b3	C b4	1.39(5)	Cl a5	Cl a3[b]	3.81(4)
C b4	C b5	1.32(5)	C a4	Cl a5[b]	3.84(5)
C b5	C b6	1.43(5)	C a5	Cl a3[b]	3.98(6)
C b6	C b1	1.48(5)	C a5	Cl a5[b]	3.83(6)
C a1	Cl a1	3.61(5)	C a6	Cl a3[b]	3.38(5)

[a] Moved one cell in the -x direction.

[b] Atom transformed by (x,y,z) to (-x,½+y,-z).

Table 14. Bond angles from pyridinium hexachloroantimonate(V)

Atom 1	Atom 2	Atom 3	Angle (degrees)
Cl a2	Sb a	Cl a1	177.3(8)
Cl a3	Sb a	Cl a1	88.9(8)
Cl a4	Sb a	Cl a1	89.1(8)
Cl a5	Sb a	Cl a1	87.1(10)
Cl a6	Sb a	Cl a1	91.2(8)
Cl a3	Sb a	Cl a2	90.9(9)
Cl a4	Sb a	Cl a2	91.2(9)
Cl a5	Sb a	Cl a2	90.2(8)
Cl a6	Sb a	Cl a2	91.4(7)
Cl a4	Sb a	Cl a3	177.9(8)
Cl a5	Sb a	Cl a3	89.8(9)
Cl a6	Sb a	Cl a3	89.6(6)
Cl a5	Sb a	Cl a4	90.4(10)
Cl a6	Sb a	Cl a4	90.1(9)
Cl a6	Sb a	Cl a5	178.3(9)
Cl b2	Sb b	Cl b1	176.6(8)
Cl b3	Sb b	Cl b1	86.5(8)
Cl b4	Sb b	Cl b1	88.8(8)
Cl b5	Sb b	Cl b1	88.9(8)
Cl b6	Sb b	Cl b1	90.1(8)
Cl b3	Sb b	Cl b2	91.6(9)
Cl b4	Sb b	Cl b2	93.1(9)

Table 14 (Continued)

Atom 1	Atom 2	Atom 3	Angle (degrees)
Cl b5	Sb b	Cl b2	88.2(8)
Cl b6	Sb b	Cl b2	92.8(9)
Cl b4	Sb b	Cl b3	175.2(8)
Cl b5	Sb b	Cl b3	89.0(8)
Cl b6	Sb b	Cl b3	90.0(9)
Cl b5	Sb b	Cl b4	91.9(9)
Cl b6	Sb b	Cl b4	88.9(9)
Cl b6	Sb b	Cl b5	178.6(9)
C a1	C a2	C a3	118(4)
C a2	C a3	C a4	116(4)
C a3	C a4	C a5	116(4)
C a4	C a5	C a6	122(4)
C a5	C a6	C a1	123(4)
C a6	C a1	C a2	122(4)
C b1	C b2	C b3	117(4)
C b2	C b3	C b4	125(4)
C b3	C b4	C b5	117(4)
C b4	C b5	C b6	124(4)
C b5	C b6	C b1	114(3)
C b6	C b1	C b2	120(4)

well.) The antimony-bromine (bridged) distances are 3.031(8), 2.973(7), and 3.006Å with the average 3.003Å. Tables 15 and 16 give the important distances between atoms in this crystal. The antimony-bromine (unbridge) distances are 2.633(8), 2.618(7), and 2.638(7)Å with the average being 2.630Å.

The equation of Pauling[1] can once again be used to calculate the approximate bond orders of these bonds. Assuming the bond of 2.51Å in $SbBr_3$[2] to be of order one; the bonds averaging 2.630Å are of order 0.63, and the bonds averaging 3.003Å are of order 0.15.

It is interesting to note that the bond distances found are quite different from those found by Lawton and Jacobson in $(NH_4)_4Sb_2Br_{12}$[3]. They found 2.80Å which is interestingly just about the average of those found in this study. The nonabromodiantimonate(III) ion does seem to be isostructural with $As_2Cl_9{}^{3-}$.[4] This ion was thought to be two MX_3 molecules and three X^- ions. It seems reasonable to assume, however, that a weak bond exists between the metal atom and bridging halogen since the Pauling bond order is about one-seventh. Furthermore the $SbBr_3$ "group" has changed significantly from the

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[1] Pauling, L., <u>The Nature of the Chemical Bond</u>, <u>loc. cit.</u>

[2] Swingle, S. M., <u>op. cit.</u>

[3] Lawton, S. L. and R. A. Jacobson, Inorg. Chem., <u>op. cit.</u>

[4] Hoard, J. L. and L. Goldstein, J. Chem. Phys., <u>3</u>, 199 (1935).

geometry found by Swingle in the gaseous $SbBr_3$ molecule[1]. The bromine-antimony-bromine angle in antimony(III) bromide is 97° while in the salt done in this study the same angle is 91°. The antimony-bromine bond distance is 2.51Å in $SbBr_3$, but in the anion studied the distance is 2.63Å.

The pyridinium cation is much smaller than the nonabromodiantimonate(III) anion. Each of these cations has quite a lot of space to "rattle around in." The high standard deviations of their parameters in this crystallographic study confirm this view. The average isotropic temperature factors for each of the three rings were A, 12.1Å^2; B, 9.1Å^2; C, 7.0Å^2. These numbers are higher than the usual carbon temperature factor indicating some "smearing out" of the atoms over the time required for measurements.

One of the more interesting and puzzling aspects of the structure of this salt is the dissimilarity between it and the structure of pyridinium tetrachloroantimonate(III). While each antimony atom is six coordinated in a nearly octahedral configuration, the similarity ends here. There seems to be no simple reason why the products of two reactions which were the same, except that bromide was substituted for chloride, should be so dissimilar.

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[1] Swingle, S. M., *op. cit.*

Table 15. Distances between heavy atoms in pyridinium nonabromodiantimonate(III) dibromide

Atom 1	Atom 2	Distance (angstroms)	D (corr.)[a]
Sb	Br 1	2.633(8)	2.652(8)
Sb	Br 3	2.618(7)	2.648(7)
Sb	Br 5	2.638(7)	2.658(7)
Sb	Br 2	3.031(8)	3.042(8)
Sb	Br 4	2.973(7)	2.984(7)
Sb	Br 6	3.006(7)	3.013(7)
Sb	Sb[b]	4.008(13)	4.008(13)
Br 2	Br 4	3.85(1)	3.85(1)
Br 4	Br 6	3.88(1)	3.87(1)
Br 6	Br 2	3.89(1)	3.89(1)
Br 1	Br 3	3.76(1)	3.77(1)
Br 3	Br 5	3.72(1)	3.72(1)
Br 5	Br 1	3.77(1)	3.77(1)

[a] Averaged over thermal motion (atoms assumed to move independently) as calculated by ORFFE[1].

[b] Atom transformed by (x,y,z) to (x,½-y,z).

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[1] Busing, W. R., K. O. Martin, and H. A. Levy, ORFFE, p.25.

Table 16. Other important distances from pyridinium nonabromodiantimonate(III) dibromide

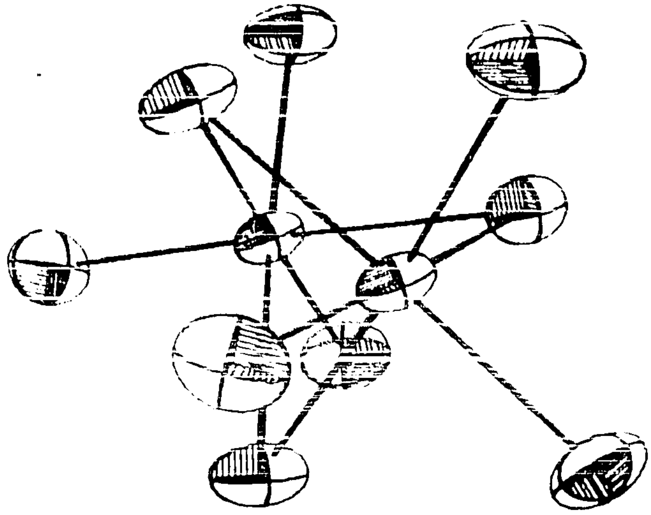
Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
C a1	C a26	1.33(8)	C a1	Br 1	4.03(4)
C a26	C a35	1.19(9)	C a1	Br 4	3.78(7)
C a35	C a4	1.27(7)	C a1	Br 6	3.79(7)
C b1	C b2	1.38(5)	C a26	Br 1	3.85(8)
C b2	C b3	1.29(6)	C b2	Br 1	4.11(5)
C b3	C b4	1.38(7)	C b2	Br 5	3.93(5)
C b4	C b5	1.72(8)	C b3	Br 1	3.83(5)
C b5	C b6	1.39(7)	C b3	Br 3	4.23(6)
C b6	C b1	1.24(4)	C c2	Br 3	4.02(5)
C c1	C c2	1.39(6)	C c2	Br 5	4.05(5)
C c2	C c3	1.48(7)	C c3	Br 3	4.10(5)
C c3	C c4	1.27(5)	C c3	Br 5	3.85(5)
C c4	C c5	1.26(5)	C c4	Br 7	3.53(4)
C c5	C c6	1.40(5)	C c3	Br 7	3.57(5)
C c6	C c1	1.24(5)	C b6	Br 7	3.68(4)
C b2	Br 7	4.07(6)	C b1	Br 7	3.10(3)

Table 17. Bond angles in pyridinium nonabromodiantimonate(III) dibromide

Atom 1	Atom 2	Atom 3	Angle (degrees)
Br 1	Sb	Br 3	91.5(2)
Br 3	Sb	Br 5	90.0(3)
Br 5	Sb	Br 1	91.4(2)
Br 2	Sb	Br 4	79.8(2)
Br 4	Sb	Br 6	80.8(3)
Br 6	Sb	Br 2	80.3(2)
Br 1	Sb	Br 6	93.5(2)
Br 1	Sb	Br 4	93.3(2)
Br 3	Sb	Br 4	94.5(3)
Br 3	Sb	Br 2	94.3(2)
Br 5	Sb	Br 2	95.1(2)
Br 5	Sb	Br 6	94.3(3)
Br 1	Sb	Br 2	171.4(1)
Br 3	Sb	Br 6	173.4(1)
Br 5	Sb	Br 4	173.4(1)
Sb	Br 2	Sb[a]	82.8(3)
Sb	Br 4	Sb[a]	84.7(3)
Sb	Br 6	Sb[a]	83.6(3)

[a] Atom transformed by (x,y,z) to (x,½-y,z).

Figure 8. The nonabromodiantimonate(III) anion



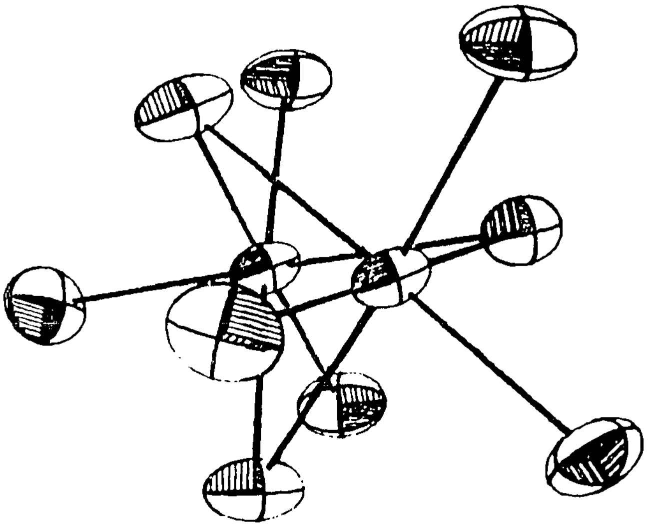
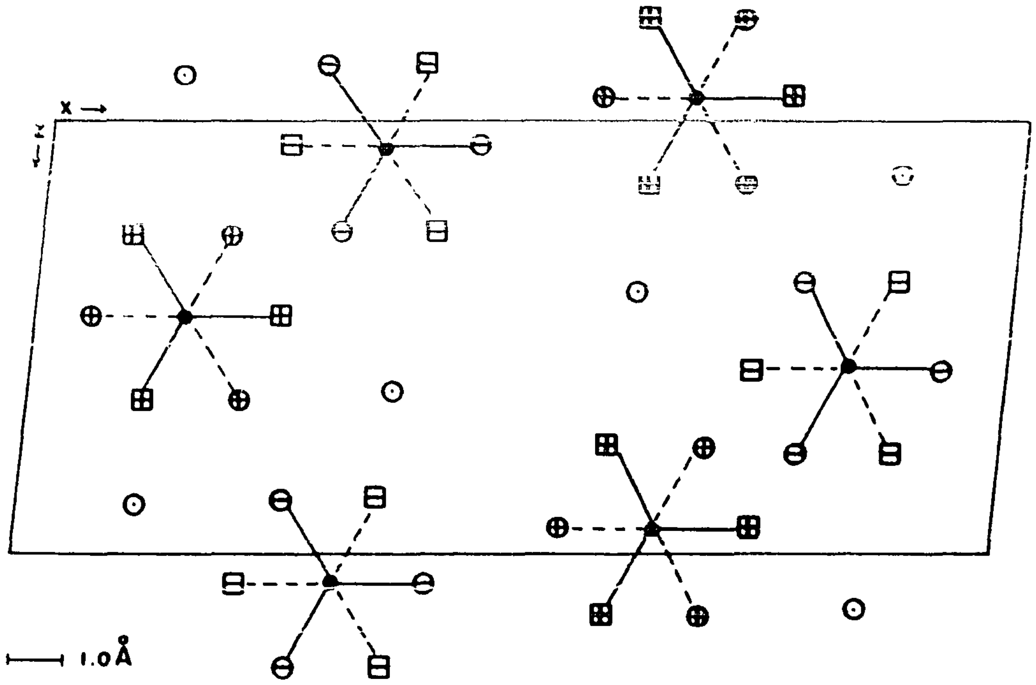


Figure 9. View of the packing of anions in pyridinium nonabromodiantimonate(III) dibromide down the y axis

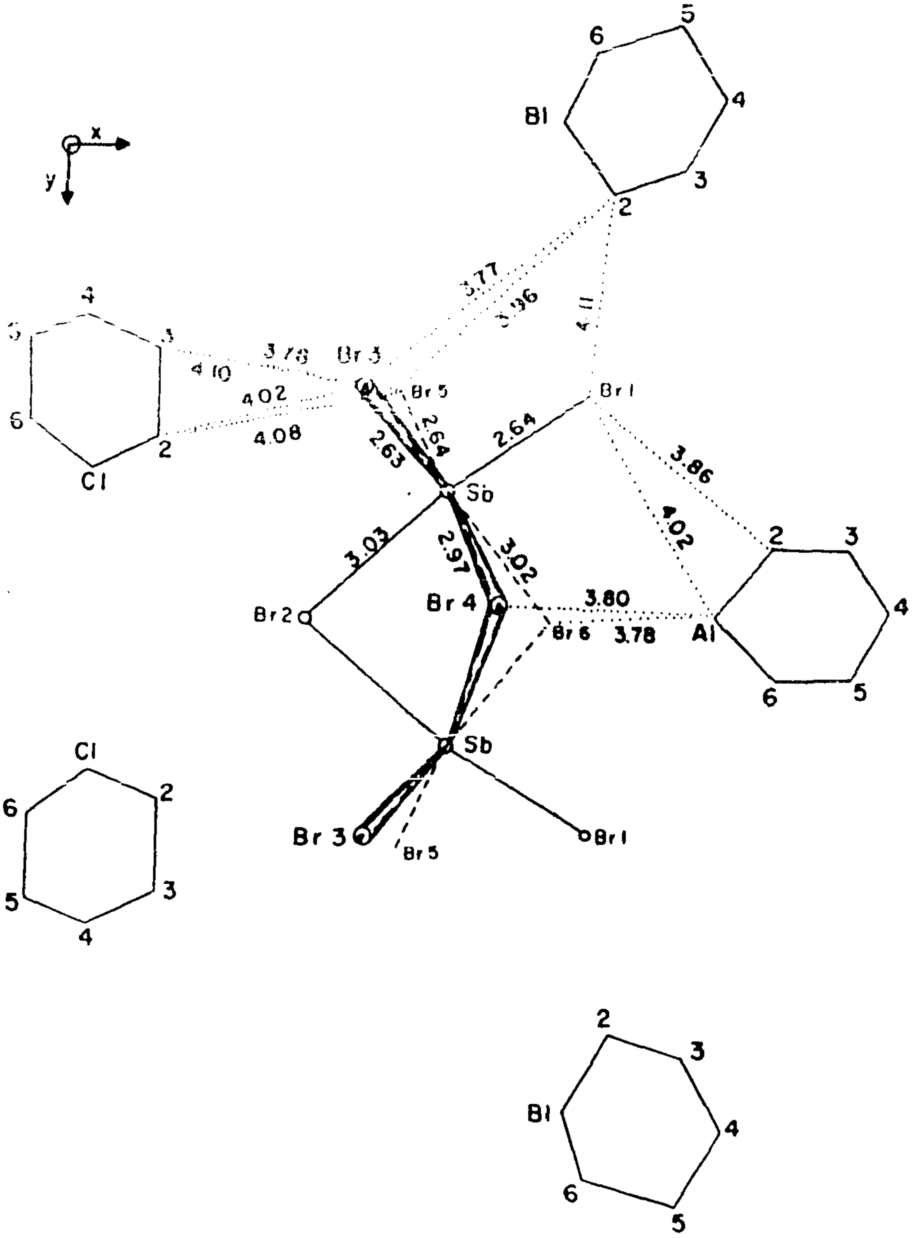


PACKING DIAGRAM OF ANTIMONY AND BROMINE ATOMS IN $(pyH^+)_5\ Sb_2\ Br_9^{3-}\ (Br^-)_2$

- ● Sb
- ⊙ Br NEAR $y=0$
- ⊖ Br (BONDED TO ONE Sb) AT $y>0$
- ⊕ Br (BONDED TO ONE Sb) AT $y<0$
- ⊟ Br (BRIDGING) AT $y=1/4$
- ⊞ Br (BRIDGING) AT $y=-1/4$

THERE ARE MIRROR PLANES AT $y=\pm 1/4$

Figure 10. The environment of the nonabromodiantimonate(III) anion



TWO ASYMMETRIC UNITS OF $(pyH^{+})_5$ $Sb_2Br_9{}^{3-}(Br^{-})_2$ RELATED BY A MIRROR PLANE AT y = 1/4. ALL Br-c DISTANCES LESS THAN 4.2 Å ARE SHOWN.

CONCLUSION

The crystal structures of three new halogen coordinated antimony anions have been solved. In all cases the pyridinium was used as the cation. Each of the antimony atoms is surrounded by six halogen atoms in a distorted octahedral arrangement. The distortion is different in each salt. Pyridinium tetrachloroantimonate(III) has an infinite chain structure with a bridging chlorine atom. This atom forms bonds of Pauling orders of 0.38 and 0.06 with two antimony atoms. The lengths of these bonds are 2.63 and 3.13Å respectively. There are two other antimony-chlorine distances in each anion of 2.38Å. This distance is the single bond distance as reported for antimony(III) chloride.

Pyridinium hexachloroantimonate(V) has two crystallographically independent $SbCl_6^-$ anions. These ions are close to being regular octahedra with bond distances averaging 2.34Å. There is considerable distortion, however, and the distances range from 2.21 to 2.44Å.

Pyridinium nonabromodiantimonate(III) dibromide contains the interesting $Sb_2Br_9^{3-}$ ion which has the form of two $SbBr_6$ octahedra sharing a face. There are also two bromide ions in this structure which appear to merely fill holes in the lattice.

SUGGESTIONS FOR FURTHER STUDY

The inter-ionic forces holding pyridinium hexachloroantimonate(V) together are not easily understood and are worthy of theoretical study.

The structure of $SbCl_3$ should be redetermined by a full three-dimensional x-ray study so as to lower the standard deviations in the bond lengths and angles. There is no "standard" antimony(III)-chlorine bond length to which one can refer.

The structure of a simple pyridinium salt should be done to determine the "normal" configuration of this elusive ion.

A structural analysis of cesium nonachloradiarsenate(III) should be undertaken to better establish the parameters of this interesting salt.

A study should be made of the correlation between the standard errors of parameters refined by least squares and the extent to which data is taken (in terms of $\sin\theta/\lambda$). There is a good inverse correlation between the two, but it may be possible to estimate what fraction of the error is due to lack of high order data and what fraction is due to atomic vibration.

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