tron affinities for the elements. In these cases polyatomic anions of the general sort deduced by Zintl[5] are presumably better candidates. However the thermal stabilities of these must be limited, and the entropy change for decomposition of at least the more complex examples should be substantial at the temperatures necessary to observe solution in simple molten salts such as the alkali metal halides. Unfortunately the intermetallics of interest readily reduce the useful solvent $NaAlCl_4$.

Particularly for bismuth and antimony the explorations reported here indicate the existence of an interesting solution chemistry involving unusual anions, and additional characterization by several means is needed. Emf methods could be particularly useful if electronic conduction in the melts is not bothersome. The small changes in conduction properties generally observed on fusion of pure semiconductors[32] suggest that there should not be a substantial electronic conduction in the solutions of NaSb or Na_3Sb, but this property for the Na_3Bi solutions is more uncertain.

(32) A. F. Ioffe and A. R. Regel in "Progress in Semiconductors," Vol. IV, A. F. Gibson, R. E. Burgess, and F. A. Korger, Ed., Heywood and Co., London, 1960, p 238.

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The Crystal Structure of α-Picolinium Nonabromoantimonate(V), $(C_6H_7NH)_2Sb^VBr_9$[1]

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The crystal structure of α-picolinium nonabromoantimonate(V), $(C_6H_7NH)_2SbBr_9$, has been solved by single-crystal X-ray diffraction techniques at room temperature (25 ± 3°) using three-dimensional scintillation counter data and a full-matrix anisotropic least-squares refinement procedure (final $R = 0.069$). The salt crystallizes in the triclinic crystal system of centrosymmetric space group $P\bar{1}$, with reduced cell lattice parameters $a = 9.249 \pm 0.002$ Å, $b = 9.750 \pm 0.001$ Å, $c = 7.645 \pm 0.002$ Å, $\alpha = 90.074 \pm 0.016°$, $\beta = 107.461 \pm 0.024°$, and $\gamma = 70.520 \pm 0.016°$. The structure consists of one tetragonally distorted octahedral $Sb^VBr_6^-$ ion (D_{4h} symmetry), one linear symmetrical Br_3^- ion, and two planar α-picolinium cations per unit cell; no trivalent antimony was found. The tribromide ion forms approximately linear chains with the Sb(V) ion and each cation forms a sandwich-type arrangement about the Br···Br bridge of the chains with its π cloud normal to the bridge. The crystallographically independent Sb–Br bond lengths in $SbBr_6^-$, corrected for rigid-body libration (after Cruickshank), are 2.565, 2.547, and 2.548 Å (each ±0.003 Å). Only the first is directly involved in charge transfer and so is lengthened by ~0.018 Å. The Br–Br bond in Br_3^- is 2.543 ± 0.002 Å (no correction for thermal motion assumed). The Br···Br van der Waals contact along the chain is fairly short, 3.491 ± 0.002 Å, and the average cation–$SbBr_6^-$ contact along the normal to the ring (π-cloud interaction) is 3.87 Å. The results of this investigation are extended to the related salts $(\beta\text{-pic})_2SbBr_9$ and $(\gamma\text{-pic})_2SbBr_9$ in an attempt to explain their unusual dependence of color on temperature.

Introduction

The crystal structure determination[3] of $R_6Sb_4Br_{24}$, R = pyridinium, has revealed the presence of both trivalent and pentavalent antimony in an orthorhombic unit cell. Substitution of a methyl group into the 2, 3, or 4 position of the pyridinium ring relative to nitrogen (position 1) was found, however, to result in a complete change of structure, as indicated by an examination of unit cell dimensions and space group.[4,5] Examination of several of their physical properties has also revealed an entirely different behavior of color and stability with change in temperature.[4] For example, the pyridinium salt, which is jet black at room temperature, remains jet black at all temperatures between room temperature and liquid nitrogen temperature; it has a melting point of 201–202° and decomposes upon melting. The three salts which contain the methyl-substituted pyridinium (picolinium) cations, on the other hand, are also jet black (the color of reflected light) at room temperature but lose their black color as the temperature is lowered below room temperature. They have a low melting point, occurring in the range 115–140° for the three salts, and remain stable as jet black liquids. Finally, the ratio of elements in the three salts also differs markedly from the pyridinium salt, being R:Sb:Br of 6:4:24 for R = pyridinium and 2:1:9 for R = α-, β-, and γ-picolinium.

It thus became readily apparent that substitution of a methyl group into the pyridinium ring resulted in a drastic change not only in the structure of the resulting salts but in their charge-transfer properties as well.

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(1) This work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

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(3) S. L. Lawton and R. A. Jacobson, to be submitted for publication.

(4) S. L. Lawton, and R. A. Jacobson, *J. Am. Chem. Soc.*, **88**, 616 (1966).

(5) The crystal symmetry and unit cell parameters of the pyridinium salt $(C_5H_5NH)_6Sb^{III}Sb^V{}_3Br_{24}$ are orthorhombic, possible space groups $Cmc2_1$, C2cm, and Cmcm (based on the observed extinction conditions: hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$), with $a = 17.51 \pm 0.02$, $b = 23.77 \pm 0.03$, $c = 16.46 \pm 0.02$ Å. The crystal data for the three picolinium salts are: $(\alpha\text{-pic})_2SbBr_9$, see text; $(\beta\text{-pic})_2SbBr_9$, possible space groups C2, Cm, and C2/m, with lattice parameters $a = 18.61 \pm 0.03$, $b = 7.54 \pm 0.02$, $c = 9.69 \pm 0.02$ Å, $\beta = 113° 17' \pm 10'$; $(\gamma\text{-pic})_2SbBr_9$, possible space groups C2, Cm, and C2/m, with lattice parameters $a = 18.38 \pm 0.03$, $b = 7.43 \pm 0.02$, $c = 9.83 \pm 0.02$ Å, $\beta = 113° 08'$. The β-picolinium crystals show a pronounced tendency to twin; the others do not. The errors cited represent maximum deviations.

What changes actually occurred were not obvious and could only be resolved by the structure determination of any one of the three picolinium salts. The α-picolinium salt was ultimately chosen for X-ray study as it gave high-quality untwinned crystals.

Experimental Section

Preparation.—The salt was prepared by the reaction of α-picoline (2-methylpyridine) and antimony tribromide in a solution of concentrated hydrobromic acid (48%) and liquid bromine. The antimony tribromide solution was first prepared by dissolving 2.50 g (0.0069 mol) of reagent grade antimony tribromide and 0.6 ml of liquid bromine in 10 ml of warm (approximately 50°), concentrated hydrobromic acid (48%). To this was added 1.2 ml (0.0125 mol) of α-picoline. A thick, black, crystalline precipitate which formed instantly was filtered by vacuum filtration through a sintered-glass funnel, rinsed with a small amount of cold, concentrated hydrobromic acid (48%), and dried on a porous porcelain plate in a desiccator containing concentrated sulfuric acid as the desiccant and a small partial pressure of bromine vapor.

Single crystals suitable for the X-ray investigation were obtained by recrystallization of the raw material, using the following procedure. A small quantity of the black material was first dissolved in 2-3 ml of hot, concentrated hydrobromic acid (48%) followed by the addition of 1–2 drops of liquid bromine. The solution was swirled, reheated slightly, and set aside to cool. The addition of bromine replenished that which was lost by heating (excess bromine is to be avoided). Crystals of high quality were produced from a cool solution which is dark yellow rather than from one which is red, which would indicate the presence of too much bromine. After crystal growth was completed, an eye dropper was used to transfer a small portion of the crystals, together with the mother liquor, to flat filter paper for inspection under a microscope. The mother liquor on the paper served to delay debromination of the salt during examination. Single crystals were mounted in 0.3-mm diameter Lindemann glass capillaries whose inner walls were coated with a thin film of the mother liquor. Long-range stability of the crystals was found to be increased considerably if two or more crystals were sealed within each capillary of approximate length equal to 1.5 cm.

Crystal Data.—Crystals of (α-pic)$_2$SbBr$_9$, examined by precession and Weissenberg-film techniques, were found to belong to the triclinic crystal system with lattice parameters of the primitive reduced cell $a = 9.249 \pm 0.002$ Å, $b = 9.750 \pm 0.001$ Å, $c = 7.645 \pm 0.002$ Å (needle axis), $\alpha = 90.074 \pm 0.016°$, $\beta = 107.461 \pm 0.024°$, and $\gamma = 70.520 \pm 0.016°$. These observed lattice constants were checked with the computer program of Lawton and Jacobson[6] to verify that the correct reduced cell was chosen and that no higher symmetry was present. The volume of the unit cell is 616.25 Å^3; the observed density is 2.57 ± 0.20 g/cm^3 (by flotation) and the calculated density for 1 unit of $(C_6H_7NH)_2SbBr_9$ per unit cell is 2.75 g/cm^3. The centrosymmetric space group, $P\bar{1}$, was indicated by an analysis of the Patterson map and was confirmed by the successful refinement of the derived structure.

The lattice constants were determined by a least-squares fit[7] to 43 independent reflection angles (each with a separate α_1–α_2 angular measurement) in the region $120° \leq 2\theta \leq 165°$ which were carefully measured on Weissenberg films calibrated with superimposed aluminum powder lines; the Nelson–Riley extrapolation function was employed. The high-angle reflections were obtained from four independent zero-level zones taken with Cu Kα radiation (λ(Kα_1) 1.54050 Å and λ(Kα_2) 1.54434 Å). The value of a_0 used for aluminum was 4.03310 Å,[8] a value which includes a correction for thermal expansion to a temperature of 25.5°.

The unit cells of both (β-pic)$_2$SbBr$_9$ and (γ-pic)$_2$SbBr$_9$ are essentially isomorphous with the (α-pic)$_2$SbBr$_9$ salt studied in this investigation except that they are monoclinic with space group C2, Cm, or C2/m (b unique). This same C-centered cell occurs in the α-picolinium salt but is triclinic, with lattice parameters $a = 17.770 \pm 0.003$ Å, $b = 7.645 \pm 0.002$ Å (needle axis), $c = 9.750 \pm 0.001$ Å, $\alpha = 89.926 \pm 0.016°$, $\beta = 110.279 \pm 0.014°$, and $\gamma = 83.233 \pm 0.024°$. The primitive reduced cell is related to the C-centered cell by the transformation matrix 201 001 0$\bar{1}$0.

Collection and Treatment of X-Ray Intensity Data.—Complete three-dimensional X-ray diffraction intensity data ($0° < 2\theta_{\mathrm{Mo}} \leq 55°$) were taken at room temperature ($25 \pm 3°$) with zirconium-filtered molybdenum radiation from a crystal of dimensions $0.073 \times 0.176 \times 0.389$ mm. A General Electric single-crystal orienter equipped with a scintillation counter was used with the moving-crystal, moving-counter measurement technique (θ–2θ coupling) and a 3.0° takeoff angle. A 100-sec scan, covering 3.33° in 2θ, was used for each of 2849 independent reflections. Three standard reflections were measured periodically as a check on crystal decomposition; the average decrease in their intensities *vs.* reflection number was used to correct for decomposition effects. The maximum decrease in intensity was 8%.

The raw intensity of each reflection was corrected for background, streak (produced by noncharacteristic radiation in the wavelength range $\lambda_K < \lambda < 2\lambda_K$ and by excitation of the bromine K-absorption edge caused by the noncharacteristic radiation), decomposition, absorption, and Lorentz polarization. The background was determined by one of two methods, depending upon the intensity of the reflection. The background for reflections which were moderate to strong in intensity, a total of 817 such reflections, was read from background plots. These plots were prepared from reflections whose intensities were essentially zero, as determined by the lack of any visible contribution in intensity detectable above the background level on the recorder trace, neglecting those considered to be affected by streak. (This eliminated the need of taking background intensity measurements in empty regions of the reciprocal space while the data were being taken.) A total of 18 plots of background intensity *vs.* 2θ were prepared in 20° intervals of ϕ since the background was found to be moderately dependent upon ϕ owing to absorption by the crystal. Reflections whose intensities were very close to the background level are subject to considerable statistical counting errors, thus requiring a different treatment for the determination of these intensities. In this case the net intensity of each reflection was obtained by integration of the peak area of the recorder trace; this resulted in an additional 1254 observed reflections to give a total of 2071 observed reflections. Streak corrections were made using a modification of the method of Williams and Rundle.[9] Because of significant absorption ($\mu = 147$ cm^{-1}), an absorption correction was made using the transmission factors calculated by the program of Wehe, *et al.*;[10] the ratio of the maximum to minimum transmission factors was 4.55.

The estimated error in each intensity measurement was calculated by

$$[\sigma(I)]^2 = [C_{\mathrm{T}} + C_{\mathrm{B}} + C_{\mathrm{S}} + (K_{\mathrm{T}}C_{\mathrm{T}})^2 + (K_{\mathrm{B}}C_{\mathrm{B}})^2 + (K_{\mathrm{S}}C_{\mathrm{S}})^2 + (K_{\mathrm{A}}C_{\mathrm{R}})^2]/A^2$$

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(6) S. L. Lawton and R. A. Jacobson, "TRACER, A General Fortran Lattice Transformation—Cell Reduction Program," in "The Reduced Cell and Its Crystallographic Applications," Report IS-1141, Ames Laboratory, Iowa State University, Ames, Iowa, 1965. This program is written in Fortran II for the IBM 7074. It transforms any cell in any crystal system to its reduced cell. The output consists of all transformation matrices used and generated and the new cell parameters. The reduction procedure is based on the method of L. V. Azaroff and M. J. Buerger, "The Powder Method," McGraw-Hill Book Co., Inc., New York, N. Y., 1958.

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

(8) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 122.

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

(10) D. J. Wehe, W. R. Busing, and H. A. Levy, "A Fortran Program for Single-Crystal Orienter Absorption Corrections," Report ORNL-TM-299, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

where C_T, C_B and C_S are the total count, background count, and streak count, respectively, $C_R = C_T - C_B - C_S$, A is the transmission factor, and K_T, K_B, K_S, and K_A are fractional random errors in C_T, C_B, C_S, and A, respectively. A value of 0.03 was arbitrarily assigned to K_T, K_B, and K_S and 0.10 to K_A. The estimated standard deviation in each structure factor was calculated by

$$\sigma(F_o) = [(I_o + \sigma(I_o))/\mathrm{Lp}]^{1/2} - |F_o|$$

a function based on the finite-difference method, where Lp is the Lorentz-polarization factor. These standard deviations were used during the least-squares refinements to weight the observed structure factors, where w, the individual weighting factor, was defined as $1/\sigma(F_o)^2$.

Solution of the Structure

An unsharpened Patterson function was calculated using all observed reflections. An $SbBr_6$ octahedron was readily found and placed such that the antimony was at the origin of the unit cell. This resulted in an R factor of 0.397 in the space group $P\bar{1}$. A three-dimensional electron density function revealed the location of a Br_3^- ion, also on a center of symmetry.[11] A second electron density function ($R = 0.148$) led to the location of the α-picolinium cations, two per unit cell, each occupying a general position related by a center of symmetry. Except for the hydrogen positions, all electron density in the unit cell was now accounted for.

Using the full-matrix least-squares program of Fitzwater,[12] an isotropic refinement was undertaken on all atoms. After several iterations the weighting scheme was modified by employing the method of Cruickshank[13,14] in which $w = f(|F_o|)$ was adjusted such that the condition $w\Delta^2$ = constant is fulfilled. The R factor was reduced to 0.085. The scattering factors for all atoms in this and subsequent refinements were those of Hanson, *et al.*[15] The calculated structure amplitudes were corrected for the real and imaginary parts of anomalous dispersion due to bromine and antimony;[16] contribution from the imaginary part was found to be negligible, however. The nitrogen atom was initially assigned a carbon form factor.

The low reliability factor at this point suggested that the initial choice, $P\bar{1}$, was probably correct. This was confirmed by undertaking four iterations of least-squares refinement in the acentric space group P1, primarily for determining the true symmetry of the Br_3^- ion. The unweighted R factor decreased to only 0.079 with meaningless distortions resulting in both anions and the cations. The structure was henceforth assumed to be centrosymmetric.

A total of 92 primarily weak reflections ($|F_o| \leq 5$ electrons) which appeared to be in poor agreement, satisfying the condition $|\Delta F| > 2|F_o|$ or $|\Delta F| > 2|F_c|$, were removed, subsequently reducing the R factor to 0.078. Precalculated hydrogen positions were then included in the refinement but not allowed to vary. The ring C–H and methyl C–H distances were assigned values of 1.08 and 1.09 Å, respectively; the methyl hydrogen positions were treated as six half-hydrogen atoms.[17] With antimony and bromine anisotropic and carbon isotropic, the R factor continued to drop to 0.075.

The α-, β-, and γ-picolinium R_2SbBr_9 salts exhibit slight variations in their unit cell lattice parameters and crystal symmetry,[5] suggesting that the nitrogen atom in the ring is ordered in the crystal. Within the ring it is restricted to only two possible sites; within the structure one of these sites is favored structurally over the other in regard to proximity of negative charge. An examination of the isotropic temperature factor of this favored ring position clearly revealed a value of B_i lower than the other five, namely, 3.7 Å^2 *vs.* an average 4.2 Å^2 for the other five ring atoms and 5.1 Å^2 for the methyl group, where B_i is defined by $-B_i(\sin^2\theta)/\lambda^2$. Computation of an electron density map unambiguously verified this atomic position as the correct choice for nitrogen. Further, a difference map clearly revealed slight anisotropic motion of the ring with marked anisotropy of the methyl group. The structure was largely overdetermined at this stage (25 reflections per variable) and full anisotropic treatment of the ring was therefore considered to be justified. Two iterations of least-squares refinement were henceforth run with all atoms anisotropic and the nitrogen position was now assigned a nitrogen form factor; hydrogen positional and thermal parameters ($B_H = 4.0$ Å^2) were kept fixed. The residual decreased to 0.073.

Refinement of the structure was completed by first carefully examining all reflections for any which may have been measured incorrectly.[18] Seven fairly strong reflections which satisfied the condition $|\Delta F| > 3\sigma$ were removed; these were primarily low first-order reflections seriously affected by streak near the origin. An additional 71 weak reflections which satisfied the condition $|\Delta F| > 2|F_o|$ or $|\Delta F| > 2|F_c|$ were also removed. In addition, 37 reflections were found which satisfied the condition $2\sigma < |\Delta F| < 3\sigma$ but for which $|\Delta F| \ll 2|F_o|$ and $|\Delta F| \ll 2|F_c|$; removal of these reflections did not appear to be justified and so, rather than removing them, their σ values were arbitrarily multiplied by a factor of 2.5. Finally, the 92 reflections removed earlier were reexamined, and, of these, five were readmitted.

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[11] There existed the possibility at this stage that the space group was actually acentric and that the Br_3^- ion was only Br_2 with one of the two bromine atoms occupying the center of the unit cell face. However, further refinement of the structure confirmed the space group to be centrosymmetric and that the true chemical composition was R_2SbBr_9 rather than R_2SbBr_8, as had been reported earlier from preliminary studies.[4]

[12] D. R. Fitzwater, "A Crystallographic Full-Matrix Least-Squares Program for the IBM 7074," Department of Chemistry, Iowa State University, Ames, Iowa, 1963. The discrepancy factors are defined as follows: unweighted $R = \Sigma||F_o| - |F_o||/|F_o|$ and the weighted value $wR = \Sigma||F_o/\sigma| - |F_c/\sigma||/\Sigma|F_o/\sigma|$.

[13] D. W. J. Cruickshank and D. E. Pilling in "Computing Methods and the Phase Problem in X-Ray Crystal Analysis," R. Pepinsky, J. M. Roberts, and J. C. Speakman, Ed., Pergamon Press Inc., New York, N. Y., 1961.

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

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

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

[17] L. G. Guggenberger, "A Fortran Program for the Calculation of Assumed Hydrogen Atom Positions," Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Del.

[18] For comments on weak reflections which are in error and their influence on positional parameters and standard errors, see C. J. Fritchie, *Trans. Am. Cryst. Assoc.*, **1**, 30 (1965).

Convergence for the fully anisotropic refinement was reached after completing two iterations of full-matrix least-squares refinement on an IBM 360 computer using the program of Busing, *et al.*[19] The final values of the unweighted and weighted R factors were $R = 0.069$ and $wR' = 0.068$ ($wR' = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2}$). The standard deviation for an observation of unit weight (*i.e.*, the "goodness of fit") was 0.82, where the "goodness of fit" is defined by $[\Sigma w(|F_o|^2 - |F_c|^2)^2/(n - m)]^{1/2}$, with n being the number of observations (1913) and m the number of variables (112). On the final cycle the shift in each positional and thermal parameter averaged 0.006 times its own σ. The average decrease in the standard deviation of each atomic parameter was 10%, justifying the preceding analysis and removal of "bad" reflections.

The final positional and anisotropic thermal parameters with standard deviations are given in Tables I and II. The root-mean-square thermal displacements along the principal axes and the isotropic temperature factor equivalent to the anisotropic form for each atom are given in Table III. The hydrogen positions, based on the final atomic positions in Table I, are given in Table IV; the six hydrogen atoms designated with the letters a–f were treated as half-hydrogen atoms in the structure factor calculation. A listing of the 1920 observed and calculated structure factors is given in Table V. The seven strong reflections for which $|\Delta F| > 3\sigma$ are indicated in Table V by a dashed line under F_o.

TABLE I

FINAL POSITIONAL PARAMETERS FOR $(\alpha\text{-}C_6H_7NH)_2SbBr_9$[a]

Atom	Position	x	y	z
Sb	1a	0.0	0.0	0.0
Br_1	2i	0.30271 (15)	−0.14833 (18)	0.12151 (20)
Br_2	2i	0.05287 (17)	0.16324 (16)	−0.21350 (18)
Br_3	2i	0.03888 (17)	0.17006 (16)	0.24777 (18)
Br_4	1g	0.0	0.5	0.5
Br_5	2i	0.29562 (18)	0.33484 (19)	0.61437 (24)
N_1	2i	0.4066 (15)	0.2067 (15)	0.1844 (21)
C_2	2i	0.3804 (17)	0.3514 (19)	0.1765 (20)
C_3	2i	0.5083 (18)	0.3925 (18)	0.2699 (21)
C_4	2i	0.6471 (18)	0.2988 (19)	0.3617 (22)
C_5	2i	0.6755 (18)	0.1560 (21)	0.3758 (22)
C_6	2i	0.5489 (24)	0.1120 (19)	0.2891 (27)
C_7	2i	0.2181 (22)	0.4667 (22)	0.0733 (24)

[a] Numbers in parentheses represent standard deviations occurring in the last digit of the parameter.

TABLE II

FINAL ANISOTROPIC THERMAL PARAMETERS ($\times 10^4$) FOR $(\alpha\text{-}C_6H_7NH)_2SbBr_9$[a,b]

Atom	Position	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Sb	1a	83 (2)	63 (1)	117 (2)	−31 (1)	23 (1)	−10 (1)
Br_1	2i	94 (2)	122 (2)	196 (3)	−20 (2)	23 (2)	−2 (2)
Br_2	2i	169 (2)	94 (2)	158 (3)	−66 (2)	63 (2)	−10 (2)
Br_3	2i	156 (2)	94 (2)	148 (3)	−59 (2)	43 (2)	−41 (2)
Br_4	1g	139 (3)	79 (2)	151 (4)	−48 (2)	49 (3)	−17 (2)
Br_5	2i	145 (3)	122 (2)	265 (4)	−40 (2)	57 (2)	−12 (3)
N_1	2i	155 (22)	97 (19)	405 (44)	−40 (17)	61 (24)	−50 (24)
C_2	2i	134 (24)	128 (24)	197 (32)	−36 (19)	20 (22)	−28 (23)
C_3	2i	168 (26)	113 (22)	239 (35)	−65 (20)	85 (24)	−58 (23)
C_4	2i	155 (25)	123 (24)	253 (38)	−62 (20)	82 (25)	−85 (25)
C_5	2i	131 (25)	160 (30)	221 (35)	−3 (22)	47 (23)	−27 (26)
C_6	2i	255 (39)	88 (23)	371 (53)	−25 (24)	107 (37)	35 (29)
C_7	2i	212 (33)	169 (31)	234 (40)	20 (26)	6 (28)	26 (29)

[a] The form of the anisotropic temperature factor expression is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$. [b] Numbers in parentheses are standard deviations occurring in the last digit of the parameter.

TABLE III

FINAL ROOT-MEAN-SQUARE THERMAL DISPLACEMENTS ALONG PRINCIPAL AXES AND THE EQUIVALENT ISOTROPIC TEMPERATURE FACTORS[a] FOR $(\alpha\text{-}C_6H_7NH)_2SbBr_9$

	Rms displacement, Å			Equiv isotropic temp factor, Å²
Atom	Min	Med	Max	
Sb	0.154	0.170	0.184	2.28
Br_1	0.178	0.239	0.240	3.86
Br_2	0.163	0.213	0.244	3.46
Br_3	0.164	0.217	0.236	3.41
Br_4	0.173	0.199	0.220	3.10
Br_5	0.221	0.234	0.269	4.62
N_1	0.20	0.23	0.34	5.5
C_2	0.20	0.23	0.27	4.3
C_3	0.19	0.23	0.27	4.2
C_4	0.18	0.22	0.28	4.3
C_5	0.20	0.24	0.30	5.0
C_6	0.18	0.30	0.33	6.1
C_7	0.20	0.28	0.36	6.5

[a] The isotropic temperature factor equivalent to the anisotropic form was calculated by the formula $B_{iso} = (4/3)(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + 2B_{12}ab \cos \gamma + 2B_{13}ac \cos \beta + 2B_{23}bc \cos \alpha)$, where B_{ij} are the anisotropic thermal parameters defined in Table II and a, b, c, α, β, and γ are the unit cell lattice parameters: W. C. Hamilton, *Acta Cryst.*, **12**, 609 (1959).

TABLE IV

CALCULATED POSITIONAL PARAMETERS FOR HYDROGEN IN $(\alpha\text{-}C_6H_7NH)_2SbBr_9$

Atom	Position	x	y	z
H_1	2i	0.3128	0.1674	0.1063
H_3	2i	0.4919	0.5076	0.2664
H_4	2i	0.7441	0.3378	0.4297
H_5	2i	0.7930	0.0783	0.4520
H_6	2i	0.5641	−0.0025	0.3057
H_{7a}	2i	0.2125	0.4891	−0.0687
H_{7b}	2i	0.2041	0.5668	0.1404
H_{7c}	2i	0.1214	0.4267	0.0741
H_{7d}	2i	0.1461	0.4994	0.1659
H_{7e}	2i	0.1546	0.4216	−0.0431
H_{7f}	2i	0.2373	0.5617	0.0232

Description of the Structure

Structural Aspects.—The unit cell of crystalline $(\alpha\text{-pic})_2SbBr_9$ is illustrated in Figure 1, produced by Johnson's thermal-ellipsoid plot program.[20] The cell is composed of one tetragonally distorted octahedral $Sb^VBr_6^-$ ion (D_{4h} symmetry), one linear symmetrical Br_3^- ion, and two planar α-picolinium cations. Both anions lie on crystallographic centers of symmetry, and the two cations occupy general positions related by a center of symmetry.

The dimensions of the ions are summarized in Table VI. The standard deviations reported here (except where indicated) were derived from the complete var-

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[19] W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least-Squares Program," Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

[20] C. K. Johnson, "ORTEP, A Fortran Thermal-Ellipsoid Plot Program for the Crystal Structure Illustrations," Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

TABLE V

OBSERVED AND CALCULATED STRUCTURE FACTORS (IN ELECTRONS) FOR $(\alpha\text{-}C_8H_7NH)_2SbBr_9$

H	K	FO	FC
H K 0			
0	0		468.0
0	1	77.6	71.9
0	2	46.7	-39.6
0	3	106.4	-102.2
0	4	61.4	-58.0
0	5	36.2	32.7
0	6	161.7	163.8
0	7	42.2	43.7
0	9	22.2	-19.6
1	0	126.6	116.5
1	1	34.3	41.1
1	-1	--	98.9
1	2	151.4	132.4
1	-2	49.9	-38.7
1	3	--	-78.2
1	-3	99.0	-93.7
1	4	21.5	16.4
1	-4	71.5	71.5
1	5	69.2	66.1
1	-5	36.6	36.9
1	6	74.0	71.7
1	-6	104.7	102.7
1	-7	53.8	52.8
1	8	38.9	36.8
1	-8	17.8	-15.2
1	9	25.6	-23.7
1	-9	33.0	-31.7
1	10	14.1	10.9
1	-10	20.4	10.9
1	11	27.8	26.0
1	12	26.1	24.9
2	0	--	75.9
2	1	9.4	8.8
2	-1	129.1	116.3
2	2	72.2	-64.6
2	-2	164.7	154.9
2	3	103.7	-93.3
2	-3	41.7	-40.5
2	4	149.0	137.3
2	-4	6.2	-5.3
2	5	117.8	111.4
2	-5	21.7	18.3
2	6	90.6	84.1
2	-6	18.4	16.9
2	-7	28.9	27.3
2	8	36.4	-32.2
2	-8	49.4	47.1
2	9	41.7	-41.2
2	-9	14.8	-11.2
2	10	50.9	47.8
2	-10	11.6	9.8
2	11	34.9	33.4
2	12	29.1	30.6
3	0	219.1	211.9
3	1	7.4	-7.4
3	-1	126.8	116.1
3	2	152.7	-139.6
3	-2	93.6	87.0
3	3	54.5	-48.8
3	-3	36.8	-33.5
3	4	85.3	87.3
3	-4	79.0	-78.0
3	5	83.3	76.2
3	-5	18.8	-20.5
3	6	148.8	145.1
3	-6	88.1	86.9
3	-7	40.6	40.2
3	8	40.2	-39.1
3	-8	40.7	40.3
3	9	22.4	-21.3
3	10	27.8	26.4
3	-10	14.8	-11.6
3	11	24.4	24.2
3	12	40.3	39.7
4	0	112.5	109.4
4	1	31.9	-33.1
4	-1	72.6	67.8
4	2	52.9	49.2
4	-2	21.6	21.4
4	3	15.7	-14.0
4	-3	17.2	-16.5
4	4	18.1	27.5
4	-4	18.4	17.2
4	5	75.8	75.7
4	-5	14.5	-10.5
4	6	71.4	65.0
4	-6	58.3	57.4
4	7	32.9	-30.7
4	-7	35.8	33.7
4	8	24.9	17.1
4	-8	14.7	10.3
4	10	33.0	32.9
4	11	32.4	31.9
4	12	23.0	23.1
5	0	15.7	-12.4
5	1	50.6	-57.0
5	-1	65.9	62.5
5	2	12.1	9.5
5	-2	102.9	96.3
5	3	9.1	7.6
5	4	155.1	149.9
5	-4	31.3	30.8
5	5	90.3	89.1
5	-5	10.3	-8.7
5	6	13.1	11.3
5	7	59.6	-54.8
5	-7	15.6	15.8
5	8	17.4	-14.2
5	-8	24.8	23.6
5	10	65.4	66.5
5	11	42.8	41.3
5	12	15.9	13.7
6	0	51.9	48.3
6	1	39.3	-37.4
6	-1	54.4	51.7
6	2	61.0	-59.9
6	-2	104.8	100.3
6	-3	16.1	17.7
6	4	119.9	115.8
6	-4	30.3	-30.3
6	5	54.5	53.4
6	-5	18.5	-18.5
6	6	50.6	49.9
6	-6	11.1	12.3
6	7	18.0	-13.6
6	-7	18.6	16.4
6	8	27.7	-24.5
6	10	55.5	55.0
6	11	22.8	20.6
6	12	20.2	18.8
7	0	52.5	47.4
7	1	9.0	-9.0
7	-1	18.7	20.5
7	2	20.6	20.2
7	-2	19.8	17.0
7	3	33.9	33.5
7	-3	10.9	9.1
7	4	38.1	36.9
7	5	17.0	16.2
7	6	33.1	31.7
7	-6	28.0	25.0
7	7	33.2	-32.2
7	8	23.8	16.4
7	9	35.4	34.1
7	10	35.5	35.9
7	12	11.3	9.0
8	0	22.9	-19.2
8	1	35.4	-34.6
8	-1	15.0	11.3
8	2	46.5	47.2
8	-2	30.7	30.1
8	3	45.9	45.1
8	-3	19.3	21.6
8	4	64.8	64.6
8	-4	31.4	30.6
8	5	30.4	28.5
8	6	22.2	-22.5
8	7	38.9	-38.5
8	8	25.6	25.3
8	9	27.9	26.7
8	10	47.6	47.2
8	11	18.5	16.3
9	0	4.6	-4.2
9	1	13.4	-10.3
9	-1	14.1	13.4
9	-2	49.4	47.3
9	3	14.7	15.3
9	-3	17.3	14.3
9	4	64.2	67.6
9	5	18.7	15.3
9	7	12.2	-7.5
9	9	13.5	13.6
9	10	41.7	39.3
10	0	24.6	23.0
10	3	21.0	19.2
10	6	16.6	13.8
10	8	23.5	20.8
10	9	25.8	25.6
11	2	32.7	32.6
11	3	24.8	25.6
11	4	15.6	13.0
H K 1			
0	0	25.9	31.9
0	1	--	143.3
0	-1	101.0	98.0
0	2	38.6	31.4
0	-2	16.4	18.7
0	3	16.1	-11.1
0	-3	36.2	-33.8
0	4	18.8	20.4
0	-4	12.8	-10.3
0	5	25.2	28.9
0	-5	108.3	108.6
0	6	9.7	-10.4
0	-6	32.7	32.4
0	7	73.1	73.3
0	-7	45.4	46.3
0	8	18.9	20.4
0	9	24.7	25.0
0	10	11.9	9.8
0	-10	12.9	-7.6
0	-11	29.5	28.4
1	0	34.9	34.4
-1	0	35.0	32.7
1	1	94.5	91.3
1	-1	19.2	-17.0
-1	1	61.1	57.8
-1	-1	--	140.5
1	2	8.1	-7.4
-1	2	15.0	16.6
-1	-2	23.1	19.4
1	3	169.4	156.7
1	-3	102.2	104.0
-1	3	16.1	13.1
-1	-3	15.6	15.7
1	4	30.3	32.7
1	-4	7.3	-5.7
-1	-4	21.3	22.7
1	-5	61.0	63.7
-1	5	104.6	107.0
-1	-5	13.7	14.7
1	6	16.9	14.7
1	-6	27.1	27.9
-1	6	18.4	18.9
1	7	22.9	22.9
1	-7	15.4	15.7
-1	7	19.8	22.4
-1	-7	77.8	76.9
-1	8	13.5	10.5
1	9	51.5	50.1
1	-9	24.3	21.9
-1	9	10.8	8.1
-1	-9	24.8	21.8
1	10	18.5	18.2
1	11	17.1	14.7
1	-11	21.9	20.1
-1	11	24.4	27.1
2	0	35.5	32.6
-2	0	16.0	16.3
2	1	33.7	-23.6
2	-1	160.5	153.4
-2	1	9.2	-12.2
-2	-1	64.9	60.0
2	2	30.1	-28.0
-2	-2	12.3	-9.6
2	-3	78.6	77.4
-2	3	137.4	138.3
-2	-3	172.3	162.3
-2	4	17.8	19.4
2	5	130.6	132.5
2	-5	12.9	-8.0
-2	5	36.8	38.6
-2	-5	23.7	26.7
2	6	33.3	33.9
2	-6	13.0	13.1
-2	6	11.4	7.1
-2	-6	25.8	29.0
2	-7	40.6	43.5
-2	-8	20.4	-18.9
2	9	24.1	22.6
2	-9	22.0	25.4
-2	9	35.0	38.4
-2	-9	42.4	40.7
-2	10	18.5	10.8
-2	-10	15.3	14.4
2	11	29.4	31.2
-2	11	12.5	14.7
-2	-11	31.8	27.6
2	12	12.1	9.3
3	0	15.8	17.6
-3	0	9.2	12.0
3	1	104.9	103.0
3	-1	132.2	130.2
-3	1	150.9	147.1
-3	-1	9.4	-6.4
3	2	10.1	17.4
3	-2	26.6	28.3
-3	2	6.7	6.4
3	3	17.6	-14.6
3	-3	40.0	-38.8
-3	3	61.8	60.1
-3	-3	17.6	22.5
3	-4	17.6	-14.4
-3	4	14.8	20.8
3	5	70.2	69.0
3	-5	31.4	33.4
-3	-5	133.6	140.3
3	-6	14.9	14.4
-3	-6	26.3	28.9
3	7	69.1	68.3
3	-7	56.0	59.8
-3	-7	15.7	16.1
3	8	27.8	26.0
3	-8	18.6	18.9
-3	9	25.2	27.0
-3	10	14.9	13.2
3	11	20.4	18.8
-3	-11	35.4	37.2
-3	-12	11.8	11.1
4	0	14.5	13.8
-4	0	6.8	4.5
4	1	79.0	82.1
4	-1	13.4	-12.7
-4	1	64.1	63.0
-4	-1	128.1	131.2
4	2	12.2	-9.0
4	-2	19.8	20.5
-4	2	16.5	14.7
-4	-2	31.8	35.6
4	3	75.4	79.3
4	-3	43.2	44.4
-4	3	22.4	-22.7
-4	-3	12.0	7.7
4	4	46.2	51.5
-4	4	13.2	10.3
4	-5	48.0	50.1
-4	5	54.1	55.7
-4	-5	31.5	32.5
4	-6	19.0	18.2
-4	6	10.7	7.8
4	7	46.1	46.0
4	-7	10.0	7.6
-4	7	31.6	34.0
-4	-7	71.4	73.4
4	8	17.1	-14.1
-4	8	14.0	9.8
-4	-8	22.7	19.1
4	9	45.9	45.6
-4	-9	17.2	16.6
4	10	24.6	22.7
-4	-11	20.6	19.2
5	0	17.3	18.0
-5	0	9.6	11.0
5	1	36.0	-37.8
5	-1	64.8	59.8
-5	1	37.8	-38.0
-5	-1	68.5	69.8
5	2	14.6	-18.7
5	-2	31.9	32.6
-5	-2	11.3	8.1
5	3	84.2	84.9
5	-3	68.8	69.3
-5	3	66.7	66.9
-5	-3	94.2	98.6
5	4	24.0	26.4
-5	4	19.1	20.4
-5	-4	36.8	39.1
5	5	72.5	76.5
5	-5	11.5	-9.9
-5	5	50.6	52.7
5	6	25.1	22.6
-5	6	14.3	13.1
5	7	19.7	-13.8
5	-7	17.4	16.4
-5	7	12.2	-9.4
-5	-7	29.1	31.9
-5	-8	14.2	-13.9
-5	9	17.4	13.8
-5	-9	46.5	50.4
-5	-10	22.8	22.2
5	11	32.0	30.9
-5	-11	16.3	15.6
-6	0	15.7	16.5
6	1	22.8	20.4
6	-1	85.6	86.0
-6	1	60.5	58.5
-6	-1	14.9	-14.8
6	2	15.1	11.0
6	-2	19.0	16.9
-6	2	16.4	8.6
-6	-2	8.2	6.8
-6	3	52.7	51.7
-6	-3	60.8	61.9
6	4	13.1	8.6
-6	4	16.8	11.6
6	5	69.2	72.4
-6	-5	70.0	73.3
6	6	13.8	9.1
-6	-6	23.0	22.9
6	7	34.8	35.3
6	-7	31.6	33.0
-6	7	16.8	13.7
6	8	14.6	10.9
-6	-9	29.1	29.1
6	11	25.6	23.9
-6	-11	31.7	31.5
-7	0	12.8	11.8
7	1	56.5	56.1
-7	1	64.7	56.5
-7	-1	59.7	60.2
7	-2	15.6	14.3
-7	-2	24.9	25.7
7	3	39.0	40.4
7	-3	15.0	12.6
-7	-3	12.2	-13.5
7	4	26.4	27.8
7	-5	26.5	27.7
-7	5	20.8	21.1
-7	-5	42.3	44.7
7	6	16.9	-12.7
7	7	31.5	33.9
-7	7	24.6	23.8
-7	-7	52.0	54.8
-7	-8	22.6	18.2
7	9	33.7	32.1
7	10	23.5	20.2
-7	-11	18.0	17.0
8	0	12.0	-8.2
-8	0	11.8	11.5
8	1	9.6	-8.4
-8	1	12.8	-10.8
-8	-1	64.4	64.1
8	-2	20.2	18.0
-8	-2	12.7	9.6
8	3	62.0	64.1
8	-3	40.5	42.0
-8	-3	37.3	39.7
8	4	28.7	29.5
-8	-4	16.1	12.3
8	5	26.5	23.9
-8	5	33.5	34.1
-8	-7	35.1	37.4
8	9	36.7	35.5
-8	-9	32.4	32.5
8	10	17.1	11.8
-8	-10	14.5	14.0
8	11	19.7	17.6
-9	1	15.7	15.0
9	-1	32.8	33.0
9	-2	16.3	13.6
9	3	16.3	14.8
9	-3	15.6	12.7
-9	3	29.5	29.0
-9	-3	40.8	40.6
9	5	37.6	38.2
-9	-5	29.0	29.9
-9	-6	17.5	15.4
9	7	14.4	9.8
9	8	13.8	8.7
9	9	18.8	14.3
-9	-9	24.1	24.1
-9	-11	18.7	17.1
10	1	24.7	26.9
-10	1	28.2	32.6
-10	-1	17.4	15.9
10	2	17.5	15.9
-10	-5	33.8	34.4
10	6	12.5	-8.0
-10	-6	22.1	17.7
10	7	23.0	23.8
-10	-7	20.3	23.6
10	8	19.2	15.5
-10	-8	15.4	10.4
-11	-1	26.2	29.6
-11	-2	11.4	10.0
-11	-3	8.7	6.4
-11	-7	26.9	26.2
H K 2			
0	0	--	-49.8
0	1	25.5	-22.0
0	-1	72.2	-67.6
0	2	258.0	242.2
0	3	132.5	122.9
0	-3	78.7	79.5
0	4	38.8	38.4
0	-4	146.1	152.1
0	5	50.9	-53.3
0	6	41.9	-38.9
0	-6	17.4	17.0
0	7	20.1	-20.6
0	8	89.7	93.8
0	9	48.5	49.1
0	-9	21.5	22.6
0	10	21.1	19.0
0	-10	32.6	34.6
1	0	136.4	-128.7
-1	0	140.0	126.4
1	-1	71.8	-67.8
-1	1	56.7	-54.6
-1	-1	39.1	-36.9
1	2	169.7	171.5
1	-2	118.6	117.5
-1	2	31.8	29.3
-1	-2	123.5	121.5
1	3	85.9	85.0
1	-3	86.8	90.1
-1	3	93.5	93.8
-1	-3	106.8	105.7
1	4	115.7	111.1
1	-4	127.4	133.1
-1	4	54.1	59.7
-1	-4	13.9	13.6
1	5	28.5	-30.3
1	-5	20.0	22.7
-1	5	27.3	-29.4
-1	-5	41.9	-45.3
1	6	52.3	-51.5
1	-6	54.9	-58.6
-1	6	33.5	34.5
-1	-6	21.8	20.0
1	-7	32.9	-34.2
-1	-7	14.7	-12.4
1	8	63.2	64.7
1	-8	31.0	33.1
-1	8	28.7	31.0
-1	-8	61.1	64.8
1	9	30.3	30.3
1	-9	20.4	23.3
-1	9	33.9	38.7
-1	-9	45.3	45.6
1	10	40.5	41.5
1	-10	42.0	42.0
-1	10	25.8	24.1
-1	-10	13.9	16.8
1	11	11.5	-8.7
-1	-11	14.9	-10.7
2	0	47.3	47.1
-2	0	162.9	-153.0
2	1	44.6	46.6
2	-1	46.0	-46.7
-2	1	69.3	-66.6
-2	-1	12.1	-7.7
2	2	42.6	44.0
2	-2	63.9	65.1
-2	2	36.1	36.7
-2	-2	286.9	261.3
2	3	66.6	71.1
2	-3	51.2	55.5
-2	3	80.3	83.0
-2	-3	125.2	112.0
2	4	52.2	57.2
2	-4	29.5	31.9
-2	4	168.3	176.0
-2	-4	81.6	77.2
2	5	68.3	-67.0
2	-5	12.5	10.3
-2	5	13.7	13.1
-2	-5	40.2	-42.4
2	6	37.8	36.9
2	-6	22.1	19.2
-2	6	23.8	-24.4
-2	-6	67.2	-66.0
2	7	38.6	38.6
2	-7	20.1	-19.3
-2	7	18.5	-20.5
-2	-7	20.1	-17.8
2	8	48.7	50.0
2	-8	30.8	37.7
-2	-8	90.6	91.4
2	9	27.0	29.8
2	-9	22.2	22.5
-2	9	19.5	20.3
2	-10	16.2	15.5
-2	10	40.6	41.4
-2	-10	27.9	30.0
2	11	24.5	-25.0
3	0	68.1	65.4
-3	0	53.8	-53.9
3	1	59.7	62.2
3	-1	64.3	-65.4
-3	1	66.3	-67.7
-3	-1	26.6	25.7
3	2	171.7	175.0
3	-2	41.2	-42.2
-3	2	126.2	125.3
-3	-2	84.2	85.3
3	3	51.4	54.5
3	-3	28.3	29.3
-3	3	77.0	80.9
-3	-3	70.6	73.3
3	4	54.7	-58.4
3	-4	77.8	80.8
-3	4	80.0	82.1
-3	-4	105.6	105.9
3	5	73.2	-73.9
3	-5	25.5	25.6
-3	5	21.3	19.6
-3	-5	39.7	-42.3
3	6	24.6	21.1
3	-6	41.7	41.7
-3	6	42.6	-42.9
-3	-6	17.9	-12.3
3	7	43.5	41.9
-3	7	34.8	-36.1
-3	-7	24.0	19.9
3	8	100.7	103.0
-3	8	40.4	42.7
-3	-8	43.6	45.6
3	9	35.2	36.0
-3	9	25.7	25.9
-3	-9	28.0	25.2
-3	10	29.6	32.1
-3	-10	36.5	37.8
3	11	26.1	-26.4
-3	-11	15.8	-14.3
4	0	23.7	-25.3
-4	0	90.8	89.0
4	1	40.8	42.6
4	-1	41.5	-43.4
-4	-1	53.6	55.2
4	2	149.9	154.7
-4	-2	83.3	86.4
4	3	34.5	37.3
4	-3	17.9	16.1
-4	3	38.2	41.5
-4	-3	63.1	65.2
4	4	18.9	22.0
4	-4	96.5	100.3
-4	-4	11.2	-7.2
4	5	30.8	-33.4
4	-5	32.4	32.9
-4	5	12.9	11.6
-4	-5	76.6	-77.6
-4	6	41.9	44.5
-4	-6	48.0	49.1
4	7	23.0	19.9
4	-7	14.8	-13.9
-4	7	14.7	-14.6
-4	-7	42.6	43.1
4	8	78.9	80.8
-4	8	13.2	12.1
-4	-8	66.1	69.8
4	9	20.9	18.5
-4	9	19.1	17.3
-4	-9	28.6	34.7
4	10	14.1	9.1
4	11	14.6	-10.3
-4	-11	25.4	-27.8
-4	-12	13.7	11.4
5	0	37.1	37.3
-5	0	15.9	15.7
5	1	42.3	44.4
5	-1	14.6	-10.6
-5	1	59.1	-61.2
-5	-1	55.7	56.1
5	2	32.6	34.0
5	-2	42.9	43.9
-5	2	40.2	-40.0
-5	-2	196.3	200.5
5	3	15.3	-10.5
5	-3	12.3	12.2
-5	3	20.9	20.0
-5	-3	39.5	44.0
5	4	28.4	29.1
5	-4	19.1	18.5
-5	4	99.9	105.4
-5	-4	42.1	-46.2
5	5	23.5	-23.8
5	-5	16.9	16.7
-5	5	32.5	34.3
-5	-5	53.1	-56.2
5	6	44.3	46.3
-5	6	19.1	18.0
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-5	-7	29.4	30.4
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-5	8	12.5	-9.5
-5	-8	99.9	107.7
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5	12	24.5	20.4
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6	-4	13.7	14.6
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-6	5	28.6	29.1
-6	-5	26.6	-27.3
6	6	65.7	70.0
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6	7	47.0	51.6
-6	7	17.9	-13.1
-6	-7	36.7	37.8
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-6	8	10.3	7.3
-6	-8	49.3	55.0
6	10	18.6	-17.7
-6	-10	18.2	17.2
6	11	17.6	-15.4
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-7	0	69.3	71.7
7	1	22.9	23.0
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-7	-1	55.6	57.7
7	2	70.0	72.7
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-7	5	16.9	17.1
-7	-5	30.1	-30.8
-7	6	22.3	22.9
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7	7	23.5	22.1
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7	8	46.0	48.7
-7	-8	36.4	40.1
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-7	-12	23.4	25.1
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8	1	21.7	19.0
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-8	1	12.0	-10.9
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8	2	9.3	11.5
8	-2	23.5	25.7
-8	2	30.0	-32.8
-8	-2	67.3	70.1
8	3	16.8	-17.7
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8	4	26.4	25.8
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-8	-4	40.6	-43.4
8	5	14.0	14.2
-8	5	18.9	21.5
-8	-5	25.0	-22.9
8	6	33.3	35.1
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-8	-6	50.1	51.5
8	7	29.3	31.3
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8	8	15.4	11.6
-8	-8	50.3	53.7
8	9	23.8	-20.9
-8	-10	16.0	-16.1
9	0	40.7	43.1
-9	0	9.8	10.0
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-9	-1	14.4	16.8
-9	-2	44.4	45.7
9	3	20.9	-15.2
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9	7	28.8	28.3
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9	8	16.8	9.8
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-9	-9	18.7	-14.2
-10	0	26.0	29.9
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-10	-4	19.7	15.8
-10	-5	11.0	10.4
10	6	25.1	23.0
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-10	-7	32.8	32.8
-10	-9	24.2	-19.0
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H K 3			
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0	5	32.0	-28.5
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0	7	37.7	35.3
0	9	45.2	42.9
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0	10	14.5	13.5
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-1	1	86.9	93.2
-1	-1	74.1	76.2
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-1	-2	32.7	35.1
1	3	90.2	95.7
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-1	-4	16.2	17.5
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-1	-5	54.3	53.5
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-1	6	12.0	-14.7
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-1	7	60.6	58.6
-1	-7	35.5	37.3
-1	8	23.8	25.4
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1	9	26.8	30.3
1	-9	39.6	42.2
-1	9	18.3	17.4
-1	-9	20.0	18.2
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-2	-3	83.4	86.0
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-2	5	75.3	76.3
-2	-5	23.0	-27.0
-2	6	15.5	13.2
-2	-6	24.1	-25.0
2	7	63.2	60.7
2	-7	27.5	32.0
-2	7	17.3	12.9
-2	-7	53.8	54.1
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2	-8	12.2	9.8
-2	8	12.0	8.9
-2	-8	26.8	24.9
2	9	12.2	11.0
2	-9	13.6	13.0
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-2	-9	45.4	47.4
-2	-10	14.3	12.7
-3	0	8.8	-10.0
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3	-1	39.8	-41.0
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3	2	44.8	46.4
3	-2	12.6	-10.8
-3	-2	23.0	23.1
3	3	56.4	60.3
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-3	3	111.7	116.3
-3	-3	152.1	140.2
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-3	4	25.2	25.0
-3	-4	13.0	11.4
3	5	27.3	-27.9
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-3	5	10.5	13.0
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3	-6	10.6	7.6
3	7	70.1	70.0
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-3	9	31.3	33.4
-3	-9	50.6	47.2
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4	-4	26.1	24.6
-4	4	14.2	13.0
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-4	-9	17.2	14.1
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5	0	15.8	16.5
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-5	-3	24.2	26.0
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5	-4	14.8	14.0
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5	-5	15.2	12.7
-5	5	45.6	46.6
-5	-5	11.5	-8.6
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5	7	44.9	47.5
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-5	7	25.6	24.8
-5	-7	73.7	76.7
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-5	-9	24.7	23.2
5	10	19.0	-14.1
5	11	22.0	17.8
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6	1	83.0	83.1
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-6	-1	36.3	36.3
6	2	21.9	20.9
6	-2	16.0	-12.8
-6	-2	13.0	9.2
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6	-4	11.1	9.9
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6	7	53.7	58.7
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-6	-9	36.4	37.4
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7	0	12.3	9.5
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7	1	29.5	27.4
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-7	-4	9.4	-9.1
7	5	16.0	11.8
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7	6	18.4	15.1
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7	7	23.8	24.4
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-7	-8	18.8	13.8
7	9	19.9	18.5
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8	0	18.3	20.4
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8	-1	30.3	29.9
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-8	-2	14.9	16.1
8	5	39.8	39.3
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8	7	19.4	19.5
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9	0	16.7	17.6
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-10	-6	18.2	14.8
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-11	-5	23.8	23.5
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-12	-3	15.2	13.9
H K 4			
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0	-3	28.1	-29.6
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0	-7	19.9	21.8
0	-8	18.4	18.2
0	9	23.5	-24.5
0	10	22.7	25.3
0	-10	20.4	14.1
0	11	26.9	23.5
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-1	2	48.0	51.4
-1	-2	40.5	-43.0
1	3	40.0	-44.4
1	-3	22.0	-21.8
-1	3	39.1	-44.9
-1	-3	55.3	-60.3
1	4	80.2	81.9
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-1	-4	24.9	24.0
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-1	5	24.9	24.2
-1	-5	22.3	22.5
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-2	-4	35.4	-37.3
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2	-6	58.1	57.5
-2	6	100.5	105.2
-2	-6	84.9	88.5
2	-7	26.4	26.1
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-2	-7	24.4	19.4
2	-8	15.6	15.7
-2	-8	31.0	28.3
-2	9	20.0	-19.0
2	10	21.1	18.1
2	11	18.5	18.5
3	0	15.1	15.9
-3	0	28.6	26.8
3	1	27.3	-27.6
3	-1	38.8	36.3
-3	1	66.9	66.0
-3	-1	16.7	14.9
3	2	38.7	36.9
3	-2	39.9	39.3
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-3	-2	55.3	49.7
3	3	11.1	8.5
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3	4	66.4	67.6
3	-4	36.9	36.2
-3	4	41.0	41.0
-3	-4	59.9	57.7
3	5	54.7	57.2
-3	5	20.9	21.1
-3	-5	57.0	57.2
3	6	21.7	21.5
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-3	6	37.2	39.1
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3	7	39.1	-37.8
3	-7	14.1	12.9
-3	7	26.0	28.3
-3	-8	21.1	12.0
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3	10	35.6	37.2
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3	11	34.0	30.3
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-4	1	75.0	68.7
4	2	25.3	-25.4
4	-2	83.9	82.2
-4	2	107.5	102.8
-4	-2	74.3	-76.9
4	-3	15.9	13.5
-4	3	18.9	-20.0
-4	-3	44.7	-46.0
4	4	100.5	99.6
-4	4	36.5	-35.3
-4	-4	86.5	85.0
4	5	55.2	55.2
4	-5	12.1	-11.4
-4	-5	66.3	64.4
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-4	6	32.3	28.4
-4	-6	82.6	82.1
4	7	15.4	-14.8
4	-7	14.8	10.5
-4	7	24.2	23.0
4	8	13.2	-17.6
-4	8	40.4	39.1
-4	-8	28.7	-29.5
-4	-9	29.0	-24.8
4	10	43.1	46.0
-4	-10	31.0	29.5
4	11	23.1	22.9
-4	-11	21.3	20.0
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5	-1	25.8	23.7
-5	1	66.7	63.8
-5	-1	14.6	-12.0
5	2	15.7	-12.1
5	-2	33.6	31.7
-5	2	29.9	29.7
-5	-2	29.1	-30.3
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-5	4	26.9	-28.7
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-5	-5	47.1	47.0
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5	-6	22.0	20.2
-5	6	63.6	62.4
-5	-6	82.2	86.1
-5	7	32.2	30.1
-5	8	15.9	17.3
-5	-9	10.8	-6.7
5	10	29.7	29.0
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-5	-11	17.2	17.8
-6	0	24.1	24.1
6	1	17.4	-15.9
6	-1	10.4	7.5
-6	1	43.8	42.9
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6	2	36.7	38.3
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-6	-2	38.9	39.2
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6	4	33.1	32.6
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-6	6	13.5	16.2
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-6	-7	28.3	-28.9
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6	9	24.0	23.6
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7	0	13.0	-10.5
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7	-1	11.1	12.4
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7	4	55.3	55.6
-7	-4	103.1	106.9
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-7	-6	21.8	20.2
7	7	16.0	-13.8
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-7	-8	21.8	-19.7
7	9	13.1	9.6
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-7	-11	21.3	25.2
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8	-1	12.2	8.3
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-8	-2	19.9	-21.0
8	3	11.2	7.2
-8	3	14.5	11.4
-8	-3	11.8	10.8
8	4	28.8	27.2
-8	4	16.4	-15.3
-8	-4	48.0	49.2
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8	6	18.7	14.6
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-8	-6	36.7	37.3
-8	-7	15.4	-11.8
-8	-10	32.8	30.6
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-9	-1	16.3	-13.5
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-9	-2	34.2	32.8
9	3	15.8	18.7
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-9	-4	29.2	30.9
-9	-5	16.2	13.7
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-9	-9	23.6	24.4
-9	-10	25.9	28.7
-10	0	18.4	-13.6
-10	-1	21.2	-18.9
-10	2	31.8	31.1
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-10	3	14.5	15.6
-10	-3	23.8	23.9
-10	-4	53.1	52.5
-10	-5	20.7	17.9
-10	-6	15.9	-11.8
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-10	-8	11.4	10.7
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-11	-4	27.6	31.8
H K 5			
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0	-4	16.0	-13.0
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0	-5	12.7	11.7
0	6	29.5	32.0
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0	-7	23.5	24.2
0	8	20.0	-19.1
0	9	22.5	16.8
0	-9	17.5	13.9
1	0	39.5	35.0
-1	0	44.2	38.4
1	1	18.4	20.3
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1	-2	18.5	18.2
-1	2	10.3	-8.3
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1	-8	17.5	11.7
-1	9	23.2	17.9
-1	10	18.8	13.0
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-2	0	43.3	42.2
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2	9	19.0	20.7
2	10	19.9	19.6
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-3	-9	17.4	15.4
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-4	0	21.1	21.6
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5	10	18.6	17.8
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-6	-4	24.0	25.2
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-6	-5	18.8	17.5
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-6	-10	20.5	20.7
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7	3	25.8	28.8
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-7	-10	19.4	18.0
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8	3	12.3	11.8
-8	3	13.6	12.8
-8	-3	15.2	18.1
-8	-5	47.6	50.0
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-9	1	17.9	17.4
-9	-1	34.3	33.8
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-9	-3	10.7	10.2
-9	-4	16.2	12.2
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-10	-9	30.2	28.1
-11	-3	14.9	17.1
-11	-5	23.5	21.8
H K 6			
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0	-3	31.9	29.9
0	4	48.4	50.5
0	-4	31.2	31.4
0	5	18.9	-15.5
0	8	26.7	24.9
0	-8	19.9	20.5
0	9	17.5	16.0
0	10	16.3	17.5
1	0	43.2	42.0
-1	0	37.7	-37.7
1	1	28.5	28.3
1	-1	19.7	-19.6
-1	-1	27.8	-26.8
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-1	2	86.2	93.7
-1	-2	32.1	31.8
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1	-3	16.9	14.8
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1	6	19.7	17.2
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1	7	24.9	23.4
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-3	-9	21.2	23.4
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4	2	19.9	17.7
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H K 7			
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-1	-5	15.9	10.7
-1	-6	14.7	-12.6
1	7	37.2	39.6
1	8	18.9	19.4
1	9	18.4	15.8
-2	0	23.2	-22.7
2	1	37.0	33.6
2	-1	15.3	-18.2
-2	-1	13.7	-9.9
2	2	23.9	24.5
-2	2	29.4	30.1
-2	-2	14.7	15.8
2	3	40.8	40.6
2	-3	32.4	31.4
-2	3	38.3	48.5
-2	-3	35.0	38.9
2	-4	19.7	21.1
-2	-4	16.8	19.0
2	-5	23.8	23.4
-2	5	20.1	-9.6
-2	-5	25.5	26.4
-2	6	17.2	-15.4
-2	-6	17.4	-12.1
2	7	25.6	25.2
-2	7	21.4	21.0
2	8	13.4	13.9
-2	-8	14.2	10.0
-3	0	17.7	-16.9
3	1	19.7	20.8
3	-1	12.3	14.4
-3	1	18.6	14.1
-3	-1	37.4	38.1
3	2	15.8	19.1
-3	2	19.8	19.1
-3	-2	22.1	23.3
3	3	15.6	11.9
3	-3	18.7	16.8
-3	3	24.3	21.4
-3	-3	30.7	31.1
3	4	15.2	-13.4
3	-4	16.7	12.8
-3	-4	13.1	10.7
3	5	13.3	14.7
-3	5	24.5	20.9
3	6	20.2	14.5
-3	-6	14.7	-13.9
3	7	24.4	25.3
-3	7	18.4	15.8
-3	-7	21.6	21.8
-3	8	20.4	13.9
-3	-8	18.6	17.9
4	0	16.7	14.6
-4	0	16.0	-13.6
4	1	40.2	40.9
4	-1	14.8	10.2
-4	1	14.2	-13.1
-4	-1	24.8	26.4
4	2	19.7	16.8
-4	-2	28.6	29.0
-4	3	50.4	50.9
-4	-3	60.3	62.6
4	4	18.2	-17.4
-4	4	15.1	15.9
-4	5	22.1	20.3
-4	-5	19.9	-13.6
-4	-6	19.1	-15.3
4	7	35.2	34.9
-4	-7	19.4	17.1
-4	-8	17.7	17.4
-5	0	14.0	-14.2
5	1	31.4	30.2
-5	1	16.5	12.5
-5	-2	23.4	23.5
-5	3	42.0	42.3
-5	-3	48.3	45.4
-5	4	20.4	19.5
-5	-5	17.1	12.1
-5	-8	18.6	16.4
-5	-9	26.1	19.9
-6	1	22.6	21.1
-6	-1	40.1	35.3
-6	-2	26.3	25.1
-6	5	17.3	15.1
-6	-7	32.4	35.7
-6	-8	21.6	22.5
-7	1	12.8	-8.9
-7	-1	45.4	45.5
-7	-2	22.8	21.6
-7	3	16.2	15.5
-7	-3	31.6	27.1
-7	4	16.0	11.4
-7	5	20.1	21.5
-7	-7	29.4	33.5
-7	-8	18.4	15.8
-8	-1	15.1	13.4
-8	3	27.0	25.1
-8	-3	24.0	26.0
-9	1	13.9	21.4
-9	-1	22.9	18.1
-9	-4	11.6	-9.9
-9	-5	21.9	19.1
-9	-6	17.2	13.3
-9	-7	23.4	23.8
-10	-1	27.8	27.8
-10	-2	12.8	7.8
H K 8			
0	0	44.6	42.5
0	-1	20.9	20.9
0	-2	16.0	19.0
0	3	16.3	-12.2
0	4	8.5	13.5
0	5	17.5	15.7
0	6	30.7	33.7
1	0	21.2	21.7
-1	0	22.0	23.3
-1	-1	22.5	22.8
1	2	20.1	15.7
-1	-2	34.8	33.8
-1	3	16.0	-11.9
1	4	15.1	13.7
1	-4	17.7	13.1
-1	4	25.7	27.6
1	5	13.3	14.4
-1	5	25.8	21.9
1	6	20.0	19.7
-1	6	32.4	28.7
-2	0	29.3	26.8
2	-1	11.8	13.6
-2	1	12.7	9.0
-2	-1	17.9	13.5
2	-2	26.1	25.5
-2	2	22.1	24.3
2	4	29.0	31.4
-2	-4	20.6	18.4
2	5	14.2	22.2
2	6	15.5	13.0
-2	6	19.0	19.7
-2	-6	18.1	18.3
3	0	21.4	19.1
-3	0	60.7	57.8
3	-1	17.3	13.0
-3	1	22.8	19.3
-3	-1	17.6	15.1
-3	3	18.1	-14.1
-3	-3	16.2	-16.1
3	4	19.3	23.0
3	5	14.2	13.1
-3	6	34.3	34.3
-3	-6	34.0	36.4
-3	7	20.3	14.0
-3	-7	17.3	14.7
-4	0	42.0	39.5
-4	1	16.4	16.5
-4	-2	21.2	23.0
-4	3	11.3	-15.5
-4	-5	15.3	9.6
-4	6	27.8	27.9
-4	-6	25.7	22.3
-5	0	20.8	15.5
-5	1	22.5	21.5
-5	2	28.1	27.7
-5	-4	29.2	28.3
-5	-5	18.3	19.2
-5	-6	24.5	20.1
-6	0	45.3	40.9
-6	1	20.2	22.3
-6	2	25.0	27.8
-6	-2	20.2	-16.8
-6	-4	23.6	19.5
-6	-5	17.7	18.6
-6	-6	30.5	35.0
-7	0	32.4	28.2
-7	1	18.7	18.7
-7	2	14.3	10.0
-7	-2	11.9	7.9
-7	-6	27.8	23.5
-8	1	18.8	13.2
-8	2	26.3	22.0
-8	-4	24.5	28.0
-8	-5	25.1	19.1
-9	-2	9.9	-8.0
-9	-4	28.3	30.0
-9	-5	19.4	15.7
H K 9			
0	0	7.3	12.8
0	1	14.9	14.4
0	-1	26.4	30.0
0	4	13.1	9.6
0	5	22.9	23.9
-1	0	20.4	19.3
-1	-1	39.1	38.4
1	2	13.5	-10.1
-1	2	12.7	-14.5
1	3	19.0	16.0
1	4	14.3	17.0
-1	5	30.6	33.8
-2	0	19.8	18.4
-2	1	17.4	12.8
-2	-1	20.5	20.1
-2	2	16.3	-12.2
-2	5	14.0	20.0
-3	0	20.9	21.3
-3	1	30.9	30.9
-3	-1	26.2	20.0
-3	-3	15.6	-10.4
-3	5	22.7	15.6
-4	0	21.1	22.2
-4	1	18.1	22.5
-4	-1	27.9	30.0
-4	-5	17.1	17.6
-5	0	16.2	16.8
-5	1	16.2	17.8
-5	3	13.8	8.8
-5	-5	19.6	21.0
-6	0	14.0	10.5
-6	1	28.4	30.1
-6	-5	30.7	32.1
-7	0	14.0	10.1
-7	1	25.3	25.1
-7	-1	12.8	9.7
-8	-3	19.0	15.1

iance–covariance matrix using the function and error program of Busing, *et al.*[21] The $SbBr_6^-$ ion appears to deviate from perfect octahedral symmetry by the lengthening of two Sb–Br bonds to form an ion which has a tetragonal-bipyramidal configuration, disregarding the slight deviations of the Br–Sb–Br angles from 90°. This lengthening, to be discussed in more detail below, is due to the direct participation of these two apical bromine atoms in the charge-transfer process which occurs in the crystal. The two significantly different Sb–Br bond lengths are 2.565 ± 0.003 and 2.547 ± 0.003 Å (after correction for rigid-body libration[22]) and differ by 0.018 Å, or six standard deviations

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(21) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, a Fortran Crystallographic Function and Error Program," Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

(22) (a) D. W. J. Cruickshank, *Acta Cryst.*, **9**, 754 (1956); (b) C. L. Coulters, P. K. Gantzel, and K. N. Trueblood, A.C.A. Computer Program 232 (UCLA-TOI), Department of Chemistry, University of California, Los Angeles, Calif.

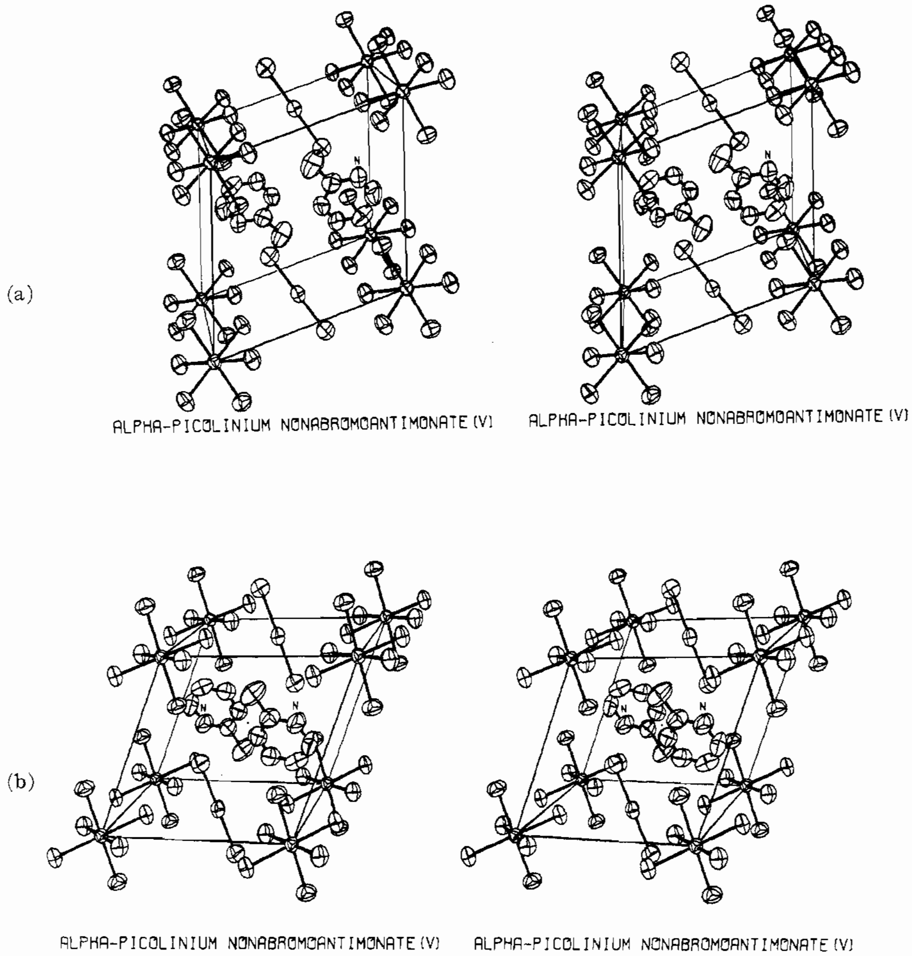

Figure 1.—The complete unit cell of $(\alpha\text{-}C_6H_7NH)_2SbBr_9$, shown as stereographic pairs, depicting the nearly octahedral $Sb^VBr_6^-$ and linear Br_3^- anions and the planar $\alpha\text{-}C_6H_7NH^+$ cations. The thermal ellipsoid boundaries are at the 75% probability level. The origin in both views is in the upper right forward corner with x down, y to the left, and z into the paper. (a) View of the sandwich arrangement of the cation between Br···Br contacts in the anion chains. (b) Generalized view of the packing.

in bond lengths. They appear to agree extremely well with the two crystallographically independent Sb(V)–Br bond lengths of 2.560 ± 0.008 and 2.541 ± 0.008 Å found in $(NH_4)_4Sb^{III}Sb^VBr_{12}$.[16,23]

The Br–Br bond in the Br_3^- ion is 2.543 ± 0.002 Å in length if no thermal correction is applied and appears to agree very well with the two independent values 2.53 and 2.54 Å observed for Br_3^- in $(CH_3)_3NHBr_2$.[24] If a "riding motion" of each terminal bromine atom on the central bromine atom is assumed,[25] the bond length increases to 2.554 ± 0.002 Å (Table VI); this correction assumes that the central bromine atom is stationary relative to the terminal atom. As can be seen in Figure 1, the Br_3^- ion librates to some extent along its linear axis, a fact visible by the shape of the thermal ellipsoid of the central bromine. The terminal atoms, whose thermal ellipsoids are more spherical, are probably involved in a small amount of riding motion in addition to a possible rotation of the ion about its linear axis. The correction for a riding motion may therefore be considered as an upper limit.

The least-squares plane through the α-picolinium ring (Table VII) shows that the ring atoms and the methyl group do not deviate significantly from coplanarity. The dimensions of the ring are summarized in Table VI and illustrated in Figure 2. Figure 1 clearly shows some anisotropic motion of the ring. Some of this motion may be influenced by van der Waals contact with vibrating bromine atoms. Application of the Cruickshank correction results in an increase of only 0.01 Å in all bonded distances, an increase of less than one standard deviation, and so is not significant. Thermal motion of the cation is greatest in the region of the $SbBr_6^-$ ions (Table III). The methyl group is affected the most, and, if it is assumed to ride on C_2, an increase of 0.03 Å in bond length is obtained, a value which may be considered as an upper limit. The average corrected ring distances C–N (1.35 Å) and C–C (1.35 Å) and the ring–methyl C–C distance (1.52–1.55 Å) are reasonably consistent with values found for related rings previously reported. The microwave structure determination of pyridine has shown the C–N and

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(23) The bond lengths reported here for $(NH_4)_4Sb_2Br_{12}$ have been corrected for rigid-body libration of each ion about its center of gravity, using the Cruickshank treatment, and are considered to be much more meaningful than the "riding-motion" treatment of bromine on antimony originally used in ref 16.

(24) C. Romers and E. W. M. Keulemans, *Koninkl. Ned. Akad. Wetenschap., Proc.*, **B61**, 345 (1958).

(25) W. R. Busing and H. A. Levy, *Acta Cryst.*, **17**, 142 (1964).

TABLE VI

DIMENSIONS OF THE IONS IN $(\alpha\text{-}C_6H_7NH)_2SbBr_9$[a]

Atoms	Length, Å Uncor	Length, Å Cor[b]	Atoms	Angle, deg[c]
		(a) $Sb^VBr_6^-$ Anion		
Sb–Br_1	2.556 (0.002)	2.565 (0.003)	Br_1–Sb–Br_2	89.72 (0.05)
Sb–Br_2	2.538 (0.002)	2.547 (0.003)	Br_1–Sb–Br_3	89.53 (0.06)
Sb–Br_3	2.539 (0.002)	2.548 (0.003)	Br_2–Sb–Br_3	89.27 (0.05)
Br_1–Br_2	3.594 (0.002)	3.605 (0.003)		
Br_1–Br_3	3.588 (0.002)	3.601 (0.003)		
Br_2–Br_3	3.567 (0.002)	3.580 (0.003)		
		(b) Br_3^- Anion		
Br_4–Br_5	2.543 (0.002)			
		(c) α-Picolinium Cation		
N_1–C_2	1.35 (0.02)	1.36 (0.03)	C_6–N_1–C_2	119.9 (1.4)
C_2–C_3	1.37 (0.02)	1.38 (0.03)	N_1–C_2–C_3	116.8 (1.4)
C_3–C_4	1.29 (0.02)	1.30 (0.03)	C_2–C_3–C_4	122.3 (1.6)
C_4–C_5	1.33 (0.02)	1.34 (0.03)	C_3–C_4–C_5	122.4 (1.5)
C_5–C_6	1.37 (0.03)	1.37 (0.04)	C_4–C_5–C_6	116.7 (1.5)
C_6–N_1	1.34 (0.02)	1.35 (0.03)	C_5–C_6–N_1	121.8 (1.7)
C_2–C_7	1.52 (0.02)	1.53 (0.03)	N_1–C_2–C_7	123.1 (1.5)
			C_3–C_2–C_7	120.1 (1.7)

[a] Numbers given in parentheses refer to the standard deviation. [b] The corrected bond lengths were obtained by assuming rigid-body libration of each ion about its center of gravity using the Cruickshank treatment;[22] they are considered to be more meaningful in this case than the "riding motion" of one atom on another. The esd's in this correction include an (arbitrary) uncertainty of 0.001 Å in bond lengths for $SbBr_6^-$ and 0.01 Å for $\alpha\text{-}C_6H_7^+$ for the rigid-body assumption. For comparison in corrections, the "riding-motion" treatment (using ORFFE) gives the following corrected bond lengths: $SbBr_6^-$ (bromine riding on antimony): Sb–Br_1 = 2.568 (0.002), Sb–Br_2 = 2.547 (0.002), and Sb–Br_3 = 2.548 (0.002) Å; Br_3^- (Br_5 riding on Br_4): 2.554 (0.002) Å; $\alpha\text{-}C_6H_7^+$ (C_7 riding on C_2): 1.55 (0.02) Å. These may be considered as an upper limit. [c] The bond angles are unaffected by the rigid-body correction.

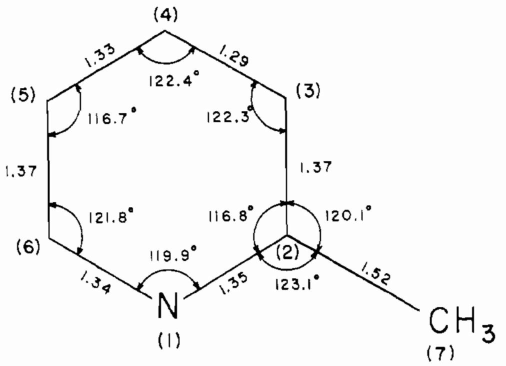

Figure 2.—Dimensions (before correction for thermal motion) of the α-picolinium cation in $(\alpha\text{-}C_6H_7NH)_2SbBr_9$.

C–C distances to be 1.340 and 1.394 Å, respectively.[26] The ring–methyl C–C distance in methylbenzene is reported to be 1.52 Å. Inspection of our C–C distances shows that they are, in general, shorter than expected and that there is considerable variation in these distances within the ring. However, it must be remembered that each atom in the cation contributes only 1.5% to the total electron density and so its position is less well defined; moreover, if the π cloud of the cation participates in charge transfer, these distances might be affected to some extent.

Although unexpected prior to this structural determination, this salt contains no trivalent antimony. Apparently for reasons of packing and existing crystal forces, a stable salt is formed only when antimony is fully oxidized as Sb(V). Nevertheless, two features predominante in this structure: infinite ···Br–Br–Br···Br–Sb–Br··· chains in the (120) crystal planes involving the Br_3^- and $SbBr_6^-$ ions and α-picolinium cations forming a sandwich about the –Br···Br– bridge of that chain. Such environments provide suit-

TABLE VII

EQUATIONS OF ATOMIC PLANES AND DISTANCES (Å) OF ATOMS FROM THESE PLANES[a]

(a) Plane[b] through N_1, C_2, C_3, C_4, C_5, C_6

$$-0.584X - 0.032Y + 0.811Z + 0.803 = 0$$

N_1	−0.03	C_5	−0.01	$Br_{1(a)}$	3.55
C_2	0.01	C_6	0.03	$Br_{1(c)}$	−3.75
C_3	0.01	C_7	0.06	Br_5	3.65
C_4	−0.01			$Br_{5(c)}$	−3.65

(b) [011] Crystal Plane through Sb_2, Sb_3, Sb_5, Sb_8, Br_4 $Br_{4(f)}$

$$-0.2180X + 0.6163Y + 0.7567Z - 6.0089 = 0$$

$Br_{1(a)}$	−0.161	$Br_{2(b)}$	0.302	Br_5	0.305

(c) [120] Crystal Plane through Sb_4, Sb_8, Br_4, $Br_{4(e)}$

$$-0.2007X - 0.9772Y - 0.0686Z + 4.7641 = 0$$

$Br_{1(a)}$	0.029	N_1	0.86	C_5	0.05
$Br_{2(a)}$	1.807	C_2	−0.40	C_6	1.08
$Br_{3(a)}$	1.806	C_3	−1.40	C_7	−0.72
Br_5	0.165	C_4	−1.17		

[a] The coordinate system used for the least-squares planes was: $X = xa \sin \gamma + zc(\cos \beta - \cos \alpha \cos \gamma)/\sin \gamma$; $Y = xa \cos \gamma + by + cz \cos \alpha$; $Z = zV/ab \sin \gamma$. [b] The atoms defining the plane were assigned unit weights.

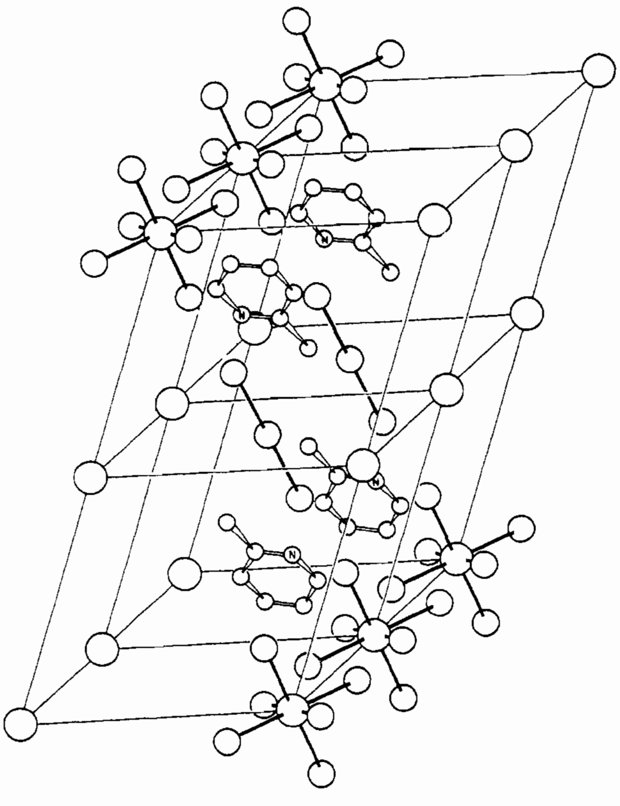

Figure 3.—Four unit cells of $(\alpha\text{-}C_6H_7NH)_2SbBr_9$ showing one set of parallel charge-transfer chains extending diagonally through the crystal in a (120) crystal plane.

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(26) B. Bak, L. Hansen-Nygaard, and J. Rastrup-Anderson, *J. Mol. Spectry.*, **2**, 361 (1958).

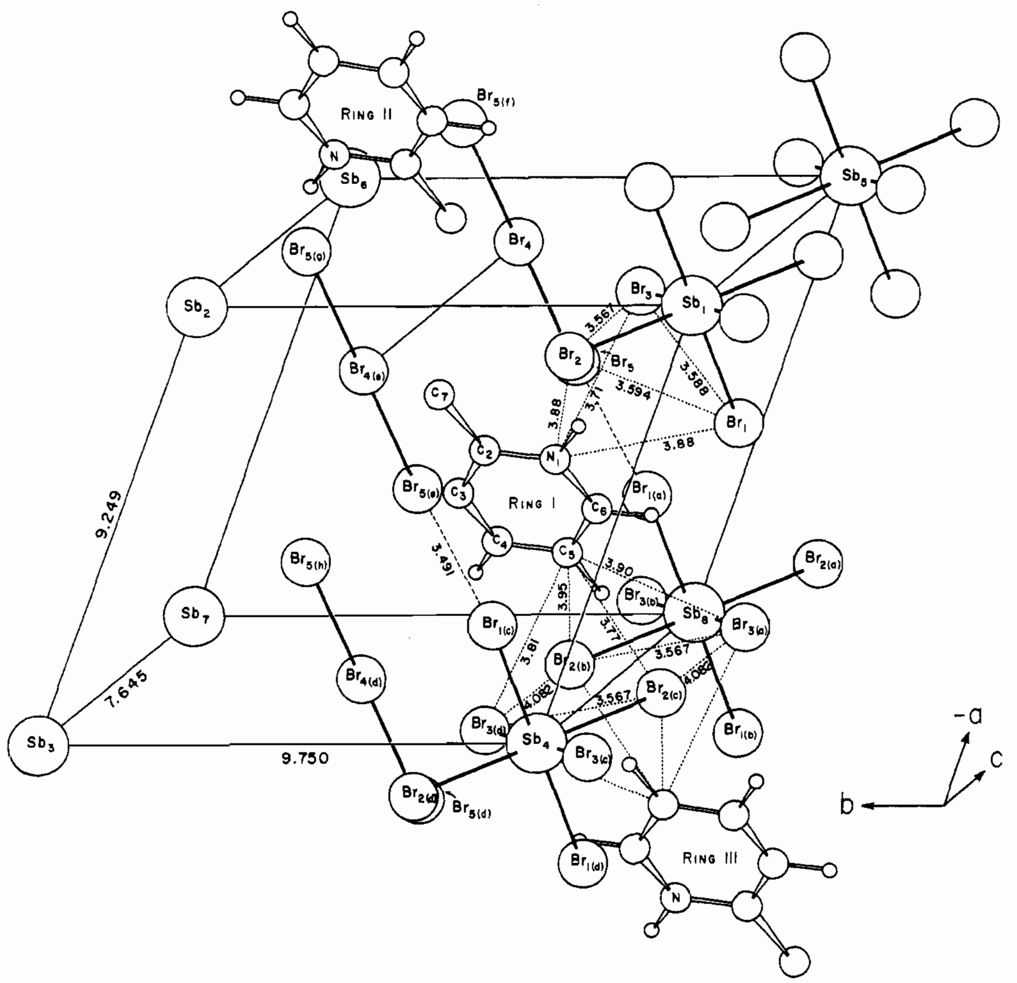

Figure 4.—Unit cell of $(\alpha\text{-}C_6H_7NH)_2SbBr_9$ showing the environment of several symmetry-related cations and anions.

able charge-transfer paths. These features are illustrated in Figures 3–7.

The nitrogen atom in the cation would be expected to carry most of the positive charge and so its location relative to regions of surrounding negative charge is highly influential in determining the final crystal symmetry. Specifically, the position occupied by nitrogen is directed toward the midpoint of one of the faces of an $SbBr_6^-$ ion (Figure 4) and thus, with the three bromine atoms, forms the corner of a nearly regular tetrahedron. The average distance of N_1 from the three bromine atoms is 3.83 Å (Table VIII) and the three Sb_1–Br–N_1 angles are very nearly 90° (Table IX).

The Charge-Transfer Paths.—This structure contains two different electron-donor groups, Br_3^- and $C_6H_5NH^+$, and one electron-acceptor group, $Sb^VBr_6^-$. This results in at least two possible paths along which transfer of charge might conceivably occur; these are illustrated in some detail in Figures 3–6 and schematically in Figure 7. The two paths appear to be (1) Br_3^- to $SbBr_6^-$ *via* the –Br···Br– bridges (through van der Waals contact) and (2) $C_6H_7NH^+$ to $SbBr_6^-$ *via* interaction of bromine with the π cloud. The existence of the first path is indicated by the short van der Waals Br···Br contact (3.491 Å) between the donor group and the acceptor group and by a slight lengthening of the Sb–Br bond (by 0.018 Å) of the acceptor in the chain. The second path is evident by the orientation of the cation. In contrast to the manner in which benzene is oriented relative to halogen molecules in $C_6H_5 \cdot X_2$ charge-transfer complexes,[27] the plane of the α-picolinium cation straddles the –Br···Br– bridge of the chain and is tilted in such a manner that its π cloud is approximately normal to terminal bromine atoms of both Br_3^- and $SbBr_6^-$. Such an orientation, in fact, suggests the capability of Br_3^- to feed electron density into one end of the π cloud of the cation as $SbBr_6^-$ withdraws electron density from the other end. The $\cdots Br_3^- \cdots Sb\text{-}Br_6^- \cdots$ chain is somewhat nonlinear and the angles Br_4–Br_5–$Br_{1(a)}$ and Br_5–$Br_{1(a)}$–Sb_8 are about 165° rather than 180° (see Figure 5). The corresponding tilt of the ring prevents maximum overlap of bromine ($Br_{1(a)}$, $Br_{1(c)}$, Br_5, and $Br_{5(e)}$) with the π cloud. Clearly, the one efficient π-cloud interaction involves Br_5 with N_1, C_2, and C_3 (average distance, 3.85 Å) and $Br_{1(c)}$ with C_5, C_6, and N_1 (average distance, 3.89 Å). Effective interaction of $Br_{5(e)}$ with this ring is considerably reduced but $Br_{1(a)}$ interaction with C_5 is maintained at 3.79 Å.

It was stated earlier that the carbon–carbon distances can be expected to vary in length over the ring, depend-

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[27] O. Hassel and Chr. Rømming, *Quart. Rev.* (London), **16**, 1 (1962).

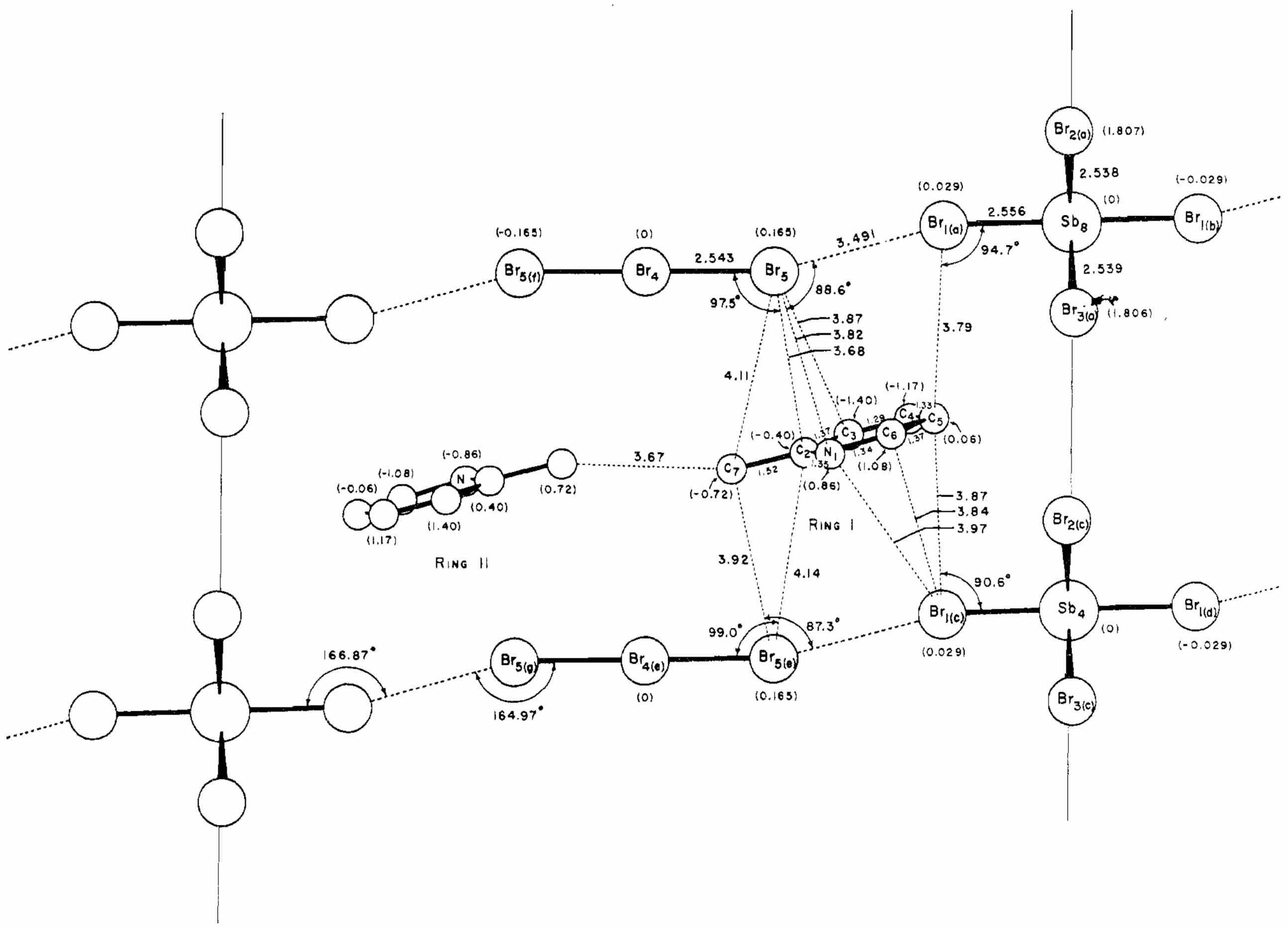

Figure 5.—View of the (120) crystal plane in $(\alpha\text{-}C_6H_7NH)_2SbBr_9$, illustrating the packing of the aromatic cations between two chains formed by Br_3^- and $SbBr_6^-$ anions. A number within parentheses refers to the perpendicular distance of the atom from the plane. All distances and angles result from atomic coordinates before correction for thermal motion (Table I). The numbering scheme of all atoms corresponds to that used in Figure 4.

ing upon the amount of interaction that exists between the π cloud and surrounding bromine atoms. If this assumption is correct, then since the π-cloud electron density surrounding C_4 interacts the least with bromine, it would be expected that the C_3–C_4 and C_4–C_5 bonds will have more double-bond character than the others and therefore be shorter in length; this is precisely what is observed.

Influence of the Nitrogen Position on the Structure. —In crystals of $(pic)_2SbBr_9$ the position of nitrogen in the ring relative to the methyl group appears to have a noticeable effect both on the packing of the ions and on the colors the crystals exhibit at low temperatures. Examinations of single-crystal X-ray photographs of the three salts $(\alpha\text{-pic})_2SbBr_9$, $(\beta\text{-pic})_2SbBr_9$, and $(\gamma\text{-pic})_2SbBr_9$ indicate that although the ionic packing is essentially the same, there exist slight variations in the unit cell parameters and crystal symmetry.[5] These variations are reflected in their melting points. The γ-picolinium salt (mp 135–138°) appears to exhibit a more efficient packing of ions, since it is slightly more stable to heat than either the α-picolinium salt (mp 116.5–117°) or the β-picolinium salt (mp 119.5–120°). A look at the colors exhibited by these salts also quite clearly reflects a sensitivity to nitrogen location. As the temperature is lowered below room temperature, they lose their black color, a change which is reversible with temperature. Both the α- and β-picolinium salts begin to lose their black color at about −41° and become bright orange at the temperature of liquid nitrogen (approximately −174°). The γ-picolinium salt, in contrast, begins to lose its black color at about −125° and becomes red at −174°.

It has been found that in $(\alpha\text{-pic})_2SbBr_9$ the nitrogen position is fixed (not disordered) and to minimize crystal forces the ring is tilted to allow nitrogen and the acidic hydrogen to be directed toward the center of a face of the $SbBr_6^-$ ion and thereby reside midway from all three bromine atoms (Figure 4). This presumably accounts for the apparent nonlinearity of the $\cdots Br_3^- \cdots SbBr_6^- \cdots$ chain and also explains why the salt is triclinic. Crystals of $(\gamma\text{-pic})_2SbBr_9$ are monoclinic, and, on the basis of the results of $(\alpha\text{-pic})_2SbBr_9$, nitrogen would be in a very favorable position electrostatically; it would be midway between $Br_{1(a)}$ and $Br_{1(c)}$ and, being in the 4 position on the ring, also directed toward the center of a square formed by the four bromine atoms $Br_{2(b)}$, $Br_{3(d)}$, $Br_{2(c)}$, and $Br_{3(a)}$. The 2

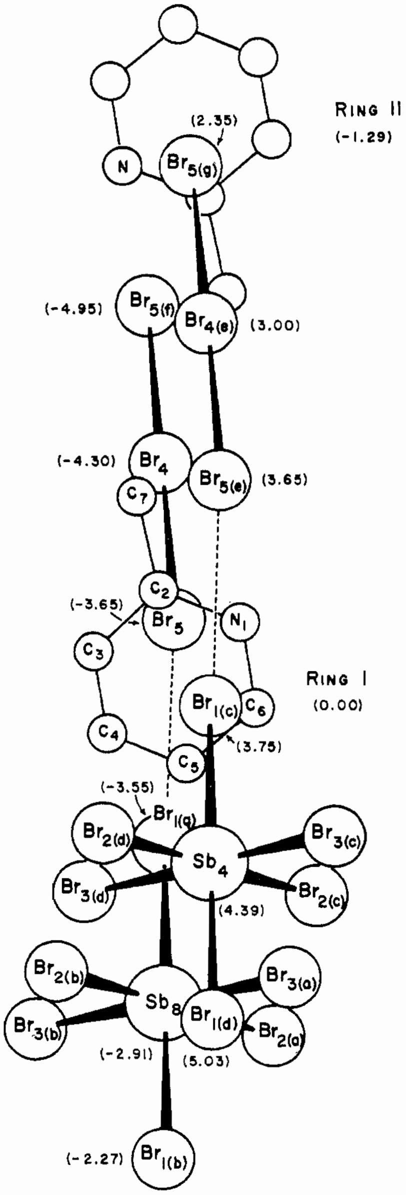

Figure 6.—Projection of atoms in (α-$C_6H_7NH)_2SbBr_9$ onto the least-squares plane of the cation (ring I). A number within parentheses refers to the perpendicular distance of the atom from that plane. The numbering scheme of all atoms corresponds to that used in Figures 4 and 5. This view is approximately 90° to the view in Figure 5.

TABLE VIII

SELECTED INTERATOMIC DISTANCES BETWEEN IONS IN (α-$C_6H_7NH)_2SbBr_9$

Atoms[a]	Distance, Å[b,c]	Atoms[a]	Distance, Å[b,c]
$Br_{1(a)}$–Br_5	3.491 (0.002)	C_4–$Br_{4(d)}$	4.22 (0.02)
$Br_{2(b)}$–$Br_{3(d)}$	4.082 (0.002)	C_4–Br_5	4.17 (0.02)
$Br_{2(j)}$–Br_4	3.758 (0.002)	C_4–$Br_{5(c)}$	5.61 (0.02)
Br_3–Br_4	3.718 (0.002)	C_5–$Br_{1(a)}$	3.79 (0.02)
Br_3–Br_5	3.823 (0.002)	C_5–$Br_{1(c)}$	3.87 (0.02)
N_1–Br_1	3.88 (0.01)	C_5–$Br_{2(b)}$	3.95 (0.02)
N_1–$Br_{1(a)}$	5.11 (0.01)	C_5–$Br_{2(c)}$	3.77 (0.02)
N_1–$Br_{1(c)}$	3.97 (0.02)	C_5–$Br_{3(a)}$	3.90 (0.02)
N_1–Br_2	3.88 (0.01)	C_5–$Br_{3(d)}$	3.81 (0.02)
N_1–Br_3	3.71 (0.01)	C_5–Br_5	4.30 (0.02)
N_1–Br_5	3.82 (0.02)	C_5–$Br_{5(e)}$	5.74 (0.02)
N_1–$Br_{5(e)}$	4.25 (0.02)	C_5–$C_{5(i)}$	5.47 (0.02)
C_2–$Br_{1(a)}$	5.29 (0.01)	C_6–Br_1	3.92 (0.02)
C_2–$Br_{1(c)}$	4.22 (0.02)	C_6–$Br_{1(a)}$	4.35 (0.02)
C_2–Br_5	3.68 (0.02)	C_6–$Br_{1(c)}$	3.84 (0.02)
C_2–$Br_{5(e)}$	4.14 (0.01)	C_6–Br_5	4.06 (0.02)
C_3–$Br_{1(a)}$	4.77 (0.02)	C_6–$Br_{5(e)}$	5.12 (0.02)
C_3–$Br_{1(c)}$	4.25 (0.02)	C_7–$Br_{1(c)}$	5.13 (0.02)
C_3–Br_5	3.87 (0.02)	C_7–$Br_{1(k)}$	4.08 (0.02)
C_3–$Br_{5(e)}$	4.91 (0.02)	C_7–$Br_{2(l)}$	4.00 (0.02)
C_3–$Br_{5(h)}$	3.66 (0.02)	C_7–$Br_{3(l)}$	3.89 (0.02)
C_4–$Br_{1(a)}$	4.05 (0.02)	C_7–Br_4	4.28 (0.02)
C_4–$Br_{1(c)}$	4.07 (0.01)	C_7–$Br_{4(e)}$	4.20 (0.02)
C_4–$Br_{2(b)}$	3.97 (0.02)	C_7–Br_5	4.11 (0.02)
C_4–$Br_{3(d)}$	3.78 (0.01)	C_7–$Br_{5(e)}$	3.92 (0.02)
		C_7–$C_{7(h)}$	3.67 (0.02)

[a] The subscript letters in parentheses refer to all atoms (except antimony) related by symmetry to those in the original aysmmetric unit (Table I). These letters define the following positions: no subscript letter in parentheses: x, y, z; (a) $1 - x, \bar{y}, 1 - z$; (b) $1 + x, y, 1 + z$; (c) $1 - x, \bar{y}, \bar{z}$; (d) $1 + x, y, z$; (e) $x, y, z - 1$; (f) $\bar{x}, 1 - y, 1 - z$; (g) $x, 1 - y, \bar{z}$; (h) $1 - x, 1 - y, 1 - z$; (i) $2 - x, \bar{y}, 1 - z$; (j) $x, y, 1 + z$; (k) $x, 1 + y, z$; (l) $x, 1 - y, \bar{z}$. See also Figures 4–6 for the numbering scheme. [b] All distances correspond to the *uncorrected* distances in that no correction for any thermal motion has been applied. [c] Numbers given in parentheses refer to the standard deviation.

position, being the least favorable of the three, would not involve maximum attractive forces with neighboring groups of bromine atoms and so the ring is probably much less tilted (or not tilted at all) in the β-picolinium salt. In the α-picolinium salt the nonlinear $\cdots Br_3^- \cdots SbBr_6^- \cdots$ chain produces a $Br_4 \cdots Sb_8 \cdots Sb_4$ angle of 82.901°; in the β- and γ-picolinium salts this angle is restricted to 90° by monoclinic symmetry, strongly suggesting that the $-Br_4-Br_5 \cdots Br_1-Sb$ chain is linear in these salts. It is also of interest to note that the distance between the chains (Sb_4–Sb_8) varies systematically among the three salts. This distance corresponds to the c dimension of the unit cell; it is 7.645 Å in the α-picolinium salt, 7.54 Å (a reduction) in the β-picolinium salt, and 7.43 Å (a further reduction) in the γ-picolinium salt. Thus, in the γ-picolinium salt the distance between $Br_{1(a)}$ and $Br_{1(c)}$ with position 5 of the ring is reduced by as much as 0.1 Å.

Conclusion

The compound (α-$C_6H_7NH)_2Sb^VBr_9$ represents an example of a salt containing ions which are capable of exhibiting charge transfer under appropriate environments. The presence of charge transfer in this particular salt becomes one of a speculative nature when attempting to explain its jet black color and must await spectral studies for confirmation. It is known that the tribromide ion is red and that, in the presence of the $Sb^VBr_6^-$ ion, it may produce the observed deep color without involving charge transfer at all; we find that light transmitted by very thin crystals does appear deep red. It is also known that, upon cooling any material, its absorption bands become much narrower and often result in color changes; an absorption band in the near-ultraviolet spectrum whose edge overlaps the blue end of the visible spectrum will appear deep red and, upon cooling, will disappear as the peak sharpens to produce color changes from red to orange, yellow, and colorless.

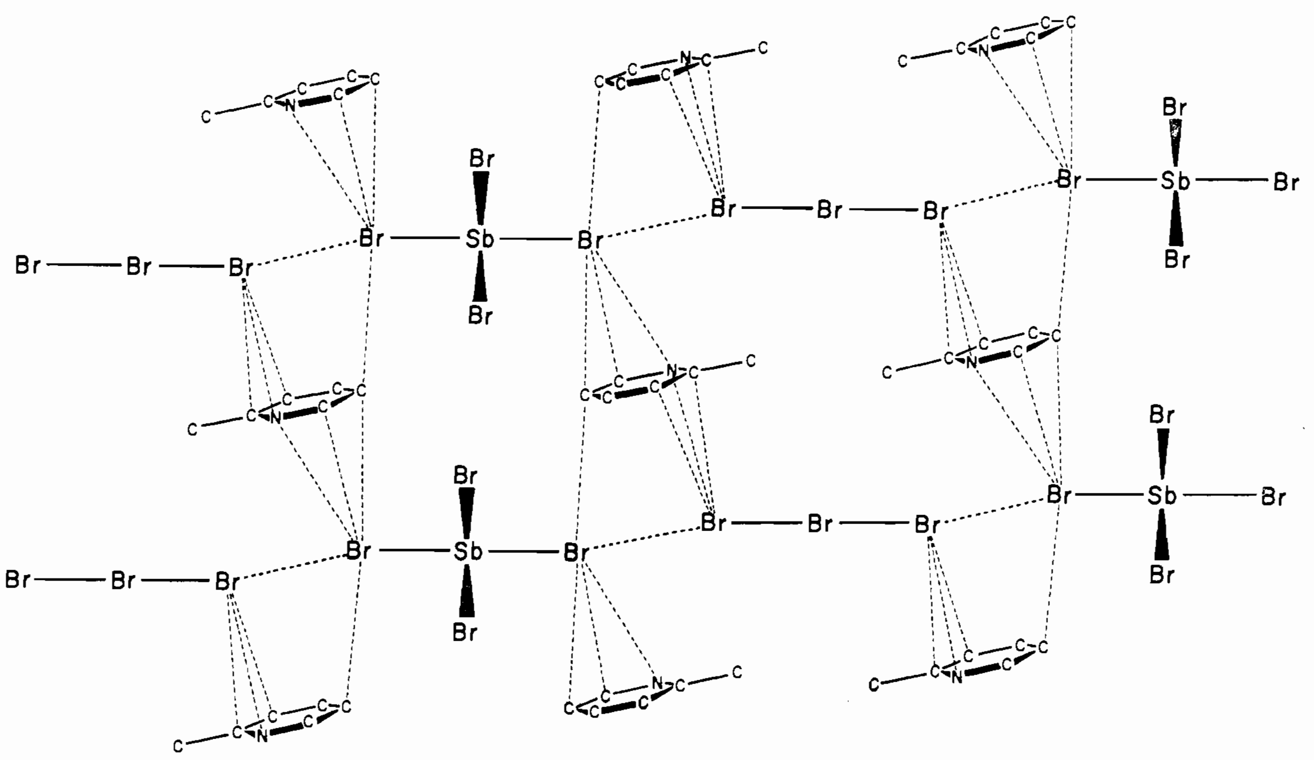

Figure 7.—A schematic representation of the proposed charge-transfer system in (α-$C_6H_7NH)_2SbBr_9$. The view is an expansion of Figure 5.

TABLE IX

SELECTED INTERATOMIC ANGLES BETWEEN IONS IN (α-$C_6H_7NH)_2SbBr_9$

Atoms[a],[b]	Angle,[c] deg	Atoms[a],[b]	Angle,[c] deg
$\mathrm{Sb_1-Br_1-N_1}$	91.3 (0.2)	$\mathrm{Br_{1(c)}-C_4-N_1}$	68.6 (0.5)
$\mathrm{Sb_1-Br_2-N_1}$	91.5 (0.2)	$\mathrm{Br_{1(c)}-C_5-C_2}$	77.5 (0.5)
$\mathrm{Sb_1-Br_3-N_1}$	95.7 (0.2)	$\mathrm{Br_{1(c)}-C_6-C_3}$	79.5 (0.6)
$\mathrm{Sb_4-Sb_8-Br_4}$	82.90 (0.03)	$\mathrm{Br_2-N_1-Br_3}$	56.0 (0.2)
$\mathrm{Sb_4-Br_{1(c)}-Br_5}$	114.53 (0.05)	$\mathrm{Br_{2(b)}-Br_{3(d)}-Br_{2(c)}}$	90.07 (0.05)
$\mathrm{Sb_4-Br_{1(c)}-N_1}$	123.2 (0.2)	$\mathrm{Br_{2(b)}-C_5-Br_{3(a)}}$	54.8 (0.2)
$\mathrm{Sb_4-Br_{1(c)}-C_2}$	129.0 (0.2)	$\mathrm{Br_{2(b)}-C_5-Br_{3(d)}}$	63.4 (0.3)
$\mathrm{Sb_4-Br_{1(c)}-C_3}$	114.6 (0.2)	$\mathrm{Br_{2(c)}-C_5-Br_{3(a)}}$	64.3 (0.3)
$\mathrm{Sb_4-Br_{1(c)}-C_4}$	97.5 (0.2)	$\mathrm{Br_{2(c)}-C_5-Br_{3(d)}}$	56.9 (0.2)
$\mathrm{Sb_4-Br_{1(c)}-C_5}$	90.6 (0.2)	$\mathrm{Br_{3(a)}-Br_{2(b)}-Br_{3(d)}}$	89.93 (0.05)
$\mathrm{Sb_4-Br_{1(c)}-C_6}$	103.7 (0.3)	$\mathrm{Br_4-Br_5-N_1}$	106.0 (0.2)
$\mathrm{Sb_4-Br_{2(c)}-C_5}$	93.2 (0.3)	$\mathrm{Br_4-Br_5-C_2}$	97.5 (0.2)
$\mathrm{Sb_4-Br_{3(d)}-C_5}$	92.0 (0.3)	$\mathrm{Br_4-Br_5-C_3}$	109.4 (0.2)
$\mathrm{Sb_8-Br_{1(a)}-C_5}$	94.7 (0.2)	$\mathrm{Br_4-Br_5-C_4}$	127.3 (0.2)
$\mathrm{Sb_8-Br_{1(a)}-Br_5}$	166.87 (0.06)	$\mathrm{Br_4-Br_5-C_5}$	136.4 (0.2)
$\mathrm{Sb_8-Br_{2(b)}-C_5}$	91.1 (0.3)	$\mathrm{Br_4-Br_5-C_6}$	124.9 (0.3)
$\mathrm{Sb_8-Br_{3(a)}-C_5}$	92.3 (0.3)	$\mathrm{Br_{4(e)}-Br_{5(e)}-C_2}$	99.0 (0.2)
$\mathrm{Br_1-N_1-Br_2}$	55.1 (0.2)	$\mathrm{Br_5-N_1-C_4}$	77.9 (0.5)
$\mathrm{Br_1-N_1-Br_3}$	56.4 (0.2)	$\mathrm{Br_5-C_2-Br_{5(c)}}$	155.7 (0.4)
$\mathrm{Br_{1(a)}-Br_5-Br_4}$	164.97 (0.08)	$\mathrm{Br_5-C_2-C_5}$	82.9 (0.5)
$\mathrm{Br_{1(a)}-Br_5-N_1}$	88.6 (0.2)	$\mathrm{Br_5-C_3-C_6}$	74.6 (0.6)
$\mathrm{Br_{1(a)}-C_5-Br_{1(c)}}$	174.6 (0.4)	$\mathrm{Br_5-C_4-N_1}$	63.4 (0.4)
$\mathrm{Br_{1(a)}-C_5-C_2}$	107.6 (0.6)	$\mathrm{Br_5-C_5-C_2}$	58.1 (0.4)
$\mathrm{Br_{1(c)}-Br_5-Br_4}$	115.16 (0.05)	$\mathrm{Br_5-C_6-C_3}$	66.7 (0.5)
$\mathrm{Br_{1(c)}-Br_{5(e)}-C_7}$	87.3 (0.2)	$\mathrm{Br_5-C_7-Br_{5(e)}}$	144.4 (0.5)
$\mathrm{Br_{1(c)}-N_1-C_4}$	72.7 (0.5)	$\mathrm{Br_{5(e)}-Br_{1(c)}-C_6}$	88.4 (0.3)
$\mathrm{Br_{1(c)}-C_2-C_5}$	63.4 (0.4)	$\mathrm{Br_{5(e)}-C_7-C_5}$	89.2 (0.4)
$\mathrm{Br_{1(c)}-C_3-C_6}$	62.9 (0.5)		

[a] See Table VIII, footnote *a*, for definition of subscript letters. See also Figures 4–6 for the numbering scheme. [b] The subscript numbers for antimony are defined as shown in Figures 4–6 and correspond to the corners of the unit cell as follows: 1, [000]; 2, [010]; 3, [110]; 4, [100]; 5, [001]; 6, [011]; 7, [111]; 8, [101]. Numbers given in parentheses refer to the standard deviations.

Our proposal for the presence of charge transfer in this salt, disregarding the mechanisms involved, is based upon the following two observations. First, location of nitrogen relative to the methyl group in the α-, β-, and γ-picolinium cations has an effect on the temperature at which the respective salts begin to lose their black color as the temperature is lowered. Since the picolinium cations themselves do not produce absorption bands in the visible region of the spectrum, they must apparently be involved in a process which does affect the observed colors. Second, an abnormally short Br···Br van der Waals contact (3.491 Å, compared with the sum of the Pauling van der Waals radius of bromine, 3.90 Å) and the lengthened Sb–Br bond (by 0.018 Å) along the infinite ···Br–Br–Br···Br–Sb–Br··· chains suggest that an interaction exists between the two anions which is other than of a purely electrostatic nature. It thus appears to us that the charge-transfer paths most likely involved are those shown in Figure 7.

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