cated short C-O bond lengths (1.21-1.25 Å) and C-S (1.75-1.78 Å) and C-N (1.36-1.37 Å) bond lengths longer than values found in dithiocarbamate structures.[6] Present values of 1.283 (7) Å for the C-O distance, 1.735 (6) Å for the C-S distance, and 1.342 (7) Å for the thiocarbamate C-N distance indicate a more delocalized π system for the SOCN group. The multiple character of the thiocarbamate C-N bond is reflected in the geometry of the pyrrolidine ring. An interior C(2)-N(2)-C(5) angle of 113.5 (5)° for the thiocarbamate pyrrolidine is significantly larger than the value of 104.7 (5)° for the amine ligand. Enlargement of this angle further seems to result in considerable anisotropy for atoms C(8) and C(9) of the ring.

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Registry No. $Co(SOCN(C_4H_8))_2(NC_4H_9)_2$, 51286-76-1.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th Street, N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy of $2.00 for microfiche, referring to code number INORG-74-1674.

Contribution from the Ames Laboratory-USAEC and
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Crystal Structure of Potassium Pentachloroantimonate(III)

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The crystal structure of potassium pentachloroantimonate(III) (K_2SbCl_5, monoclinic, $P2_1/c$, $a = 8.8686$ (07) Å, $b = 12.4577$ (13) Å, $c = 8.9280$ (13) Å, $\beta = 110.512$ (11)°, $Z = 4$, Mo Kα radiation) has been determined by three-dimensional X-ray analysis. The structure was solved by conventional Patterson and Fourier techniques and refined by full-matrix least squares to a final conventional discrepancy factor of 0.055 for the 1546 observed reflections. The $SbCl_5^{2-}$ anion displays a distorted square-pyramidal configuration in which the axial antimony-chloride bond (2.385 (2) Å) is shorter than the mean basal antimony-chloride bond. Two of the four basal antimony-chloride bonds (2.622 (2), 2.625 (2) Å) are undistorted while the other two basal bonds (2.799 (2), 2.509 (2) Å) are distorted by interionic and packing forces.

Introduction

Structural investigations of antimony halide complexes have been actively pursued in this laboratory during recent years, beginning with the work of Lawton and Jacobson.[1] The structures of species containing antomony(III) are of particular interest because of questions concerning the stereochemical role of the lone pair of electrons.

Only a very few antimony(III) chloride structures have been reported in the literature. $SbCl_3$ exhibits a trigonal-pyramidal structure with antimony at the apex,[2] while in $(NH_4)_2SbCl_5$ the chlorine atoms are arranged in a square-pyramidal coordination geometry around the antimony.[3] In $[C_5H_5NH][Sb^{III}Cl_4]$, the halogen configuration around the antimony can be described as tetragonally distorted octahedral with two of the equatorial atoms removed,[4] and $SbCl_6^{3-}$ forms perfect octahedra in $Co(NH_3)_6SbCl_6$.[5]

Because of the seeming variety of structural geometries possible for antimony(III) and because the structure of $(NH_4)_2SbCl_5$ was determined only from film projection data, we decided to undertake a structure determination of K_2SbCl_5.

Experimental Section

Preparation. A sample of K_2SbCl_5 was kindly supplied by Dr. Donald Macalady, who prepared the compound in the following manner. Two solutions, one of $SbCl_3$ in 3 *N* HCl and one of KCl in 3 *N* HCl, were combined so that the molar ratio of potassium to antimony in the resulting solution was 5:7. This solution was allowed to stand, and crystals formed by slow evaporation. Microscopic examination revealed many different crystal morphologies. Thin plates appeared to be the basic unit of all these morphologies, however.

Crystal Data. A crystal was cut from one of these plates and mounted on the end of a glass fiber with Duco cement thinned with amyl acetate. Preliminary Weissenberg and precession photographs exhibited $2/m$ Laue symmetry, indicating a monoclinic space group. The following systematic absences were observed: $h0l$ when $l = 2n + 1$ and $0k0$ when $k = 2n + 1$. These absences are only consistent with the space group $P2_1/c$. The unit cell parameters at 25° are $a = 8.8686 \pm 0.0007$, $b = 12.4577 \pm 0.0013$, $c = 8.9280 \pm 0.0013$ Å, and $\beta = 110.512 \pm 0.011°$. These parameters and their standard deviations were obtained by a least-squares fit[6] to the 2θ values of 16 independent high-angle reflections whose centers were determined by left-right, top-bottom beam splitting on a previously aligned four-circle diffractometer (Mo Kα radiation, λ 0.71069 Å). A calculated density of 2.711 g/cm^3 for four molecules per unit cell agrees quite well with an observed density of 2.72 ± 0.01 g/cm^3, determined by flotation techniques.

Collection and Reduction of X-Ray Intensity Data. For data collection, the crystal described above, measuring approximately 0.2 mm along each of the crystal axes, was mounted so that the *c* axis coincided with the ϕ axis of the diffractometer. Data were collected at room temperature using an automated four-circle diffractometer designed and built in the Ames Laboratory. The

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Table I. Final Atomic Coordinates and Thermal Parameters (×10^4) for K_2SbCl_5[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sb	0.1836 (1)	−0.0068 (1)	0.2025 (1)	75 (1)	42 (1)	80 (1)	−2 (0.4)	20 (0.8)	−0.3 (0.4)
Cl(1)	0.2414 (3)	0.0959 (2)	0.0510 (3)	141 (4)	55 (2)	98 (3)	−3 (2)	47 (3)	3 (2)
Cl(2)	−0.0097 (3)	0.1519 (2)	0.2070 (3)	90 (3)	51 (2)	160 (4)	6 (2)	47 (3)	2 (2)
Cl(3)	0.4157 (3)	−0.1400 (2)	0.2121 (3)	143 (4)	68 (2)	115 (4)	35 (2)	41 (3)	0.8 (2)
Cl(4)	0.3885 (3)	0.1137 (2)	0.3563 (3)	89 (3)	61 (2)	99 (3)	−17 (2)	26 (3)	−9 (2)
Cl(5)	0.1706 (3)	−0.0770 (2)	0.4611 (3)	118 (4)	67 (2)	100 (3)	−11 (2)	40 (3)	16 (2)
K(1)	0.1853 (3)	0.1746 (2)	0.5939 (3)	135 (4)	56 (1)	112 (3)	2 (2)	52 (3)	−1 (2)
K(2)	0.3742 (3)	−0.1285 (2)	0.8452 (2)	106 (3)	94 (2)	129 (4)	5 (2)	43 (3)	−24 (2)

[a] Anisotropic thermal parameters are defined by $T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{33})]$.

upper full circle was purchased from STOE and is equipped with encoders (Baldwin Optical) and drive motors. The design of the base allows the encoders to be directly connected to the main θ and 2θ shafts, using solid and hollow shaft encoders, respectively. The diffractometer is interfaced to a PDP-15 computer in a real-time mode and is equipped with a scintillation counter. Zirconium-filtered Mo Kα radiation was used for the data collection. A scan rate of 0.1 sec/step of 0.01° in θ was employed with a variable-scan range of 35 steps plus 1 step/1° in θ. Stationary-crystal, stationary-counter background counts of a quarter of the scan time were taken at the beginning and end of each scan. Before the scan was made, a peak height measurement was used to determine if the reflection was observed. To be scanned, the reflection had to exceed the background by more than six counts. If the reflection met this criterion, the ω setting was then adjusted slightly, if necessary, to maximize the peak height. Within a 2θ sphere of 50° ($(\sin\theta)/\lambda = 0.595$ Å^{-1}), all data in the hkl and $\bar{h}kl$ octants were measured in this manner, using a takeoff angle of 4.5°. Of the 1750 reflections examined, 1614 met the peak height criterion and were scanned.

As a general check on electronic and crystal stability, the intensities of three standard reflections were remeasured every 25 reflections. These reflections did not vary to any significant degree during the entire period of data collection.

The intensity data were corrected for Lorentz-polarization effects and for effects due to absorption. An absorption correction was made using the Tompa–Alcock absorption correction program[7] using a linear absorption coefficient of $\mu = 52.28$ cm^{-1}. The maximum and minimum transmission factors were 43.95 and 35.98%, respectively. The estimated error in each intensity was calculated by

$$\sigma_I^2 = C_T + 2C_B + (0.03C_T)^2 + (0.03C_B)^2 + (0.03C_I)^2 T_a^2$$

where C_T, C_B, C_I, and T_a are the total count, the background count, the net count, and the transmission factor, respectively, and the factor 0.03 represents an estimate of nonstatistical errors. The estimated deviations in the structure factors were calculated by the finite-difference method.[8] Of the 1614 independent reflections, 1546 were considered observed ($>2.0\sigma_F$).

Solution and Refinement of Structure

The position of the antimony atom was obtained from analysis of a sharpened three-dimensional Patterson function.[9] The remaining atoms were found by successive structure factor[10] and electron density map calculations.[11] These atomic positions were refined by a full-matrix least-squares procedure,[10] minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma_F^2$, to a conventional discrepancy factor of $R = \Sigma(|F_o| - |F_c|)/|F_o| = 0.169$. The scattering factors used were those of Hanson, *et al.*,[12] modified for the real and imaginary parts of anomalous dispersion.[13]

Table II. Bond Lengths (Å), Bond Angles (deg), and Significant Nonbonded Distances (Å) in K_2SbCl_5[a]

Sb–Cl(1)	2.799 (2)	Sb–Cl(2)	2.625 (2)
Sb–Cl(3)	2.622 (2)	Sb–Cl(4)	2.385 (2)
Sb–Cl(5)	2.509 (2)		
Cl(4)–Sb–Cl(1)	81.92 (7)	Cl(4)–Sb–Cl(2)	83.54 (8)
Cl(4)–Sb–Cl(3)	87.06 (8)	Cl(4)–Sb–Cl(5)	87.77 (8)
Cl(1)–Sb–Cl(2)	88.50 (7)	Cl(2)–Sb–Cl(5)	90.43 (8)
Cl(5)–Sb–Cl(3)	92.19 (3)	Cl(3)–Sb–Cl(1)	87.22 (8)
Cl(1)–Sb–Cl(5)	169.69 (8)	Cl(2)–Sb–Cl(3)	170.13 (8)
Sb–Sb′	3.932 (1)	Sb–Cl(2)′	3.881 (3)
Cl(1)–Sb′	3.701 (2)	Cl(1)–Cl(2)′	3.699 (3)
Cl(2)–Cl(5)$_{\mathrm{i}}$	3.768 (3)	Cl(1)–Cl(3)$_{\mathrm{ii}}$	3.832 (4)
Cl(1)–K(1)$_{\mathrm{iii}}$	3.187 (3)	Cl(1)–K(2)$_{\mathrm{iii}}$	3.290 (3)
Cl(2)–K(2)$_{\mathrm{iii}}$	3.168 (3)	Cl(1)–K(1)$_{\mathrm{iv}}$	3.247 (3)
Cl(2)–K(1)$_{\mathrm{iv}}$	3.147 (3)	Cl(3)–K(2)$_{\mathrm{v}}$	3.190 (4)
Cl(2)–K(1)	3.289 (3)	Cl(4)–K(1)	3.317 (3)

[a] Primed atoms are those related by the center of inversion, as in Figure 1. Other symmetry operations referred to: (i) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $1 - x, -y, -z$; (iii) $x, y, z - 1$; (iv) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (v) $x, -\frac{1}{2} - y, z - \frac{1}{2}$.

An electron density difference map verified that all the atoms had been accounted for but indicated that some anisotropic motion, particularly of the antimony, was present. Accordingly, anisotropic refinement was begun and after four cycles of refinement, values of R and R_w ($= [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$) of 0.055 and 0.080, respectively, were obtained.

A final electron density difference map showed no peaks greater than 0.9 e/Å^3. A final statistical analysis of $\overline{w\Delta^2}$, where $\Delta = (|F_o| - |F_c|)$, as a function of the scattering angle and magnitude of F_o revealed no unusual trends and suggests that the relative weighting scheme used is a reasonable one.

The final positional and thermal parameters are listed in Table I. The standard deviations were calculated from the inverse matrix of the final least-squares cycle. Bond lengths, bond angles, and significant nonbonded distances[14] are listed in Table II.[15]

Description and Discussion

The configuration of $SbCl_5^{2-}$ in K_2SbCl_5 is essentially that of a square pyramid which has been distorted by inter-

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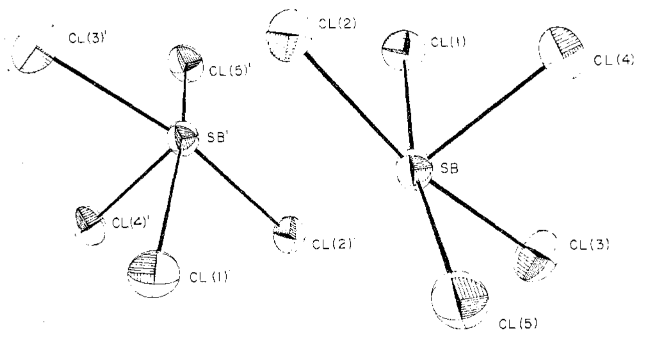

Figure 1. Two inversion-related $SbCl_5^{2-}$ anions.

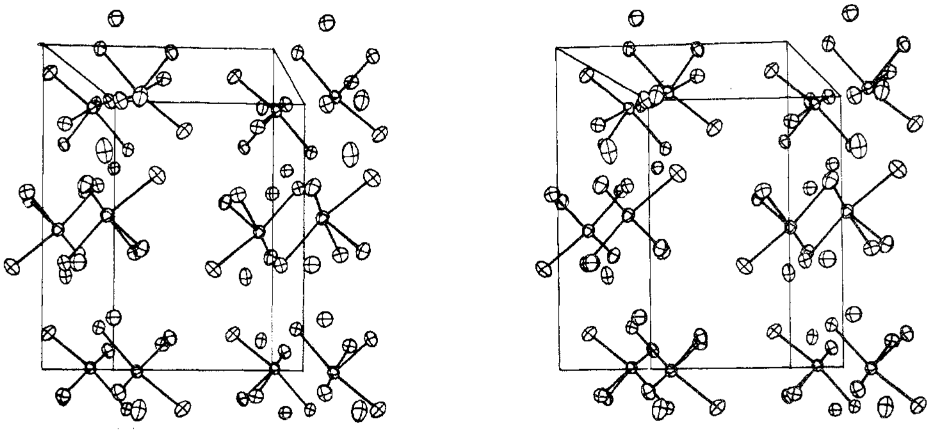

Figure 2. Packing diagram of K_2SbCl_5.

ionic and packing forces. The inversion-related anions are packed approximately base to base, as depicted in Figure 1.[16] The axial antimony-chlorine bond length is 2.385 (2) Å in good agreement with the axial distance in $(NH_4)_2SbCl_5$ (2.36 Å)[3] and the shorter distance (2.38 Å) in $[C_5H_5NH]$-$[Sb^{III}Cl_4]$[4] and is only slightly longer than the distance (2.32 Å) in $SbCl_3$.[2]

The antimony-chlorine bond distances in the base are all considerably longer than the axial distance. Two of these distances are almost identical (2.622 (2), 2.625 (2) Å) and involve chlorines trans to each other. The other pair of chlorines form bonds of 2.799 (2) and 2.509 (2) Å length, with an average of 2.654 Å. In $(NH_4)_2SbCl_5$ all basal antimony-chlorine bonds were found to be essentially of equal length (2.62 Å average) while in $[C_5H_5NH][SbCl_4]$ the corresponding bond length for chlorines trans to one another is 2.63 Å.

In the present study, the lengthening of the Sb-Cl(1) distance to 2.799 (2) Å appears to be due to electrostatic repulsions and packing effects, as it is this chlorine that is involved in the closest nonbonded contacts; significant nonbonded distances are given in Table II. An antimony atom is only 3.701 (2) Å from Cl(1), whereas the sum of the van der Waals radii is 4.0 Å. Also, the shortest chlorine-chlorine distance found, 3.699 (3) Å, is between this chlorine and Cl(2)'. Both these distances would become significantly shorter if the Sb-Cl(1) bond were shortened. Thus, it can be inferred that this bond can be readily distorted if more efficient packing of the ions results. The shortening of the Sb-Cl(5) bond appears to be a trans effect in response to the lengthening of the Sb-Cl(1) bond. The observed bond lengths of the basal antimony-chlorine bonds described above are consistent with characterizing the antimony bonding orbitals as being composed primarily of p orbitals as in the three-center four-electron bonding scheme described by Porter and Jacobson.[17] The lone pair appears to have a comparatively small stereochemical effect. This is supported by the relatively short antimony-antimony distance of 3.932 (1) Å, where localized lone pairs, if present, would have to be directed toward one another. Distortions of the Cl-Sb-Cl bond angles from the expected 90° (*cf.* Table II) can be explained by interionic repulsions between inversion-related complexes.

The arrangement of the $SbCl_5^{2-}$ complexes in the unit cell is such that the chlorine atoms approximate a closest packed arrangement in the *bc* plane, as is evident in Figure 2, with the shortest chlorine-chlorine distances approximating the sum of the van der Waals radii. The potassium ions lie in these planes, located between three of the chlorines. The shortest potassium-chlorine distance is 3.147 (3) Å.

Registry No. K_2SbCl_5, 42201-07-0.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-1678.

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