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THE CRYSTAL STRUCTURES OF HEXAMMINECOBALT
HEXACHLOROANTIMONATE(III) AND HEXAMMINECOBALT
NONAFLUOROANTIMONATE(III)

MS. Thesis Submitted to Iowa State University, November 1972

Donald Ray Schroeder

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The crystal structures of hexamminecobalt
hexachloroantimonate(III) and hexamminecobalt
nonafluoroantimonate(III)

by

Donald Ray Schroeder

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ABSTRACT

Hexamminecobalt hexachloroantimonate(III), $\text{Co}(\text{NH}_3)_6\text{SbCl}_6$, crystallizes in the orthorhombic space group $P_{bca}^{15} (D_{2h}^{15})$ with unit cell parameters $a = 11.50(3) \text{ \AA}$, $b = 11.53(3) \text{ \AA}$ and $c = 11.51(2) \text{ \AA}$. The observed and calculated densities were both found to be 2.19 g cm^{-3} with $Z = 4$. Data were collected on an automated four-circle diffractometer equipped with scintillation counter using the θ - 2θ step scan technique and Mo K_α radiation ($\lambda = 0.71069 \text{ \AA}$). The structure was solved by Patterson and Fourier methods and refined by full matrix least-squares techniques to a final discrepancy index $R = 0.061$ for the 416 independent reflections significantly above background. The structure consists of SbCl_6^{3-} anions and $\text{Co}(\text{NH}_3)_6^{3+}$ cations both of which have exact $\bar{1}$ crystallographic symmetry. Both also have approximately octahedral symmetry with all Sb-Cl bond lengths in $\text{Sb}^{\text{III}}\text{Cl}_6$ of $2.643(6) \text{ \AA}$ ($2.652(6) \text{ \AA}$ when corrected for thermal motion); the mean Co-N bond distance is $1.982(10) \text{ \AA}$.

The crystal structure of hexamminecobalt nonafluoroantimonate(III), $\text{Co}(\text{NH}_3)_6\text{Sb}_2\text{F}_9$, has been solved by single-crystal X-ray diffraction techniques at room temperature ($25 \pm 2^\circ$) using three-dimensional scintillation counter data and a full-matrix anisotropic least-squares refinement procedure ($R = 0.060$). The compound crystallizes in the monoclinic crystal system of space group $P2_1/c$, with cell lattice parameters $a = 7.223(5)$, $b = 7.298(3)$, $c = 12.432(7) \text{ \AA}$ and $\beta = 93.15(8)^\circ$.

The observed and calculated densities are 2.84 and 2.89 g cm⁻³, respectively. The asymmetric unit consists of one octahedral Co(NH₃)₆³⁺ ion and one distorted Sb₂F₉³⁻ ion. The Sb₂F₉³⁻ ion resembles two octahedra sharing a corner with each octahedra possessing a lone pair. It was also found that the bridging fluorine in this compound is statistically disordered. The bridge is asymmetric with Sb-F bonds of 2.249(12) and 2.449(4) Å. The Sb-F bond length opposite the lone pair is 1.948(7) Å while the Sb-F distance opposite the bridging fluorine is 2.015(5) Å. The remaining two Sb-F bonds are trans to one another with distances of 2.080(11) and 2.078(8) Å, respectively. The mean Co-N distance is 1.990(5) Å.

INTRODUCTION

In recent years there has been increased interest in the bonding exhibited by non-transition element compounds. It has been postulated by Gillespie and Nyholm¹ that the stereochemistry of most of these compounds is dictated by electrostatic repulsions between valence electron pairs including lone pairs, with the lone pair occupying a definite coordination site. However it has also been suggested that in some of these compounds the s-orbital may not interact strongly with the ligand orbitals and that the lone pair resides in this spherically symmetrical s-orbital². Various types of spectroscopy have been employed in attempts to examine the bonding in $:XL_6$ complexes and to draw conclusions as to the inertness of the s-orbital on the central atom. Even these results have been many times inconclusive and contradictory assignments have appeared pertaining to various frequencies^{3,4,5}. This has been particularly true for complexes involving antimony halides.

The crystal structure investigations of hexaminecobalt hexachloroantimonate(III) and hexaminecobalt nonafluoroantimonate(III) were undertaken as part of a series of investigations of halo-coordinated antimony compounds being performed at this laboratory⁶⁻¹². Through these studies an attempt is being made to evaluate the effects of cation size and type on the stereochemistry of different antimony halides and to determine what effect, if any, the lone pair plays in the coordination geometry. In particular this study was undertaken so that more information would be made available about the coordination of Sb(III).

The structures of a number of bromide complexes have previously been reported including $(\text{NH}_4)_4\text{Sb}^{\text{III}}\text{Sb}^{\text{V}}\text{Br}_{12}$ ⁷, $\text{Rb}_4\text{Sb}^{\text{III}}\text{Sb}^{\text{V}}\text{Br}_{12}$ ⁸, $(\text{C}_5\text{H}_5\text{NH})_6\text{Sb}^{\text{III}}\text{Sb}^{\text{V}}\text{Br}_{24}$ ⁹ and $(\text{C}_7\text{H}_{13}\text{NH})_4\text{Sb}^{\text{III}}\text{Sb}^{\text{V}}\text{Br}_{12} \cdot 2\text{Br}_2$ ¹⁰, all of which contain octahedral SbBr_6^{3-} units. Of the chloride complexes, accurate crystal structure determinations of only $(\text{C}_5\text{H}_5\text{NH})\text{SbCl}_4$ ¹¹, K_2SbCl_5 ¹² and $(\text{NH}_4)_2\text{SbCl}_5$ ¹³ have been reported. The vibrational spectra of $\text{Co}(\text{NH}_3)_6\text{SbCl}_6$ was first published by Day⁴, and later by Martineau and Milne⁵ along with their powder diffraction data which led them to believe that this compound belonged to the cubic crystal system and probably isostructural with $\text{Co}(\text{NH}_3)_6\text{TlCl}_6$. Day postulated on the basis of the half widths present in his vibrational spectra that the SbCl_6^{3-} anion had octahedral geometry while on the other hand Milne stated that his results were consistent with a distorted octahedral environment. In addition to interest in the coordination geometry in this compound it was also of particular interest to determine an accurate Sb(III)-Cl bond distance, hence it was felt that a structural study of this complex would be a worthwhile endeavor. It should be noted that a structural study of such an anion has not been reported previously.

Antimony trifluoride is typical of the other antimony halides in the sense of forming a variety of cation-antimony (III) halide complexes. Crystallographic structural results on some fluoride complexes have been reported by Wilhelmi and coworkers^{14,15,16} although their conclusions have recently been questioned by Mastin and Ryan¹⁷. In this laboratory structures of $[(\text{CH}_3)_4\text{N}]_3\text{Sb}_2\text{Br}_9 \cdot \text{Br}_2$ ¹⁸, $(\text{C}_5\text{H}_5\text{NH})_5\text{Sb}_2\text{Br}_9 \cdot \text{Br}_2$ ¹⁹ and $\text{Cs}_3\text{Sb}_2\text{Cl}_9$ ²⁰, all of which contain $\text{Sb}_2\text{X}_9^{3-}$ ions have recently been

investigated by X-ray diffraction techniques. It is worthwhile to note the different bridging observed in the three cases. In $(C_5H_5NH)_5Sb_2Br_9 \cdot Br_2$ the $Sb_2Br_9^{3-}$ anion was found to consist of two $SbBr_6$ octahedra sharing a face. In $[(CH_3)_4N]_3Sb_2Br_9 \cdot Br_2$ the same anion is found but in this case the anions are bridged by Br_2 molecules ($Br-Br_2$ distance of $2.89(1) \text{ \AA}$). However in $Cs_3Sb_2Cl_9$, although three chlorines are of the bridging type, all form linear bridges producing a three-dimensional network in the crystal. Since a fluorine complex with formula $Co(NH_3)_6Sb_2F_9$ has been recently prepared, it was felt a structural investigation of this complex would form a significant addition to the $Sb_2X_9^{3-}$ series.

THE STRUCTURE OF HEXAMMINECOBALT HEXACHLOROANTIMONATE(III)

Experimental

Preparation

The salt was prepared by the reaction of hexamminecobalt(III) chloride and antimony trioxide in a solution of 2.0 molar hydrochloric acid. Hexamminecobalt(III) chloride was first prepared by adding 24.0 grams (0.1 mole) of cobalt(II) chloride hexahydrate and 16.0 grams (0.3 mole) of ammonium chloride to 20.0 ml of H_2O . To this was added 0.4 grams of activated decolorizing charcoal and 50.0 ml of concentrated NH_3 . Air was then bubbled vigorously through the mixture for approximately four hours to enhance oxidation of Co(II). The crystals were filtered and then added to a solution of 3.0 ml of concentrated hydrochloric acid in 150 ml of H_2O . Hexamminecobalt(III) chloride was then precipitated by adding 40.0 ml of concentrated hydrochloric acid and cooling to $0^\circ C$. The precipitate was next filtered and washed first with 60% and then with 95% alcohol before drying at $90^\circ C$. Then, a hot solution of 0.15 grams of antimony trioxide in 50.0 ml of 2.0 molar hydrochloric acid was added to 50.0 ml of 0.02 molar hexamminecobalt(III) chloride in H_2O . The crystalline product which resulted was of superior quality, consisting of tetragonal prisms which exhibited a bright orange color. They were also found to be stable in the atmosphere; therefore, the crystal used for data collection was mounted on a glass fiber.

Crystal Data

Crystals of $\text{Co}(\text{NH}_3)_6\text{SbCl}_6$, examined by precession and Weissenberg film techniques, were found to exhibit mmm Laue symmetry indicating an orthorhombic space group. The following systematic absences were observed: $0k\ell$ when $k = 2n+1$, $h0\ell$ when $\ell = 2n+1$ and $hk0$ when $h = 2n+1$. These absences are consistent only with the space group P_{bca} .

The unit cell parameters at $25^\circ\text{C} \pm 2^\circ$ are $a = 11.50(3)$, $b = 11.53(3)$ and $c = 11.51(2)$ Å. 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 left-right, top-bottom beam splitting on a previously aligned Hilger-Watts four-circle diffractometer (Cu K_α radiation, $\lambda = 1.5418$ Å). Any error in the instrument zero was eliminated by centering the reflection at both $+2\theta$ and -2θ .

Data were collected at room temperature utilizing an automated four-circle diffractometer designed and built in the Ames Laboratory. The upper full circle was purchased from STOE and equipped with encoders (Baldwin optical) and drive motors. The base was so designed that encoders could be directly connected to the main ω and 2θ shafts, using solid and hollow shaft encoders, respectively. The diffractometer is interfaced to a PDP-15 computer and is equipped with scintillation counter. Zirconium-filtered Mo K_α radiation ($\lambda = 0.71069$ Å) was used for data collection on an approximately spherical crystal of dimensions $0.104 \times 0.106 \times 0.100$ mm and mounted such that the b^* axis was coincident with the ϕ axis of the diffractometer. The θ - 2θ scan technique was employed to measure 710 reflections in

one octant within a 2θ sphere of 40° , of which 416 were found to be $\geq 3\sigma(F)$. A take-off angle of 3° and scan rate of $0.01^\circ/0.1$ sec. were employed for the symmetric scan ranges of 1.12° in 2θ at low two-theta values to 1.72° at large two-theta. Stationary crystal, stationary counter background counts of one half the time required to scan the peak were taken at each end of the scan. Before the scan was made a peak height measurement was used to determine if the reflection was observed. The reflection had to exceed the background by seven counts or more to be scanned, which corresponds to approximately three standard deviations in the background for larger $\sin \theta/\lambda$ values.

As a general check on electronic and crystal stability, the intensities of three standards were measured every twenty-five reflections. Those reflections showed no decrease over the entire period of data collection.

The intensity data were also corrected for Lorentz-polarization effects. The estimated error in each intensity was calculated by

$$[\sigma(I)]^2 = [Ct + Cb + (0.03Ct)^2 + (0.05Cb)^2 + (0.04Cr)^2]$$

where Ct, Cb, and Cr are the total count, background count, and net count, respectively. The estimated standard deviation in each structure factor was calculated by $\sigma(F_o) = [(I_o + \sigma(I_o))/Lp]^{1/2} - |F_o|$, a function based on the finite-difference method²¹, where Lp is the Lorentz-polarization factor. These standard deviations were used during the least-squares refinement to weight the observed structure factors, where w , the individual weighting factor, was defined by $1/\sigma(F_o)^2$. Transmission factors ranged from 0.71 to 0.68 based on a

linear absorption coefficient of 39.24 cm^{-1} ; no absorption corrections were therefore applied.

Solution and Refinement

Since there are eight general positions and only four formula units per unit cell, both the antimony and cobalt atoms must lie on special positions of $\bar{1}$ site symmetry. Atoms at such positions contribute only to those reflections with $h+k$, $k+l$, and $h+l = 2n$, and indeed all the strong reflections are in this subgroup. A Patterson map was computed from sharpened data²² and revealed peaks consistent with such special positions for these atoms. The remaining atoms were found by successive structure factor and electron density map calculations after care was exercised to separate the structure from its mirror image, since both heavy atoms are positioned on planes with $y = 0, \frac{1}{2}$.

These positions were then refined by full matrix least-squares techniques²³ with isotropic thermal parameters to a conventional discrepancy factor of $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.070$ and a weighted R-factor $\omega R = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{\frac{1}{2}} = 0.071$. The scattering factors were those of Hanson *et al.*²⁴, with antimony, cobalt and chlorine modified for the real and imaginary parts of anomalous dispersion²⁵. A difference electron density map²⁶ at this stage verified that all non-hydrogen atoms had been accounted for, but that some anisotropic motion, particularly of the heavier atoms was quite evident. Accordingly, anisotropic refinement of all atoms

heavier than nitrogen was begun and after four cycles of least-squares, the discrepancy factor dropped to 0.061 ($wR = 0.060$).

A final electron density map showed no peaks higher than $0.6e^-/\text{\AA}^3$. A final statistical analysis of the F_o and F_c values as a function of the indices, the scattering angle and the magnitude of F_o showed no unusual trends and suggests that the relative weighting scheme used is a reasonable one. The final positional parameters are given in Table I and the final thermal parameters in Table II, along with their standard deviations as derived from the inverse matrix of the final least-squares cycle²⁷.

Description of the Structure

The SbCl_6^{3-} and $\text{Co}(\text{NH}_3)_6^{3+}$ moieties are illustrated in Figure 1 and the interatomic distances and angles and their standard deviations are given in Table III. The average Sb-Cl bond length is 2.652(6) Å when corrected assuming a riding model. A stereoview of the unit cell of $\text{Co}(\text{NH}_3)_6\text{SbCl}_6$ is illustrated in Figure 2 produced by Johnson's thermal-ellipsoid plot program²⁸. The unit cell contains four SbCl_6^{3-} anions and four $\text{Co}(\text{NH}_3)_6^{3+}$ cations, and these anions and cations pack in a NaCl-type structure. Indeed, the unit cell dimensions are all equal to within a standard deviation, although the symmetry is clearly only orthorhombic. A portion of the unit cell has been illustrated in Figure 3 along with important non-bonding distances. The dihedral angle between the planes formed by Sb, Cl(1), Cl(3), and Co, N(1), N(3) is $64.26(5)^\circ$ giving rise to an efficient

packing of cations. Although no hydrogen atom positions were clearly evident on the difference map, hydrogen bonding is clearly indicated by the shorter nitrogen-chlorine distances ranging from 3.245 to 3.399 Å, well within that expected for such hydrogen bonds²⁹. Also, the Co-N-Cl angles are indicative of such bonding, ranging from 108.02 to 114.78°. Table IV consists of the observed and calculated structure factors (in electrons $\times 10$) for $\text{Co}(\text{NH}_3)_6\text{SbCl}_6$.

Discussion

Gillespie and Nyholm¹ have suggested that the stereochemistry of most non-transition element compounds seems to be dictated by the electrostatic repulsion between pairs of valence electrons located on the central atom, regardless of the nature of the pair of electrons, bonding or lone. Using this type of argument one would expect an XL_6 compound such as SbCl_6^{3-} to be either seven-coordinate with the lone-pair occupying a bonding site, or, an irregular octahedron. However, the three crystallographically independent bonds in SbCl_6^{3-} average 2.643(6) Å with no significant difference between them. The Cl-Sb-Cl angles all range from 88.90° to 91.10°. The equality of all the Sb-Cl distances and the very slight variation of the Cl-Sb-Cl angles from 90° indicate that the lone pair in SbCl_6^{3-} does not occupy a coordination site, but rather is in a spherically symmetric s orbital; this is also consistent with the Mössbauer work of Della Valle et al.³⁰. Essentially octahedral symmetry was also found for the SbBr_6^{3-} anions⁷⁻¹⁰. Moreover if in each case the

bond length in the anion is compared to that in the simple trihalide, lengthenings of 0.28 and 0.27 Å are found for the chloride and bromide, respectively. In both cases the bonding can be viewed to a first approximation as use of the 5s orbital for the lone pair, and primarily the 5p orbitals for bonding to the halogens. In this way the bonding in the SbX_6^{3-} specie can be viewed to a first approximation as three three-center-four-electron bonds. In this simple approach no outer d-orbitals are necessary to describe the bonding. This description is essentially that proposed by Rundle³¹ for I_3^- and other polyhalides; it should also be noted that the lengthening of the I-I distance in I_3^- relative to I_2 is 0.27 Å.

Table I. Final positional parameters^{a,b} for $\text{Co}(\text{NH}_3)_6 \text{SbCl}_6$

Atom	Position	x	y	z
Sb	4a	0.0*	0.0*	0.0*
Co	4b	0.0*	-0.5*	0.0*
Cl(1)	8c	0.1621(5)	-0.0781(6)	0.1436(5)
Cl(2)	8c	0.3559(5)	-0.1612(5)	0.4208(6)
Cl(3)	8c	0.0790(6)	-0.3564(5)	0.3383(5)
N(1)	8c	0.4438(17)	-0.0955(17)	0.1312(16)
N(2)	8c	0.3668(15)	-0.4440(16)	0.4050(16)
N(3)	8c	0.0963(17)	-0.3667(16)	0.0556(16)

^aNumbers in parentheses in this and succeeding tables represent standard deviations occurring in the least significant digits of the parameter.

^bAn atomic coordinate fixed by symmetry is indicated with an asterisk.

Table II. Final anisotropic thermal parameters^{a,b} ($\times 10^4$) for
 $\text{Co}(\text{NH}_3)_6\text{SbCl}_6$

Atom	Position	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sb	4a	34(1)	36(1)	30(1)	0(2)	0(1)	0(2)
Co	4b	30(3)	35(3)	30(3)	-6(3)	2(3)	1(3)
Cl(1)	8c	41(5)	81(7)	48(5)	16(5)	-9(5)	-1(5)
Cl(2)	8c	53(5)	51(6)	74(6)	-11(5)	0(5)	-8(5)
Cl(3)	8c	78(6)	49(5)	41(5)	0(5)	11(5)	5(5)
N(1)	8c	2.4(4)					
N(2)	8c	1.8(4)					
N(3)	8c	2.3(4)					

^aThe isotropic temperature factor and its corresponding standard deviation for nitrogens are listed under the heading β_{11} .

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

Table III. Selected distances and angles in $\text{Co}(\text{NH}_3)_6\text{SbCl}_6$ a) Distances ($\text{\AA}$)

Atoms	Length	Atoms	Length
Sb-Cl(1)	2.643(6)	N(1)-N(2)	2.814(26)
Sb-Cl(2)	2.643(6)	N(1)-N(3)	2.801(27)
Sb-Cl(3)	2.643(6)	N(2)-N(3)	2.808(26)
Co-N(1)	1.972(19)	Cl(1)-N(3)	3.545(22)
Co-N(2)	1.984(18)	Cl(3)-N(3)	3.254(21)
Co-N(3)	1.992(19)	Cl(3)-N(1)	3.341(21)
Cl(1)-Cl(2)	3.999(10)	Cl(2)-Cl(3')	3.774(11)
Cl(1)-Cl(3)	4.013(10)	Cl(1')-Cl(3)	3.767(11)
Cl(2)-Cl(3)	4.002(11)		

b) Angles (deg)

Atoms	Angle	Atoms	Angle
Cl(1)-Sb-Cl(2)	90.7(2)	N(1)-Co-N(2)	90.7(7)
Cl(1)-Sb-Cl(3)	90.9(2)	N(1)-Co-N(3)	89.9(8)
Cl(2)-Sb-Cl(3)	91.1(2)	N(2)-Co-N(3)	89.8(7)

Table IV. Observed and calculated structure factors (in electrons $\times 10$) for $\text{Co}(\text{NH}_3)_6\text{SbCl}_6$

L = 0	1	4	1718	1194	1	6	1127	1062	7	7	878	908	4	9	432	-495	6	1	279	-323	H	K	F _o	F _c	L = 0	P	FO	FC
H	K	F _o	F _c	3	4	412	426	2	6	1677	1852	4	8	269	-214	5	9	305	-210	8	1	266	228	H	K	F _o	FC	
2	0	2193	3178	5	4	965	-930	3	6	650	674	5	8	144	-252	0	10	1336	1336	0	2	2329	2180	0	0	1678	1492	
6	0	2177	2297	7	5	389	410	4	6	1470	1395	7	8	346	276	2	10	1039	1063	2	2	1689	1684	1	0	600	-572	
8	0	1566	1460	8	5	326	339	5	6	432	-442	1	9	487	556	4	2	1646	1556	4	2	1646	1556	2	0	1450	1459	
10	0	666	599	9	5	474	523	6	6	1709	1783	3	9	309	412	L = 5				2	2	1738	1809	4	0	1624	1672	
2	1	321	316	0	6	165	353	7	6	365	336	5	9	325	370	H	K	F _o	FC	8	2	1310	1239	5	0	718	904	
4	1	752	643	1	6	284	297	8	6	1365	1337	0	10	335	-616	1	1	987	942	7	3	678	712	6	0	1498	1486	
6	1	329	338	2	6	294	169	0	6	337	-137	2	1	446	427	2	1	446	427	3	3	499	543	7	0	288	-273	
8	1	474	-530	4	6	267	-115	2	7	291	-327	L = 4				3	1	897	507	7	3	427	-383	1	1	395	-451	
10	1	508	-508	6	6	155	-500	3	7	154	-464	H	K	F _o	FC	4	1	904	-14	0	4	1460	1463	1	1	593	-546	
2	0	2919	3344	5	6	310	-314	4	7	231	125	1	0	737	707	6	1	949	-345	2	2	1469	1461	5	1	789	361	
2	2	2327	2465	8	6	344	-219	0	8	1359	1417	2	0	2147	2254	7	1	276	217	4	4	1489	1548	6	1	251	-204	
4	2	2202	2258	1	7	830	869	2	8	1486	1427	3	0	400	-398	8	-1	542	527	6	4	1678	1715	0	2	1881	2003	
6	2	1352	1422	2	7	1033	1037	4	8	1444	1419	4	0	3139	3100	9	1	376	467	7	4	261	-277	1	2	326	-243	
8	2	1104	1090	3	7	526	483	6	8	1261	1222	5	0	1415	-1351	2	2	323	293	9	4	1433	1400	4	2	1238	1210	
2	3	716	747	5	7	284	218	7	8	232	251	5	0	1451	1465	3	2	358	277	1	5	402	-374	6	2	1403	1371	
4	3	458	-451	7	7	491	419	3	9	321	190	7	0	339	406	6	2	421	-458	2	5	533	-446	4	3	409	-457	
10	3	371	-448	0	8	532	-544	6	9	233	-117	8	0	1666	1627	1	3	818	772	3	5	342	388	5	3	256	263	
2	4	1765	1845	1	8	431	-419	0	10	1130	1075	9	0	904	922	4	3	448	499	4	5	391	-370	0	4	1689	1665	
4	4	2927	3053	5	8	490	501	1	10	468	-480	10	0	1545	1565	5	3	560	531	0	6	1195	1137	2	4	1391	1455	
6	4	1889	1988	6	8	504	530	2	10	1211	1259	1	1	1237	1191	6	3	366	399	1	6	317	-296	4	3	310	-271	
8	4	1559	1605	3	7	515	465	3	10	514	-516	3	1	326	-423	7	3	450	420	6	6	240	-209	7	4	1161	1109	
10	4	1721	1836	4	9	385	447	4	10	1187	1199	5	1	270	-253	8	3	470	-253	4	6	1620	1690	5	4	380	-430	
2	5	1367	-1372	0	10	530	-498	L = 3				10	1	243	257	9	3	337	362	6	6	572	593	6	4	1043	1009	
4	5	803	841	L = 2				H	K	F _o	FC	2	2	2704	2385	0	4	1352	-1314	2	7	301	-313	1	5	547	500	
6	5	2156	2244	H	K	F _o	FC	3	1	1471	1491	2	2	2173	2201	1	4	575	-637	4	7	240	-43	3	5	274	-271	
8	5	2151	2141	0	0	3077	3342	4	1	528	407	2	4	1494	1419	2	4	723	97	0	8	1463	1481	0	6	630	643	
10	5	1399	1409	2	0	2402	2635	5	1	802	705	10	2	1510	1463	3	4	321	-418	2	8	1388	1353	1	6	709	217	
2	6	1169	1074	2	0	818	747	7	1	487	461	1	3	1158	1226	4	4	630	606	4	8	967	955	2	6	1294	1245	
4	6	1393	1440	4	0	1885	1846	9	1	730	704	2	3	277	-342	6	4	433	-372	L = 7				4	6	1390	1414	
6	6	162	-676	6	0	1885	1846	0	2	780	699	4	1	591	505	9	4	240	-212	H	K	F _o	FC	L = 9				
8	6	401	349	8	0	1728	2182	1	2	1461	-1451	5	1	383	306	1	1	911	912	H	K	F _o	FC	L = 9	F _o	FC		
10	6	491	515	8	0	1750	-666	1	2	1461	-1451	6	1	517	-619	2	1	547	547	2	1	367	-266					
2	8	1640	1494	10	0	1852	1849	2	3	307	-360	7	1	407	461	1	5	405	416	5	1	467	425	3	1	509	576	
4	8	1804	1945	10	0	1190	-1155	3	1	1543	-1326	0	4	3052	3226	5	5	288	187	7	1	416	-437	4	1	381	502	
6	8	1600	1588	2	1	762	-705	4	2	342	-290	2	4	2083	2181	7	5	288	187	7	1	416	-437	5	1	381	502	
8	8	106	599	4	1	1510	-1454	6	2	601	684	4	4	562	515	0	6	419	-347	0	2	733	-699	5	1	395	536	
10	8	765	795	1	1	1081	1031	10	2	515	-504	4	4	1569	1461	5	6	298	156	1	2	1035	1022	1	3	752	724	
2	10	529	549	1	1	725	-744	1	3	1436	1474	5	4	606	604	1	7	470	408	2	2	277	-328	2	3	379	227	
4	10	1121	1137	2	2	2450	2472	2	3	1501	-1376	6	4	1461	1519	2	7	388	-360	3	2	824	781	3	3	457	446	
6	10	1545	1532	1	2	785	-743	3	3	825	765	7	4	343	-320	7	7	668	695	4	2	781	183	4	3	286	-197	
L = 1				2	2	2703	2610	6	3	579	558	8	4	1112	1103	5	7	385	399	5	2	311	-357	5	3	266	239	
H	K	F _o	FC	3	2	365	-316	8	3	376	-359	9	4	427	-484	0	8	861	823	6	2	353	339	0	4	732	808	
1	1	1039	907	4	2	2352	2395	9	4	426	434	1	5	899	-941	1	9	306	331	9	2	295	225	4	4	477	-502	
3	1	1240	1164	5	2	1337	2982	10	5	252	-933	2	5	425	440	3	4	425	440	1	3	389	-402	5	0	589	509	
5	1	998	919	7	2	376	-309	1	4	482	-384	5	5	379	397	1	9	500	501	5	3	711	702	1	6	264	196	
6	1	242	236	8	2	1470	1459	3	4	221	180	8	5	428	-429	3	9	300	225	7	3	854	931	1	6	228	121	
7	1	827	861	10	2	1221	1275	4	4	525	532	0	6	1937	1994	L = 6				0	4	450	400					
8	1	486	-463	2	3	395	-357	5	4	481	508	2	6	1558	1524	H	K	F _o	FC	4	4	261	-331	H	K	F _o	FC	
5	2	766	-681	3	3	1492	-1399	6	4	788	-213	4	6	1418	1515	0	0	2271	2255	7	4	345	383	0	0	631	647	
2	2	467	468	7	3	840	805	7	4	420	-389	5	6	332	-335	1	0	288	349	3	5	1003	969	1	0	533	-540	
4	2	1181	1100	0	4	2237	2291	8	4	463	-469	6	6	1637	1691	2	2	2454	2271	5	5	432	426	2	0	1164	1131	
7	2	77	301	2	4	2257	2428	1	5	881	872	5	6	995	972	1	0	2030	2018	6	5	279	77	3	0	396	-445	
9	2	288	-257	3	4	316	-336	5	4	358	-391	7	7	425	-392	5	0	340	-298	0	6	544	516	4	0	1381	1373	
10	2	480	-493	4	4	2142	2193	5	5	430	509	7	7	278	359	5	0	1216	1122	1	6	359	-205	2	1	433	-517	
2	3	1259	1337	5	4	1461	1430	7	6	557	668	7	8	1638	16

Figure 1. SbCl_6^{3-} anion and $\text{Co}(\text{NH}_3)_6^{3+}$ cation in $\text{Co}(\text{NH}_3)_6\text{SbCl}_6$.

Figure 2. Stereogram of $\text{Co}(\text{NH}_3)_6\text{SbCl}_6$ with Sb at $(0,0,0)$ and Co at $(\frac{1}{2},0,0)$.

Figure 3. A portion of the unit cell of $\text{Co}(\text{NH}_3)_6\text{SbCl}_6$ illustrating intermolecular contacts.

THE STRUCTURE OF HEXAMMINECOBALT NONAFLUOROANTIMONATE(III)

Experimental

A sample of the compound was kindly supplied by Dr. Birchall³² of McMaster University. The crystals obtained were of good quality and no recrystallization was necessary. Microscopic examination revealed that the crystals were cubic in shape with sharply defined faces and exhibited a bright orange color. They were also found to be stable in the atmosphere; therefore the crystal used for data collection was mounted on a glass fiber.

Crystal Data

Crystals of $\text{Co}(\text{NH}_3)_6\text{Sb}_2\text{F}_9$, examined by precession and Weissenberg film techniques were found to exhibit 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 consistent only with the space group $P2_1/c$. The unit cell parameters at 25° are $a = 7.223(5)$, $b = 7.298(3)$, $c = 12.432(7)$ Å and $\beta = 93.15(8)^\circ$. These parameters and their standard deviations were obtained by a least-squares fit to 12 independent reflection angles whose centers were determined by left-right, top-bottom beam splitting on a previously aligned Hilger-Watts four circle diffractometer (Mo K_α radiation, $\lambda = 0.71069$ Å). Any error in the instrumental zero was eliminated by centering the reflection at both $+2\theta$ and -2θ . A calculated density of 2.89 g cm^{-3} for 2 molecules per unit cell agrees quite well with the observed density of 2.84 g cm^{-3} which was determined by flotation techniques.

For data collection, a crystal having approximate dimensions $0.081 \times 0.104 \times 0.095$ mm along the a, b, and c crystal axes, respectively, was mounted such that the b axes was coincident with the spindle axes.

Data were collected at room temperature utilizing a Hilger-Watts four-circle diffractometer equipped with scintillation counter and using Zr-filtered Mo K_{α} radiation. Within a two-theta sphere of 50° , all data in each of two octants were recorded using the θ - 2θ scan technique with a take-off angle of 3° . Symmetric scan ranges of 1.00° in 2θ at low two-theta values and 2.20° at the high two-theta limit were used. Stationary-crystal, stationary-counter background measurements were made at the beginning and end of each scan for one-half the total scan time. The counting rate used was 0.2048 sec per step of 0.02° in two-theta. The rest of the experimental arrangement used has already been discussed in some detail³³. A total of 1317 reflections were measured in this way of which 1037 were found to be $\geq 3\sigma(F)$ and therefore considered observed.

As a general check on electronic and crystal stability, the intensities of three standard reflections were remeasured every twenty-five reflections during the data collection period. These reflections showed no decrease in intensity over the entire period of data collection.

The intensity data were also corrected for Lorentz-polarization effects. The estimated error in each intensity was calculated by $[\sigma(I)]^2 = [C_t + C_b + (0.03 C_t)^2 + (0.05 C_b)^2 + (0.04 C_r)^2]$ where C_t , C_b and C_r are the total count, background count, and net count, respectively.

The estimated standard deviation in each structure factor, $\sigma(F_o)$, was calculated by the finite-difference method²¹. These standard deviations were used during the least-squares refinement to weight the observed structure factors, where ω , the individual weighting factor, was defined as $1/\sigma(F_o)^2$. Transmission factors ranged from 0.67 to 0.62 based on a linear absorption coefficient of 53.32 cm^{-1} ; no absorption corrections were therefore applied.

Solution and Refinement

Examination of the Patterson function, which was calculated from sharpened data²², coupled with restrictions imposed by the space group led to ready location of the heavy atoms. Since there are four general positions but only two molecules per unit cell, the cobalt atoms must lie on positions of $\bar{1}$ site symmetry while the two antimony atoms must be related by $\bar{1}$ symmetry. The remaining atoms were found by successive structure factor and electron density map calculations. No fluorine atom was found on a center of symmetry site; however, two statistically disordered bridging fluorines were found and given half-occupancy.

These positions were then refined by full-matrix least-squares techniques²³ with isotropic thermal parameters to a conventional discrepancy factor of $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 10.3\%$ and a weighted R-factor $\omega R = [\sum \omega (|F_o| - |F_c|)^2 / \sum \omega |F_o|^2]^{1/2} = 11.5\%$. The scattering factors were those of Hanson et al.²⁴, with antimony and cobalt modified for the real and imaginary parts of anomalous dispersion²⁵.

A difference electron density map²⁶ at this stage illustrated that all non-hydrogen atoms had been accounted for, but that some anisotropic motion, particularly of the heavier atoms was quite evident. Anisotropic refinement of all atoms heavier than hydrogen was begun and after six cycles of least-squares the discrepancy factor converged at 0.060 ($\omega R = 0.072$). On the final cycle the shift in each positional and thermal parameter averaged 0.004 times its own σ . A final electron density map showed no peaks higher than $0.5 \text{ e}^-/\text{\AA}^3$. A final statistical analysis of the $|F_o|$ and $|F_c|$ values as a function of the indices, the scattering angle and the magnitude of F_o showed no unusual trends and suggests that the relative weighting scheme used is a reasonable one. The final positional parameters are given in Table V and the final thermal parameters in Table VI, along with their standard deviations as derived from the inverse matrix of the final least-squares cycle²⁷. A table of observed and calculated structure factors are found in Table VII.

Discussion of the Structure

The unit cell consists of $\text{Co}(\text{NH}_3)_6^{3+}$ cations and $\text{Sb}_2\text{F}_9^{3-}$ anions. In the cation, the coordination of the NH_3 ligands around the cobalt atom is approximately octahedral and the distances and angles, presented in Table VIII agree quite well with those found for the same cation in $\text{Co}(\text{NH}_3)_6\text{SbCl}_6^{34}$.

The $\text{Sb}_2\text{F}_9^{3-}$ anion is shown in Figure 4 and could be described as two square pyramids sharing a corner. A stereoview of the

structure is illustrated in Figure 5, produced by Johnson's thermal-ellipsoid plot program²¹. In the pyramid, the antimony atom is displaced below the least-squares plane formed by the four basal fluorines by 0.37 Å when the plane is calculated using the shorter bridging fluorine atom and by 0.35 Å when the longer bridging fluorine is used (Table IX). The F(axial)-Sb-F(basal) angles range from 78.2(4) to 86.0(3) Å. It appears therefore, that this antimony fluoride complex can be best described as consisting of two distorted octahedral units sharing a vertex, with a lone pair occupying the sixth position in each octahedron.

A second peculiar feature of this anion is the statistical disordering of the fluorine bridge and its asymmetric nature. One Sb-F distance is 2.249(12) Å while the other is appreciably lengthened, 2.449(4) Å. The angles to the neighboring basal fluorines are 82.6(6) and 102.8(7)° (66.3(7) and 120.1(6)° if the longer bridge is used). The Sb-F(5)-Sb' angle was found to be 142.1(8)° which is similar to the bridging angle found in the Sb_2F_7^- anion³⁵. In this case the Sb-F-Sb angle is 125.3°. It is difficult to see why such an asymmetric arrangement is preferred over a symmetric one. It is worthwhile to note that in the compound CsSb_2F_7 a bent fluorine bridge is also found, with the bridging fluorine on a crystallographic two fold axis. However, in the salt $\text{K}^+[(\text{C}_2\text{H}_5)_3\text{Al}-\text{F}-\text{Al}(\text{C}_2\text{H}_5)_3]^-$ the fluorine bridge is linear³⁶. It has been stated that in the absence of π bonding fluorine bridges tend to be bent. Therefore, the linearity of this bridge can be attributed to the fact that fluorine

possesses filled 2p orbitals which can overlap with the empty 3d orbitals of the aluminum atoms forming a π type bond. If this is actually the case then the non-linearity of the Sb-F-Sb bridge can be explained in terms of a greatly reduced overlap integral. A dimeric bridge involving fluorine would be very unlikely because the size of the fluorine atoms would cause great Sb-Sb repulsion. It should also be noted that the Sb-Sb distance in the $\text{Sb}_2\text{F}_9^{3-}$ anion is 4.44 Å compared to a Van der Waals distance of 4.40 Å³⁷.

A third aspect of interest in this anion is the variation of the Sb-F non-bridging distances that is observed. In order of increasing bond length, the distance opposite the lone pair is the shortest at 1.948(7) Å, while the Sb-F distance opposite the bridge is next at 2.015(5) Å. The other two fluorines in the base and trans to one another have essentially identical distances, 2.078(8) and 2.080(11) Å, respectively.

In this salt as in the bromide and chloride salts containing the $\text{Sb}_2\text{X}_9^{3-}$ species, the antimony-bridging halogen distance is lengthened with respect to the terminal halogen distance. In the bromide and chloride anions this lengthening was found to be 0.37 and 0.36 Å, respectively. If the asymmetric Sb-F bridge distances are averaged in the present compound, the corresponding lengthening is 0.33 Å, and is thus indicative of an effect which is essentially independent of the halogen present.

Although no hydrogen atoms were clearly indicated in the difference map, weak hydrogen bonding could well be present. The

shorter nitrogen-fluorine distances range from 2.84 to 2.94 Å while the corresponding Co-N-F angles range from 97.5 to 120.2°.

Table V. Final positional parameters for $\text{Co}(\text{NH}_3)_6\text{Sb}_2\text{F}_9$ ^{a,b}

Atom	Position	x	y	z
Sb	4e	0.03496(11)	0.01997(9)	0.32524(6)
Co	2b	0.5*	0.0*	0.0*
F1	4e	0.3163(15)	0.0077(13)	0.3721(14)
F2	4e	0.1314(12)	0.1066(11)	0.1864(6)
F3	4e	0.7878(10)	0.1425(11)	0.2688(7)
F4	4e	0.0832(9)	0.2674(9)	0.3771(6)
F5	4e	0.0988(33)	0.5315(26)	0.0175(14)
N1	4e	0.7595(13)	0.0857(13)	0.0137(8)
N2	4e	0.4171(14)	0.2361(13)	0.0576(8)
N3	4e	0.4771(13)	0.3991(14)	0.3496(7)

^aIn this and succeeding tables, numbers in parentheses indicate standard deviations in least significant digits.

^bAn asterisk indicates an atomic coordinate fixed by symmetry.

Table VI. Final anisotropic thermal parameters ($\times 10^4$) for
 $\text{Co}(\text{NH}_3)_6\text{Sb}_2\text{F}_9^a$

Atom	Position	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sb	4e	131(2)	55(1)	25(0)	-11(1)	0(0)	0(0)
Co	2b	74(4)	62(3)	23(1)	-4(3)	5(1)	0(1)
F1	4e	243(27)	252(27)	348(25)	135(21)	-193(22)	-185(20)
F2	4e	336(26)	156(17)	56(6)	14(17)	73(10)	-3(9)
F3	4e	129(17)	219(20)	103(8)	19(15)	-4(9)	-35(10)
F4	4e	148(15)	87(13)	60(6)	-6(11)	-14(7)	-15(7)
F5	4e	605(91)	210(47)	41(13)	71(53)	63(29)	-6(19)
N1	4e	102(21)	100(19)	42(7)	-26(16)	18(10)	0(10)
N2	4e	158(23)	79(18)	43(7)	-9(17)	23(11)	3(10)
N3	4e	118(21)	140(22)	25(6)	-5(17)	25(9)	-1(10)

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

Table VII. Observed and calculated structure factors (in electrons $\times 10$) for $\text{Co}(\text{NH}_3)_6\text{Sb}_2\text{F}_9$

L = 0	h	k	l	F _o	F _c	L = 1	h	k	l	F _o	F _c	L = 2	h	k	l	F _o	F _c	L = 3	h	k	l	F _o	F _c	L = 4	h	k	l	F _o	F _c	L = 5	h	k	l	F _o	F _c	L = 6	h	k	l	F _o	F _c	L = 7	h	k	l	F _o	F _c	L = 8	h	k	l	F _o	F _c	L = 9	h	k	l	F _o	F _c	L = 10	h	k	l	F _o	F _c	L = 11	h	k	l	F _o	F _c	L = 12	h	k	l	F _o	F _c	L = 13	h	k	l	F _o	F _c	L = 14	h	k	l	F _o	F _c	L = 15	h	k	l	F _o	F _c	L = 16	h	k	l	F _o	F _c	L = 17	h	k	l	F _o	F _c	L = 18	h	k	l	F _o	F _c	L = 19	h	k	l	F _o	F _c	L = 20	h	k	l	F _o	F _c	L = 21	h	k	l	F _o	F _c	L = 22	h	k	l	F _o	F _c	L = 23	h	k	l	F _o	F _c	L = 24	h	k	l	F _o	F _c	L = 25	h	k	l	F _o	F _c	L = 26	h	k	l	F _o	F _c	L = 27	h	k	l	F _o	F _c	L = 28	h	k	l	F _o	F _c	L = 29	h	k	l	F _o	F _c	L = 30	h	k	l	F _o	F _c	L = 31	h	k	l	F _o	F _c	L = 32	h	k	l	F _o	F _c	L = 33	h	k	l	F _o	F _c	L = 34	h	k	l	F _o	F _c	L = 35	h	k	l	F _o	F _c	L = 36	h	k	l	F _o	F _c	L = 37	h	k	l	F _o	F _c	L = 38	h	k	l	F _o	F _c	L = 39	h	k	l	F _o	F _c	L = 40	h	k	l	F _o	F _c	L = 41	h	k	l	F _o	F _c	L = 42	h	k	l	F _o	F _c	L = 43	h	k	l	F _o	F _c	L = 44	h	k	l	F _o	F _c	L = 45	h	k	l	F _o	F _c	L = 46	h	k	l	F _o	F _c	L = 47	h	k	l	F _o	F _c	L = 48	h	k	l	F _o	F _c	L = 49	h	k	l	F _o	F _c	L = 50	h	k	l	F _o	F _c	L = 51	h	k	l	F _o	F _c	L = 52	h	k	l	F _o	F _c	L = 53	h	k	l	F _o	F _c	L = 54	h	k	l	F _o	F _c	L = 55	h	k	l	F _o	F _c	L = 56	h	k	l	F _o	F _c	L = 57	h	k	l	F _o	F _c	L = 58	h	k	l	F _o	F _c	L = 59	h	k	l	F _o	F _c	L = 60	h	k	l	F _o	F _c	L = 61	h	k	l	F _o	F _c	L = 62	h	k	l	F _o	F _c	L = 63	h	k	l	F _o	F _c	L = 64	h	k	l	F _o	F _c	L = 65	h	k	l	F _o	F _c	L = 66	h	k	l	F _o	F _c	L = 67	h	k	l	F _o	F _c	L = 68	h	k	l	F _o	F _c	L = 69	h	k	l	F _o	F _c	L = 70	h	k	l	F _o	F _c	L = 71	h	k	l	F _o	F _c	L = 72	h	k	l	F _o	F _c	L = 73	h	k	l	F _o	F _c	L = 74	h	k	l	F _o	F _c	L = 75	h	k	l	F _o	F _c	L = 76	h	k	l	F _o	F _c	L = 77	h	k	l	F _o	F _c	L = 78	h	k	l	F _o	F _c	L = 79	h	k	l	F _o	F _c	L = 80	h	k	l	F _o	F _c	L = 81	h	k	l	F _o	F _c	L = 82	h	k	l	F _o	F _c	L = 83	h	k	l	F _o	F _c	L = 84	h	k	l	F _o	F _c	L = 85	h	k	l	F _o	F _c	L = 86	h	k	l	F _o	F _c	L = 87	h	k	l	F _o	F _c	L = 88	h	k	l	F _o	F _c	L = 89	h	k	l	F _o	F _c	L = 90	h	k	l	F _o	F _c	L = 91	h	k	l	F _o	F _c	L = 92	h	k	l	F _o	F _c	L = 93	h	k	l	F _o	F _c	L = 94	h	k	l	F _o	F _c	L = 95	h	k	l	F _o	F _c	L = 96	h	k	l	F _o	F _c	L = 97	h	k	l	F _o	F _c	L = 98	h	k	l	F _o	F _c	L = 99	h	k	l	F _o	F _c	L = 100	h	k	l	F _o	F _c
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Table VIII. Selected bond distances and angles in $\text{Co}(\text{NH}_3)_6\text{Sb}_2\text{F}_9$ a) Distances ($\text{\AA}$)

Atoms	Length	Atoms	Length
Sb-F(1)	2.080(11)	Sb-F(5')	2.449(4)
Sb-F(2)	2.015(5)	Sb-Sb'	4.444(0)
Sb-F(3)	2.078(8)	Co-N(1)	1.973(3)
Sb-F(4)	1.948(7)	Co-N(2)	1.980(9)
Sb-F(5)	2.249(12)	Co-N(3)	2.017(4)

b) Angles (deg)

Atoms	Angle	Atoms	Angle
F(1)-Sb-F(2)	82.5(5)	F(3)-Sb-F(4)	80.9(3)
F(2)-Sb-F(3)	84.8(4)	F(4)-Sb-F(5')	78.3(5)
F(3)-Sb-F(5)	82.6(6)	F(4)-Sb-F(5)	75.6(6)
F(3)-Sb-F(5')	120.1(6)	F(1)-Sb-F(5)	102.8(7)
F(3)-Sb-F(4)	80.9(3)	F(1)-Sb-F(5')	66.3(7)
F(2)-Sb-F(5)	159.1(6)	Sb-F(5)-Sb'	142.1(8)
F(2)-Sb-F(5')	147.3(6)	N(1)-Co-N(2)	89.9(4)
F(1)-Sb-F(4)	78.2(4)	N(1)-Co-N(3)	89.1(4)
F(2)-Sb-F(4)	86.0(3)	N(2)-Co-N(3)	89.3(4)

Table IX. Equations of atomic planes and distances ($\text{\AA}$) of atoms from these planes^a in $\text{Co}(\text{NH}_3)_6 \text{Sb}_2\text{F}_9$

a) Plane^b through F1, F2, F3, F5

$$-0.171X + 0.958Y - 0.231Z - 3.561 = 0$$

Sb -0.37

F1 0.02

F2 -0.03

F3 0.03

F5 -0.02

b) Plane through F1, F2, F3, F5'

$$-0.169X + 0.952Y - 0.255Z - 3.464 = 0$$

Sb -0.35

F1 0.05

F2 -0.05

F3 0.03

F5' -0.04

^aThe coordinate system used for the least-squares planes was:
 $X = xa + zc \cos \beta$; $Y = by$; $Z = zV/ab$.

^bThe atoms defining the planes were assigned unit weights.

Figure 4. $\text{Sb}_2\text{F}_9^{3-}$ anion in $\text{Co}(\text{NH}_3)_6\text{Sb}_2\text{F}_9$.

Figure 5. Stereogram of $\text{Co}(\text{NH}_3)_6\text{Sb}_2\text{F}_9$ with Co at $(\frac{1}{2}, 0, 0)$.

RESEARCH PROPOSALS

The compounds $M_3^I\text{SbX}_6$ ($X = \text{Cl}, \text{Br}, \text{I}$) form a very interesting series of antimony halides. To date a structure of this stoichiometry has not been published. A structural investigation of one of these compounds would be a significant contribution to the Sb(III) work being done. Presently there is a conflict in opinion as to the geometry possessed by the anions. Della Valle *et al.*³⁰, have stated that their work is consistent with a distorted environment about the antimony atom, increasing in the order K_3SbCl_6 , Cs_3SbCl_6 and $(\text{NH}_4)_3\text{SbCl}_6$. This study revealed the hexamminecobalt(III) salt as having a symmetric environment about the antimony atom and that Martineau and Milne's⁵ Raman data could be explained in terms of reduced site-symmetry, as they suggested. Adams³⁸, on the other hand, believes the compounds $M_3^I\text{SbX}_6$ to contain the SbX_5^{2-} anion, which would be consistent with the Mössbauer and Raman data now available on these compounds.

Another compound of considerable interest related to this series is $(\text{C}_4\text{H}_9\text{NH}_3)_3\text{SbCl}_6$. The vibrational spectra of this compound has been interpreted to be consistent with the $M_3^I\text{SbX}_6$ compounds, indicating distortion from an octahedral geometry. Preliminary work on these compounds indicates that the potassium, ammonium and rubidium salts belong to the monoclinic crystal system with essentially the same lattice constants, while the cesium salt is cubic⁵. The compound $(\text{C}_4\text{H}_9\text{NH}_3)_3\text{SbCl}_6$ has been found to be orthorhombic by a structural investigation underway at the present time at this laboratory. A

structural investigation of a compound of this type would produce further significant structural information about the coordination of Sb(III) and the effect of the lone pair on the coordination geometry.

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