chloride (1.75 Å)[12] and markedly longer than in diboron tetrafluoride (1.67 Å).[13] The B–P and P–F bond distances are very similar to those observed in trifluorophosphine–borane ($F_3P\cdot BH_3$),[14] while the P–F distances are equal and the B–P distance is only slightly shorter in the borane adduct (0.012 Å). However, the trifluorophosphine group in the borane adduct has $C_{3v}$ symmetry but not in the refined structure of model A. A planar projection of the trifluorophosphine group shows two FPF angles of 122 ± 0.6°, which reduces the symmetry to $C_{2v}$. The deviation from $C_{3v}$ symmetry is such as to increase the nearest fluorine–hydrogen nonbonded distance.

Model A does show one unusual structural feature. The HBH angle of 146 ± 12° is much larger than that reported for diborane(6) and tetraborane(10), 122°;[9] in trifluorophosphine–borane and carbonyl–borane, these are 115 and 113°,[15] respectively. The small BBH angle of 92.3° is associated with a short nonbonded boron–hydrogen distance of 2.23 Å. In contrast, the hydrogen positions in model B are not significantly different from those reported for diborane(6).

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# The Crystal Structure of Tetraethylammonium Hexabromoantimonate(V), $(C_2H_5)_4NSbBr_6$[1]

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Tetraethylammonium hexabromoantimonate(V) has been prepared and its crystal structure determined by three-dimensional X-ray analysis. The dark red-brown compound crystallizes in the tetragonal space group $I4_1md$ with four molecules in a unit cell of dimensions $a = b = 8.7008$ (7) and $c = 24.797$ (3) Å. Data were collected with an automated diffractometer using the $\theta$–$2\theta$ step scan technique and Mo Kα (λ 0.7107 Å). The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares techniques to a discrepancy index $R = 0.042$ for the 276 independent reflections used in the analysis. The structure consists of slightly distorted octahedral $Sb^{V}Br_6^-$ anions and $(C_2H_5)_4N^+$ cations which are twofold disordered about intersecting mirror planes. The average Sb–Br distances corrected for thermal motion assuming a riding model are 2.561 (5), 2.564 (5), and 2.570 (4) Å. The only close Br–Br van der Waals contact is along the *a* axis at 3.584 Å. The similar sizes of the tetraethylammonium and the more spherical hexabromoantimonate(V) ions permit efficient packing which contributes to the stability of this compound.

## Introduction

The crystal structure investigation of tetraethylammonium hexabromoantimonate(V) was undertaken as part of a series of investigations of halo-coordinated antimony compounds being performed in this laboratory.[4–11] A series of intervalence antimony bromide complexes of varying stoichiometries has been investigated to relate, if possible, their crystal structures and charge transfer properties and to evaluate the effects of cation size, type, and stereochemistry on the antimony bromide anion and on the resulting solid-state structure. The structure of the tetraethylammonium salt was undertaken as a result of preliminary investigations[8] on the physical and chemical properties of this material and other intensely colored $R_xSb_yBr_z$ complexes. The tetraethylammonium complex was shown to be unusually stable in comparison to the other antimony bromide complexes studied, being stable in air and more slowly hydrolyzed in water. Although the tetraethylammonium complex is also deeply colored,[12] appearing a dark red-brown, the preliminary X-ray results indicated the stoichiometry was $RSb^{V}Br_6$ with only four formula units per unit cell. Intervalence charge transfer could not occur if indeed all the $SbBr_6$ species present were equivalent. Also, the saturated cation would not be expected to participate in any other possible type of charge-transfer path.

## Experimental Section

Tetraethylammonium hexabromoantimonate(V), $(C_2H_5)_4NSbBr_6$, mol wt 479.5, crystallizes in the tetragonal space group $I4_1md$, with $F(000) = 1344$ e, $Z = 4$, $a = b = 8.7008$ (7) Å, $c = 24.797$ (3) Å, temperature ~24°, $V = 1877.3$ Å$^3$, $d_m = 2.62$ g/cm$^3$, $d_c = 2.59$ g/cm$^3$, Mo Kα (λ 0.7107 Å), and $\mu = 150.7$ cm$^{-1}$.

The $(C_2H_5)_4NSbBr_6$ salt was prepared by the method of Law-

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(1) Work was performed at the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2784.

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(3) Ames Laboratory undergraduate summer student trainee,1968.

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TABLE I

FINAL ATOMIC POSITIONAL[a] AND THERMAL PARAMETERS[b] AND STANDARD ERRORS[c] FOR $SbBr_6^-$

| Atom | Position | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Sb | 4a | $0^d$ | $0^d$ | $0^d$ | 87 (5) | 117 (6) | 13 (1) | $0^d$ | $0^d$ | $0^d$ |
| Br(1) | 8b | $0^d$ | 0.2034 (7) | 0.0732 (2) | 244 (12) | 217 (11) | 22 (1) | $0^d$ | $0^d$ | −29 (3) |
| Br(2) | 8b | $0^d$ | −0.2057 (6) | −0.0734 (2) | 135 (8) | 155 (8) | 20 (1) | $0^d$ | $0^d$ | −16 (2) |
| Br(3) | 8b | 0.2940 (4) | $0^d$ | −0.0027 (3) | 97 (6) | 175 (7) | 24 (1) | $0^d$ | −13 (3) | $0^d$ |

[a] Positional parameters are in fractional unit cell coordinates. [b] $\beta$'s $\times 10^4$; the form of the anisotropic temperature factor is exp $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [c] Estimated standard deviations are given in parentheses for the least significant figures. [d] Atomic parameter fixed by symmetry.

ton.[6] Microscopic examination revealed the fourfold symmetry of the crystals, square pyramidal with sharply defined faces. Although the tetraethylammonium salt was observed to be air stable, crystals were selected and mounted in thin-walled Lindemann glass capillaries to limit exposure in the atmosphere. Preliminary Weissenberg and precession photographs exhibited $4/mmm$ Laue symmetry, indicating a tetragonal space group. The following systematic absences were observed: $hkl$ when $h + k + l = 2n + 1$ and $hhl$ when $2h + l = 4n + 1$. The absences are consistent with either space group $I4_1md$ or $I\bar{4}2d$. The unit cell parameters and their standard deviations were obtained by a least-squares fit to 12 independent reflection angles whose centers were determined by a left–right, top–bottom beam-splitting technique using a previously aligned Hilger-Watts four-circle diffractometer (Mo K$\alpha$ radiation, $\lambda$ 0.71069 Å). The observed density was determined by flotation techniques using ethylene bromide and 1,1,2,2-tetrabromoethane solutions.

A crystal having approximate dimensions 0.10 × 0.10 × 0.09 mm was mounted on a glass fiber such that the $c$ axis (0.09 mm) was nearly coincident with the spindle axis. Data were collected at room temperature utilizing a Hilger-Watts four-circle diffractometer equipped with scintillation counter and using Zr-filtered Mo K$\alpha$ radiation. Within a $2\theta$ sphere of 60° all data in one full octant were recorded using a $\theta$–$2\theta$ step scan technique with a takeoff angle of 4.5°. Symmetric scan ranges of 1.00° in $2\theta$ at low $2\theta$ values to 2.20° at the high $2\theta$ limit were used. Stationary-crystal, stationary-counter background measurements were made at the beginning and end of the step scan, each measurement being made for half the total scan time. The counting rate used was 0.2048 sec/step of 0.02° in $2\theta$. The rest of the experimental arrangement used has already been discussed in some detail.[13] A total of 1535 reflections were measured in this way. Based on the measurements of three standard reflections, no decomposition correction was made; total decomposition was less than 3%.

The intensity data were also corrected for Lorentz–polarization effects and for effects due to absorption ($\mu$ = 150.7 cm$^{-1}$). The absorption correction[14] was made using ABCOR;[15] the maximum and minimum transmission factors were 0.414 and 0.322, respectively. The error assigned each intensity measurement was calculated from the estimated statistical and nonstatistical errors by

$$[\sigma(I)]^2 = [C_T + C_B + (0.03C_T)^2 + (0.05C_B)^2 + (0.04C_R)^2]/A^2$$

where $C_T$, $C_B$, $C_R$, and $A$ are the total count, background count, net count, and transmission factor, respectively. The equivalent values of $F_o^2$ were then averaged. The estimated standard deviation in each structure factor was calculated from the mean deviation of intensity by the method of finite differences.[16] The reciprocals of the structure factor variances were used as weights in the least-squares refinement. Based on the measurements of symmetry extinct data, it was decided that only those reflections with $I \geq 2\sigma(I)$ would be considered observed. The results reported are based on the remaining 276 independent reflections.

TABLE II

FINAL ATOMIC PARAMETERS AND STANDARD ERRORS FOR $(C_2H_5)_4N^+$

| Atom | Position | $x$ | $y$ | $z$ | $B$, Å$^2$ |
|---|---|---|---|---|---|
| N | 4a | $0^b$ | $0^b$ | 0.4333 (16) | 4.0 (9) |
| C(1) | 8b | 0.2158 (52) | $0^b$ | 0.3666 (17) | 5.9 (10) |
| C(2) | 8b | 0.2170 (47) | $0^b$ | 0.5064 (23) | 5.5 (10) |
| C(3)[a] | 16c | 0.1005 (64) | 0.1185 (62) | 0.3976 (18) | 4.1 (11) |
| C(4) | 16c | 0.0999 (63) | −0.0998 (70) | 0.4684 (21) | 5.0 (11) |

[a] Atoms C(3) and C(4) are disordered and refined with half-occupancy. [b] Atomic parameter fixed by symmetry.

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTORS (×10)

| L | H | K | FO | FC |
|---|---|---|---|---|
| L = 0 | 2 | 0 | 2729 | 2709 |
| | 4 | 0 | 4762 | 4826 |
| | 6 | 0 | 2388 | 2476 |
| | 8 | 0 | 898 | 884 |
| | 10 | 0 | 1134 | 1217 |
| | 3 | 1 | 2867 | 2823 |
| | 5 | 1 | 1291 | 1281 |
| | 7 | 1 | 1286 | 1305 |
| | 2 | 2 | 4015 | 3905 |
| | 5 | 3 | 2453 | 2488 |
| | 9 | 3 | 568 | 555 |
| | 4 | 4 | 2649 | 2728 |
| | 6 | 4 | 1366 | 1395 |
| | 10 | 4 | 564 | 699 |
| | 7 | 5 | 1157 | 1217 |
| | 6 | 6 | 809 | 711 |
| L = 1 | 1 | 0 | 2949 | 3216 |
| | 3 | 0 | 3468 | 3370 |
| | 5 | 0 | 2291 | 2310 |
| | 7 | 0 | 1425 | 1449 |
| | 9 | 0 | 542 | 524 |
| | 2 | 1 | 1500 | 1438 |
| | 4 | 1 | 1719 | 1655 |
| | 6 | 1 | 877 | 916 |
| | 3 | 2 | 1143 | 1140 |
| | 5 | 2 | 1440 | 1492 |
| | 7 | 2 | 490 | 540 |
| | 4 | 3 | 1402 | 1390 |
| | 6 | 3 | 664 | 719 |
| | 5 | 4 | 1207 | 1253 |
| | 7 | 4 | 778 | 775 |
| | 6 | 5 | 773 | 778 |
| L = 2 | 1 | 1 | 2555 | 2549 |
| | 3 | 1 | 1407 | 1434 |
| | 5 | 1 | 1107 | 1077 |
| | 7 | 1 | 792 | 811 |
| | 3 | 3 | 1147 | 1149 |
| | 5 | 3 | 968 | 981 |
| | 7 | 3 | 744 | 694 |
| | 5 | 5 | 837 | 910 |
| | 7 | 5 | 590 | 564 |
| L = 3 | 1 | 0 | 2393 | 2246 |
| | 3 | 0 | 2480 | 2447 |
| | 5 | 0 | 1534 | 1517 |
| | 7 | 0 | 1239 | 1327 |
| | 9 | 0 | 509 | 539 |
| | 4 | 1 | 1396 | 1316 |
| | 6 | 1 | 558 | 552 |
| | 3 | 2 | 1110 | 1142 |
| | 5 | 2 | 411 | 435 |
| | 7 | 2 | 841 | 818 |
| | 4 | 3 | 1525 | 1533 |
| | 6 | 3 | 785 | 807 |
| | 8 | 3 | 507 | 478 |
| | 5 | 4 | 644 | 659 |
| | 7 | 4 | 902 | 859 |
| L = 4 | 0 | 0 | 3127 | 3028 |
| | 2 | 0 | 1724 | 1675 |
| | 4 | 0 | 2033 | 1975 |
| | 6 | 0 | 1043 | 1035 |
| | 8 | 0 | 510 | 565 |
| | 10 | 0 | 605 | 594 |
| | 3 | 1 | 444 | 395 |
| | 7 | 1 | 505 | 455 |
| | 2 | 2 | 620 | 591 |
| | 4 | 2 | 1116 | 1107 |
| | 6 | 2 | 564 | 535 |
| | 5 | 3 | 554 | 542 |
| | 4 | 4 | 1361 | 1335 |
| | 6 | 4 | 779 | 768 |
| L = 5 | 1 | 0 | 1834 | 1905 |
| | 3 | 0 | 2480 | 2437 |
| | 5 | 0 | 819 | 753 |
| | 7 | 0 | 943 | 990 |
| | 2 | 1 | 1391 | 1410 |
| | 4 | 1 | 643 | 648 |
| | 6 | 1 | 390 | 396 |
| | 3 | 2 | 2285 | 2227 |
| | 5 | 2 | 736 | 682 |
| | 7 | 2 | 1090 | 1120 |
| | 4 | 3 | 1569 | 1582 |
| | 6 | 3 | 935 | 957 |
| | 7 | 4 | 610 | 725 |
| L = 6 | 2 | 0 | 5622 | 5652 |
| | 4 | 0 | 1118 | 1148 |
| | 6 | 0 | 985 | 1010 |
| | 8 | 0 | 1130 | 1111 |
| | 1 | 1 | 324 | 282 |
| | 3 | 1 | 2392 | 2403 |
| | 5 | 1 | 1075 | 1030 |
| | 7 | 1 | 1220 | 1269 |
| | 4 | 2 | 2470 | 2429 |
| | 6 | 2 | 1153 | 1171 |
| | 10 | 2 | 704 | 654 |
| | 3 | 3 | 3771 | 3868 |
| | 5 | 3 | 427 | 440 |
| | 7 | 3 | 1793 | 1840 |
| | 8 | 4 | 541 | 541 |
| | 5 | 5 | 1276 | 1178 |
| | 7 | 5 | 545 | 445 |
| | 7 | 7 | 866 | 937 |
| L = 7 | 1 | 0 | 2043 | 2053 |
| | 3 | 0 | 2690 | 2656 |
| | 5 | 0 | 1383 | 1326 |
| | 7 | 0 | 1163 | 1164 |
| | 2 | 1 | 2257 | 2182 |
| | 4 | 1 | 492 | 498 |
| | 3 | 2 | 3119 | 2996 |
| | 5 | 2 | 1168 | 1076 |
| | 7 | 2 | 1381 | 1395 |
| | 4 | 3 | 1728 | 1657 |
| | 6 | 3 | 1102 | 1106 |
| | 8 | 3 | 762 | 742 |
| | 5 | 4 | 526 | 441 |
| | 7 | 4 | 863 | 865 |
| | 7 | 6 | 656 | 603 |
| L = 8 | 0 | 0 | 634 | 636 |
| | 2 | 0 | 1234 | 1223 |
| | 4 | 0 | 509 | 505 |
| | 3 | 1 | 555 | 586 |
| | 2 | 2 | 1751 | 1853 |
| | 4 | 2 | 1090 | 1074 |
| | 6 | 2 | 925 | 864 |
| | 4 | 4 | 955 | 640 |
| | 6 | 4 | 520 | 537 |
| | 6 | 6 | 507 | 450 |
| | 8 | 8 | 584 | 199 |
| L = 9 | 1 | 0 | 1372 | 1409 |
| | 3 | 0 | 1842 | 1759 |
| | 5 | 0 | 814 | 781 |
| | 7 | 0 | 1063 | 1084 |
| | 2 | 1 | 1338 | 1331 |
| | 4 | 1 | 711 | 758 |
| | 6 | 1 | 534 | 564 |
| | 3 | 2 | 1933 | 1877 |
| | 5 | 2 | 472 | 486 |
| | 7 | 2 | 978 | 1060 |
| | 4 | 3 | 1170 | 1115 |
| | 6 | 3 | 984 | 960 |
| | 8 | 3 | 547 | 454 |
| | 5 | 4 | 562 | 474 |
| | 7 | 6 | 618 | 607 |
| L = 10 | 2 | 0 | 1861 | 1894 |
| | 6 | 0 | 597 | 581 |
| | 1 | 1 | 918 | 981 |
| | 3 | 1 | 1451 | 1402 |
| | 7 | 1 | 1031 | 987 |
| | 4 | 2 | 1146 | 1148 |
| | 3 | 3 | 1755 | 1787 |
| | 5 | 3 | 551 | 558 |
| | 7 | 3 | 1048 | 1076 |
| | 7 | 5 | 519 | 468 |
| | 7 | 7 | 651 | 625 |
| L = 11 | 1 | 0 | 1781 | 1781 |
| | 3 | 0 | 1496 | 1505 |
| | 5 | 0 | 1117 | 1065 |
| | 7 | 0 | 789 | 769 |
| | 4 | 1 | 1043 | 993 |
| | 6 | 1 | 588 | 616 |
| | 3 | 2 | 639 | 654 |
| | 5 | 2 | 528 | 459 |
| | 7 | 2 | 454 | 448 |
| | 4 | 3 | 769 | 755 |
| | 6 | 3 | 607 | 560 |
| | 5 | 4 | 625 | 578 |
| L = 12 | 0 | 0 | 4725 | 4890 |
| | 2 | 0 | 1452 | 1455 |
| | 4 | 0 | 2605 | 2693 |
| | 6 | 0 | 1681 | 1707 |
| | 10 | 0 | 748 | 743 |
| | 3 | 1 | 1600 | 1607 |
| | 5 | 1 | 732 | 738 |
| | 7 | 1 | 704 | 781 |
| | 2 | 2 | 1354 | 1359 |
| | 5 | 3 | 1452 | 1498 |
| | 4 | 4 | 1328 | 1312 |
| | 6 | 4 | 916 | 862 |
| | 10 | 4 | 634 | 492 |
| | 7 | 5 | 748 | 711 |
| | 6 | 6 | 671 | 581 |
| L = 13 | 1 | 0 | 2444 | 2575 |
| | 3 | 0 | 2243 | 2256 |
| | 5 | 0 | 1535 | 1571 |
| | 7 | 0 | 1047 | 1074 |
| | 2 | 1 | 972 | 883 |
| | 4 | 1 | 1004 | 980 |
| | 6 | 1 | 650 | 644 |
| | 3 | 2 | 864 | 849 |
| | 5 | 2 | 974 | 988 |
| | 4 | 3 | 972 | 1005 |
| | 6 | 3 | 705 | 663 |
| | 5 | 4 | 1059 | 1013 |
| | 7 | 4 | 540 | 592 |
| | 6 | 5 | 597 | 612 |
| L = 14 | 2 | 0 | 926 | 929 |
| | 1 | 1 | 1364 | 1400 |
| | 3 | 1 | 797 | 809 |
| | 5 | 1 | 1308 | 1330 |
| | 4 | 2 | 471 | 408 |
| | 5 | 3 | 700 | 679 |
| | 5 | 5 | 854 | 838 |
| | 7 | 5 | 524 | 391 |
| L = 15 | 1 | 0 | 1595 | 1675 |
| | 3 | 0 | 1460 | 1422 |
| | 5 | 0 | 1002 | 1019 |
| | 7 | 0 | 694 | 799 |
| | 2 | 1 | 472 | 445 |
| | 4 | 1 | 886 | 857 |
| | 5 | 2 | 615 | 643 |
| | 4 | 3 | 944 | 950 |
| | 5 | 4 | 763 | 750 |
| | 6 | 5 | 569 | 439 |
| L = 16 | 0 | 0 | 3033 | 2993 |
| | 2 | 0 | 989 | 982 |
| | 4 | 0 | 2113 | 2160 |
| | 6 | 0 | 914 | 973 |
| | 3 | 1 | 576 | 627 |
| | 5 | 1 | 468 | 425 |
| | 7 | 1 | 529 | 546 |
| | 2 | 2 | 827 | 768 |
| | 4 | 2 | 638 | 631 |
| | 5 | 3 | 762 | 753 |
| | 4 | 4 | 1271 | 1283 |
| | 6 | 4 | 592 | 561 |
| L = 17 | 1 | 0 | 951 | 925 |
| | 3 | 0 | 907 | 955 |
| | 5 | 0 | 489 | 532 |
| | 7 | 0 | 544 | 467 |
| | 4 | 1 | 525 | 605 |
| | 3 | 2 | 438 | 466 |
| | 4 | 3 | 671 | 708 |
| L = 18 | 2 | 0 | 1189 | 1231 |
| | 3 | 1 | 1062 | 1088 |
| | 7 | 1 | 569 | 576 |
| | 3 | 3 | 1634 | 1588 |
| | 7 | 3 | 756 | 757 |
| L = 19 | 1 | 0 | 698 | 703 |
| | 3 | 0 | 1115 | 1197 |
| | 2 | 1 | 845 | 815 |
| | 3 | 2 | 1129 | 1141 |
| | 7 | 2 | 614 | 581 |
| | 4 | 3 | 801 | 833 |
| | 7 | 4 | 526 | 448 |
| L = 20 | 2 | 0 | 539 | 582 |
| | 3 | 1 | 450 | 418 |
| | 2 | 2 | 1075 | 1104 |
| | 4 | 2 | 627 | 646 |
| L = 21 | 1 | 0 | 452 | 483 |
| | 3 | 0 | 783 | 811 |
| | 2 | 1 | 702 | 670 |
| | 3 | 2 | 829 | 863 |
| | 5 | 2 | 453 | 343 |
| | 4 | 3 | 605 | 582 |
| L = 22 | 2 | 0 | 1200 | 1249 |
| | 3 | 1 | 722 | 727 |
| | 4 | 2 | 753 | 746 |
| | 3 | 3 | 977 | 1017 |
| | 7 | 3 | 581 | 640 |
| L = 23 | 1 | 0 | 462 | 440 |
| | 3 | 0 | 526 | 513 |
| | 3 | 2 | 601 | 628 |
| L = 24 | 0 | 0 | 889 | 886 |
| | 2 | 0 | 471 | 522 |
| | 4 | 0 | 588 | 543 |
| | 6 | 0 | 683 | 538 |
| | 4 | 4 | 541 | 258 |
| | 6 | 6 | 603 | 296 |
| L = 25 | 1 | 0 | 755 | 696 |
| | 3 | 0 | 621 | 547 |
| L = 26 | 1 | 1 | 610 | 562 |
| | 5 | 1 | 543 | 442 |
| L = 28 | 0 | 0 | 1213 | 1108 |
| | 2 | 0 | 478 | 386 |
| | 4 | 0 | 689 | 669 |
| | 4 | 4 | 590 | 492 |
| L = 30 | 3 | 3 | 561 | 308 |

## Solution and Refinement of the Structure

With only four formula units per unit cell, the antimony and nitrogen atoms must have either $mm$ ($I4_1md$) or $\bar{4}$ ($I\bar{4}md$) site symmetry. The orientation of the hexabromoantimonate(V) group was obtained from a three-dimensional Patterson map and indicated that the space group was $I4_1md$. These heavy-atom positions were then refined by full-matrix least-squares techniques with isotropic thermal parameters to a conventional discrepancy factor of $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.081$ and a weighted $R$ factor of $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2} = 0.104$. The remaining nonhydrogen atoms were found by an electron density map calculation.

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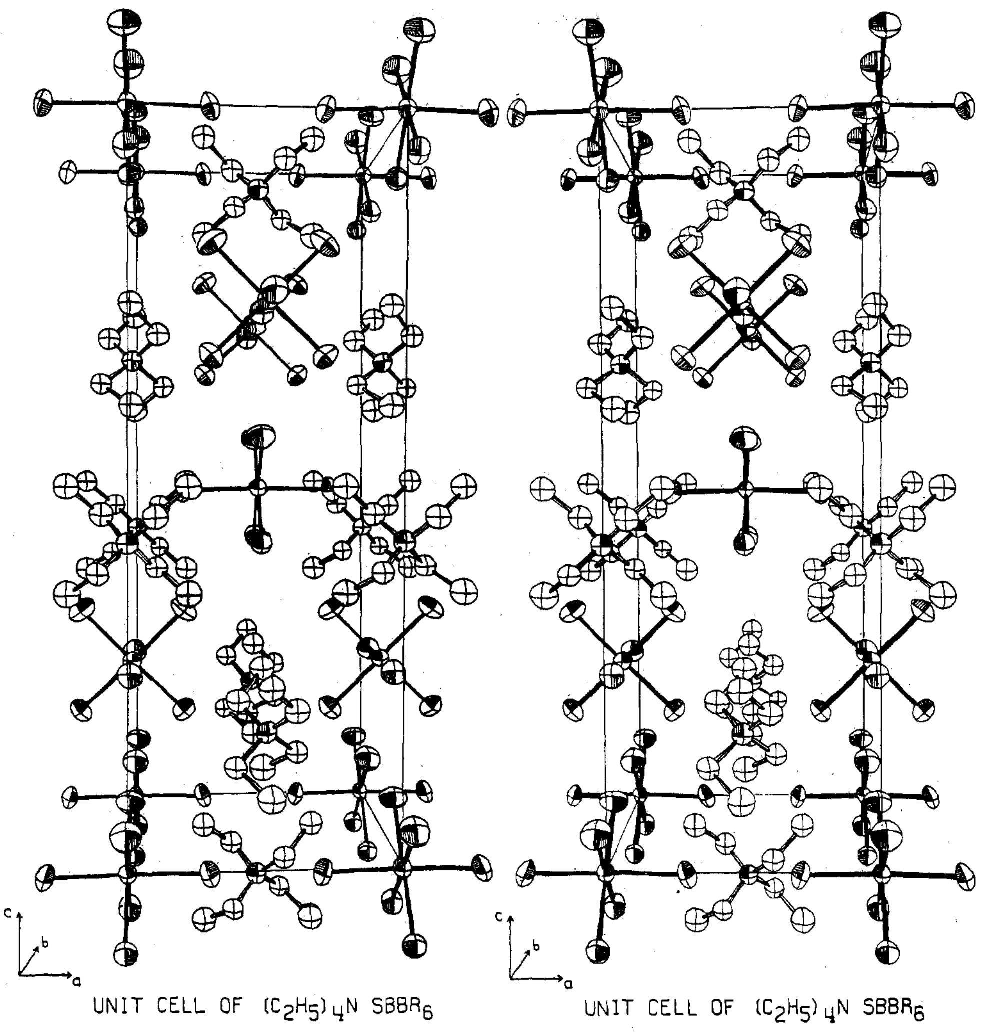

Figure 1.—Stereogram of unit cell showing packing of $(C_2H_5)_4NSbBr_6$ units; hydrogens not shown.

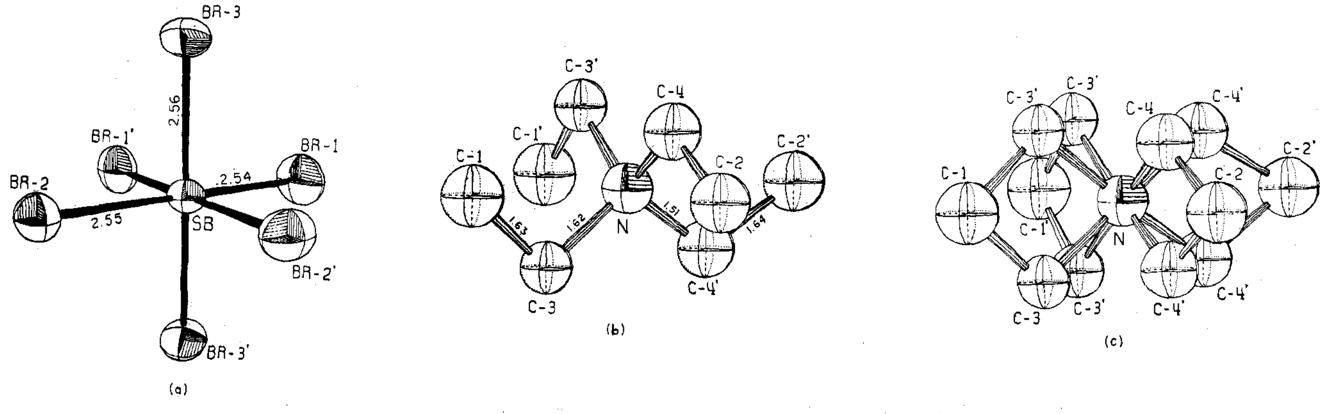

Figure 2.—Ions present in $(C_2H_5)_4NSbBr_6$: (a) $SbBr_6^-$; (b) $(C_2H_5)_4N^+$; (c) disordered $(C_2H_5)_4N^+$.

A tetraethylammonium group has two preferred orientations, the swastika configuration or a trans arrangement. Although found in a trans arrangement, the inner carbon atoms do not lie on the mirror planes and are twofold disordered. These inner carbons were refined with half-occupancy in a general 16-fold position. The outer carbons appeared to lie on the mirror planes and were treated as ordered and restrained to these mirror planes. Subsequent refinement using anisotropic thermal parameters for only the heavy atoms lowered the $R$ factor to 0.042 and $R_w = 0.044$.

The relativistic Hartree–Fock X-ray scattering factors for neutral atoms of Doyle and Turner[17] were used with those of antimony and bromine modified for the real and imaginary parts of anomalous dispersion.[18] Based on the agreement of the large structure factors, no extinction correction was necessary. A final electron density difference map showed no peak heights

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(17) P. A. Doyle and P. S. Turner, *Acta Crystallogr., Sect. A*, **24**, 390 (1968).

(18) D. H. Templeton, "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, pp 215, 216, Table 3.3.2C.

greater than 0.3 $e^-/\text{Å}^3$. The final standard deviation for an observation of unit weight ($[\Sigma w\Delta^2/(NO - NV)]^{1/2}$ where $\Delta = |F_o| - |F_c|$, $NO$ is the number of observations (276), and $NV$ is the number of variables (38)) was 0.95 electron. During the final cycle, the largest shift in any parameter was less than 0.01 times its own $\sigma$. The final positional and thermal parameters are given in Tables I and II, along with their standard deviations as derived from the inverse matrix of the final least-squares cycle. In Table III are listed the magnitudes of the observed and calculated structure factors in electrons × 10.

## Discussion

The crystal structure of tetraethylammonium hexabromoantimonate(V) is shown in Figure 1. Bond distances and angles of interest are given in Table IV and Figure 2. The $Sb^VBr_6^-$ ion has crystallographic $C_{2v}$ symmetry but is somewhat distorted from $O_h$ symmetry. The most significant deviation involves the Br(3)–Sb–Br(3)′ angle which is 177.0 (3)°. This slight distortion can be ascribed to packing effects since the closest approach between anions is 3.584 (5) Å along the *a* direction (Br(3)---Br(3)′$_i$) which is significantly shorter than the 3.9-Å sum of the van der Waals radii.[19] The average Sb–Br bond length is 2.549 (5) Å before correction for thermal motion and 2.565 (5) Å when corrected assuming a riding model. These averages are in good agreement with those previously reported.[9] The tetraethylammonium ion has the trans configuration in which the ethyl groups lie on intersecting mirror planes ($C_{2v}$ symmetry) as required by this space group. However, the inner carbon atoms do not lie on the mirror planes and are therefore disordered with apparent $D_{2h}$ symmetry, as shown in Figure 2. Disorder within the swastika configuration of the tetraethylammonium ion has also been reported.[20] The long bond lengths indicate that the light-atom positions are not well defined and reflect both the disorder and the heavy-atom nature of this problem.

The crystal structure (Figure 1) can be viewed as an efficient packing arrangement of the rather spherical hexabromoantimonate(V) ions and of the nearly equal in size but slightly flattened tetraethylammonium ions. The similar sizes of these two large, rather diffuse ions contribute to the crystal stability. The usual type of intervalence charge transfer cannot occur in this structure. The structure consists of only one kind of $SbBr_6$ species, has a saturated cation, and has only the one bromine---bromine contact (Br(3)---Br(3)′$_i$, 3.58 Å) which is less than the sum of the van der Waals radii. This distance does not appear to be short enough for any type of interspecies charge-transfer interaction since the Br(3)---Br(2) and Br(3)---Br(1) intraion distances are 3.58 and 3.64 Å, respectively. We believe, therefore, that the deep color of this complex probably results from normal charge transfer of the intraspecies ligand to metal type, involving transitions between molecular orbitals of the $Sb^VBr_6^-$ species.

TABLE IV

SELECTED INTERATOMIC BOND DISTANCES AND ANGLES FOR $(C_2H_5)_4NSbBr_6$[a]

| Atoms | Distance, Å | Atoms | Angle, deg |
|---|---|---|---|
| Sb–Br(1) | 2.536 (5) | Br(1)–Sb–Br(1)′ | 88.5 (3) |
| Sb–Br(2) | 2.553 (5) | Br(1)–Sb–Br(2)′ | 91.2 (1) |
| Sb–Br(3) | 2.559 (4) | Br(1)–Sb–Br(3) | 91.1 (1) |
| Br(1)--Br(1)′ | 3.540 (12) | Br(2)–Sb–Br(2)′ | 89.0 (3) |
| Br(1)--Br(2)′ | 3.636 (5) | Br(2)–Sb–Br(3) | 88.9 (1) |
| Br(1)--Br(3) | 3.636 (5) | Br(1)–Sb–Br(2) | 179.8 (5) |
| Br(2)--Br(2)′ | 3.579 (10) | Br(3)–Sb–Br(3)′ | 177.0 (3) |
| Br(2)--Br(3) | 3.581 (5) | C(3)–N–C(4) | 112 (3) |
| Br(3)---Br(3)′$_i$ | 3.584 (5) | C(3)–N–C(4)′ | 105 (3) |
| Br(1)---Br(2)′$_{ii}$ | 4.053 (6) | C(3)–N–C(3)′ | 113 (4) |
| N–C(3) | 1.62 (5) | C(3)′–N–C(4) | 105 (3) |
| N–C(4) | 1.51 (5) | C(4)–N–C(4)′ | 109 (5) |
| C(3)–C(1) | 1.63 (6) | N–C(3)–C(1) | 101 (3) |
| C(4)–C(2) | 1.64 (7) | N–C(4)–C(2) | 113 (4) |
| Sb–Br(1) | 2.561 (5)[b] | | |
| Sb–Br(2) | 2.564 (5)[b] | | |
| Sb–Br(3) | 2.570 (4)[b] | | |

[a] Primed atoms refer to the symmetry-related atom in the group (Figure 2). Other symmetry operations referred to: (i) $1 + x, y, z$; (ii) $x, \frac{1}{2} + y, \frac{1}{4} + z$. [b] Interatomic distance corrected for thermal motion using a riding model where the second atom is assumed to ride on the first.

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[19] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 260.

[20] G. D. Stucky, J. B. Folkers, and T. J. Kistenmacher, *Acta Crystallogr.*, **23**, 1064 (1967).

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# Notes

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## Bromine Perchlorate

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Recently we reported the synthesis of a novel chlorine oxide, chlorine perchlorate.[1] This preparation was accomplished by the reaction

$$MClO_4 + ClSO_3F \longrightarrow MSO_3F + ClOClO_3 \qquad (M = NO_2, Cs) \qquad (1)$$

It has now been found that the related bromine compound bromine perchlorate can be prepared by this method using bromine(I) fluorosulfate.

$$MClO_4 + BrSO_3F \xrightarrow{-20°} MSO_3F + BrOClO_3 \qquad (2)$$

In addition, a second method involving the oxidation of elemental bromine with chlorine perchlorate was discovered

$$Br_2 + 2ClOClO_3 \xrightarrow{-45°} Cl_2 + 2BrOClO_3 \qquad (3)$$

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[1] C. J. Schack and D. Pilipovich, *Inorg. Chem.*, **9**, 1387 (1970).